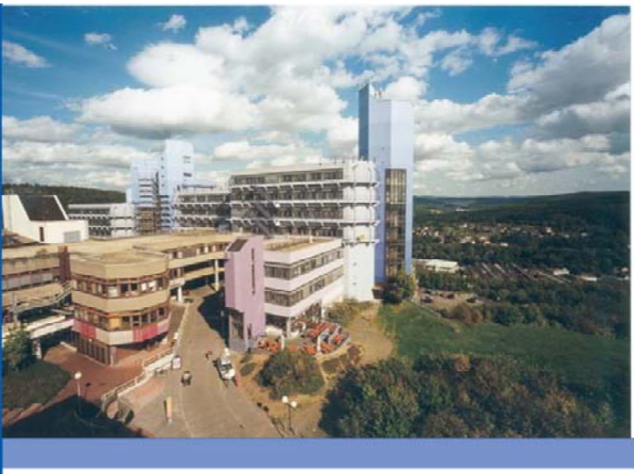

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World Forum on Advanced Polymeric Materials Synthesis, Properties, Characterisation

IUPAC sponsored conference

POLYCHAR 18

April 7 – 10, 2010
in Siegen, Germany

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Editors:

Prof. Dr. Werner Mormann
Macromolecular Chemistry
mormann@chemie.uni-siegen.de
http://www.uni-siegen.de/fb8/makro/index.html.en?lang=en

Prof. Dr. Holger Schönherr
Physical Chemistry
schoenherr@chemie.uni-siegen.de
http://www.uni-siegen.de/fb8/pc/hs/index.html.en?lang=en

both

Universität Siegen, Fachbereich 8 Chemie - Biologie
Adolf-Reichwein-Straße 2
57068 Siegen, Germany

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Contents

Welcome

Dear colleagues, friends and guests. It is a great honour and pleasure for us to warmly welcome you to Siegen. We took over the organization of POLYCHAR 18 on short terms with a rather small team. We do hope, however, that our efforts to establish a stimulating atmosphere for science and exchange of views have been somehow successful.

POLYCHAR has become a renowned conference over the years thanks to those who started it and made it grow. In terms of quantity we seem to have reached an optimum size, as for quality it will be you, the speakers, who can improve it and certainly will. With this in mind we have tried to eliminate, at least to drastically reduce, the number of “no-show” contributions, which can spoil a conference.

We are proud to have contributions from all continents with an increasing number from far-east (China, Korea and Thailand). We are happy to see scientific contributions not only from South Africa and Egypt but also from Nigeria; we regret that colleagues from other developing and underprivileged countries did not react on our offer for support. Finally it is worth mentioning that we have a significant number of contributions from industry, and we do hope that the exchange between academia and industry will stimulate new ideas and research.

What remains is to wish you a nice stay in Siegen, in Germany and in Europe, where some of you will spend time before and after the conference. We will do our best to make the conference pleasant and effective and we count on your understanding, where we will have to be strict in order to keep the meeting running smoothly.

In this former mining area people greeted each other with “Glück Auf” (good luck) before going into a mine. We adopt this word and say

Gück Auf
to all of you

Werner Mormann
For the whole team

Siegen, April 2010

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World Forum on Advanced Polymeric Materials

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Hewlett Packard Str. 8
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Germany

Atomic Force F&E GmbH
Hauptstrasse 161
DE-68259 Mannheim
Germany

Bruker Optik GmbH
Rudolf-Plank-Str. 27
76275 Ettlingen
Germany

CEM GmbH
Carl-Friedrich-Gauß-Str. 9, 47475 Kamp-Lintfort
Postfach 10 11 63, 47456 Kamp-Lintfort
Germany

Evonik Degussa GmbH
Rellinghauser Straße 1-11
45128 Essen
Germany

JPK Instruments AG
Bouchéstrasse 12
Haus 2, Aufgang C
12435 Berlin, Germany

PSS Polymer Standards Service GmbH
In der Dalheimer Wiese 5
D-55120 Mainz
Germany

Q-Sense AB
Hängpilsgatan 7
SE-426 77 Västra Frölunda
Sweden

Wyatt Technology Europe GmbH
Hochstrasse 18
56307 Dernbach
Germany

Exhibition

Location: Conference registration office

Atomic Force Microscopes

Atomic Force F&E GmbH
Hauptstrasse 161
DE-68259 Mannheim
Germany

Polymer Standards

PSS Polymer Standards Service GmbH
In der Dalheimer Wiese 5
D-55120 Mainz
Germany

Quartz Crystal Microbalance

Q-Sense AB
Hängpilsgatan 7
SE-426 77 Västra Frölunda
Sweden

General Information

Instructions for oral presentations

The duration of presentations (including discussion) is limited as shown in the program to

- 40 minutes for keynote lectures
- 30 (20) minutes for invited lectures
- 20 minutes for oral contributions

In view of the 3 parallel sessions we are bound to enforce the given time specifications to ensure a smooth program.
During POLYCHAR 18 we will have three parallel sessions. To avoid compatibility problems of hard and software - and delays due to several other reasons - we kindly ask the presenters to follow the guideline below:

1. Create on your computer a new folder. Rename the folder with the full name of the speaker, beginning with the last name (e.g. 'Schoenherr_Holger').

2. Save your PowerPoint-presentation into this folder.
If your presentation contains hyperlinks to other files (e.g. videos, pictures) don't forget to copy these files into the same folder!

3. Start PowerPoint and open your presentation from the folder.

4. Save your presentation additionally as 'PowerPoint – Pack & Go Presentation':
- From the PowerPoint main menu select File
- Save as
- A window opens where you can
- select the filetype: 'PowerPoint –Pack & Go Presentation'
- ensure that the filename is still the same
- Save it.
Afterwards you should find two files with the same name but different extensions, filename.pps and filename.ppt.

5. Use a standard USB storage device or CD/DVD, and save the complete folder to your storage device.

6. To avoid any other unexpected complications please also provide your presentation in PDF-format!!!

After registration ALL SPEAKERS are kindly requested to bring your PowerPoint-presentation to the presentation center as soon as possible.

Presentations from morning sessions should be uploaded on the day before. Speakers of the afternoon sessions should upload their file(s) following the closure of the morning session.

Instructions for poster presentations

For the poster session on Wednesday (18.00-20.00), please put up your poster latest during the afternoon coffee break at the poster board (marked with the ID number of your poster). Posters should remain until lunch break on Thursday April 8 for inspection by the prize committee. The organizers do not take responsibility for posters not removed in time.

Publication of papers presented at POLYCHAR 18

The POLYCHAR Forum as a rule does not publish conference proceedings for participants but publishes instead in worldwide archive journals. Presenters have an opportunity – but not an obligation – to submit manuscripts for publication. The format of the presentation (poster, oral, etc) does not matter for publication. Each manuscript will be peer-reviewed.

Conference volumes of POLYCHAR 18 will published in the following journals:

- Macromolecular Symposia
- Polymer Engineering and Science

Manuscripts should be prepared according to the guidelines on the conference website. Submission of manuscript in pdf format to polychar18@uni-siegen.de **for pre-review** is due by **June 1st 2010** the latest.

Manuscripts not prepared according to the guidelines will be automatically rejected.

Authors will be informed **within 2 weeks** which journal is suitable for final submission of the manuscript. Further details on the online submission procedure will be communicated. Then only upon invitation, manuscripts have to be submitted **within 1 week** to the corresponding journal via the online portal (final deadline: **June 21st 2010**). Direct electronic submissions to the publishers cannot be considered for the special issues devoted to POLYCHAR 18.

The total number of manuscripts that can be considered is limited to 30 - 35 papers for Macromolecular Symposia and 20 - 25 papers for Polymer Engineering and Science. Selection will be based on quality and in case of comparable quality on a *first-come, first-served* basis.

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Congress badges

Congress participants are required to wear their name badges at the congress site in order to get access to the scientific sessions and social events. You will receive your congress badge along with your congress bag, the lunch vouchers and further information during the registration. In case of loss please contact the registration desk.

Registration and information desk - opening hours

Monday April 5,	14.00 – 19.00
Tuesday to Friday	8.00 – 18.00

Awards

POLYCHAR Prizes:

- Paul J. Flory Polymer Research Prize
- International Materials Science Prize
- Bruce Hartmann Prize for a Young Scientist (Presentation)
- Jürgen Springer Prize for a Young Scientist (Presentation)
- Carl Klason Prize for the best Student Presentation
- Diploma of Distinction for a Student Presentation
- IUPAC Poster Award
- Wiley-VCH Poster Award

Coffee and poster sessions

During the poster sessions and the coffee breaks in the morning and the afternoon refreshments will be served free of charge for participants wearing their identification badges.

Lunch

Lunch is included in the registration fee and will be available in the Mensa of the University (please follow the signs). For payment of each lunch you will find a corresponding voucher in the registration material. Students are required to present their valid student identification along with their vouchers at the cashier in the Mensa.

Social events

Welcome reception and poster session on **Wednesday April 7**
Conference dinner **Friday April 9**
Conference tour **Saturday April 10**

Information on an individual touristic program is available in the registration office. Suggested locations to visit include:

Freudenberg, historic town center from the year 1667 (Bus R 38, 7.00 Euros return ticket)
Oberes Schloß (upper residence) in Siegen (Burgstraße, 57072 Siegen) (*not for those who participate in tour #1 on Saturday!)*
Museum für Gegenwartskunst (Unteres Schloß 1, 57072 Siegen)

Internet access

Free WLAN access will be provided (access code together with registration)

Timetable / Program

Short course (POLYCHAR 18), April 6, 2010

Time	Topic	Speaker
9.00-9.45	Atomic force microscopy: morphology and surface analysis beyond topography	Holger Schönherr
10.00-10.45	Dynamic mechanical thermal analysis	Michael Hess
11.00-12.30	Comprehensive characterization of macromolecules by liquid chromatography	Peter Kilz Christoph Johann
12.30-13.30	Lunch	
13.30-14.15	Characterization of thin polymer films by quartz crystal microbalance with dissipation monitoring (QCM-D)	Sofia Svedhem
14.30-15.15	Assessing transport properties of polymers by experimental techniques and simulation methods	Ulf W. Gedde
15.30-16.15	Electron microscopy to study morphology and micromechanics of polymers	Goerg Michler
16.30-17.15	Time resolved measurements for polymer processing	Anthony J. Ryan

A certificate of participation will be given to attendees

Timetable / Program: Wednesday April 7

	Wednesday April 7		
9.00	Opening		
9.25	Schönherr	**Decher** Toward soft matter thin film devices	
10.05	**Grainger** Molecular sorting at surfaces: Protein-polymer capture to patterns and their analysis		
10.45	Hvilsted A	Break Gedde B	Wenz C
11.10	**Ritter** Ring-opening polymerization of lactones	**Spencer** Tribological properties of polymer brushes: grafting-from and grafting-to	**Jin, Jung-Il** Materials Science of DNA
11.40	**Spadaro** Metallocene catalyzed polyolefines for improving thermal and mechanical properties of bitumen blends	**Pihan** The mechanical properties of brush-coated nanoparticles in a homopolymer matrix	**Feng C. L.** Dendrimer based functional nanotubes for detecting DNA hybridization
12.00	**El Gamel** Synthesis and characterization of polymeric silyl-cyamelurates versus silyl-cyanurates	**Graf** (Visco-)elastic nano- and microstructuring of polystyrene surfaces: from rippling to solvent drops	**Nöll** Electron transfer between enzymes and electrodes mediated by redox polymer hydrogels
12.20	**Causin** Electrospun nylon fibers: A cheap and effective filler for poly(ε-caprolactone)	**Jin, Jian** Spontaneous growth of free-standing conducting polymer thin films at the air/liquid interface	**Piorkowska** Modification of polylactide properties by plasticization with biodegradable polymers
12.40	Fradet A	Lunch He B	Tieke C
14.00	**Yagci** Synthetic strategies to combine high performance bezoxazine thermosets with polymers	**Butt** Surface forces across polymer melts	**Wenz** Functional systems from cyclodextrins and polymers
14.30	**Klee** Synthesis and dental application of novel hydrolysis stable adhesive monomers	**Tranchida** Mechanical properties of morphologies studied by AFM nanoin–dentation: polymer brushes and polymeric nanophases	**Jurczuk** All polymer composites
14.50	~~**Mehdipour** Synthesis and characterization of heat resistant polyamides with bulky anthraquinone unit~~	**Kazim** Morphology and optical processes in silver nanoparticles/conjugated polyelectrolyte systems: application to SERS	**Zhou, Yi** Black Polymers in bulk heterojunction solar cells
15.10	**Gorbunova** New polysulfones: Synthesis characterization, properties	**Svedhem** Real-time characterisation of polymer interactions using quartz microbalance with dissipation monitoring	**Wilberforce** T_q behaviour and viscoelastic properties of polylactide-co-glycolide /〈-tricalcium phosphate nanocomposites
15.30	**Zhunusbekova** Biopolymeric complexes of Fe(III)-porphyrin: synthesis and characterization	**Papadopoulos** Comparison of micro- and macroscopic mechanical properties of spider silk: effects of hydration	**Gutmann** Integrated approaches in templated hybrid polymer materials
15.50		Break	

	Yagci A	Butt B	Jo, B.-W. C
16.10	**Hvilsted** Efficient "electroclick" and other orthogonal "click" methods in development of challenging biopolymer Materials	**Michler** Influence of length scale of heterogeneous polymers on mechanical properties	**Brostow** Glass transition temperatures of binary systems containing polymers
16.40	**Singh** High performance polymeric flocculants- microwave assisted synthesis	**Lee**, **Kee-Y.** Micromechanics of viscoelastoplastic response of unidirectional epoxy resin composite	**Trettin** Challenges to polymers for advanced cementitious systems
17.00	**Yu, Lu** Preparation of carboxyl functionalized and fluorescently labelled polystyrene nanoparticles	**Arabeche** Enthalpy relaxation in PC/PMMA multilayered films from micro to nano scale	**Martínez-Barrera** Post-irradiation effects on nylon-fiber reinforced concretes
17.20	**Zhang**, **Y.** Influence of the sequence distribution on the properties of aromatic copolysulphonamides	**Baukh** NMR imaging of water absorption by multilayer coatings	**Dietz** Flame retardants based on phosphorus chemistry for thermosets
17.40	**Bhajantri** Effect of $FeCl_3$ doping on mechanical and microstructural properties of poly(vinyl alcohol)	**Amanat** Transmission-laser welding of poly(ether ether ketone) for medical device applications and characterisation using X-ray tomographic techniques	**Jahani** Thermal stability and degradation kinetics of PC/ABS composites with halogen free flame retardant
18.00-20.00	**Poster session and Welcome Reception**		

Timetable / Program: Thursday, April 8

	Thursday, April 8		
8.30	Mormann	**Ryan** The Quest for motility: making polymers swim	
9.10		**He** Microfoaming of polymers by supercritical CO_2 technique	
9.50	Aranguren A	Break Ryan B	Mallon C
10.15	**Geckeler** Supramolecular polymer systems: from design to reality	**Williams** Reversible epoxy networks with physical crosslinks based on tail-to-tail associations of alkyl chains	**Rowan** Polyisocyanopeptide nanoworms: 'stiff helical polymers and their applications'
10.45	**Saiter** 100% green composites and thermoplastic materials. Materials for the future?	**Patrickios** Functional end-linked conetworks based on cleavable bifunctional initiators: synthesis by GTP, ATRP and RAFT polymerization, characterization and cleavage	**Xu** Stimuli responsive polymers: exemplified on switchable windows
11.15	**Adhikari** Fully biodegradable polymer composites based on bamboo flour: morpholgy and mechanical behaviour	**v. Haeringen** Water-based coatings- film formation and film build-up	**Serpe** Janus pNIPAm microgels: anisotropic building blocks for advanced materials
11.35	**Forstner** High performance impact modification of PLA and PLA –man made cellulose fiber compounds	**Drozdzak** Poly-bicyclopentadiene (DCPD): a speciality thermoset with a bright future	**Tieke** Thermoresponsive copolymer hydrogels based on N-isopropylacrylamide and cationic surfactant monomers
11.55	**Sharmin** Organic-inorganic hybrid materials en route green chemistry	~~**Pfeil** Thermoset resins in chemical anchoring- structure property relationships~~	**Savina** Macroporous hydrogels by cryogelation
12.15	**Zafar** Microwave assisted Pongamia Pinnate oil based hyperbranched waterborn polymer- a "green" material	~~**Chemtob** Bridged polysilsesquioxane films via photoinduced sol-gel chemistry~~	**Pretsch** Thermo-mechanical effects of hydrolytic aging on an active polymer with triple-shape properties
12.35		Lunch	

	Geckeler A	Williams B	Chiardelli C
14.00	**Ax. Müller** Block terpolymer sunrise: the wondrous world of block terpolymer micelles	**Pasch** Analysis of block copolymers by 2D-LC and on-line coupled LC-NMR	**Carfagna** PVC: restyling of an old polymer
14.30	**Kroeger** Structures and dynamics of complex block copolymer aggregates: a model system	**Ginzburg** Characterisation of polyolefins with high temperature two-dimensional liquid chromatography	**Breuer** Open celled thermoplastic sheet foams
14.50	**Kuckling** Synthesis of smart nano-materials based on poly(gycidol) and poly(N-isopropylacrylamide)	**Hiller** The coupling of liquid chromatography at critical conditions and NMR- a new tool for the characterization of polymers	**Spinelli** Influence of polymer and surfactant on the aphroon-based drilling fluids characteristics correlating with fluid invasion controlling
15.10	**Lazarev** Controlled radical polymerization of methyl methacrylate catalyzed by polymer-supported complexes of copper	**Berek** Two-dimensional liquid chromatography of synthetic polymers	**Dey** Structuring edible oils by polymer gelation
15.30	**Magaraphan** Peroxide cured natural rubber/fluorelastomer/ high density polyethylene via dynamic vulcanization	**Kilz** Investigation of starch degradation by comprehensive size-exclusion chromatography	**Vuillequez** Glass transition and enthalpy relaxation in glassy materials: from polymers to food industry
15.50	Ax. Müller A	Break Pasch B	Brostow C
16.20	**Strumia** Synthesis, properties and applications of dendronized chitosan	**Jo, Byung-W.** Depolymerization and anticoagulant activity of fucoidan	**Ciardelli** Control of macromolecular architecture of polyolefins during functionalization in the melt
16.50	**Ferbitz** BASF sustainable development - renewable resources for polyurethanes	**Macko** High-temperature adsorption chromatography- a new tool for characterisation of polyolefins	**Mallon** Synthesis, morphology and electrospinning of poly(dimethylsiloxane) based copolymers
17.10	**Türe** A novel approach to extrude wheat gluten based on addition of urea	**Scherrers** Determination of molecular parameters of polyacrylamide solutions	~~**Altstädt** Thermal, mechanical and rheological properties of PA 6 nanocomposites based on halloysite nanotubes~~
17.30		**Otte** Molecular characterization of UHMW-polyethylene: asymmetric flow field-flow fractionation contra size exclusion chromatography	

Timetable / Program: Friday, April 9

	Friday, April 9		
8.30	Jin, Jung-Il **Buchmeiser** Ring-opening metathesis polymerization derived materials for heterogeneous catalysis, separation science and tissue engineering		
9.10	**Lee, Kw.-S.** Recent advances in two-photon stereolithography		
9.50	Kubisa A	Break Galeski B	van Reenen C
10.15	**Massonne** Ionic liquids and cellulose: industrial aspects	**Gedde** Small-molecule diffusion in semicrystalline polymers as revealed by combined experimental and simulation studies	**Das** Development and characterization of in situ polymerized nanocomposites based on polypyrrole and polyaniline in the presence of multiwall carbon nanotubes
10.55	**Rosenau** Side reactions in the system cellulose / 1-alkyl-3-methyl-imidazolium ionic liquid	**Matsuo** Gauche-trans transitions in amorphous polymers under annealing: lattice model and polarized light scattering	**Henning** Droplet structures in styrenic blockcopolymer blends and their nanocomposites
11.15	**Fradet** Polyesterification in ionic liquids	**Martins** Analysis of the adequacy of representation of entanglements' effects by chain loops	**Ding, Yunsheng** Magnesium hydroxide modified by 1-N-tetra-decyl-3-carboxymethyl imidazolium chloride and its effects on the properties of LLDPE
11.35	**Ahmad** Thiophene based conjugated polyelectrolytes bearing ionic moiety layers assisted by electrodeposition in ionic liquids	**Celestino** Use of dielectric analysis to complement mechanical and rheological studies in nitrile rubber/acrylic acid blends	**Hillborg** Effect of interfacial strength on mechanical properties of Al_2O_3/ epoxy nanocomposites
11.55	**Fleury** Synthesis and rheology of biodegradable poly(glycolic acid) prepared by melt ring-opening polymerisation of glycolide	**Sylvestre** Structural and dielectric properties of chlorinated and not chlorinated poly (p-xylylene)	**Yadav** Anomalous enhancement of thermal conductivity of poly vinyl alcohol
12.15	**Thiminlioglou** Preparation and transport properties of chitosan-layered silicate nanocomposite films	**Sangappa** Microstructural parameters and surface morphology of 8 MeV electron irradiated NB7 Bombyx Mori silk fibers	
12.35		Lunch	

	Rosenau A	Henning B	Das C
14.00	**Kubisa** Ionic polymerizations in ionic liquids	~~**Maurer** Characterization of free volume in polymer membranes by positron annihilation lifetime spectroscopy~~	**Rivas** Functional polymers to remove ions in conjunction with membranes
14.30	**Zhang, Jun** New results in dissolution of cellulose in ionic liquids	~~**Al. Müller** Morphology, crystallization, melting, and biode-gradation of poly(ε-caprolactone-co-ε-caprolactam) polymers~~	**Thomas** Micro and nanostructured epoxy resin based polymer blends
15.00	**Schmidt** Ionic liquids and polymers	**Obadal** Industrial consequences of polypropylene phase morphology	**Bayley** Carbon nano-tube filled electrospun polyacrylonitrile-*g*-poly(dimethylsiloxane) fibers for silicone elastomer composites
15.20	**Aranguren** Comparison of different methods of crosslinking sodium caseinate	**van Reenen** Solution crystallization analysis by laser light scattering (SCALLS)- application examples for polyolefins.	**Choi**, **Hyoung** Magnetorheological polymeric magnetic composite materials
15.40	**Bröcher** Retention technologies for improved ash retention and productivity in paper processes	**Zhang, W.** Origin of melt memory effect in polymer crystallization	**Dalle Vacche** The effect of processing conditions on the morphology, mechanical and electrical properties of $BaTiO_3$-polymer composites.
16.00	**Hedenquist** Wheat gluten - a renewable source for plastic products	**Hossain** Effects of radiation iodinization and ionization on the opto-electrical properties of polymer	**Chabukswar** Studies on morphology and conductivity of poly (N-methylaniline) nanoparticles prepared in non-stirred medium
16.20		Break	
16.45	**Flory award ceremony** **Hans Wolfgang Spiess** Interplay of structure and dynamics in polymers and supramolecular systems **Andrzej Galeski** Initiation of cavitation during drawing of crystalline polymers		
18.10	**Awards / Closing remarks**		
18.30			
19.00	**Conference dinner** (until 22.30)		

List of Posters

~~p1~~	~~Alireza~~	~~Shirazi Amin~~	~~Atom transfer radical polymerization of acrylamide in reverse suspension~~
p2	Chenyi	Wang	Highly organosoluble and transparent polyamides containing trifluoromethyl pendant groups
p3	Geeta	Saini	Synthesis and characterization of oligo and polythiophenes with thiophene side chains
p4	Navid	Nikooseresht	A new natural polymeric catalyst based on starch for Knoevenagel condensation
p5	Bum-Jae	Lee	Novel synthetic methodology of 1,2,3-triazole-embedded copolyether polyol by azide-alkyne click chemistry
p6	~~Shahram~~	~~Mehdipour-Ataei~~	~~Novel fluorene based poly(ester imide)s: synthesis, characterization and properties~~
p7	Mirta	Aranguren	Effect of cellulose nanofiber addition to a segmented polyurethane with shape memory properties
p8	Sadegh	Jamshidi	High performance thermally curable polyurethanes containing benzoxazine or naphtoxazine groups in the main chain
p9	Elahe	Gharekhani	Preparation and characterization of novel pyridine-based polyimides containing amide and ether units
p10	Yunsheng	Ding	Effect of two kinds of ionic liquids on the kinetics of methyl methacrylate microemulsion polymerization
p11	Shazia	Abrar	Characterisation of amphiphilic polymers of complex architecture using different liquid chromatography modes
p12	Rajesh	Chitta	Determination of chemical composition distribution of ethylene-butylacrylate copolymers by CRYSTAF and high-temperature HPLC
p13	Wael K.	Elhrari	2-D Chromatographic analysis of polystyrene-*b*-poly(methyl methacrylate) copolymers synthesized using borane chemistry
p14	Tibor	Macko	Chromatographic separation of copolymers according to their tacticity
p15	Anton	Ginzburg	Separation of polyethylene and polypropylene with high-temperature liquid chromatography
p16	Harald	Pasch	Characterization of blends of polyisoprene by on-line hyphenation of critical chromatography and nuclear magnetic resonance spectroscopy
p17	Nadine	Pretorius	The combination of liquid chromatography and mass spectrometry techniques for the characterization of aliphatic polyesters
p18	Margaretha	Brand	Solution crystallization analysis by laser light scattering (SCALLS)

p19	Triinu	Poltimäe	Study of tertiary crystallization process and morphology in LLDPE and HDPE
p20	Pawel	Sajkiewicz	Isothermal crystallization of polymers by depolarized light intensity – possibilities and limitations
p21	~~Uzma~~	~~Khalil~~	~~A study of XRD analysis of a ternary polymer blend system~~
p22	Abdelkader	Kahouli	Semi-crystalline study and dielectric properties of low-k poly(tetrafluoro-p-xylylene) (VT-4) for microelectronic applications
p23	Ye	Chen	Characterization of polysulfonamide in dilute solution by laser light scattering
p24	Paul Achile	Akpa	Characterization of polyelectrolyte complexes of oppositely charged polymethacrylate copolymers prepared in methanol
p25	Souren	Grigorian	X-ray investigations of semicrystalline poly(3-hexylthiophene) thin films
p26	Nima	Sanandaji	Innate confinement effects as a route to confined space crystallisation
p27	Fritjof	Nilsson	Modelling the permittivity of anisotropic composites
p28	Louise	Byers	Characterisation and ageing of fluoropolymer binders for polymer bonded explosives (PBX’s)
p29	Wissam	Abdallah	Preparation and characterization of thermally stable layered silicates for use in polymer based nanocomposites
p30	Basem	Alsawy	The dependence of sound velocity in polypropylene containing varying proportions of nano-fillers and binder
p31	Svetlana	von Gratowski	Study of the dispersity of polymer nanocomposite fillers using dielectric properties
p32	Karol	Bula	Influence of spherical and platelet nanoparticle content and processing parameters on mechanical behaviour of polypropylene composites
p33	Micheli Lucia	Celestino	Mechanical properties of nitrile rubber/acrylic rubber blends: effect of nanofiller
p34	Vera S.	Cruz	Semi-quantitative evaluation of the interactions between multiwall carbon nanotubes and polymer melts
p35	~~Sven~~	~~Friedrich~~	~~Effect of nanoclay on the vibration welding of LLDPE nanocomposites in presence and absence of compatibilizer~~
p36	Eileen	Harkin-Jones	Effects of composition and processing conditions on clay dispersion in polypropylene nanocomposites

p37	Aravind	Kalambettu	Tribologic and bioactivity studies of sulphonated polyether ether ketone (PEEK) / nano hydroxy apatite composites
p38	Olena	Kudina	New comb-like maleic anhydride copolymers for fabrication of silver nanoparticles
p39	Nattaya	Muksing	Evidences of anionic guests intercalated layered double hydroxide host on morphology and thermal properties of LDPE based nanocomposites
p40	~~Roberta~~	~~Magalhães Mariano~~	~~Evaluation of vulcanization kinetics, processability and interactions of natural rubber/cellulose II/montmorillonite nanocomposites~~
p41	Giridhar	Mishra	Synthesis and ultrasonic characterization of copper nanoparticle/poly(vinyl alcohol) nanofluids
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p46	Roza	Tchoudakov	Inorganic nano and micro fillers in PP/PA composites: processing/morphology/property relationships
p47	Yadolla	Teymouri	Physical and mechanical properties of LDPE/org-MMT nanocomposites prepared by melt intercalation method
p48	Adriana dos Anjos	Silva	Effect of organophilic montmorillonite and acrylic copolymers on nanostructure and properties of epoxy resin networks
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p112	Jose	Jesmy	Preparation and rheological characterisation of model nanocomposites based on laponite and poly(ethylene xide)

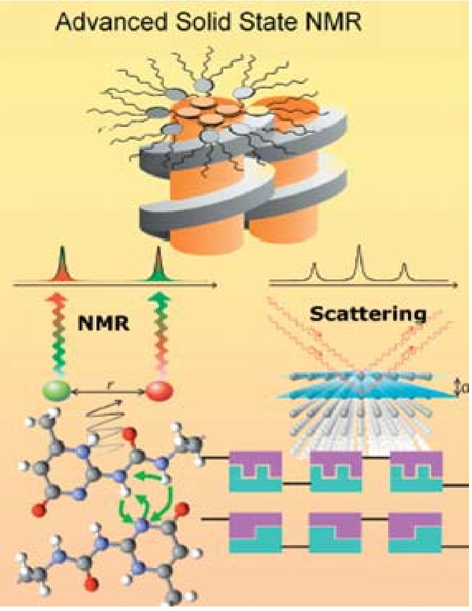
INTERPLAY OF STRUCTURE AND DYNAMICS IN POLYMERS AND SUPRAMOLECULAR SYSTEMS

Hans Wolfgang Spiess

Max Planck Institute for Polymer Research, P. O. Box 31 48, 55021 Mainz, Germany
E-mail spiess@mpip-mainz.mpg.de

Keywords: *structure, dynamics, NMR spectroscopy*

Traditionally, the determination of structure and the elucidation of dynamics of matter are considered separately. With the advancement of characterization techniques, however, this separation becomes increasingly artificial. For instance, advanced solid state NMR spectroscopy provides information on the geometry and the time scale of molecular motions independently[1]. This site-selective and specific information is highly valuable, as in soft matter the function of complex synthetic as well as natural systems is often achieved by separating regions of order and disorder. Even if highly ordered on a local scale, such systems often do not crystallize. Therefore, their atomic resolution structures cannot be determined by using conventional scattering techniques. Alternatives are needed which should provide structural and dynamic information, preferably requiring only small amounts of as-synthesized samples. For that purpose solid state NMR techniques have been developed combining fast magic angle spinning (MAS) and double quantum (DQ) NMR spectroscopy, which make use of the homonuclear and heteronuclear dipole-dipole couplings in analogy to scattering techniques.



Solid state NMR can thus be applied to tackling many problems in polymer science[2]. For instance, differences of the chain organization in polyethylene crystallized from solution, or from the melt have pronounced effects on the segmental mobility in the non-crystalline regions and the rate of medium range translational motion of the chains between non-crystalline and crystalline regions (chain diffusion)[3]. Moreover, incorporation of defects in the crystals induces torsional deformation of the chain and can lead to cooperative motion of the stems[4]. Conformational effects are also very important in synthetic macromolecules composed of aminoacid residues and can conveniently be studied by NMR[5].

Solid state NMR also provides highly specific information on local structure and transport in functional polymers for proton exchange membranes for fuel cells, or supramolecular structures for photonics. Examples of such studies will be presented for new polymeric proton conductors based on phosphonic acid[6], as well as substituted hexabenzocoronenes (HBC)[7] and perylenes[8], which are promising as active semiconductors in organic field-effect transistors and photovoltaic devices. For the processing of these materials collective motion of the residues in the column can be detected, which is particularly important for processing these materials.

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Flory award

INITIATION OF CAVITATION DURING DRAWING OF CRYSTALLINE POLYMERS

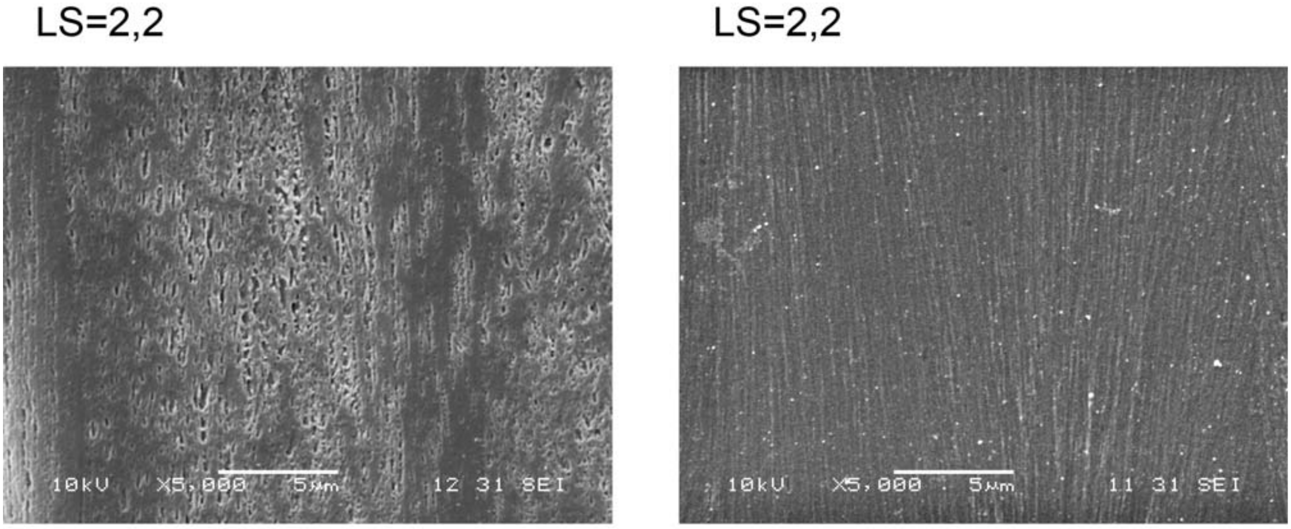
Andrzej Galeski, **Artur Rozanski**

Department of Polymer Physics , Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland
e-mail andgal@cbmm.lodz.pl

Keywords: *polypropylene, nanoclay, nanocomposite*

In crystalline polymers the cavitation occurs preferentially in amorphous layers. However, there are no information concerning the nature of the nuclei initiating cavitation and about the physical parameters of the amorphous phase that control the course and intensity of a cavitation process.

However, purified polypropylene and polyethylene using supercritical CO_2 and non-solvent extraction show more intense cavitation. PALS experiment indicated a significant increase in free volume after purification. Hence, it was anticipated that filling the excessive free volume with low molecular weight liquids it would be possible to reduce the cavitation. The modification of the amorphous phases of polypropylene, polyethylene and polyamide 6 was conducted by introduction of low molecular weight substances. Chosen liquids penetrate amorphous phases of those polymers but do not influence the crystalline phases. A gradual saturation of the amorphous phases with penetrants really leads to a decrease in the intensity of the cavitation process. With complete saturation the cavitation was completely eliminated in these materials (see Figures 1a and 1b for comparison).



Figures 1a and 1b. SEM images of etched interior of compression molded polypropylene samples deformed to the local strain of 2.2 with the same strain rate of 15%/min, a.) polypropylene untreated, b.) polypropylene with chloroform infused into its amorphous phase.

Apparently the nuclei of cavitation in crystalline polymers are thermal fluctuations of polymer's free volume and have homogenous character. When cavitation is supressed the lamellae deform without fragmentation. It follows that lamellae fragmentation is triggered by cavitation and it is not an inherent attribute of crystal yielding.

Swollen and stretched amorphous phase impresses the adjacent crystals with a force equal to the observed difference in the stress values at the yield point. That force was determined from a desorption of a penetrant for the cases of PP, PE and PA6 with fixed ends. These observations account for a decrease in the stress at yield of swollen polymers without the revision of crystallographic slip mechanisms of plastic deformation.

Flory award

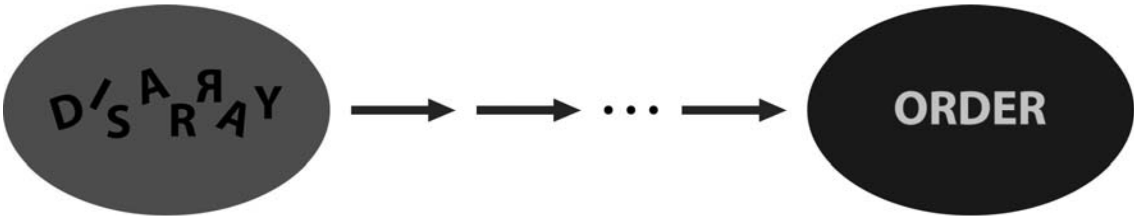
TOWARD SOFT MATTER THIN FILM DEVICES

Gero Decher

C.N.R.S. Institut Charles Sadron, 23 rue du Loess, 67034 Strasbourg, France, and
Faculté de Chimie, Univ. de Strasbourg, 1 rue Blaise Pascal, 67008 Strasbourg, France
E-mail: Decher@ics.u-strasbg.fr

Keywords: *Layer-by-layer assembly, soft matter, nano fabrication*

Materials Science has always been driven by the desire to transform matter into something more useful, even simple devices are often multi-material composites with a complex and sometimes hierarchical structure. It is evident that basic self-assembly methods will not be able to address molecular organization at this level and, as a consequence, multistep assembly procedures will need to be employed for the (nano)fabrication of such materials or devices. Layer-by-layer (LbL) assembly has, over the last years, developed into a method, which begins to enable the construction of multi-material soft-matter devices by rational design.



Since the LbL-technique allows to interface a wide variety of (bio)materials with predefined spatial arrangement, it has successfully been introduced to both materials science and applied bio-sciences. Starting with some key examples, it will be outlined where this nanofabrication technology has arrived today reviewing work from our own and from other teams. This journey will take us from examples of LbL-films containing e.g. simple polyelectrolytes and extend to films in which the composition of the film controls the interaction with living cells. Nanometric LbL-coatings can be produced on classic substrates such as silicon wafers or glass plates but also on surfaces relevant to applications such as paper, membranes or textiles. It is even possible to multi-functionalize nanoparticles using LbL-assembly, to render eye contact lenses biocompatible or to produce self-cleaning coatings on cars.

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MOLECULAR SORTING AT SURFACES: PROTEIN-POLYMER CAPTURE TO PATTERNS AND THEIR ANALYSIS

David Grainger*, David Castner, Manish Dubey,** Hiro Takahashi***

**Department of Pharmaceutics and Pharmaceutical Chemistry – University of Utah, Salt Lake City, UT 84112 USA;*
***Department of Bioengineering, NESAC/Bio - University of Washington, Seattle, WA 98195 USA*
E-mail: david.grainger@utah.edu

Keywords: *polymer patterns, surface analysis, protein immobilization*

Bioactive patterns of immobilized molecules are commonly employed in devices for assays, molecular electronics, bio-computing, and advanced molecular architectures based on affinity recognition. Surface structures of such biomolecules relies on (1) reliable surface immobilization efficiencies, (2) retention of surface bioactivity, (3) analytical tools that can provide density and bioactivity information, (4) capabilities to control multiple immobilizations of different molecules with spatial control. Many surfaces used for biomolecule capture and their exploitation are polymers,[1] used for their proven capabilities to feature both reactive chemistry for specific immobilization and unreactive background chemistry that limits non-specific reactions (noise, fouling). These surfaces can also be patterned with both photo- and mechano- lithographic means for multiplexed purposes. Characterizing the resulting patterns of surface chemistry and immobilized molecules is tedious if one seeks spatial chemical and bioactivity correlations. Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is very sensitive for surface analysis and is useful for trace element detection. With the advent of improved analyzers, imaging ToF-SIMS provides spatial distribution of different species to yield surface reactivity maps. Use of multivariate analysis, especially Principal Component Analysis (PCA), makes this technique even more powerful by differentiating regions with different chemistries. ToF-SIMS and PCA have been used to study a commercial, patterned polymer chemistry[1] with applications in diagnostics, assays, bio-chips and cell-based biosensors. The chemistry is based on N-hydroxysuccinimide (NHS) esters, widely used as leaving groups to activate covalent coupling of amine-containing biomolecules onto surfaces.

Our previously studied model system -- NHS molecules self-assembled on gold -- and XPS and ToF-SIMS were used to characterize and understand the NHS hydrolysis and regeneration at surfaces[2] on commercial poly(ethylene glycol) (PEG)-based reactive films on glass slides.[3] NHS and methoxy-capped non-reactive regions photolithographically patterned were imaged with ToF-SIMS/PCA.[3,4] NHS surface reactive zones are clearly resolved at high sensitivity despite the complexity of the polymer matrix chemistry. Surface-specific protein coupling was observed by surface-selective reaction of streptavidin with the NHS patterns.[3] Patterns of two coplanar affinity ligands (biotin and chloroalkane) were used for specific immobilization of two different proteins (streptavidin and HaloTag® enzyme). Spontaneous formation of high-fidelity surface patterns of the two proteins in a single surface exposure from their mixed aqueous solution was observed and characterized, a process termed “surface self-selection’.[5] ToF-SIMS amino acid-derived ion fragment yields, summed to produce surface images, can reliably correlate patterned surface regions to bound proteins, but cannot readily discriminate different proteins. However, PCA of ToF-SIMS data improves discrimination of ions specific to each protein, facilitating surface pattern discrimination based on protein type – either HaloTag or streptavidin. ToF-SIMS imaging also detects regions where trace UV-exposed photoresist residue remained, despite no previous reports for residue detection, reflecting the sensitivity of the analytical technique.[4,5] Most recent work is focused on use of PCA to discriminate protein orientation at surfaces, specifically for patterned antibodies.[6]

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THE QUEST FOR MOTILITY: MAKING POLYMERS SWIM

Anthony J Ryan, **Richard A L Jones, Paul D Topham, Jonathan R Howse**

Department of Chemistry, The University of Sheffield, Brookhill, Sheffield S3 7HF, United Kingdom
E-mail: tony.ryan@shef.ac.uk

Keywords: *nanotechnology, polymer devices, motility*

The first wave of polymer nanotechnology has concerned itself with what is in effect an incremental continuation of long-existing trends in materials science, in which ever-greater control over the nanoscale structure of materials leads to better properties and more functionality. Modern materials rely on being able to control both interfacial structure and grain boundaries in order to develop improved properties. Functional materials for electronics and photonics are changing the way we live and modern materials can enhance our lives further through medical applications of nanotechnology. What is now at issue is the form a second wave of nanotechnology might take – one in which attention is focused, beyond simple materials, to fully functional nanoscale devices.

What might such functional nanoscale devices look like? There are (perhaps unfortunately) plenty of futuristic science-fiction visions of nano-assemblers and nanoscale submarines to be found in newspapers and on television, but what these have in common is a total neglect of the way the laws of physics work at the nanoscale and the constraints this puts on the design of devices. (For a gallery of rather more realistic nano-images and short films which aim to explain nanotechnology to a broad audience, see http://www.nanofolio.org/images/gallery05.php.)

One piece of classic nanotechnology iconography seems unshakeable in its appeal: the tiny submarine that first appeared in the film *Fantastic Voyage*. But why is this dream so enduring? Obviously human beings are captivated by the idea that they can live long and healthy lives, and science, technology, and medicine mean that people are living longer. There is something very attractive about the science-fiction story of a device that swims around the body with the capability to do cell-by-cell surgery. Of course, the science-fiction vision remains entirely unrealistic, but the creation of a device that is able to propel itself is a very attractive target for experimentalists. Herein we review work at The University of Sheffield that aims to create such a device.

We have built polymer vesicles that are all the same size[1] and we can fill them with a payload for delivery into a cell[2,3]. We have built a synthetic muscle that generates forces[4,5] but we cannot yet fit it into the capsule. We have developed a different strategy to propel particles[6] – and found something that swims patterns just like a bacteria.

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MICROFOAMING OF POLYMERS BY SUPERCRITICAL CO_2 TECHNIQUE

Jian Yu, Wentao Zhai, Jiasong He

Key Laboratory of Engineering Plastics, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
E-mail: hejs@iccas.ac.cn

Keywords: *Microcellular polymer, supercritical carbon dioxide, multi-component polymer system*

Microcellular polymers, foamed by using supercritical CO_2 as a foaming agent, possess excellent material properties. Diffusion of CO_2 molecules into polymers results in the increase of mobility of macromolecular chains and segments, which mainly occurs in amorphous region of the polymer. After CO_2 saturation in the polymer a microfoaming process occurs by quick depressurization or temperature increase, which brings about the changes of material properties. The large amount of microcells (cell density above 10^9 cells/cm^3) of size smaller than 10 μm decrease the weight of plastic parts without impairing their mechanical properties[1,2]. This talk overviews the research results accumulated in the authors' laboratory in the aspects of mass transfer behaviour of CO_2 in polymers, evolution of cell structure during foaming process, and microfoaming behaviour of multi-phase/multi-component polymer systems.

Except for the well-known factors such as temperature, pressure and polymer characteristics, the introduction of ultrasonic irradiation affects the dissolution and diffusion of CO_2 in polymers[3], and the modified interface does as well[4]. The microstructure of microcells such as cell density[3,5,6], cell size and material expansion ratio[6] was correlated with and controlled by the nucleation, growth and coalescence of cells[7]. Microstructure of multi-component polymer materials such as miscible[8], partially miscible[9] and immiscible blends[4,8,10,11], nano-composites[12] and crystalline polymers[13,14] was controlled by long-chain branching, crosslinking, grafting, nanoparticle filling, blending, crystallization, and adding outer energy field utilized at different stages of polymer microfoaming. Microcellular polymer systems with potential applications were explored such as microcellular composites with biomimetic structure[11,15,16], microcellular polypropylene[17], and ultrasound-aid microfoaming technique[17].

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RING-OPENING METATHESIS POLYMERIZATION DERIVED MATERIALS FOR HETEROGENEOUS CATALYSIS, SEPARATION SCIENCE AND TISSUE ENGINEERING

Michael R. Buchmeiser

**a. - Lehrstuhl für Makromolekulare Stoffe und Faserchemie, Institut für Polymerchemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart, b. – Institut für Textilchemie und Chemiefasern, Deutsche Institute für Textil- und Faserforschung, Körschtalstr. 26, D-73770 Denkendorf*
E-mail: michael.buchmeiser@ipoc.uni-stuttgart.de

Keywords: *ring-opening metathesis polymerization, heterogeneous catalysis, separation science*

Ring-opening metathesis polymerization (ROMP) of cyclic olefins with high ring strain such as norborn-2-ene (NBE) and cyclooctene (COE), can be accomplished in a truly living manner with the aid of well-defined Schrock- and Grubbs-type initiators.[1-4] The copolymerization of NBE or COE with polycyclic di- or trienes, e.g., tris(norborn-5-ene-2-ylmethyl)methylsilane or tris(cyclooct-4-ene-1-yloxy)methylsilane allows for generating cross-linked beaded polymers in a precipitation polymerization setup.[5-7] Alternatively, the copolymerization can be accomplished within the confines of a certain device in the presence of a mixture of suitable poor and good polymer solvents acting as macro- and microporogens. There, cross-linked, monolithic matrices form under phase separation conditions. Under certain synthetic conditions, these monoliths are characterized by transport channels >1 μm in diameter and by virtually non-porous, structure-forming monoliths. Due to the lack of micro- and mesopores, diffusion from a liquid (mobile phase), which can be pumped through these porous supports, to the polymeric support and back is very fast and only eddy diffusion is present. Additionally, the back pressures are low (<20 bar) even at high linear velocities (20 mm/s). Alternatively, monolithic supports with a continuous or discontinuous micro- and mesopore distribution can be prepared in a way that diffusion-related restrictions in mass transfer from the liquid to the solid and back are still low. The advantage of such supports is that they offer a higher specific surface area, particularly important for the fast separation of small molecules. In terms of functionalization of such supports, ROMP provides a straight forward access. Taking advantage of the living polymerization character and of the fact that the initiator-terminated polymer ends accumulate at the phase boundaries, a simple addition of functional monomer to the monolithic support that still contains the living initiator termini results in the formation of surface-grafted polymer chains carrying the functional groups of interest.[1,2]
This presentation will address the basic concepts and then provide recent examples of applications of functional monolithic supports in the areas of separation chemistry[8,9] and molecular heterogeneous catalysis.[10,11] Finally, the synthesis of unfilled and nanoparticle-reinforced supports as scaffolds from biodegradable monomers and their use in regenerative medicine will be presented.[12,13]

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RECENT ADVANCES IN TWO-PHOTON STEROLITHOGRAPHY

Kwang-Sup Lee, Jinsoon Park, Kyung Kook Jang, Prem Prabhakaran

Department of Advanced Materials, Hannam University, 305-811 Daejeon, South Korea
E-mail: kslee@hnu.kr

Keywords: *Two-Photon Polymerization, Lithographic Microfabrication, Spatial Resolution.*

One of the important nonlinear optical properties is two-photon absorption (TPA) in which some molecules can absorb simultaneously two photons, when irradiated by intense laser pulses. The rate of TPA scales quadratically whereas the rate of one-photon absorption linearly increase with the intensity of the incident radiation. The rate also depends upon the TPA cross-section of the molecule. TPA materials with a large cross-section can be utilized for photonic and bio applications such as for two-photon-excited fluorescence microscopy, optical power limiting, three-dimensional optical data storage, photodynamic therapy and two-photon induced biological caging studies.[1,2] To expand the utility of TPA materials, the enhancement of TPA activity by the increase of the chromophore number density is required. For this purpose, various conjugated molecules have been synthesized in our lab (Figure 1). In addition, most two-photon absorption (TPA) compounds based on pi-conjugated double bond presented a problem of reduction in TPA activities due to the quenching of fluorescences resulting from the formation of pi-complex by the chromophore-chromophore interaction. To solve such problem, we have also developed site isolated dendrimers and J-aggregated molecules. In this presentation, TPA activities evaluated by both nonlinear transmission experiments and two-photon excited fluorescence measurements of above materials will be reported.

Also, considerable efforts focusing on two-photon polymerization (TPP) have been put forth in the area of two- and three-dimensional (2D and 3D) nano/ microfabrication for the development of new conceptive nano/micro-devices.[1-5] Since TPP first came out as a novel technique over a decade ago, a great number of diverse micro-objects have been fabricated using TPP with a variety of effective two-photon chromophores. In TPP, when a near-infrared ultrashort-pulsed laser is closely focused into a volume of photocurable resins, real 3D microstructures can be fabricated using a layer-by-layer accumulating technique; therefore, TPP is considered to be a promising technique for 3D nano/ microfabrication (Figure 2). Recent reports have shown that the spatial resolution of TPP is achieved at approximately the sub-100 nm scale over diffraction limit of incident light. However, a few studies have been carried out especially based on improving the fabrication efficiency and precision of TPP. In this presentation, we report our attempts to improve the fabrication efficiency of nano/ microfabrications based on TPP.

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RING-OPENING POLYMERIZATION OF LACTONES

Helmut Ritter, **Jiawen Zhou, Olga Jazgewitsch**

Heinrich-Heine-Universität, Institut für Organische Chemie und Makromolekulare Chemie, Universitätsstr 1, 40225 Düsseldorf, Germany
E-mail: H.Ritter@uni-duesseldorf.de

Keywords: *Ring opening polymerisation; lactones, networks, shape memory*

Ring-opening polymerization (ROP) of lactones has been widely investigated in recent years.[1] 3,5,5'-Trimethylcaprolactone (TMCL-1) and 3,3',5-trimethylcaprolactone (TMCL-2) are two lactones which are not sufficiently investigated. The ROP of them affords new challenges to the chemists. The lactones can be obtained as an isomer mixture through hydrogenation of isophorones and subsequent Baeyer-Villiger-oxidation. The ability of this lactone mixture has been investigated.[2]

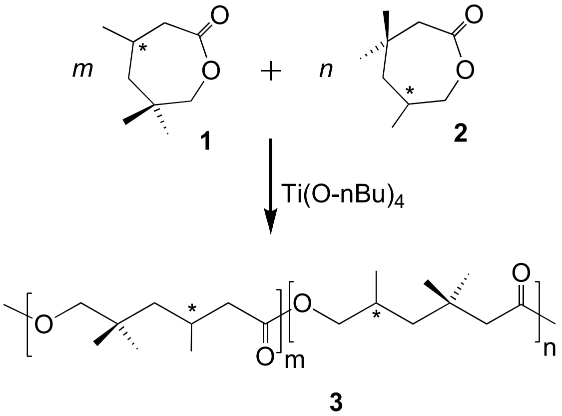

Fig. 1: Lactone polymerisation

Unsaturated polyesters are of high scientific interest and commercial importance for decades. They are preferently obtained via polycondensation reactions of diols with maleic anhydride. Another way to synthesize unsaturated polyesters is the ROP of methylene lactones. The polymerization and copolymerization of α-methylene-γ-butyrolactone with ε-caprolactone has been investigated.[3] The unsaturated polyesters were radically cross-linked with methacrylates to obtain elastic bicomponent networks with shape memory effect. Unlike conventional shape memory polymers, the new material is transparent, rubbery, and can be tailored to various transition temperatures by macromolecular engineering.

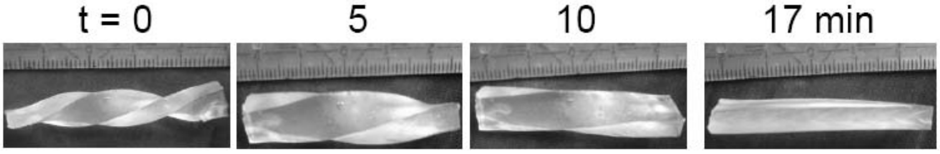

Fig. 2: Shape memory behaviour of polylactone networks

Finally, some recent results about polyesters bearing cyclodextrins via click chemistry are reported.

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METALLOCENE CATALYZED POLYOLEFINS FOR IMPROVING THERMAL AND MECHANICAL PROPERTIES OF BITUMEN BLENDS

Spadaro Chiara, Plummer Christopher J.G., Månson Jan-Anders E.

Laboratoire de Technologie des Composites et Polymères (LTC) – École Polytechnique Fédérale de Lausanne (EPFL),
Address: LTC-IMX-STI, Station 12, EPFL, CH-1015, Lausanne, Switzerland
E-mail: chiara.spadaro@epfl.ch

Keywords: *metallocene, LLDPE, bitumen.*

Bitumen is a complex viscoelastic material used as a binder in applications ranging from road paving to waterproof membranes for roofing [1]. In such applications, bitumen is often blended with a polymer in order to improve its elasticity. The resulting polymer modified bitumens (PMBs) also generally show improvements in thermal and fatigue cracking resistance, and temperature susceptibility [2, 3]. A wide range of polymers have been used in PMBs, including thermoplastic elastomers, thermoplastics and thermosets [1], but among the most successful are styrene-butadiene-styrene (SBS) block copolymers, in which the polystyrene blocks provide cohesive strength and the rubbery polybutadiene blocks provide elasticity [3]. Because SBS is relatively expensive, the possibility of mixing bitumen with other polymers remains of interest [2-4] and metallocene-catalyzed linear low density polyethylenes (m-LLDPE) have recently been discussed as a possible alternative, combining low cost and elasticity with improved storage stability compared with conventional polyolefins [5, 6].

In the present study, PE/octene and PE/butene based m-LLDPE copolymers with different melt flow indices, glass transition temperatures, melting temperatures and degrees of crystallinity have been used to modify a roofing grade gel bitumen. The morphology, the thermal behaviour and the viscoelastic properties of the PMBs have been studied in the composition range 5 to 50 wt% m-LLDPE. In the case of the butene-based copolymer, fluorescence microscopy indicated a continuous m-LLDPE-rich phase matrix containing discrete asphaltene-rich domains at all polymer contents, although at 5 wt% of the octene-based copolymer; the continuous phase remained asphaltene-rich, and there was some evidence for phase inversion, the discrete m-LLDPE-rich domains containing additional asphaltene-rich domains. It follows that the melt rheological response of the PMBs was dominated by the m-LLDPE, but the excellent flow characteristics of this latter resulted in relatively modest increases in shear viscosity compared to those obtained with equivalent concentrations of SBS. Significant swelling by the maltene-rich components of bitumen led to a decrease of the melting point of both types of m-LLDPE, although the degree of crystallinity relative to the polymer content increased somewhat at low m-LLDPE concentrations. Time temperature superposition was used to provide an indication of the dynamic viscoelastic response in shear over a wide range of frequencies. The pure bitumen exhibited liquid-like behaviour over the entire temperature and frequency range investigated, the loss modulus, *G"*, generally being significantly higher than the storage modulus, *G'*. However, whereas blending with the relatively crystalline octene-based m-LLDPE resulted in more elastic behaviour (*G'* greater than *G"*) the less crystalline butene-based m-LLDPE showed a crossover in *G'* and *G"* for all the concentrations investigated. The crossover frequency was found to shift towards lower frequencies as the m-LLDPE content increased, suggesting it to be possible to fine tune the viscoelastic response, depending on the required end-properties. In view of the relative stability of the PMB microstructures referred to above, these results confirm the promise of m-LLDPE as additives to gel bitumen, and suggest there to be considerable flexibility in the range of m-LLDPE contents that may be envisaged, without compromising processing requirements. The consequences for applicative properties will be discussed.

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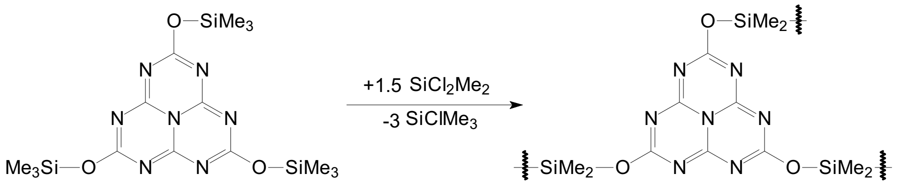
SYNTHESIS AND CHARACTERIZATION OF POLYMERIC SILYL-CYAMELURATES VERSUS SILYL-CYANURATES

Nadia E. A. El-Gamel*, Marcus Schwarz, Erica Brendler,** Edwin Kroke**

**Chemistry Department, Faculty of Science, Cairo University, 12613 Giza, Egypt.*
***Institute of Inorganic chemistry. Technical University of Freiberg, 09596 Freiberg, Germany.*
E-mail: nadinealy@hotmail.com

Keywords: *s-triazine, s-heptazine, chlorosilane.*

The synthesis of organc–inorganic polymer hybrids has been widely investigated and has received a growing interest.[1] This is due to many interesting properties, which arise from the combination of organic and inorganic components. s-Triazine and tris-s-triazine (heptazine) derivatives have recently gained attention due to interesting thermal and optical properties.[2] In this study we report the combination of s-triazines and s-heptazine units with polymeric siloxane chemistry. Herein we represent a novel hybrid type, which may be considered as ‘‘trigonally expanded silica, silsesquioxanes and siloxanes’’. The synthesis is based on the elimination of Me_3SiCl similar to the formation of Si–C–N and B–C–N gels upon reactions of chlorosilanes and trichloroborazine with bis(trimethylsilyl)carbodiimide.[3]



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Tris(trimethylsilyl)cyamelurate and tris(trimethylsilyl)cyanuratesilylcyamelurate[4] were used as precursors for exchange reactions with chlorosilanes. We prepared ‘‘expanded dimethylsiloxane’’ polymers via exchange reactions of dichlorodimethyl silane with the mentioned precursors. Afterwards several trials were done in order to prepare network structures which have stronger cross-links, using $SiCl_4$ and $MeSiCl_3$, surprisingly instead of obtaining potentially crystalline covalent porous network structures, the reactions turned out to generate gels. After gelation the gels were stored at room temperature for four weeks. Only minor linear shrinkage in the range of 10% and little syneresis was observed during this ageing period. All manipulations were performed under inert atmosphere using standard Schlenk techniques or in a glovebox. The obtained Xerogels were characterized by FT-IR and ^{29}Si-NMR. They were analyzed with respect to their structure and morphology using XRD, EDX, HR-SEM and HR-TEM. Specific surface areas were determined and calculated using the BET model. XRD measurements gave no indication for the presence of any crystalline phases. This result was confirmed by HR-TEM. FTIR spectra of all the prepared xerogels clearly indicate the presence of Si–O units showing characteristic absorption bands between 1000 and 1100 cm^{-1}. Further bands at 1262(vs) cm^{-1} and around 2830 to 3000(w) cm^{-1} are attributed to Si–CH_3 units. Relatively weak absorption bands around 604 cm^{-1} and at 530– 534(m) cm^{-1} was attributed to Si–Cl vibrations indicating the presence of chlorine in the products. EDX examinations show that relatively low chlorine concentrations (ranged from 1.5 to 3.5 mass %) are present in the xerogels. A basic feature of the products is an alternating arrangement of the heterocylic unit (C_6N_7 or C_3N_3) and the inorganic or organometallic SiO-motives. With respect to the analytical techniques; the gels are based on three-dimensionally cross-linked networks, comprised of linear and ringlike features as well as branched units while the number of Si–Cl and $OSiMe_3$ end groups and therefore the degree of cross-linking varies depending on the trimethylsiloxy-precursor, the chlorosilane and the reaction conditions (T, c etc.).The new inorganic–organic hybrid materials might show potentially useful, ceramic forming, metal coordination, or ion exchange properties.

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ELECTROSPUN NYLON FIBERS: A CHEAP AND EFFECTIVE FILLER FOR POLY(ε-CAPROLACTONE)

Valerio Causin*, Ramesh Neppalli*, Carla Marega*, Antonio Marigo*, Roberta Saini*, Madhab Prasad Bajgai, Hak Yong Kim****

** Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, 35131 Padova, Italy*
*** Department of Textile Engineering, Chonbuk National University, 561-756 Jeonju, South Korea*
E-mail: valerio.causin@unipd.it

Keywords: *polycaprolactone, electrospinning, composites*

The use of fibers to reinforce polymeric matrices is well known in the academia and in the industry. Addition of glass or carbon fibers allowed to obtain high-performance materials in a variety of applicative fields. The diameter of such fibrous fillers normally exceeds the tens of micrometers, therefore producing microcomposites, when dispersed in a polymeric matrix. The idea at the basis of the production of nanocomposites is that, decreasing the size of the dispersed filler, a large increase in interfacial area can be attained, thus largely changing the macroscopic properties of the material. As a consequence, it is of interest to be able to decrease the diameter of fibrous reinforcements, in order to further improve their effectiveness. Due to the possibility of obtaining fibers of small size, electrospinning attracted a huge interest in the research community, as testified by the ever increasing scientific literature on the subject. Most of these reports are focused on the use of nanofibers in fields such as nanocatalysis, tissue scaffolds, protective clothing, filtration, and optical electronics. It is very surprising, though, that very few works exist on the use of such fibers as fillers in polymer-based composites.[1,3]

In this communication, a fabrication approach is presented that allows to prepare composites based on polycaprolactone (PCL) filled with nylon 6 nanofibers by compression moulding. PCL was chosen as a matrix because it is a very attractive biodegradable and biocompatible material, although not with outstanding physical mechanical properties. The possibility to improve the performance of such material could open a wide array of possible applications, also allowing the substitution of some less environmentally friendly materials. Care was taken to use a small amount of nylon fibers, since the availability of electrospun nanofibers on a large scale is still difficult, and also to avoid possible problems in the waste management of the materials.

At very low filler contents (3%), the obtained composites exhibited improved stiffness (+ 51% modulus) with a simultaneous increase in ductility (+29% elongation at break), differently from what is usually found in PCL nanocomposites with a variety of fillers, in which increases in modulus happen at the expense of elongation at break. The presence of fibers with a very small diameter, typical of the products of electrospinning favored a good interfacial adhesion between matrix and filler. Although the increases in tensile properties were not spectacular in magnitude, very encouraging indications for future improvements emerged from this work:

- decreasing the diameter of the fibers will most likely bring about a more effective reinforcement: the finest fibers were the ones that best adhered to the matrix;
- by this approach it is possible to simultaneously increase modulus and elongation at break, a quite difficult task with traditional nanofillers like montmorillonite clay or carbon nanotubes;
- being of a similar order of magnitude than polymer lamellae, electrospun fibers can be used to shape the morphology of lamellar stacks, and therefore the final properties of the composites.

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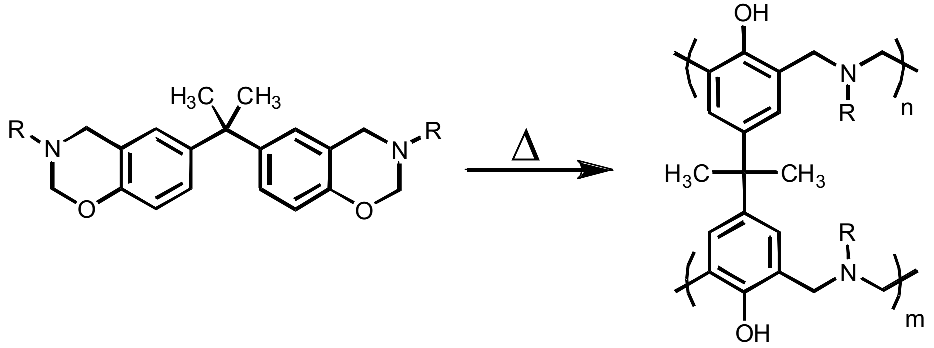
SYNTHETIC STRATEGIES TO COMBINE HIGH PERFORMANCE BENZOXAZINE THERMOSETS WITH POLYMERS

Baris Kiskan, Yusuf Yagci

Istanbul Technical University, Department of Chemistry, 34469, Maslak, Istanbul, Turkey.
e-mail: yusuf@itu.edu.tr

Keywords: *Benzoxazine, polybenzoxazine, thermosetting, cross-linking, ring-opening*

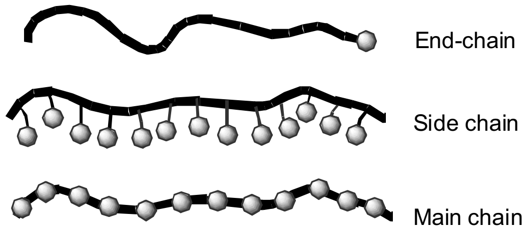
Polybenzoxazines are a relatively new class of versatile materials that can be used in many fields, such as electronics and aerospace industries, because they have a good combination of attractive properties. These include nearly zero shrinkage upon curing, thermal stability, and chemical resistance. Polybenzoxazines formed by thermally activated ring-opening of the corresponding benzoxazines without any catalyst and without generating any by-products (Scheme 1).



Scheme 1

Moreover, benzoxazine monomers can be prepared simply from inexpensive and commercially available phenols, primary amines and formaldehyde. Therefore, the chemistry of benzoxazine synthesis offers a wide range of molecular design flexibility by using appropriate starting materials and polybenzoxazine properties can be tailored[1]. However, until recently almost all benzoxazine studies were concerned with the polybenzoxazines prepared from the precursor monomers. This brings some limitations on their use in practical applications. The monomers are usually powder and processing into thin films is rather difficult. We have reported on several synthetic strategies to combine benzoxazine structures with conventional polymers, namely polystyrene, poly(ε-caprolactone), poly(methyl methacrylate) and poly(propylene oxide). The polymers containing one or two benzoxazine functionalities per chain can undergo thermally activated ring-opening copolymerization with low molar mass benzoxazines to yield cross-linked polybenzoxazines with dangling chains. Aiming at expanding their industrial applicability, it seemed appropriate also to prepare a family of highly flexible benzoxazine polycondensates, tailored to meet different requirements, depending on the specific application. Our working concept is based on creating polymeric backbones integrating segments that induce molecular flexibility, and that comprise thermally curable benzoxazine moieties either in the main chain or side chain[2] (see Figure 1).

Figure 1



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SYNTHESIS AND DENTAL APPLICATION OF NOVEL HYDROLYSIS STABLE ADHESIVE MONOMERS

Joachim E. Klee, **Uwe Lehmann**

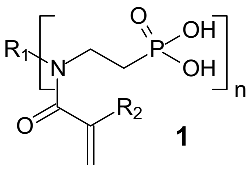
DENTSPLY De Trey, De-Trey-Str. 1, 78467 Konstanz, Germany
E-mail: joachim.klee@dentsply.de

Keywords: *stable adhesive monomers, dental application*

The successful dental treatment of lesions requires for fixation of direct or indirect restorations a dental adhesive. In the middle of 80th of the last century the first adhesives were composed of three-part systems. The systems consisted of an etch gel, a primer and a bonding. In order to reduce the complexity of the adhesives during application and to make the adhesion procedure more safe, robust and convenient new generations of adhesives have been developed. These generations combine either the prime and the etch function or the prime and the bond function. Today the one-part self-etching adhesives which combine all three steps of adhesive procedures in one are demanded. This kind of new adhesives shall contain polymerizable monomers, acidic monomers and water. Because of the fact that common ester monomers are prone to hydrolysis under these conditions novel hydrolysis stable monomers with and without acidic function were needed.

In the past years several new approaches to hydrolysis stable monomers on basis of (meth)acrylamides [1-8] and 2-oxamethyl acrylic acid esters with phosphonic acid moieties [9], phosphoric acid [10] and sulfonic acid groups [11] as well as carboxylic acid groups [11] have been developed.

Now we have synthesized novel hydrolysis stable acidic monomers **1-4** on basis of acrylamide, 2-oxamethyl acrylic acid esters and allyl compounds with sulfonic, phosphonic or phosphoric acid moieties.



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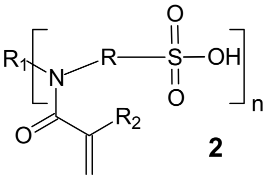

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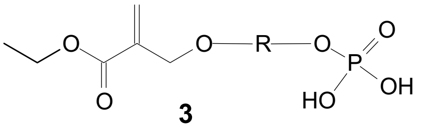

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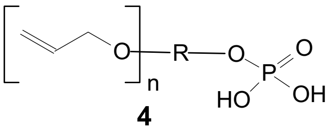

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Acidic monomers **1-4** show an improved hydrolytic stability compared to carboxylic esters. Their stability decreases in the order of acrylamide > methacrylamide > methacrylester. Acrylamides **1** show a higher polymerisation enthalpy ranging from -50 to -70 $kJ \cdot mol^{-1}$ per double bond compared to (meth)acrylamides which show -8.57 to -25.1 $kJ \cdot mol^{-1}$ per double bond only. The acidic monomers **1** exhibits a polymerisation enthalpy of 29.3 to 53.2 $kJ \cdot mol^{-1}$ which is slightly lower than the one of methacrylic esters.

The usage of the acidic monomers **1-4** in a one-part self-etching system provides an adhesion to dentin and enamel of at least 15 MPa.

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NEW POLYSULFONES: SYNTHESIS, CHARACTERIZATION, PROPERTIES

Gorbunova Marina*, **Vorob'eva Antonina****

** Institute of Technical Chemistry Ural Branch of Russian Academy of Sciences, Korolev st., 3, 614013, Perm, Russia*
*** Institute of Organic Chemistry Ufa Scientific Centre of Russian Academy of Sciences, Octyabrya pr., 71, 450054, Ufa, Russia*
E-mail: mngorb@newmail.ru

Keywords: *radical polymerization, allyl monomers, polysulfones*

The interest in the purposive synthesis of polyfunctional polymers is growing steadily. It is conditioned by a wide set of the useful properties of these polymers [1, 2]. Among allyl monomers only quaternary salts of diallylammonium found an application as monomers for the synthesis of polyfunctional polymers [3]. Therefore, a task of creation of the polymers based on new allyl monomers, is a quite topical one. N-allyl derivatives of hydrazine, diethylaminoguanidine, aminophosphonium salts are promising as monomers from this point of view.

Allyl compounds, destinguished by a tendency to degradative chain transfer to the monomer, are known to exhibit low activity in reactions of radical polymerization [4]. However, it was determined, that new monomers – *N,N*-diallyl-*N'*-acylhydrazine, 2,2-diallyl-1,1,3,3-tetraethylguanidiniumchloride, tris(diethylamino) diallylaminophosphonium tetrafluoroborate and chloride are active at copolymerization with sulphur dioxide, exhibiting high electron-acceptor activity. A study of copolymerization of new monomers with SO_2 showed the content of copolymers obtained to be of no dependence on the monomers ratio, reaction conditions - temperature, nature of initiator, medium, polymerization degree and to correspond to monomer:SO_2 ratio 1:1. Composition constancy regardless of the monomer ratio in the reaction mixture allowed to suppose, that copolymerization of these new monomers with SO_2 proceed via formation of the complexes, that was justified by UV- and NMR–spectroscopy data.

A study of kinetic regularities of copolymerization of new allyl monomers with SO_2 showed an extremal dependence of reaction rate on the monomer ratio to be observed. The maximum rate was observed at equimolar ratio of monomers. Deviation of the comonomers ratio from equimolar both to higher and lower values of one of comonomers results in reaction rate reduction, the fact being explained probably by the change of the reactive complex concentration in the system.

Analysis of polysulfone spectra shows these new monomers to copolymerize with SO_2, both double bonds participating, with formation of cis-, trans-stereoisomeric pyrrolidine structures in cyclolinear polymer chain. Cyclolinear copolymers obtained are soluble owing to intramolecular cyclization of allyl monomers when formation of the polymer chain and to the absence of intermolecular crosslinks.

Physico-chemical and biological properties of the polysulfones have been investigated. It was determined, that polysulfones on the basis of *N,N*-diallyl-*N'*-acylhydrazines have a high flocculating activity at precipitation of $Cu(OH)_2$. All the polysulfones are nontoxic (the LD_{50} values were more 1000 mg kg^{-1}) and can be used for medicine aims. The studies on antibacterial activity showed that the polysulfones of 2,2-diallyl-1,1,3,3-tetraethylguanidiniumchloride, tris(diethylamino) diallylaminophosphonium tetrafluoroborate and chloride have a pronounced antimicrobial activity with respect to gram-positive microflora. Becides that, polysulfones showed protection effect of gastric ulcers on chosen model (indometacine), ulcer quantity reduces in times as compared with control. This clearly confirms that polysulfones obtained can be used in medicine and biotechnology.

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BIOPOLYMER COMPLEXES OF Fe(III)-PORPHYRIN: SYNTHESIS AND CHARACTERIZATION

Nazym Zhunusbekova,[*] **Dolgova N.A.**,[*] **Berdykulova K.A.**,[**] **Jumadilov T.K.**,[*] **Bekturov E.A.**[*]

**Department of synthesis and physical chemistry of Polymers - Institute of Chemical Sciences named A.B. Bekturov, Sh. Ualikhanov str. 106, 050010, Almaty, Kazakhstan,*
***K.I.Satpaev's Kazahk national technical University, Satpaev str. 22, 050013, Almaty, Kazakhstan*
Email: znazym@mail.ru

Keywords: *biopolymers, porphyrin, hydrogel*

In recent years much attention has been focused on artificial carriers based on porphyrins. Porphyrins are π-conjugated macrocycles, which play a vital role in living organisms. They are parts of many enzymes, vitamins, the crucial role of porphyrins in hemoglobin or chlorophyll is generally known. In all these systems, porphyrins are present as metal complexes. Metal complexes of porphyrin are used as photosensitizes for photodynamic therapy of tumors because of their interaction with DNA[1]. The catalytic capabilities make them useful as catalyst in many reactions[2].

In our study, the polymer was modified with porphyrins by coordination interactions. For this purpose porphyrin was extracted from plant raw materials[3]. The metal ions Fe^{3+} were used for metalloporphyrins obtaining. In this contribution we will report about capabilities of interpenetrating networks based on biopolymers to fix the metal complex of the nature porphyrin. For this aim the interpenetrating polymer networks (IPN) based on agar-agar (Ag-Ag), chitosan (Chs) and synthetic polymers polyethyleneimine (PEI), polyacrylic acid (PAAc) have been developed to determine their swelling and complex-formation kinetics at various time and Fe (III)-porphyrin concentrations.

IPN were synthesized by radical polymerization at 70°C. The structure and composition of Chs-PAAc IPN were determined by FT-IR spectra. The new bands at 1731 $cm^{-1}$and 1654 cm^{-1} which correspond to C=O and amide groups, respectively, formed between the NH_2 group of polysaccharide and COOH group of PAAc, have been observed in the modified Chs spectrum. These typical absorptions confirm that PAAc has been successfully crosslinked onto the Chs backbone. The synthesis of the IPN matrix has been carried out in order to determine its swelling kinetics and complexformation properties relation to Fe (III)-phaeophytin. The method of extraction of porphyrin, swelling and adsorption ability of matrix as well as a binding degree of interpenetrating polymer networks with Fe (III)-phaeophytin were described.

The results of the swelling and complexformation study showed that the counteraction of the swelling degree suggests that specific interactions between the Chs network loaded with PAAc and the Fe (III)-Php are stronger compared to the interactions that occur with the polymeric network based on Ag-Ag and PEI. High efficiency of immobilization on IPN matrix based on Chs-PAAc (91%) was achieved.

It was estimated that the best results of the immobilization of Fe (III)-phaeophytin were achieved when the porphyrin concentration is 2.5×10^{-4} mol/l. In this case, the amount of adsorbed Fe (III)-phaeophytin is approximately 0.0013-0.0015g on Chs-PAAc sample. It was noticed that this IPN based on Chs and PAAc was a better fit for immobilization in comparison with IPN based on Ag-Ag and PEI where binding degree was 32% and amount of adsorbed porphyrin equaled 0.0002 g. This phenomenon may be explained by rigidity of a natural Ag-Ag chain. Furthermore, it was observed that because of special properties of modified Chs, the immobilized Fe (III)-phaeophytin had particularly good stability in time. The quantitative determination of interactions between porphyrins and IPN were achieved by UV-vis spectroscopy by analyzing of a liquid over the hydrogel. From the obtained experimental data one can conclude that complex formation between porphyrin and IPN has a difficult character, and can be achieved by different mechanisms.

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EFFICIENT “ELECTROCLICK” AND OTHER, ORTHOGONAL “CLICK” METHODS IN DEVELOPMENT OF CHALLENGING BIOPOLYMER MATERIALS

Søren Hvilsted

Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Technical University of Denmark, Building 423, DK-2800 Kgs. Lyngby, Denmark
E-mail: sh@kt.dtu.dk

Keywords: *interdigitated PEDOT electrodes; cholesteryl L-lysine dendron.*

The copper catalyzed cycloaddition (CuAAC) of alkynes and azides has matured resulting in new avenues for preparation of unsurpassed functional soft materials.[1,2] In this line novel azide containing, conductive (co)polymers based on poly(3,4-(1-azidomethylethylenedioxythiophene)) (PEDOT-N_3) have been prepared.[3,4] This enables introduction of new functionalities onto the conductive polymer. The CuAAC on the insoluble conductive polymer was optimized using a fluorescent alkyne. The modularity of the approach has been exploited in attempts to prepare new conductive polymers for all polymer micro sensors. Various potential receptors such as 12-crown-4 ether, biotin, or ferrocene have been covalently clicked to the surface. In a further development, it will be demonstrated that the reaction can be localized spatially and selectively on either of a pair of interdigitated electrodes. The conducting polymer microelectrodes can electrochemically generate the catalyst required for their own functionalization by ”click chemistry” with high spatial resolution. Through control of the applied potentials the electrodes are selectively functionalized in sequence by two alkyne-modified fluorophores. For this method we chose the term “electroclick”.[5]

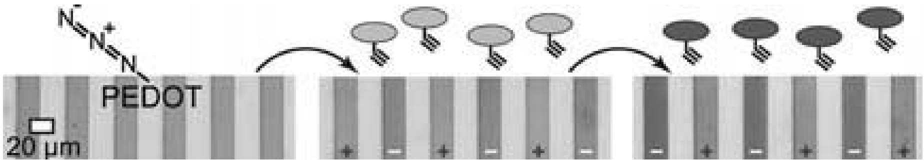

Figure 1. Sequencial functionalization of interdigitated electrodes by “electroclick”.

Another theme takes inspiration from the claim that a cholesterol rod combined through a oligo(L-lactide acid) coil to a L-lysine wedge (dendron) can interact with the cell membrane and thereby facilitate cell adhesion.[6] In addition, poly(L-lysine) seems to play a role as a functional vector for DNA transfection.[7] Therefore, the second example demonstrates the modular approach for construction of such rod-coil dendrons, where a hetero-bifunctional poly(ε-caprolactone) (PCL) plays the initial and central role as facilitator for orthogonal “click” chemistry. Alkyne and alkene terminal functionalities in this case are introduced through 5-hexyn-1-ol initiation of the ROP of CL[8] and subsequent esterification of the hydroxyl chain end with 4-pentenoic acid according to a Mitsunobu protocol. An L-lysine dendron is easily constructed by first esterifying BOC-protected L-lysine with 3-bromo-1,2-propanediol followed by conversion of the focal bromo-functionality to an azide (second generation L-lysine Dendron$_{G2}$). The PCL is then coupled (“clicked”) with the L-lysine Dendron$_{G2}$ through Cu(I) alkyne-azide 1,3-cycloaddition (CuAAC). The cholesteryl moiety was finally introduced in a UV-catalyzed (365 nm) thiol-ene “click” reaction between the alkenyl-PCL-*b*-(di-BOC-L-lysine)$_{G2}$ and thiocholesterol. The target cholesteryl-PCL-*b*-(L-lysine)$_{G2}$ was then obtained after deblocking the amine functionalities with trifluoroacetic acid. The imperative efficiencies of all synthetic steps were carefully monitored and verified by SEC, and NMR and MALDI-TOF spectroscopies.

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HIGH PERFORMANCE POLYMERIC FLOCCULANTS- MICROWAVE ASSISTED SYNTHESIS

Ram Prakash Singh*, Sagar Pal**

** Indian Institute of Science Education and Research, Pune-411008, India.*
*** Department of Applied Chemistry, Indian School of Mines, Dhanbad-826004, India.*
E-mail: singh.prakash.ram@gmail.com

Keywords: Polysaccharide, Microwave

Polysaccharides are inexpensive, biodegradable and shear stable; low efficiency flocculants used at high doses. On the other hand polyacrylamide based flocculants used in wastewater and industrial effluent treatments are highly efficient at low doses, fragile and expensive. A new generation of flocculants have been developed by optimally grafting polyacrylamide branches on purified polysaccharide backbones in authors' laboratory. These flocculants are syngistically efficient at low doses, controlled biodegradable, shear resistant, inexpensive and ecofriendly[1]. Dangling polyacrylamide branches on rigid polysaccharide backbones have easy approachability to contaminants in the suspensions. The higher the molecular weight and branching of polysaccharides, their graft copolymers show better flocculation efficiency. A flocculation model has been developed which relates the settling velocity of the contaminants particles and radius of gyration, a measure of pervaded volume of polymers in suspensions [2]. The grafted polysaccharides outperform most of the commercially available flocculants. The grafted polysaccharides can be hydrolysed/ cationised. Thus all the three classes of ionic, non-ionic and cationic flocculants can be developed based on grafted polysaccharides

Recently it has been observed in the authors' laboratory that graft copolymers synthesised by microwave initiated (using microwave energy alone to generate free radicals) and microwave assisted (using microwave energy as well as ceric ammonium nitrate as initiator to generate free radical sites) method provides a better quality of graft copolymer with much higher percentage of grafting in comparison with conventional redox grafting method. Various physicochemical characterizations (such as viscometry, molecular weight determination, elemental analysis, thermal analysis, FTIR analysis, 13C NMR analysis, SEM analysis) confirm that graft copolymerization does take place. The microwave synthesised graft copolymers shows superior flocculation characteristics when compared graft copolymers synthesised by conventional method as well as with several commercial flocculants. These systems are multifunctional and find application in agriculture, biomedical, oil field operations and recently in nano technology. The details of material synthesis, mechanism, characterizations and applications of these novel materials in the field of flocculation will be discussed in details.

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PREPARATION OF CARBOXYL FUNCTIONALIZED AND FLUORESCENTLY LABELLED POLYSTYRENE NANOPARTICLES

Lu Yu,* Iseult Lynch, Kenneth A. Dawson

Centre for BioNano Interactions, School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland
E-mail: lu@fiachra.ucd.ie

Keywords: *emulsion polymerization, functionalized nanoparticles, fluorescent labelling*

Nanomaterials have potential for use in many technical and medical fields, including diagnostics and therapeutics, and they can also serve as carries for biomolecules during drug or gene delivery.[1] Polystyrene nanoparticles are promising nanomaterials owing to their monodispersibility, controllable size, and ease of surface functionalisation with a range of biomolecules. Furthermore fluorescent labelling of the particles is a convenient method to employ in order to enable the particles to be tracked inside living matter. Here we report on the preparion of three carboxyl polystyrene particles with different sizes by emulsion polymerization. Then a bright, photostable fluorescent Alexa dye (Figure 2, left) was utilized to attach to the surface of particles using a di-functionalised PEG molecule as a spacer.

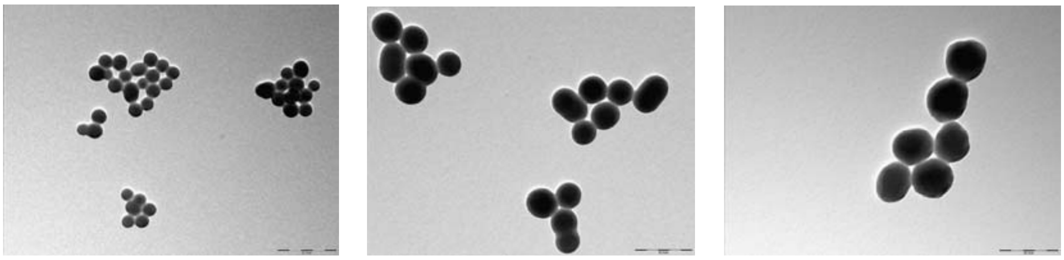

Figure 1. TEM images of PS nanoparticles with sizes 45 (PS1), 90 (PS2), 130nm (PS3) (left to right) ; scale bar: 200nm.

These carboxyl polystyrene nanoparticles were polymerized from styrene and acrylic acid monomers. Different diameters of particles can be easily achieved by changing the amount of surfactant during polymerization. The size is important because it can affect how the particles interact with proteins within living systems, and also influences whether and via which mechanism the nanoparticles are taken up by cells.[2] Carboxyl groups on the particles surface were converted to amino groups by reacting with NH_2-PEG-NH_2. The PEG chain length was around 4nm, so that it acts as a spacer between the nanoparticle surface and the ligand that is to be attached to the nanoparticles, which can be important for several applications. Then Alexa dye was then chemically attached onto the as shown in the scheme below:

$$\text{PS-COOH+ NH}_2\text{-PEG-NH}_2 \xrightarrow{\text{EDAC}} \text{PS-CONH-PEG-NH}_2 \xrightarrow{\text{Alexa dye}} \text{PS-CONH-PEG-NHCO-dye}$$

The fluorescence spectrum of one of the dye labelled nanoparticles is shown in Figure 2 (right). Biological studies of these particles, including interaction with proteins and uptake kinetics by cells are underway.

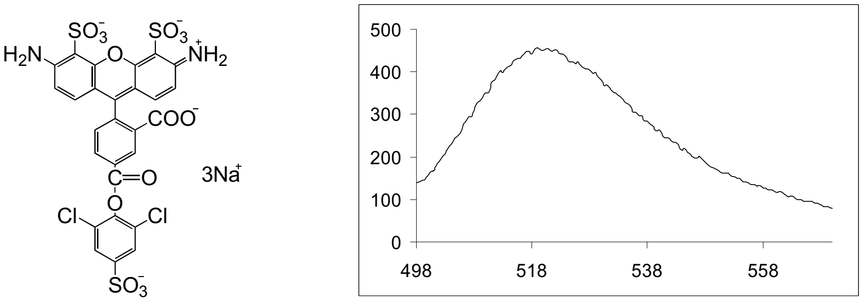

Figure 2. Left: the structure of Alexa Fluor 488 sulfodichlorophenol ester dye (Alexa dye). Right: fluorescent spectrum of PS1-PEG-Alexa (Ex=488nm, the concentration of particles is 100ug/mL in aqueous solution).

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INFLUENCE OF THE SEQUENCE DISTRIBUTION ON THE PROPERTIES OF AROMATIC COPOLYSULPHONAMIDES

Yumei Zhang, **Wantao Wu, Huaping Wang**

State Key Laboratory of Modification for Fiber Materials, Donghua University, Shanghai, 201620, China
E-mail: zhangym@dhu.edu.cn

Keywords: Aromatic polysulphonamide, sequence distribution, properties

Aromatic polysulphonamide fiber (Tanlon^{TM}) was successfully produced by Shanghai Tanlon Fiber Company as one of the novel high-performance fibers. Aromatic polysulphonamide fiber has been applied in the industrial and high-tech fields due to its excellent properties of high-temperature resistance, dimensional stability, inflaming retarding, electric insulation, acid and alkali resistance and radiation resistance. In order to improve the solubility of aromatic polysulphonamide in conventional solvents, the copolysulphonamide polymerized from 4,4,-diaminodiphenylsulfone (4,4,-DDS), 3,3,- diaminodiphenylsulfone (3,3,-DDS) and Terephthaloylchloride (TPC) was applied to produce fibers at the expense of mechanical properties because the rigid structure of the macromolecules would be destroyed in theory. The aim of this work is to get an insight into the influence of sequence distribution on the solubility, spinnability, thermal properties and the crystalline structure of the aromatic copolysulphonamides.

A series of aromatic copolylsulphonamides with various monomer ratios of 4, 4,-DDS and 3, 3,-DDS were synthesized. The sequence distribution was determined according to the results from Nuclear Magnetic Resonance (^{1}H-NMR and ^{13}C-NMR) analysis. From the results of Dynamic Mechanical Analysis (DMA) and Thermo Gravimetric Analysis (TG), it is clear that the thermal stability of the copolymers was little dependent on the sequence distribution with high thermal decomposition temperature (T_d>400) while the glass transition temperatures (Tg) decreased obviously with increasing *m*-phenylene segments. In fact, it is benefit to improve the tensile property during the spinning process and the mechanical properties would be expected to be improved by drawing. Meanwhile, the solubility increased with the presence of relatively more flexible segments of *m*-phenylene in the copolymer backbone. Therefore, concentrated dope solutions of the copolymers with more *m*-phenylene segments could be obtained for spinning, which would increase the draw ratio of the nascent filaments. In addition, the crystalline structure of the aromatic copolysulphonamides with different sequence distribution was analyzed with the Synchrotron WAXD. It is found that the crystallinity and crystallite size was influenced by the sequence distribution. The crystallinity of the copolysulphonamides was always smaller than that of the homopolymers while the crystallite size varied with the sequence distribution. From the discussion on relationship between the sequence distribution and the properties of the synthesized aromatic copolysulphonamides, it is concluded that more 3, 3,-DDS could be introduced into the copolymerization of aromatic polysulphonamides to improve the solubility and spinnability without scarifying the thermal stability and mechanical properties. So a favourable balance between spinnability and performance of the novel copolymers can be achieved by adjusting the sequence distribution.

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EFFECT OF $FeCl_3$ DOPING ON MECHANICAL AND MICROSTRUCTURAL PROPERTIES OF POLY(VINYL ALCOHOL)

Rajashekhar Bhajantri*, **V. Ravindrachary***, **Ismayil***, **A. Harisha***, **Manjunatha Pattabi****

Department of Studies in Physics, Mangalore University, Mangalagangotri-574199, India,
***Department of Materials Science, Mangalore University, Mangalagangotri-574199, India,*
E-mail: rbhajantri@yahoo.com

Keywords: *Poly(vinyl alcohol), Cross-linking, Tensile strength, Diffusion, charge transfer complex.*

Polymers have received much experimental attention recently due to their increasing technological importance. Transition metal halide doped polymers represent a new class of organic materials and among such materials, ferric chloride doped polyvinyl alcohol (PVA) seem to be suitable materials due to the important combination of thermal, structural, mechanical, optical, electrical and magnetic properties. Although PVA has good chemical resistance and good mechanical properties in the dry state, its applications were limited by its high hydrophilicity[1]. The chemical cross-linking of PVA by doping with $FeCl_3$ through hydrogen bonding may provide feasible routes for the improvement of the mechanical properties and thermal stability. In addition, PVA can form the three-dimensional network structure by cross-linking, an important characteristic of PVA as a physical hydrogel. Hence the mechanical, diffusion, thermal and optical properties of the $FeCl_3$ doped polymers should be studied extensively to understand the microstructural modifications.

Pure and $FeCl_3$ doped PVA films were prepared by solvent casting method using double distilled water. FTIR study was carried out using Shimadzu FTIR-8700 and the results shows that the intensity and wavenumber varies with $FeCl_3$ doping, suggests the interaction of Fe^{3+} with PVA. $FeCl_3$ is an efficient electron acceptor, forms the charge transfer complexes (CTC) with OH/C=O groups of PVA via intra/intermolecular hydrogen bonding. The formed complexes cross-links the PVA chains and ferric ions are acting as cross-linking agents, which increase the stiffness of the composite and make it to be insoluble in water. To confirm these properties, diffusion and mechanical studies were conducted. The diffusion study shows that the water uptake, diffusion coefficient, and penetration rate decreases with increasing $FeCl_3$ doping of PVA.

The cross-linking network modifies the microstructure of PVA and affects the mechanical properties. A Lloyd LF Plus Universal Testing Machine with a crosshead speed of 5 mm/min is used to determine the mechanical properties of the composite. The observed mechanical properties shows that the tensile strength, toughness and Young's modulus of the PVA with increasing $FeCl_3$ doping level indicates that the PVA films become more resistant to deformation due to increase in cross-linking density[2]. The X-ray diffractograms of the samples are conducted using Bruker D8 Advance X-ray diffractometer. The XRD study shows that crystallinity of the of $FeCl_3$ doped PVA decreases due to the intervention of dopant molecules in to the polymer matrix leads to a structural repositioning of the PVA chains and cross-linking(here the chain segments become more rigid and less mobile) as a result the amorphousity increases. The thermal studies of the samples were performed using Shimadzu heat flux DSC-50. The glass transition temperature (T_g) increases from 65°C for pristine PVA to 90°C for $FeCl_3$ doped one. The melting temperature T_m increases from 185 °C for pure PVA to 218 °C with increase in $FeCl_3$ dopant concentrations up to 5wt% and afterwards it decreases and attains 199 °C for 25wt% dopant concentration suggests that the thermal stability upon doping is enhanced due to cross-linking. The heat of fusion decreases with doping indicates that the main crystalline phase decreases with increasing dopant concentration and the sample becomes amorphous. The DC conductivity was carried with Keithley 236 and the result shows that the dc conductivity increases with increasing doping level which is understood that the interaction of $FeCl_3$ with PVA via hydrogen bonding gives PVA-Fe^{3+} complex. These complexes are of CTC type and considered to reduce the barrier between the trapping sites providing a conducting path through the amorphous regions of polymer matrix, which result in the enhancement of its conductivity.

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SUPRAMOLECULAR POLYMER SYSTEMS: FROM DESIGN TO REALITY

Kurt Geckeler*,**

**Department of Nanobio Materials and Electronics, World-Class University (WCU),*
***Department of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST),*
1 Oryong-dong, Buk-gu, Gwangju 500-712, South Korea
E-mail: keg@gist.ac.kr

Keywords: *Nanobiomaterials, supramolecular materials, synthons*

Supramolecular polymers have found a strong interest during the last decade and novel approaches to their synthesis and modification have become very important.[1] By introducing unorthodox approaches several novel classes of supramolecular polymers and materials with salient properties have been created and characterized (see an example in Fig. 1). In addition, different supramolecular concepts have been designed and applied for the first time to the preparation of supramolecular polymers. Thus, a series of novel and versatile synthons, applicable both in supramolecular chemistry and in nanoscience,[2-3] have been designed and prepared in our laboratory using different methods. The novel methods for the synthesis encompass supramolecular and macromolecular building blocks such as macrocycles (cyclodextrin and cucurbituril) and biopolymers (DNA, proteins). Several model systems with nanosynthons have been suggested and examples of interaction products including biopolymers based on different types of reactions and syntheses have been studied. Recent approaches presented are based on reactions in the solid state and in solution.

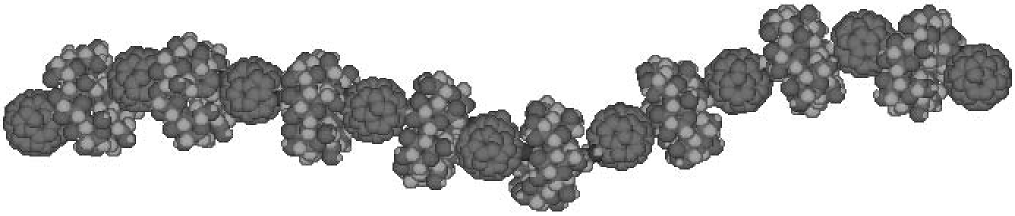

Figure 1. Space-filling model of a segment of the supramolecular cyclodextrin-[60]fullerene polymer

The different fundamental concepts are presented and highlighted both as synthetic approaches and in the context of their applications. The novel supramolecular polymer systems are expected to have an application potential in many areas such as the biomedical and electronic areas

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100% GREEN COMPOSITES AND THERMOPLASTIC MATERIALS. MATERIALS FOR THE FUTURE?

Jean Marc Saiter *, Nathalie Leblanc**

** LECAP, Institut des Matériaux de Rouen, Faculté des Sciences, Université de Rouen, BP12, 76801 Saint Etienne du Rouvray Cedex, France.*
*** LGMA, ESITPA, 3 rue du Tronquet, BP 40118, 76134 Mt St Aignan Cedex, France.*
E-mail : jean-marc.saiter@univ-rouen.fr

Keywords: *Green Polymer, Green Composite.*

A review of the development of materials during the last century shows that the new generation of material will have to respect green concepts. From this remark, we propose to show how 100% green composites having natural fibers can be prepared.

Modified wheat or Rice flours, potatoes can be used as thermoplastic matrix while sisal, flax or cotton can be added as natural fibers to build a composite.

In this work a review of our last results concerning the performances of new composites is made. We will show that we may obtain films, thin films, and bulk products using these raw materials. Then, the mechanical, thermal properties and also the durability of the different prepared composites will be presented and analyzed. Finally, in regard to the performances obtained, we will discuss about their possible use.

One important point concerning our work is to use by-products of the food industry. So, the development of these new 100% green composites respects the following concept: more food will be produced, more by-products will be obtained, and more raw materials will be produced for our goal. In other words, we do not use natural materials to the detriment of the human food production.

FULLY BIODEGRADABLE POLYMER COMPOSITES BASED ON BAMBOO FLOUR: MORPHOLGY AND MECHANICAL BEHAVIOUR

R. Adhikari*, **N. L. Bhandari***, **V. Causin****, **L. H. Hai** ***, **H. I. Khasim****** , **S. Henning******,
H.- J. Radusch ***, **G. H. Michler******, **J. M. Saiter*******

* *Central Department of Chemistry, Tribhuvan University, Kathmandu, Nepal*
** *Department of Chemical Sciences, University of Padova, Padova, Italy*
*** *Centre for Engineering Science, Martin Luther University Halle-Wittenberg, Halle (Saale), Germany*
**** *Institute of Physics, Martin Luther University Halle-Wittenberg, Halle (Saale), Germany*
***** *Institute of Materials, University of Rouen, Rouen, France*
E-mail: nepalpolymer@yahoo.com

Keywords*: Biodegradable Polymers, Composites, Mechanical Properties*

Most of the plastics materials used in everyday life originate from by-products of petroleum industries. These materials are getting more and more expensive and are also too difficult to degrade completely. Especially, in the developing countries these are posing problems of environmental degradation. On the other hand, we are all in the stage of civilization that the life is almost unthinkable without the use of polymeric materials. Thus, environmentally benign biodegradable polymeric materials are attracting attention of the polymer scientists worldwide. In this context, some chemical companies have already introduced completely biodegradable polymers, though these are still derived from petroleum based monomers. The aim of this study was to study the composites of Bamboo flour and biodegradable polymers. The polymer matrix used was a copolyester possessing lamellar morphology (see Fig. 1, left), a commercial product of BASF SE having Tradename Ecoflex. The filler was the flour of Bamboo shoots collected from Kathmandu valley. The filler was treated with caustic soda prior to the melt mixing using Brabender internal mixture followed by compression moulding. The composites thus obtained were characterized by scanning electron microscopy, X-ray diffraction and uniaxial tensile testing. The first results demonstrate that the composites having fairly good level mechanical properties can be obtained in which the lamellae morphology of the copolyester also does vary with composition. Via this method, the composites having well dispersed filler (see Fig. 1, right) and adjustable mechanical properties profile could be produced.

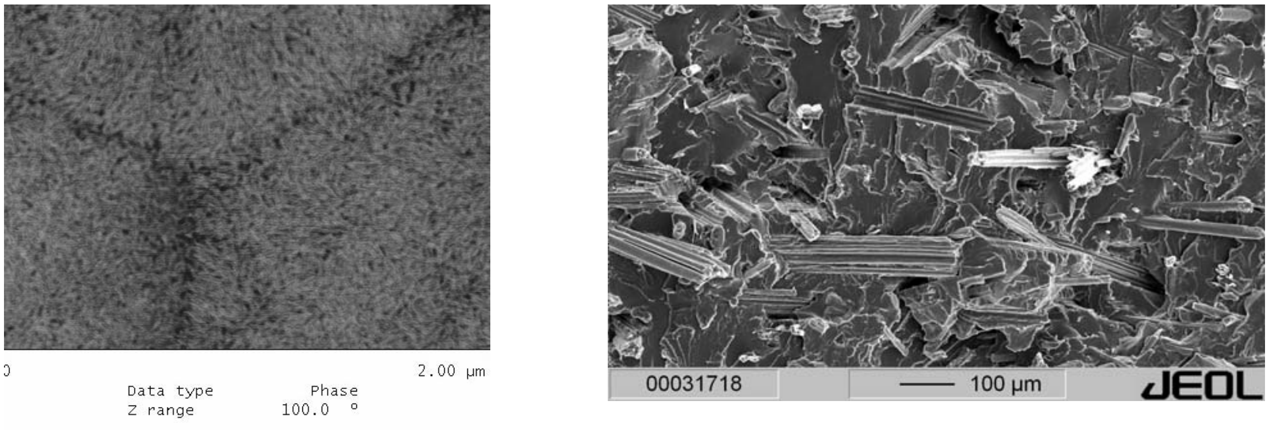

Figure 1. Tapping mode AFM phase micrograph showing lamellar morphology of Ecoflex sample (left) and SEM image of a composite material comprising 20 wt.-% Bamboo flour

HIGH PERFORMANCE IMPACT MODIFICATION OF PLA AND PLA –MAN MADE CELLULOSE FIBER COMPOUNDS

R. Forstner, **W. Stadlbauer**

Transfercenter für Kunststofftechnik GmbH, Franz-Fritsch-Straße 11, A-4600 Wels, Austria,
E-mail: reinhard.forstner@tckt.at

Keywords: *polylactic acid, mechanical properties, SEM*

INTRODUCTION

In recent years Poly-(lactic acid) as a green polymer has attracted scientific and industrial attention since PLA can be processed similar to polyolefins and is known to be biodegradable. Its good mechanical properties e.g. high stiffness and high tensile strength combined with optical good properties (transparency) made PLA successful in many packing and household applications, but due to the low thermal dimensional stability big markets are still prohibited. In order to make PLA e.g. feasible for automotive industry or other high performance markets new composites need to be developed to overcome the low thermal dimensional stability and improve toughness. In the past different attempts with reinforcements like jute[1], microcrystalline cellulose (MCC)[2] or flax[3] have been made to improve tensile properties in general on costs of impact strength. Recent studies on impact modification of PLA already showed an increase of toughness using natural rubber[4, 5] or commercial petrol based impact modifiers[6]. The goal of this study was to improve impact properties with different commercial available additives as well to improve thermal stability and stiffness of PLA by incorporating man made cellulose fibres.

RESULTS

The goal of this study was to improve impact properties with different commercial available additives as well as to improve thermal stability and stiffness of PLA by incorporating man made cellulose fibres into PLA compounds. Various impact modifier classes were tested and improvements in unnotched charpy impact strength up to factors of 10 were achieved with Core-Shell type modifiers opening the non break area for PLA even for samples tested at lower temperatures of T=-20°C.

In order to improve tensile- and HDT-properties additional PLA–compounds incorporating man made cellulose fibres were created. Impact modification of the fibre compounds was achieved (charpy impact strength of 100kJ/m^2) compared to the neat PLA-man made cellulose fibres (charpy impact strength of 50kJ/m^2) compounds and tensile as well as HDT properties increased.

Additional SEM measurements performed on these compounds revealed that the used impact modifiers also act as coupling agents to the man made cellulose fibres, which explains the better mechanical performance compared to the non modified PLA-Flax compounds

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ORGANIC-INORGANIC HYBRID MATERIALS EN ROUTE GREEN CHEMISTRY

Eram Sharmin, Deewan Akram, Fahmina Zafar, Sharif Ahmad*

Materials Research Lab., Dept. of Chemistry, Jamia Millia Islamia, New Delhi-110025, India
E-mail: eram_jmi@yahoo.co.in

Keywords: *vegetable oilpolyol, tetraethoxysilane, coatings*

The development of organic-inorganic hybrid materials from biobased precursors (e.g., carageenen, chitosan, starch, cellulose, vegetable oils) through sol-gel process and nano reinforcement techniques has been encouraged worldwide [1,2]. Such methods offer the advantages of ambient temperature reactions as well as improved performance of the final material at low content of modifiers (less than 5 wt%). Recently, organic-inorganic hybrids [OIHs] from vegetable oils have been obtained through sol-gel method with metal alkoxides (examples silicon, aluminum, titanium, and zirconium) as inorganic and virgin oil, alkyds or epoxies as organic precursors, respectively [2,3]. However, such OIHs are prepared through multi-step process, i.e., the synthesis of the organic matrix followed by the incorporation of inorganic component. The synthesis of vegetable oil based polymers such as alkyds, polyesteramides, polyetheramides, polyurethanes, polyepoxies and polyols, which may be used as matrices, for the development of nanohybrids or nanocomposites, is itself a cumbersome process, generally involving multiple steps, high reaction temperatures and time periods; in some cases, good yield is also not guaranteed due to (i) possible side reactions and, (ii) non-homogenous heating (external heating of reaction vessels).

Vegetable oil polyols consist of long, aliphatic chains with active methylene groups, double bonds, esters, and hydroxyl groups, which may undergo chemical reactions. Their interesting features are their inherent fluidity as well as abundant hydroxyl functionalities in their backbone. Vegetable oil polyols are obtained by several methods such as hydroformylation or ozonolysis followed by hydrogenation, epoxidation followed by hydration reactions and by enzymatic reactions from linseed, karanj, soybean, canola and rapeseed oil and are also found in nature as Castor or Lesquerella oils [5]. All these methods involve multiple steps and considerable time.

In the present work, a novel attempt has been made for in situ preparation of nanostructured OIHs from linseed oil through microwave [MW] assisted synthesis, for the first time by using Linpol, prepared under MW irradiations, and tetraethoxyorthosilane [TEOS] (in different % compositions by weight) as the organic and inorganic precursors. The in situ preparation of nano OIHs was carried out by (i) preparing linseed polyol (Linpol) under microwave irradiations through epoxidation and hydration of linseed oil, (ii) the hydrolysis-condensation reactions of TEOS within Linpol matrix, generating silanols and (iii) the condensation of silanols with Linpol backbone yielding SLinpol via MW assisted synthesis through a “one-pot multi-step” strategy. Similar reactions were also carried out by conventional methods. Products were characterized by spectral, physico-chemical and morphological (TEM) studies; the antibacterial behavior of OIHs was also studied. The effect of loading of TEOS on the aforementioned characteristics of OIHs was also investigated. Our results revealed that SLinpols showed nanosized (2nm) silica embedded in Linpol matrix; at higher loading agglomeration was evident. MW SLinpols were obtained in much reduced time period (6 minutes) with 100% yield compared to their conventionally obtained counterparts (in 12 hours, yield 75%). MW SLinpols yielded nanostructured coatings with good performance, curable by simple route at ambient temperature compared to the reported conventional OIHs, which require multi-step cure schedule at elevated temperatures. Our studies revealed that the in situ prepared linseed polyol OIH materials may serve as important candidates fjor corrosion protective “green”, “nanostructured” coating materials.

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MICROWAVE ASSISTED PONGAMIA PINNATE OIL BASED HYPERBRANCHED WATERBORNE POLYMER - A "GREEN" MATERIAL

Fahmina Zafar, M. Yaseen Shah, Eram Sharmin, Sharif Ahmad

Materials Research Lab., Dept. of Chemistry, Jamia Millia Islamia, New Delhi-110025, India
Email: fahmzafar@gmail.com

Keywords: *Pongamia pinnate* oil, *waterborne, hyperbranched, green material*

Recently, evolution of Green Chemistry is providing an alternate mode for chemists and industrialists to develop polymers from bio-based precursors via eco- friendly route to safe the health and environment. Green Chemistry means using green source (biomass) through green route with zero negative impact on environment (zero toxicity), and meeting green end (biodegradable) that is from source to end everything is green. Biomass such as rosin, chitosan, starch, cellulose, fats, proteins, lignin, jute, flour, cashewnut shell liquid, bagasse, seeds etc. are used as alternative of petro-based resources. Green route involves development of green polymers via solvent free, enzymatic and microwave irradiation methods.

Features of microwave irradiation, i.e., solvent-free reactions, low waste, energy efficiency, high yield, short reaction time, and possible use of alternative solvents can also play an important role in the development of green chemistry methods.

Hyperbranched polymer is a unique polymer, have non-entangled and globular structures that provide them with unusual properties from others polymers. The large number of end groups of such polymers greatly affects their properties for versatile applications. They possess high solubility, low melt-and solution viscosity, etc. in contrast to their linear analogues of same molar mass that completely overcome the use of VOCs during processing and application and can be used as waterborne, high solids, radiation curable, biodegradable materials overcome the use of volatile organic contents along with excellent properties that utilized in many applications.

In the present work we have taken an attempt to developed vegetable seed oil (biomass) based microwave assisted (green route) hyperbranched-waterborne polymer (zero toxicity), that can be used as a protective materials.

Pongamia pinnate oil based hyperbranched waterborne polymer [HWBP] was synthesised by a simple route through microwave irradiation within 4-5 min. The polymer synthesis carried out in situ by a two step reaction. 1st step reaction is amination of *Pongamia pinnate* oil with diethanol amine in the presence of sodium methoxide that results diol fatty amide and glycerol in 2-3 min. 2nd step reaction is condensation polymerization of reacting mixture of 1st step with phthalic anhydride that yields hyperbranced polymer in 1-2 min. Former reaction monitored by TLC test and while later by TLC as well as by acid value. The degree of branching of MCPUA was calculated by comparison of their ^{1}H-NMR spectra with model compounds. Solubility was checked in polar and non polar solvents that showed the resin soluble in non polar as well as polar solvent. Thermal analysis showed that these materials were stable up to 300°C, suitable for use as stable "green polymeric materials" for a variety of applications.

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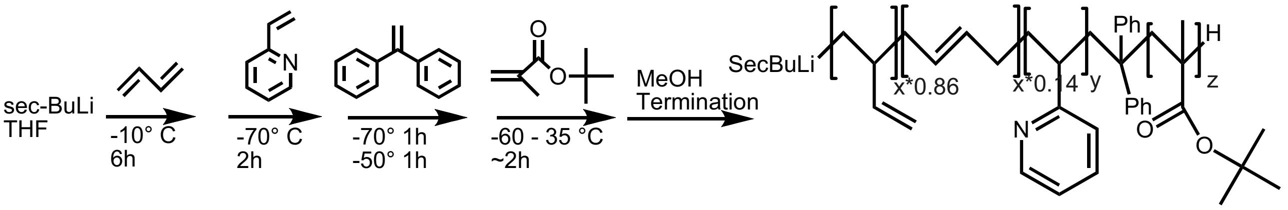
BLOCK TERPOLYMER SUNRISE: THE WONDROUS WORLD OF BLOCK TERPOLYMER MICELLES.

Felix Schacher, Christopher Synatschke, Eva Betthausen, Tobias Rudolph, Axel H. E. Müller

Macromolecular Chemistry II and Bayreuth Center for Colloids and Interfaces, University of Bayreuth, Germany
E-mail: axel.mueller@uni-bayreuth.de

Keywords: *anionic polymerization, micelles, electron microscopy.*

Using anionic polymerization, we have synthesized a new ABC triblock terpolymer, polybutadiene-*block*-poly(2-vinyl pyridine)-*block*-poly(*tert*-butyl methacrylate) (PB-P2VP-PtBMA; BVT) (Scheme 1). By quaternizing the P2VP block with methyl iodide and/or hydrolyzing the PtBMA block, forming poly(methacrylic acid) (PMAA), we obtain terpolymers of different degrees of amphiphilicity, which form interesting multicompartment core micelles with an anionic corona.[1,2]



Scheme 1: Synthesis of BVT

These micelles are studied using transmission electron microscopy (TEM) and cryogenic TEM (cryo-TEM). They further interact with bis-hydrophilic diblock copolymers with a cationic block, e.g. poly(N,N-dimethylaminoethyl methacrylate)-*block*-poly(ethylene oxide) (PDMAEMA-PEO) forming new sunray-like or core-shell-shell-corona inter-polyelectrolyte complexes (IPECs). The PB core of the micelles can be crosslinked and the obtained organic nanoparticles can be loaded with metal nanoparticles to form hybrids.[3]

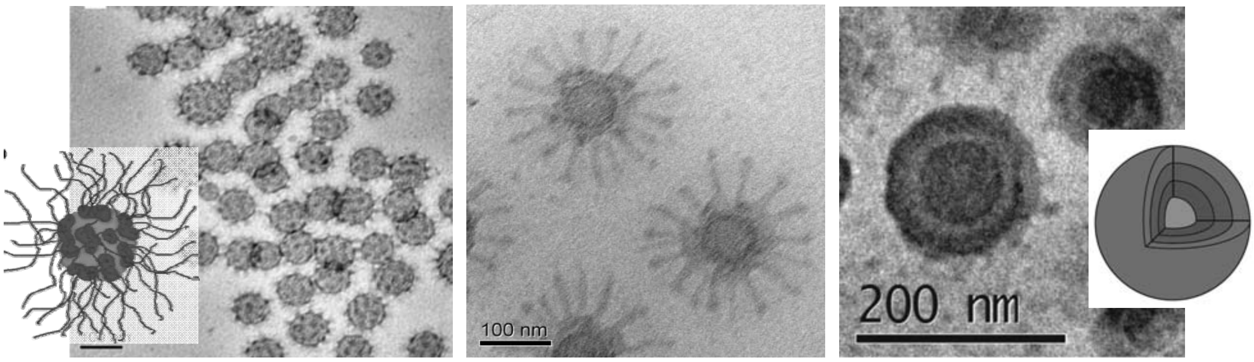


Fig. 1: PB-P2VP-PMAA micelles in water (left) and their interaction with PDMAEMA-PEO after 10 h (middle) and 10 days (right)

The charge sequence of the BVT block terpolymer was inverted by synthesizing PB-*b*-PtBMA-*b*-PDMAEMA (BTD) triblock terpolymers. The corresponding micelles with a cationic corona interact with block copolymers having an anionic block, like PAA-b-PEO.

In addition, we obtained nanoparticles of various shapes by crosslinking the PB domain of the bulk structure of BVT or BTD. Again, they can form hybrids by loading their shell or corona with metal nanoparticles.[4]

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STRUCTURES AND DYNAMICS OF COMPLEX BLOCK COPOLYMER AGGREGATES: A MODEL SYSTEM

Anja Kroeger*, **Katharina Landfester***, **Adi Eisenberg*****

Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
*** *McGill University, Department of Chemistry, 801 Sherbrooke Street West, Montreal, Quebec, H3A 2K6, Canada*
E-mail: kroeger@mpip-mainz.mpg.de

Keywords: block copolymers, structure formation, interactions

Lipid and polymer aggregates are versatile and very useful model systems and are intensely studied with respect to biomedical applications [1]. Over the past decade, a large number of publications have appeared on the topic of self-organization of highly asymmetric amphiphilic block copolymers into different morphologies, such as spherical micelles, rods, vesicles, and others [2]. Here, the long hydrophobic block forms either the core in micelles and rods, or the wall in bilayer structures, whereas the short hydrophilic block forms the corona. Compared to their low molecular counterpart, i. e. the liposomes, polymer vesicles show higher stability and robustness as well as a highly designable permeability [3]. Therefore, they have received the attention of many research groups all over the world. Furthermore, compared with the extensive research on encapsulation of biomolecules into liposomes, the studies on incorporation of large biological units into block copolymer aggregates are very limited, in part because large hydrophilic biomolecules are sensitive to organic solvents and the pH of the solution. The paucity of studies dealing with the encapsulation of biological species into block copolymer aggregates underlines the inherent difficulties of the process and suggests the need for further research. On this account a simplified synthetic model system for systematic investigations was introduced, with the aim of improving the understanding of the encapsulation and supramolecular structure formation mechanisms and controlling the parameters which influence these processes.

In the present work, the encapsulation of a amine-terminated, poly(amido amine) dendrimer (PAMAM) into block copolymer assemblies, including micelles and vesicles, is explored. A polystyrene-block poly(acrylic acid) copolymer (PS-*b*-PAA) was chosen because it is a well-known and well-understood system and the self-organization has been studied extensively [4]. On the other hand, dendrimers are very useful model compounds for complex structures, such as proteins, which have similar sizes and/or similar terminal groups. The presence of carboxylic acid moieties on the block copolymer and of amine groups on the dendrimer, in a medium of relatively low polarity, such as dioxane, undoubtedly leads to strong interactions, which manifest themselves immediately on mixing of the two components.

The complex structure of the formed aggregates as well as the distribution and the localization of the dendrimer units inside these aggregates are determined by comparative studies of dynamic light scattering and turbidity measurements and transmission electron microscopy. The strong, complex and specific interactions, which influence the dynamic behaviour of the system, have a strong influence on the structure formation, which proceeds at different hierarchical levels [5]. The PAMAM concentration as well as the character of the terminal groups of the dendrimer influence the strength of these interactions and consequently affect the structure formation process. As shown by fluorescence quenching experiments, on all supramolecular hierarchical structure levels, and specifically in vesicles, the dendrimer is coated by the PAA chains of the block copolymer due to the strong interactions; since the PAA blocks are connected to the PS blocks, which form the corona, the dendrimer is surrounded by PS chains and is thus encapsulated into the hydrophobic regions of the block copolymer aggregates [6].

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SYNTHESIS OF SMART NANO-MATERIALS BASED ON POLY(GYCIDOL) AND POLY(N-ISOPROPYLACRLAMIDE)

Dirk Kuckling

Department Chemie, Universität Paderborn, Warburger Str. 100, D-33098 Paderborn, Germany
E-mail: dirk.kuckling@uni-paderborn.de

Keywords: *hydrogel, block copolymer cross-linking.*

Responsive polymers networks are interesting materials for a variety of different applications due to the fact that they can perform a large volume transition.[1] However, the swelling transition is a diffusion limited process. Thus, the decrease of the feature size (e. g. in thin layers) is an appropriate way to create structures with reasonable response time. The possibility to pattern responsive polymer networks makes them useful for application in micro-system technology as well as in biomedicine. The transition behavior of these films showed similar trends to those of the corresponding linear polymers whereas confinement effects have been found for thin hydrogel layers. The ability to optimize the integration of these polymers is critical for the fabrication and development of platforms that harness the unique abilities of responsive polymer networks. Here, some recent developments on chemically cross-linked hydrogels with respect to synthesis, characterization and application are highlighted.

Designing functionalized nanohydrogels with specific properties is a challenging task by the fact that both the total number of functional groups and their distribution within nanohydrogels play a crucial role in controlling its properties.[2] In addition the distribution and accessibility of functional groups are critical in determining the types of applications. In order to obtain a high degree of control over these properties and the stimuli that induce property changes, complex polymer structures designed for supramolecular aggregation must be prepared. Along these lines, tailor-made block copolymers were synthesized to spatially localize chemical functionalities to a defined position, to improve colloid stability, and finally, to obtain specific physical properties of the particles.

The objectives of this work are to synthesize and characterize stimuli-sensitive core-shell nanohydrogels with controllable functional group distribution.[3-6] The general approach involve the organization of polymers into micellar assemblies followed by stabilization through cross-linking of collapsed core of the assemblies in order to produce monodispersed, stable nanohydrogels, having an amphiphilic core-shell morphology. Consequent down-scaling of core-shell particles led to the preparation of end tethered block copolymers (so-called star polymers). Controlled (radical) polymerization has been proven to be the method of choice to prepare a variety of functional (block) polymers. Different polymer constitutions have been realized by changing the order of monomer addition or by post modification of already existing blocks. In addition to standard polymer characterization (NMR, MALDI-TOF-MS, DSC etc.) the structure has been investigated by SEC with triple detection (RI, MALLS and Visco). The temperature responsive properties of block copolymers were analyzed mainly by dynamic light scattering.

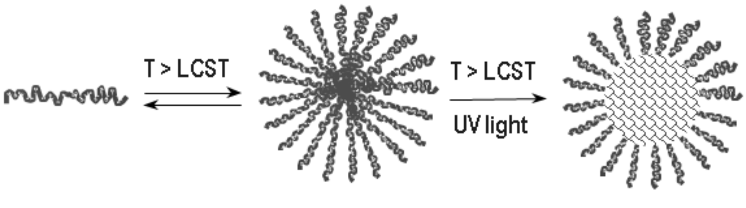

Figure1: Synthetic approach used upon preparation of PGI/PNIPAAm core-shell nano-hydrogels.

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CONTROLLED RADICAL POLYMERIZATION OF METHYL METHACRYLATE CATALYZED BY POLYMER-SUPPORTED COMPLEXES OF COPPER

Mikhail Lazarev, Egeniya Geraskina, Dmitry Grishin

Research Institute of Chemistry of Lobachevsky State University, Address: 23/5 Gagarina ave., Nizhny Novgorod 603950 Russsia,
E-mail: lazarev@ichem.unn.ru

Keywords: *controlled polymerization, immobilized catalyst, support-polymerization, polyvinylpyridine, methyl methacrylate*

The complexes of copper with 2,2-bipyridine ligands for realize the controlled atom transfer radical polymerization (ATRP) technique have been described[1,2]. The polymer-supported copper catalysts contain different nitrogen groups as 2,2-bipyridine, di-(2-pyridylethylene)amine, N',N",N"-trimethylenediamine, N',N',N",N"-tetraethyldiethylenetriamine groups have been known[4,5,6].

The soluble catalysts with poly-2-vinylpyridine, its copolymers with styrene or esters C_1-C_{14} of methacrylic acid and the non-soluble catalyst with copolymers of 2- and 4-vinylpyridine with divinylbenzene (2%) and styrene or esters C_1-C_{14} of methacrylic acid was studied in the controlled polymerization of methyl methacrylate (MMA). The catalytic complexes were prepared by ligand change reaction. The copper (I) bromide was dissolved in water/methanol mixture of ammonia or in different amines. The homogeneous solution of the complex of cuprous bromide with ammonia was blue while complexes with amines were green. The solution of copper complexes was mixed with described polymer matrixes and then solvent was evaporated under vacuum. The polymer complexes of copper contained 2-vinylpyridine were red-brown while the complexes contained 4-vinylpyridine had grass-green color. The ratio of copper per vinylpyridine units was in the range from 1 to 10.

The ethyl-2-bromoisobutyrate was used as the initiator for the polymerization. The molar ratio of components was MMA : initiator : Cu = 100 : 1 :1. Toluene, dioxane, acetone, THF, DMFA, DMSO were used as solvents for polymerization. The started concentration of MMA was 2.37 M.

It was established that different solvents exert an influence on polymerization of MMA. The yields of the polymers in toluene, acetone and dioxane are very small (<5) in 10 hours of the reaction at 90°C. The largest monomer conversion was >60% in DMSO, but polydispersity indexes (PDI) of polymers are also high (~5-7). The best solvents for polymerization in the presence of copper-supported complexes are THF, pyridine and DMFA, because polymers have the least PDI (1.2-1.5).

The complexes of copper (I) with copolymers of 2-vinylpyridine and 4-vinylpyridine have also different effect both on the polymerization and the molecular weight properties of the synthesized polymers. The polydispersity indexes of polyMMA obtained in the presence of copper complexes with copolymers of 2-vinylpyridine are less than that for complexes with 4-vinylpyridine.

The influence of water on the polymerization in the presence of copper complexes described in the paper[7] has not been established. The sequence of experiments for polymerization with different quantity of water (from 0 to 100 μl per ml of solvent) was realized. It was observed that number-average molecular weight and PDIs of the samples synthesized in the presence of complexes with cross-linked poly-4-vinylpyridine and different quantity of water in THF solution were equal 86 kDa and 3.32, respectively. The effect of DMSO on the polymerization described[7] was also not found.

The conversion of monomer in semi-logarithmic coordinates per time is linear. The molecular weight of the polymers synthesized in the presence of the copper-supported complexes increases with MMA conversion.

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PEROXIDE CURED NATURAL RUBBER/FLUORELASTOMER/HIGH DENSITY POLYETHYLENE VIA DYNAMIC VULCANIZATION

Chamaiporn Yamoun, Rathanawan Magaraphan

Polymer Processing and Polymer Nanomaterials Research Unit, Petroleum and Petrochemical College, Chulalongkorn University, Phayathai Rd., Soi Chula 12, Pathumwan, Bangkok 10330, Thailand
E-mail: rathanawan.k@chula.ac.th

Keywords: *Natural Rubber, Fluoroelastomer, Peroxide Cure, Dynamic Vulcanization*

Global warming concerns drive the increase in use of gasohol and biodiesel as alternative fuels for automobiles. These biofuels especially gasohol contain the polar component, e.g. ethanol make the fuel no longer purely hydrophobic. Therefore the oil resistant rubber materials used in fuel pipes in automobile may need to be modified to have a better resistance to polar components [1-4]. For this purpose, fluoroelastomer as well as natural rubber (NR) and high density polyethylene (HDPE) can be applied. Fluoroelastomers have excellent thermal, oil, and chemical resistance but are very expensive while natural rubber and HDPE are relatively much cheaper. Blends of these materials could be good candidates for use with gasohol. In this work, blending of both thermoplastic and rubber was carried out by dynamic vulcanization using peroxide as a curing agent. The effect of blend composition and peroxide type on the oil resistance and mechanical properties was studied.

Experimental:

High density polyethylene 30% by weight was mixed with natural rubber and fluoroelastomer (FKM or Viton GF600S) with compositions of 35-60 wt%) in an internal mixer at 150°C 50 rpm for about 15 min. Then calcium hydroxide 3 phr, stearic acid 0.25 phr, talc 3 phr and dicumyl peroxide (DCP) 0.1 phr or DBPH 1 phr were subsequently added and mixed further for about 30 min. The dynamic vulcanized blends were further mixed on two-roll mill and compression molded at 180°C. The cure characteristics were studied by Techpro MDR. Tensile properties were studied according to ISO 37 (type I). Thermal properties were determined with Perkin Elmer DSC.

Results:

The simple blends of the three component (HDPE/NR/FKM) without peroxide curing agent showed small improvement in mechanical properties with increasing NR content. The dynamic vulcanization of the blends with DCP showed slightly lower mechanical properties than those blends without DCP. This was explained by the extensive curing reaction of DCP at relatively high temperature of mixing even with its small amount. It was observed that the blends were turned to powder if higher amount of DCP or higher mixing temperature was used. This implied that the curing reaction by DCP could be so intensed making lots of small rigid crosslinks in bulk which were easily detached from each other under high shear due to its limited elongation. This crosslinks become interior defects and cause the poor mechanical properties. However, the resistance to gasohols and biodiesel of the dynamic cured blends was better as seen by less swelling, than that of the simple blends. DSC thermograms revealed the slight change in HDPE crystallinity (53-55%) with increasing NR content. The crystallinity of HDPE (49-53%) slightly decreased for the blends with DCP dynamic vulcanization.

When DBPH was used as the curing agent for the blends by dynamic vulcanization, the cure characteristic showed that the higher curing temperature (150°C and 180°C) the higher improvement in torque and faster curing rate were obtained. It was also found that the tensile strength and modulus were much more improved as compared to those of DCP cured blends. The swelling of these DBPH dynamic vulcanized blends in gasohol and biodiesel was also reduced, suggesting the improvement of gasohol and biodiesel resistances.

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SYNTHESIS, PROPERTIES AND APPLICATIONS OF DENDRONIZED CHITOSAN

Agustina Aldana, Marisa Martinelli, Miriam Strumia*

IMBIV-CONICET. Dpto. De Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba. Córdoba. ARGENTINA.
E-mail: mcs@fcq.unc.edu.ar

Keywords: *dendronized chitosan, functional polymers, dendronization.*

The dendronized polymer architecture has gained increasing attention during the latest years thanks to its controllable size, shape, and versatile functionalization possibilities. In addition, their highly branched structure with a presumably high degree of functionality, provides them with unique physical properties, such as low viscosity at high molecular weight. This subclass of comb polymers was first mentioned in a patent by Tomalia *et al*. in 1987 and then was synthesized by Hawker and Fréchet in 1992. Since then, a large number of dendronized polymers have been developed, and promising applications in nanotechnology for these new materials have been suggested.

More recently, our research group has begun to work in the chemical functionalization of polymers through dendronization methodology. Interesting properties were found in these new products, as stimuli responsive behavior in solvent of different polarity[1], rheological synergism[2] and multivalency effect in Affinity Chromatography[3]. At the moment, we are studying the effect of the dendronization of Chitosan. It is a polysaccharide formed primarily of repeating units of β (1-4)-2-amino-2-deoxy-D-glucose, although a small amount of N-acetyl-D-glucosamine is included in the structure. The free amino and hydroxyl groups of chitosan offer great potential for further derivation. Chitosan has shown interesting applications as biomaterial due to its excellent biocompatibility, low toxicity, immunostimulatory activities, antibacterial and antifungal action, and anticoagulant properties. Furthermore, the degradation products of chitosan have been shown to be nontoxic, non-immunogenic and non-cancerogenic.

It is well known that the effects of dendronization are of two types: one of them is of topological nature, according to the architecture and size of the dendrons, and the other, is of chemical nature, according to the chemical structure of the dendrons. Therefore, our goal is to obtain a new material by modification of chitosan using dendritic molecules of different generation or chemical structure. The challenge of this research is to find in these products new properties maintaining the well known advantages of the Chitosan. Consequently, it allows increasing the functional utility of this polymer to facilitate the use in a variety of applications like supports in drug delivery or affinity chromatography.

Therefore, different chitosan-based polymers were functionalized with the first and second generation of dendritic molecules. The products were chemically characterized showing the covalent incorporation of the dendrons. The studies of their properties are in progress. In a next step, is our interest to evaluate the influence of dendritic effects on the efficiency of dendrons as multivalent ligand.

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BASF SUSTAINABLE DEVELOPMENT - RENEWABLE RESOURCES FOR POLYURETHANES

Jens Ferbitz*, **Jörn Duwenhorst****, **Jens Müller*****

Elastogran GmbH, Elastogranstr. 60, 49448 Lemförde, Germany
** BASF Global PU Specialities Research GKF/U,*
*** BASF Global PU Specialities Research GKF/U*
**** Manager Technical Service Slabstock Foam - European Business Unit Comfort*
E-Mail: jens.ferbitz@elastogran.de

Keywords: *Sustainability, bio-based PU, polyols from renewable resources*

The interest in «green » materials has been growing throughout the last years. Two different types of these materials have to be differentiated: the bio-degradable polymers and the bio-based polymers. Bio-degradable polymers are those that are decomposed by microorganisms and thus can be composted. Here the functionality is “bio-degradable”. In contrast, for bio-based polymers the focus is on the raw materials. The carbon-backbone is at least partially built up by renewable resources. One of the strategic guidelines of BASF is to ensure sustainability development. Within its Growth Cluster Initiative BASF has identified four megatrends, leading to six growth clusters. Three of these growth clusters include “renewable resources” as topic. This underlines the importance of renewable resources in future development.

This presentation focuses on two products out of BASF’s polyurethane portfolio that include a significant ratio of bio-based material: BALANCE 50 and “bio-based” TPU.

BALANCE 50 is a bio-based polyol developed by BASF for the slabstock market. The castor oil based polyol contains 31 % of biomass, has a good processing profile, excellent odor and does not contain residual acidic groups. Castor oil, an OH-functionalized natural oil, is used as raw material for the synthesis of BALANCE 50. For product quality and performance reasons DMC catalyzed alkoxylation is used to obtain a polyol with a functionality of about 2.7 and an OH-number of 50 mg KOH/g. Comparison to standard slabstock polyols proves that BALANCE 50 has same processing properties, excellent mechanical properties, good aging properties and very low emissions. It is possible to not only obtain a flexible foam with a significant amount (approximately 25 %) of bio-mass but also to improve aging properties. Comparison of both flame-resistant and non-flame-resistant slabstock foams proves that aging properties are significantly enhanced, especially loss in elongation at break and of tensile strength in flame-retardant foams. For emissions BALANCE 50 based foams have significantly reduced values in FOG tests at same VOC levels. The eco-efficiency analysis shows that the ecological impacts of BALANCE 50 are lower energy consumption, less resource consumption, a significantly reduced global warming potential, less SO_2 emission and a more ecologically friendly foam. These pros by far overwhelm the cons which are a higher land use and a limited competition with the food chain. The overall rating makes BALANCE 50 a sustainable approach in flexible foam applications.

The second material in focus is bio-based TPU. Within the presentation we give an overview on routes to bio-based TPU and compare the different approaches. The possible ways to produce bio-based TPU are blending of standard TPU with bio-based materials, wood-plastic composites, as well as polyols and isocyanates based on renewable resources.

BASF chose the last approach and developed a castor oil based polyesterdiol. This new polyol enables the production of TPU over a wide Shore-hardness range. The content of renewable resources depends on the desired hardness. A TPU with 80 Shore A hardness contains about 60 % carbon based on renewable resources. The content at 60 Shore D is 40 %. So far the most intensively studied hardness is 95 Shore A . Here the content of carbon based on renewable resources is approximately 50 %. The new Elastollan types show similar mechanical properties than the standard Elastollan types. Additionally they have very good hydrolytic stability and show improved heat aging properties compared to standard non-bio-based TPU. The typical fields of application of this new TPU type are shoes, car interior and in TPU foils.

As a conclusion it can be stated that the eco-efficient use of natural resources in polyurethane applications is one of the growing market segments for the next years. The presented examples show that the use of renewable resources for material development is not necessarily combined with a loss in performance. To contribute to a high quality of life for coming generations, BASF will continue its sustainable development of materials that combine environmental protection and social responsibility with economical success.

A NOVEL APPROACH TO EXTRUDE WHEAT GLUTEN BASED ON ADDITION OF UREA

Hasan Türe*, Mikael Gällstedt, Eva Johansson***, Ramune Kuktaite***, Mikael S. Hedenqvist***

* *School of Chemical Science and Engineering, Fibre and Polymer Technology, Royal Institute of Technology (KTH), SE-10044 Stockholm, Sweden*
** *Innventia Box 5604, SE-11486 Stockholm, Sweden*
*** *Department of Agriculture – Farming Systems, Technology and Product Quality, The Swedish University of Agricultural Sciences, SE-230 53 Alnarp, Sweden*
E-mail*: tureh@kth.se*

Keywords: *Wheat gluten, extrusion, urea*

Using of biopolymers as packaging materials has received great attention due to increasing environmental concern caused by petroleum-based plastic. Among natural polymers wheat gluten (WG) is a valuable candidate for development biodegradable films because of its film forming properties, relatively low cost and biodegradability. On the other hand, extrusion of WG into the packaging film is difficult due to its protein structure and rheological properties.The goal of this study was to examine the effect of urea as a protein denaturant in processing of WG plasticized with glycerol into biodegradable film by extrusion technology. Confocal laser scanning microscopy (CLSM), Field emission scanning electron microscopy (FE-SEM), oxygen and water permeability measurements, tensile test, protein solubility, and infrared spectroscopy (IR) were used to assess the properties of the extrudates. WG films, with different urea concentrations, were successfully produced using a single screw extruder. CLSM analysis showed different protein structure in the extruded films. Scanning electron micrographs exhibited that homogenous and smooth film was obtained by increasing urea concentration. As urea concentration increased maximum stress and Young's modulus were found to decrease, while strain at maximum stress increased significantly, resulting in a more flexible structure. Water vapor and oxygen permeabilities of the film increased with increasing urea concentration. Protein solubility of urea containing films was found lower than the native gluten and glycerol-plasticized WG extrudate. It was also observed that an increasing urea concentration did not significantly change the protein solubility of the urea containing films. The interaction between the gluten network and urea was also revealed by IR analysis.

IONIC LIQUIDS AND CELLULOSE: INDUSTRIAL ASPECTS

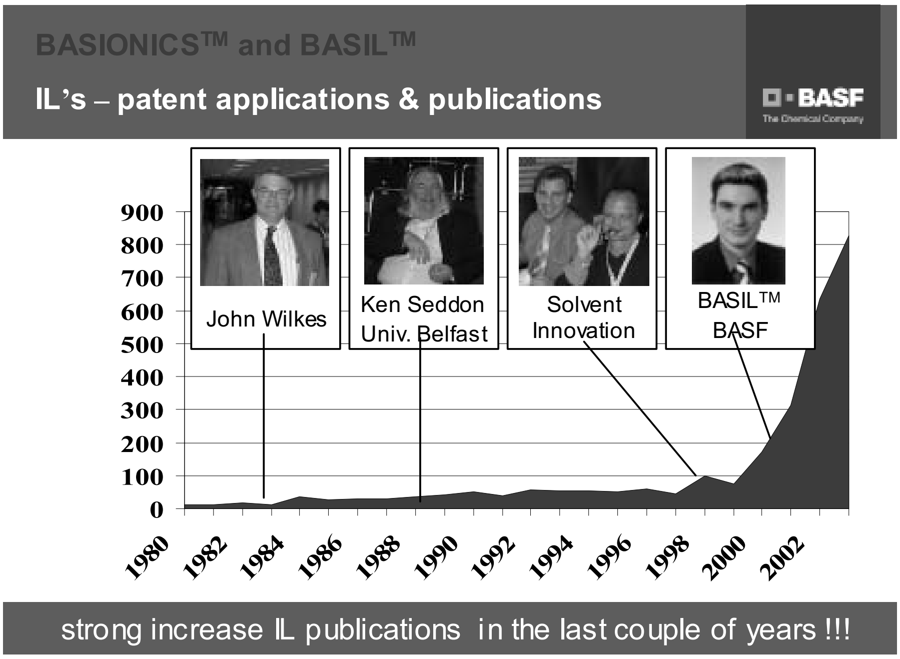
Klemens Massonne

BASF SE, Ludwigshafen, Germany
E-mail: klemens.massonne@basf.com

Keywords: ionic liquids, cellulose

Ionic liquids are mostly organic salts with melting points below 100 °C. To obtain these low melting points one has to combine a relatively complex delocalized cation with all kinds of anions. The chemical and physical properties cover a wide range and are determined by both of the constituents.

Interest in ionic liquids has grown over the past years as demonstrated by the significant increase in publications and patent applications in this field:



BASIONICS™ and BASIL™

IL's – patent applications & publications

strong increase IL publications in the last couple of years !!!

They exhibit a unique and thus far unprecedented set of properties such as non-volatility, non-flammability, electrical conductivity and very special, highly selective solubilising power. The systematic application of this property profile offers opportunities to overcome previously unsolvable problems in today's processes.

In 2002 Robin Rogers from the University of Alabama published that certain ionic liquids are able to dissolve biopolymers, especially cellulose, physically without chemical derivatisation. This was the starting point for increasing efforts in the field of cellulose processing in ionic liquids worldwide over the last years. The publications include cellulose reshaping using the unique solvating power of ionic liquids as well as chemical derivatisations of cellulose taking advantage of the chemical inertness of many molten salts.

The lecture will provide an overview on these activities focussing on the ionic liquids and their role in the processes. Aspects of solution power will be discussed as well as questions of stability, processability and recycling of the ionic liquids. To understand these opportunities and also the limitations is prerequisite for any industrial application of ionic liquids in cellulose processing.

BASF in this exciting field is offering system solutions to the market. Tailor-made and standard ionic liquids are offered under the brand name BASIONICS™, processes involving ILs as BASIL™. We are ready to support customers in optimizing their processes with ionic liquids and in the development of new products. This includes technology as well as products in bulk quantities and services concerning toxicity data, registration and recycling.

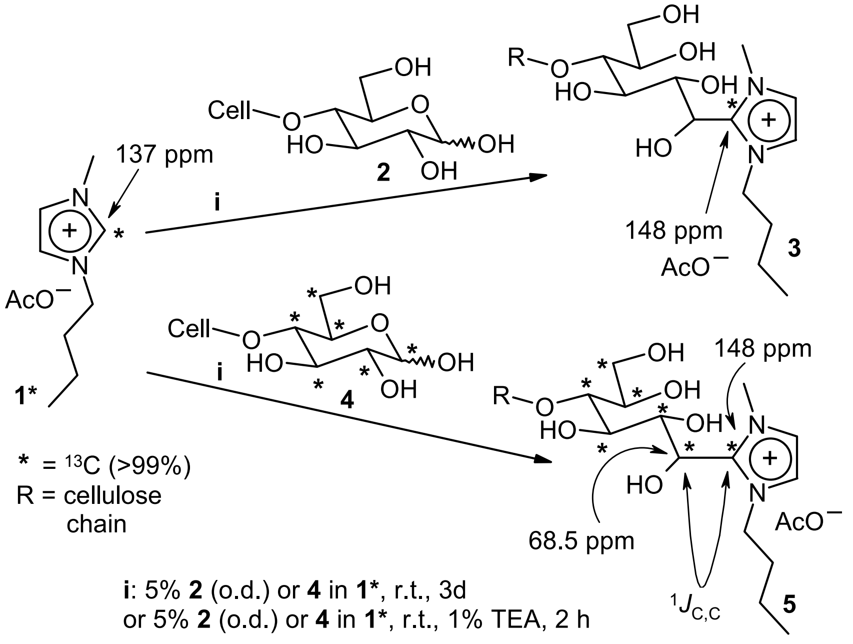
SIDE REACTIONS IN THE SYSTEM CELLULOSE / 1-ALKYL-3-METHYL-IMIDAZOLIUM IONIC LIQUID

Gerald Ebner*, Michael Schrems*, Falk Liebner*, Ernst Becker, Michael Horix**, Antje Potthast*, Thomas Rosenau***

** University of Natural Resources and Applied Life Sciences Vienna (BOKU), Department of Chemistry, Muthgasse 18, A – 1190 Vienna, Austria*
*** Blue Globe Energy GmbH, Willi-Brandt-Platz 6, D – 68161 Mannheim; Germany*
E-mail: thomas.rosenau@boku.ac.at

Keywords: *cellulose, ionic liquids, side reactions*

In solutions of cellulose in 1-alkyl-3-methyl-imidazolium ionic liquids (ILs), both the ionic liquid and the cellulose are evidently not inert. Side reactions can be distinguished according to whether they involve the cation or the anion of the ionic liquid or just autodegradation products of the IL. Ionic liquids with 1-alkyl-3-methyl-imidazolium cations react at C-2 with cellulose at its reducing end (and, if present, other aldehyde functionalities along the chain), forming a carbon-carbon bond, see Figure 1. There is a linear correlation between the carbonyl content of the cellulose and the amount of covalently bound IL. The side reaction is strongly catalyzed by bases, so that commonly present impurities in ILs, such as their thermal degradation products, promote this reaction. These thermal degradation products are mainly imidazole, *N*-alkylimidazole, *N*-methylimidazole and methylene-bridged dimers.
Side reactions of ILs anions are more diverse and depend on the respective reaction system. We have focused on acetate and chloride as the anions since they are most commonly used so far in the processing and derivatization of cellulosics. Acetate as the IL anion is generally unsuitable for esterifications by acylating agents (halides, anhydrides), both organic and inorganic ones, for methylations (alkyl halides, dialkyl sulfate), or for silylations (trimethylsilyl halides), since the reagents coreact with the IL anion rather than with the cellulosic hydroxyls. Chloride anions in the IL cannot be used for alkylations (alkyl halides, dialkyl sulfate) or oxidations (NMMO, periodate).



* = ^{13}C (>99%)
R = cellulose chain

i: 5% **2** (o.d.) or **4** in **1***, r.t., 3d
or 5% **2** (o.d.) or **4** in **1***, r.t., 1% TEA, 2 h

Figure 1. Reaction of 2-^{13}C-labeled 1-butyl-3-methyl-imidazolium acetate (**1***) with cellulose (**2**) at its reducing end to the "BMIM-cellulose" derivative (**3**) and with ^{13}C-perlabeled cellulose (**4**) to "labeled BMIM-cellulose" (**5**), both products having ^{13}C NMR-detectable cellulose-IL linkages.

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POLYESTERIFICATION IN IONIC LIQUIDS

Shaodong Zhang, Elise-Marie Dukuzeyezu, Hervé Lefebvre, Martine Tessier, Alain Fradet

Université Pierre et Marie Curie - UPMC Univ Paris 06, Laboratoire de Chimie des Polymères, Courrier 184, 4 Place Jussieu, Paris, France ; CNRS, UMR 7610, Paris France.
E-mail: herve.lefebvre@upmc.fr, alain.fradet@upmc.fr

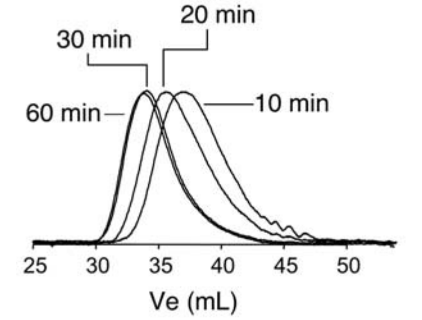
Keywords: *Polyesterification, Brønsted Acid, Ionic Liquids, Green chemistry*

Polyesters are usually synthesized by reaction between diols and diacids or diesters. In order to achieve high conversions and to obtain high-molar-mass polyesters in reasonable reaction time, such reactions are carried out in the bulk, at high temperature and in the presence of protonic acid or organometallic catalysts. The process requires several hours heating at high temperature (> 200°C) and vacuum is often applied at the end of reaction to distil off the last traces of by-product from the viscous reaction medium, in order to shift esterification equilibrium toward polymer formation.[1] Such harsh conditions favor side reactions that can lead to uncontrolled molar masses, architectures and microstructures. Alternatively, high-molar-mass polyesters can be obtained by solution reactions of acid chlorides or activated carboxylic acids and diols in milder conditions and shorter time. However, the use of expensive and/or toxic starting reactants and solvents are additional drawbacks.

Removing and/or replacing volatile and harmful solvents as well as saving energy and time are the challenges of green process research. In this context, ionic liquids (IL)s have appeared as interesting novel polymerization reaction media, owing to their unique properties: negligible vapor pressure, high thermal and chemical stabilities, non-flammability and reusability.[2] In previous studies, we reported on polyesterifications in ionic liquids, mainly dialkylimidazolium salts.[3,4] Reaction rate was in the same range as observed for common bulk polyesterifications, but the activity of common catalysts, such as $Zn(OAc)_2$, was very low. This was assigned to the formation of interactions between the catalyst and IL anions, instead of interactions between catalyst and carboxylic acid end-groups. Brønsted acid ionic liquids (**BAIL**s) are a class of ionic liquids that can be used as solvent and strong-acid catalyst for the synthesis of esters. However, to date, no polyesterification has been studied in these ionic liquids.

We report here on the first direct polyesterifications undertaken in **BAILs** at low to moderate temperature, atmospheric pressure and without any added catalyst. The polyesterification of 12-hydroxydode-canoic acid (**12-HDA**) was investigated using various 3-alkyl-(4-sulfonyl)imidazolium **BAILs** as both reaction media and catalysts. The effect of the nature of ionic liquids, of reaction time and temperature, of nitrogen flow rate and of **BAILs**/**12-HDA** molar ratio on average molar masses and yields was investigated.

High molar mass poly(**12-HDA**) (*Mw* = 40000) were obtained at low to moderate temperature (90-130°C) in short reaction time (30-60 min) and at atmospheric pressure (**Fig. 1**), reaction conditions that are considerably milder than conventional ones (5-7 h, 180-220°C, vacuum). Reaction kinetics, probable reaction mechanisms, and the post-polycondensation of various oligoesters in **BAILs** will also be discussed.



SEC chromatograms of poly(**12-HDA**) obtained at various reaction times in 3-butyl-1-(butyl-4-sulfonyl)imidazolium hydrogen sulfate at 110°C

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THIOPHENE BASED CONJUGATED POLYELECTROLYTES BEARING IONIC MOIETIES- LAYERS ASSISTED BY ELECTRODEPOSITION IN IONIC LIQUIDS

Shahzada Ahmad, Hakan Yildiz, Rüdiger Berger, Hans-Jürgen Butt

Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany
E-mail:ahmad@mpip-mainz.mpg.de,shahzada80@gmail.com

Keywords: *Conjugated polyelectrolytes, Ionic liquids, Scanning force microscopy.*

Conjugated polyelectrolytes (CPEs) are a relatively new class of conjugated polymers that can be distinguished with pendent group having ionic side moieties.[1] These CPEs polymers are of special interest because of their unique optoelectronic/redox properties. Conjugated backbone helps with solubility in polar solvents while processability occurs due to the ionic solubilizing groups.

Due to their hydrophobic backbone and hydrophilic side group, CPEs are amphiphilic and have a tendency to aggregate in aqueous solution or polar organic solvents. These polymers permit a well-controlled and facile film preparation via layer-by-layer assembly or by adsorption onto a charged substrate. Room temperature ionic liquids (RTILs) are particularly electrochemically stable and are not just liquids but with unparalled physico-chemical properties, can also totally alter the reaction pathways and now regarded as designer solvents. RTILs are flawless and powerful media for the electrodeposition of conducting polymers films, [2] and more recently it has been advocated to revisit this old synthetic route for the creation of fine nanostructured film for organic photovoltaic materials. It is known that polymerizing media has a strong influence on morphology and it controls the film microstructure.

Poly (thiophene) backbone and substituted with perfluoroalkyl anionic side groups have been prepared using 1-butyl-3-methylimidazolium-bis-(trifluoromethylsulfonyl) imide, (BMITFSI). The anion of CPEs and RTILs were chosen as such, to be of the same molecule, to overcome any side products formation. The electrodeposition results in the formation of uniform, shiny and adherent thick polymer films with an extended fine structure, on conductive glass substrates. Cyclic voltammetry studies revealed that the polymer was susceptible to both p- and n- doping. These CPEs exhibits fast electrochromic switching at low voltage from highly metallic like deep pink to almost transparent colour. Scanning force microscopy (SFM) and conductive force microscopy (CFM) have been employed to probe local heterogeneities in the topography and transport properties of the synthesized CPEs films. SFM reveals high surface area fibre like morphology while CFM suggests uniform distribution of current throughout the samples. A new phenomenon has been observed that due to the ionic moieties as a side group, these CPEs can be switched at localized level in-situ with the help of CFM cantilever tip, just with the applications of reverse potential. This is of immense interest as it will eliminate the use of any liquid electrolytes to oxidize/reduced the polymers. This facilitates its applications in data storage as well as sensor at nanometer scale. It is a facile, repeatable and controllable method to meet the challenges for polymers in electronics applications.

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SYNTHESIS AND RHEOLOGY OF BIODEGRADABLE POLY(GLYCOLIC ACID) PREPARED BY MELT RING OPENING POLYMERISATION OF GLYCOLIDE

Estelle Gautier,* Patrick Fuertes, ** Philippe Cassagnau,* Jean Pierre Pascault,* Etienne Fleury*

** Université de Lyon, Lyon, F-69003, France, CNRS UMR5223, Ingénierie des Matériaux Polymères, INSA de Lyon, Laboratoire des Matériaux Macromoléculaires, IMP/LMM, F-69621 Villeurbanne, France ;*
** Division Recherche, Roquette Frères, F-62080 Lestrem Cedex, France*
E-mail: etienne.fleury@insa-lyon.fr

Keywords: *Poly(glycolic acid), ring-opening polymerization, rheology*

Synthetic petrochemical-based polymers have been extensively used and studied since 1940s. These materials have numerous advantages, nevertheless they present two disadvantages: their non-renewable origin and their poor biodegradation. Therefore Biodegradable polymers have been considered as alternative environmentally friendly polymers. Advances in the synthesis, manufacture, and processing of these materials have given rise to a broad range of applications from packaging to biomedical devices.[1] The linear aliphatic polyesters are particularly attractive and mostly used, especially those derived from lactic acid (PLA), glycolic acid (PGA), and their copolymers (PLGA). PGA is less studied than PLA, two reasons can be proposed: glycolic acid is more expensive than lactic acid, and PGA is difficult to characterize because of its poor solubility within common organic solvents. Indeed PGA is highly crystalline and only soluble in hexafluoroisopropanol (HFIP) up to a molar mass of 45000 g/mol.[2,3] Surprisingly, Mark-Houwink parameters for HFIP solutions are not available in literature and, in addition, the power law in molten condition between molar mass and zero shear viscosity has not yet been reported in literature. In this study, PGA with controlled molar masses ranging from 2000 to 42000 g/mol were synthesized by ROP of glycolide in melt conditions and in the presence of two different initiators: 1-dodecanol and 1,4-butanediol. Their thermal properties were evaluated by DSC analysis and a glass transition temperature at infinite molar mass (Tg_∞) of 44.8 °C was thus calculated. From rheological data the critical molar mass for entanglement, Mc, was estimated to be near 11000 g/mol. *In situ* polymerizations were also performed between the plates of the rheometer within a same temperature range from 210 to 235°C. The variation of the storage and loss moduli during the polymerization step have been monitored by time sweep oscillatory experiments under an angular frequency $\omega = 10$ rad.s^{-1} and it was also possible to develop a kinetic modelling of the polymerization by inverse calculation. Such approach and few experimental data obtained are new and allow to better describe the melt ring-opening polymerization of glycolide and rheological properties of PGA. For instance, fine tools are now available to control a processing machine for continuous PGA production in extruder.

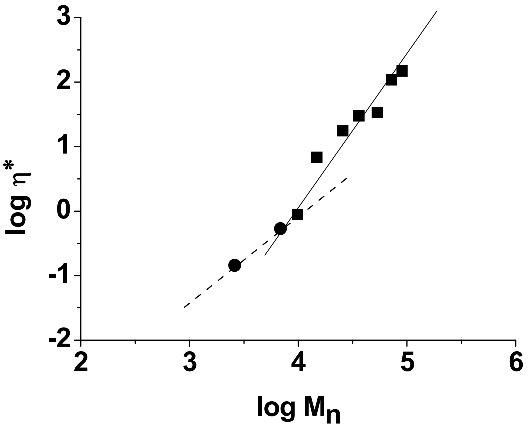

Figure 1. Poly(glycolic acid) Molar Mass dependence of the zero shear viscosity: T = 235°C

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PREPARATION AND TRANSPORT PROPERTIES OF CHITOSAN-LAYERED SILICATE NANOCOMPOSITE FILMS

Tihminlioglu Funda*, Oğuzlu Hale

Department of Chemical Engineering, İzmir Institute of ,Technology, Gulbahce Urla İzmir 35430, Turkey
E-mail:fundatihminlioglu@iyte.edu.tr

Keywords: Chitosan, layered silicate, transport properties

Use of natural polymers, such as proteins and polysaccharides, as coating or film materials for protection of food has grown extensively in recent years. Chitosan is the one of the most abundant natural biopolymer and a partially deacetylated derivative of chitin. Several researchers work on the potential of chitosan for biodegradable food packaging applications. Because of its good film-forming properties it is especially used as edible films and coatings for instance the storage of fruits and seafood products. However, the main drawback in these applications is their high water permeability and low water resistance at high relative humidity conditions due to large number of hydrogen bonds existence in chitosan. In this study, chitosan nanocomposite films were prepared using a solvent-casting method by incorporation with an organically modified montmorillonite (Cloisite 10A). The effects of filler concentration on the water vapor, gas permeability, mechanical and thermal properties were evaluated.

The water vapor and gas permeability values of the films decreased significantly depending on the filler concentration and the type of filler used. The decrease in water vapor and gas permeability of chitosan-clay nanocomposite films is believed to be due to the presence of ordered dispersed clay nanoparticle layers with large aspect ratios in the polymer matrix. This causes an increase in effective path length for diffusion of water vapour and gas into polymer matrix. Permeation data was fitted to various phenomenological models(1-2), predicting the permeability of polymer systems filled with nanoclays as a function of clay concentration and aspect ratio of nanoplatelets. Tensile strength of the composites increased with the addition of clay, however thermal properties were not much affected through the intercalation of clay into polymer matrix.

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IONIC POLYMERIZATIONS IN IONIC LIQUIDS

Przemysław Kubisa, Tadeusz Biedroń

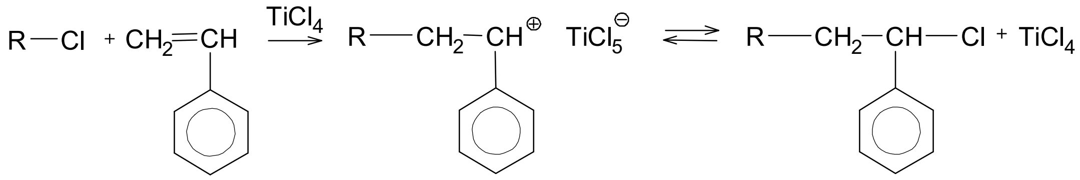
Center of Molecular and Macromolecular Studies, Polish Academy of Sciences,
112 Sienkiewicza, 90-363 Lodz, Poland,
e-mail: pkubisa@bilbo.cbmm.lodz.pl

Keywords: *ionic liquids, cationic polymerization, anionic polymerization*

Ionic Liquids (IL's) are organic salts that are liquid at ambient temperatures. IL's have emerged as a new class of solvents due to their unique combination of low volatility, chemical stability, ability to dissolve organic and inorganic solutes and tunable solvent properties. There is a growing number of papers describing application of ionic liquids as solvents for polymerization processes.[1a,b] Intuitively it can be expected that because IL's are composed of positively and negatively charged ions they should be highly polar thus their application as solvents could be especially advantageous for ionic polymerization processes.

Ability of IL's to dissolve inorganic compounds was exploited in the study in which organoborate acids were used as initiators of the cationic polymerization of styrene in IL's. M_n values were close to calculated up to DP_n~20 and dispersity was low (~1.3). The system was described as controlled polymerization.[2]

We have studied cationic polymerization of styrene in the system in which equilibrium between dormant and active species governs the concentration of growing ionic species. It has been expected that polarity of ionic liquids would favor ionization of C-Cl bond.



Although ionization of C-Cl bond indeed proceeded in IL solution even in the absence of coinitiator ($TiCl_4$) and polymerization proceeded to complete conversion, full control of polymerization could not be achieved. Ionization of C-Cl bond in IL solution was confirmed by measurements of the rate of racemization of optically active 1-phenylethyl chloride (model of dormant species). Although racemization (proceeding by reversible ionization of C-Cl bond) was observed, its rate was relatively low as compared to the rate of polymerization, therefore the requirement of fast interconversion of active and dormant species was apparently not fulfilled. More recently we have shown that ionization of C-Cl bond may proceed more efficiently in IL/SO_2 mixtures (several IL's may dissolve up to 2 moles of SO_2 per 1 mole of IL) although the rate of ionization was still not sufficient to achieve fully controlled cationic polymerization of styrene.[3]

Anionic polymerization in imidazolium IL's may be hampered by acidity of proton in 2-position in imidazolium ring although anionic polymerization of methyl methacrylate in IL's has been described. On the other hand acidic proton may be used for functionalization of IL's. We have found that when paraformaldehyde is dissolved in 1-alkyl-3-methylimidazolium chloride, reaction proceeds by which C(2)-H group is quantitatively converted into C(2)-CH_2-OH group. By this reaction acidic proton is removed and functional –OH group is introduced into imidazolium ring of IL. Alkoxide ions formed by reaction of –OH group with NaH were used to initiate anionic polymerization of ethylene oxide (EO). Polymerization gave imidazolium ionic liquids containing polyoxyethylene chains attached at 2- position with quantitative yields.[4] As IL's are used as components of PEO based solid polymer electrolytes, such materials may find practical applications.

These and other examples of ionic polymerizations in IL's will be discussed in the presentation.

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NEW RESULTS IN DISSOLUTION AND DERIVATIZATION OF CELLULOSE IN IONIC LIQUIDS

Jun Zhang

Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Engineering Plastics (KLEP), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
E-mail: jzhang@iccas.ac.cn

Keywords: *Cellulose, Ionic liquids, Dissolution and derivatization*

Since Swatloski et al [1] reported the dissolution of cellulose in alkyl substituted imidazolium based room temperature ionic liquids (RTILs), it has attracted considerable attention in this area. Recent studies on the application of RTILs in cellulose chemistry have made great progresses. [2-6] It is now accepted that RTILs have been providing a new and versatile platform for the wide utilization of cellulose resources and preparation of novel cellulose-based materials with special properties. In this work, we will report some new results in dissolution and derivatization of cellulose in RTILs.

(1) Dissolution mechanism of cellulose in RTILs has been investigated by using cellobiose and 1-ethyl-3-methylimidazolium acetate (EmimAc) as a model system under various conditions with conventional and variable-temperature NMR spectroscopy. The NMR data of the model system clearly suggest that hydrogen bonding is formed between hydroxyls of cellobiose and both anion and cation of EmimAc. The CH_3COO^- anion favors the formation of hydrogen bonds with hydrogen atoms of hydroxyls, and the aromatic protons in bulky cation $[Emim]^+$, especially the most acidic H2, prefer to associate with the oxygen atoms of hydroxyls with less steric hindrance.

(2) Taking advantage of the extremely low vapor pressure of RTILs, the solution morphology of cellulose in RTILs was observed directly by conventional high-resolution transmission electron microscopy (HR-TEM). In the fresh prepared cellulose solutions of RTILs, undissolved cellulose structures at multiscale level including elementary fibrils, microfibrils and lamellar crystals were observed. After a long-time storage, most of these cellulose structures disappeared and the relatively uniform cellulose solutions were formed.

(3) Using 4-dimethylaminopyridine (DMAP) as an organic catalyst, cellulose-g-PLLA copolymers with a wide range of composition were prepared by the homogeneous graft reaction of cellulose with L-lactide in an ionic liquid 1-allyl-3-methylimidazolium chloride. Interestingly, some cellulose-g-PLLA copolymers with relatively high molar substitution of PLLA were found to be thermoplastic.

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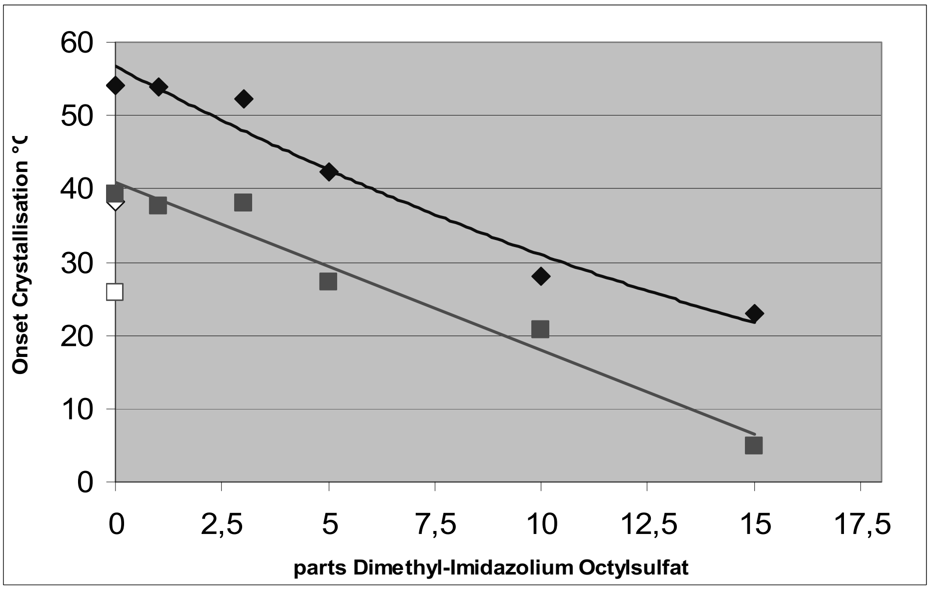
IONIC LIQUIDS AND POLYMERS

Friedrich Georg Schmidt*, Peter Schwab**

**Innovation Management New Technologies, Business Unit Coatings & Additives, Evonik Degussa GmbH, Paul-Baumann-Straße 1, D-45764 Marl*
*** Innovation Management, Business Unit Consumer Specialties, Evonik Goldschmidt GmbH, Goldschmidtstr. 100, D-45127 Essen*
E-mail: friedrich-georg.schmidt@evonik.com

Keywords : polymers, polymerisation, Ionic Liquids

During the last 30 years the interest into Ionic Liquids and the interaction or combination with polymers increased dramatically. Ionic liquids are ambient temp. molten salts and have attracted considerable attention because of their unique properties such as nonflammability, negligible volatity, high ionic cond., and thermal stability.
The presentation gives a brief overview about the state of the art of polymerisation, polykondensation, enzymic, group transfer and other polymerisation methods in or with Ionic Liquids.
Ionic Liquids are continuing as important media for various kinds of polymerisations. So e.g atom transfer radical polymisation catalysts are being attached to Ionic Liquids to make them more easily recoverable in living polymerisations. In addition, the number of polymerizable Ionic Liquids is steadily increasing. Ionic Liquids polymers of polymerizable ionic liq. monomers have been produced as exotic polyelectrolytes.
Ionic Liquids are used as plasticizers of various kinds of polymers and as key components in new classes of polymer gels.



The ionic interaction between polar polymers like polyamides and Ionic Liquids can be used to modify the bulk properties. A tuning of polymer properties by Ionic Liquids is demonstrated by an example of polyamide-elastomers. By adding of, e.g., 1-Ethyl-3-methyl-imidazolium tosylates to polyetheresteramides (VESTAMELT), which are used as hotmelts, only a very little depression of the melting point can be observed, but cristallinity and more interesting the speed of recrystallisation from the melt is increased.
As to be expected the glass transition temperature is decreased as a fourth effect.

Polymers and inorganic substrates are being used to support Ionic Liquids through covalent binding of the Ionic Liquids and polymer membranes and porous materials absorb Ionic Liquids with concomitant changes in ionic conductivity and mobility. The presentation tries to cover the newest aspects of Ionic Liquids in applications where their ion conductivity is exploited; as electrolytes in batteries and fuel cells where conventional media fail.
The influence of the polymeric material will be described briefly. The selection of the monomers e.g. with respect to polarity and the polymer structures e.g. random copolymers or block copolymers offer a huge potential to design unique materials.
Already existing applications, some application fields for the future including creating new classes of advanced materials will be shown.

COMPARISON OF DIFFERENT METHODS OF CROSSLINKING SODIUM CASEINATE FILMS

Mariana Pereda, Norma Marcovich, Mirta I. Aranguren

**INTEMA- Facultad de Ingeniería, Universidad Nacional de Mar del Plata, Argentina
E-mail: marangur@fi.mdp.edu.ar

Keywords: *protein films, crosslinking, polyelectrolyte complexation.*

The goal of this work was to investigate different methods to crosslink sodium caseinate (NaCas) films, by analyzing and comparing the final properties of the films (potentially useful as food packaging): mechanical, water vapor sorption and permeability. The crosslinking chosen methods were: a) use of glutaraldehyde (GTA) as chemical crosslinker, b) thermal treatment, c) complexation with a polysaccharide (chitosan, Chit).

The films were obtained by a casting/solvent evaporation method from dilute aqueous solutions, using glycerol (28 wt%) as plasticizer.

The first method (a) was followed by measuring the total soluble material (TSM), which indicated that the level of crosslinking increases as glutaraldehyde content increases. Visual inspection of the films showed a more intense yellow coloration as glutaraldehyde content was increased, due to the crosslinking reaction, which proceeded via Schiff-base formation.[1] Tensile and thermal degradation (TGA) properties, as well as water vapor permeability, were measured to characterize the films. Thermal gravimetric analysis showed an increase of about 15 ºC in the initial degradation temperature due to GTA crosslinking, indicating improved thermal stability of the films. Final properties showed not much improvement at concentrations below 10 wt.% with respect to those of the uncrosslinked film. This was explained as the result of the disruption of the strong H-bonding interactions present in neat caseinate films, which was barely compensated by the introduction of low amounts of covalent SC-GTA bonds.

The thermal treatment (b) was much more successful with the added advantage of not incorporating potentially toxic crosslinkers. Samples were prepared by the usual casting method and thermally treated at constant different temperatures (95-105°C) for different amount of time (0-24 hours), to investigate the effect of heating the caseinate films. Disulfide bridges formed between the protein chains were responsible of crosslinking. The properties were largely improved; by heating at 95 °C during 6 hours: total soluble mass was reduced by ~ 40wt.%, tensile modulus more than double the value for the unheated sample (251 to 525 MPa), with a slight decrease in the elongation at break. Although there was just a small decrease in the equilibrium moisture content, the permeability dropped to $7.79 \pm 1.25\ 10^{10}$ g m/(Pa s m^2), a value almost 30% lower than the corresponding to the untreated film (measured at 100:64.5% relative humidity, 24°C).

The use of chitosan to form a polyelectrolyte complex (method c) was also quite successful. Chitosan is edible and also has biocide properties, which make it an interesting crosslinker, although the pH conditions had to be carefully selected to allow for the polysaccharide dissolution and to avoid protein coagulation. The co-dissolution was done at pH =5. Tensile and impact testing showed that the complex films presented a synergistic effect, so that tensile modulus and impact energy increased with respect to the control caseinate films. Moreover, the equilibrium moisture content was lower that any of the one-component films.

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RETENTION TECHNOLOGIES FOR IMPROVED ASH RETENTION AND PRODUCTIVITY IN PAPER PROCESSES

Markus Bröcher, Nathalie Sieverling, Lotta Kanto Öqvist

Ashland Hercules Water Technologies, Ashland Deutschland GmbH, Fütingsweg 20, D-47805 Krefeld
E-mail: mbroecher@ashland.com

Keywords: *ash retention, polyacrylamide*, *formation*

Paper is a complex mixture of fibres, fillers and other functional and process additives. These additives are incorporated in the sheet to deliver desired properties such as strength, sizing, opacity, etc.. Retention programs are an essential component of any modern wet end chemistry regime because retaining these process and functional additives in the sheet as it is formed not only ensures that the desired sheet properties are met but also ensures good cost control. Retention programs can range from a single-component product to a complex program consisting of multiple components added at multiple addition points throughout the wet end (*1-3*).

Designing a retention program to provide high ash and fines retention, while not adversely impacting formation, drainage and machine runnability is the hallmark of an excellent retention program. To meet this challenge has been the focus of much R&D work. To date, a variety of multi-component programs consisting of coagulants, starch, flocculants and microparticles (silica, bentonite, etc.) have demonstrated the ability to deliver these results, but cost and complexity limit their utility. The talk will mainly focus on two new and patented retention aid technologies, that help papermakers achieve the criteria of an excellent retention system, as previously described.

Chemically the products are based on cationic polyacrylamides. Different polymerization/process technologies are used to synthesize the dual systems.

The first is a bi-molecular cationic aqueous dispersion polymer (water-in-water referred to as W/W, Fig. 1), and the second is a bi-molecular cationic inverse emulsion polymer (water-in-oil referred to as W/O, Fig. 2). The unique feature of these products is that they combine two polymers with different molecular weights and cationic charges. These new products have been successfully used as retention aids for a variety of paper grades with demonstrated improvements in key parameters such as ash retention, formation, runnability and sheet quality as compared to standard retention programs available in the market. Case histories are presented that highlight key benefits and that show, that the two dual component retention aid technologies meet the criteria of excellent retention required by papermakers. The products that contain more than one polymer often show better results than standard products on ash retention and drainage.

The new Water-in-Water dispersions (W/W) are easy to add to the process, have better mixing behavior, can be used successfully in combination with other products, can increase drainage and can provide excellent retention for tissue applications. The new dual Water-in-Oil emulsions (W/O) have shown the ability to increase ash retention and lead to less product consumption.

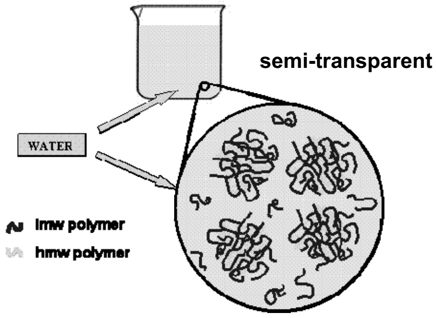

Fig. 1 Water in Water (W/W) Dispersion

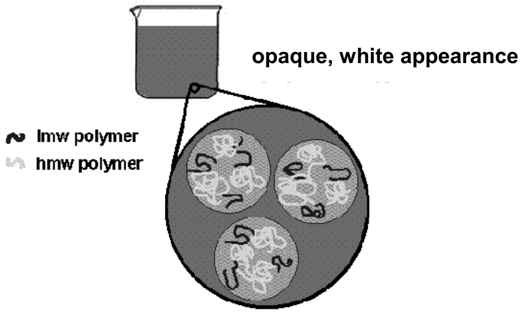

Fig. 2 Water in Oil (W/O) Emulsion

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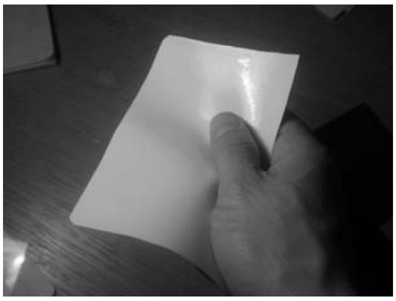
WHEAT GLUTEN – A RENEWABLE SOURCE FOR PLASTIC PRODUCTS

S.-W. Cho[1], N.H. Ullsten[1,2], M. Gällstedt[2], G. M. Spencer[3], E. Johansson[3], R. Kuktaite[3], S. Marttila[4], R. Ignell[4], Thomas O.J. Blomfeldt[1], R. T. Olsson[1], M. Menon[5], D. Plackett,[5] M. S. Hedenqvist[1]

[1]*Department of Fiber and Polymer Technology, Royal Institute of Technology, SE-10044, Stockholm, Sweden*
[2]*STFI-Packforsk, Packaging and Logistics, Box 5604, SE-114 86 Stockholm, Sweden*
[3]*Department of Agriculture – Farming Systems, Technology and Product Quality, The Swedish University of Agricultural Sciences, Box 104, SE-23053 Alnarp*
[4]*Department of Plant Protection Biology, The Swedish University of Agricultural Sciences, Box 102, SE-23053 Alnarp*
[5] *Risø National Laboratory for Sustainable Energy, Technical University of Denmark, DK-4000 Roskilde, Denmark*
E-mail: mikaelhe@polymer.kth.se

Keywords: *wheat gluten, processing, renewable resources.*

This presentation deals with wheat gluten as a source for plastics. It touches on a broad range of processing techniques to convert wheat gluten into plastic products. For several years, we have worked with vital wheat gluten and its processing properties. The processing techniques include casting[1,2], compression molding[3,4], extrusion[5,6], injection molding and freeze-drying/foaming. In this presentation the properties of plasticized vital wheat gluten materials produced from the above methods will be discussed. The effects of the different processing routes on the final molecular, mechanical and barrier will be exemplified. The sealability as well as the visual appearance will be discussed. The pictures below show a compression-molded film with white filler (left) and paperboard boxes coated on the inside with green or uncolored translucent compression molded films. As observed it is easy to color the material and the mechanical properties can be tuned from a soft flexible to a rigid and strong material.



If necessary the material can be reinforced with fibers, e.g. from renewable resources such as hemp and bacterial cellulose. Casting generates thin films with sometimes good transparency wheras compression molding is more suitable for making thicker films and if more advanced shapes are necessary. Extrusion puts more demand on the starting material. It has to have a suitable combination of melt viscosity and final mechanical properties. Injection molding requires even higher demands on the starting material. Despite this we have recently been able to injection mold plasticised wheat gluten. The final material behaves somewhat similar to the “best” extruded material, even though the recipies/material approach differ. Yet a different approach has been used in theseection of the starting material/recipie to produce foams. It has been shown that the freeze-drying approach generates rigid or semi-rigid foams with mainly open cells.

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TRIBOLOGICAL PROPERTIES OF POLYMER BRUSHES: GRAFTING-FROM AND GRAFTING-TO

Nicholas Spencer

Laboratory for Surface Science and Technology, Department of Materials, ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland
E-mail: nspencer@eth.ch

Keywords: *polymer brushes, tribology*

Polymer brushes constitute a fascinating and technologically important class of polymer coatings on surfaces, and to some extent have analogs in nature, where glycoproteins, for example, can form a brush-like coating of polysaccharide chains on surfaces, protecting them or lubricating them[1] as a consequence.

Polymer brushes have been extensively investigated, both experimentally[2] and theoretically[3], and many studies have been made on their applications in biology, in particular, where they can be used to modify protein-adsorption behavior[4].

In our laboratory we have focused on the use of polymer brushes for lubrication, in particular in an aqueous environment[5]. Our initial experiments concerned poly(ethylene glycol) brushes adsorbed on metal oxide surfaces, adsorbed by means of a graft co-polymer structure, utilizing a positively charged, poly(lysine) backbone. Further work has extended the application of these polymers to polymeric and ceramic substrates, and included the replacement of the brush-forming chains by dextran and of the backbone by poly (allyl amine).

The tribological behavior of grafting-to systems such as these has been characterized on the nano and macro scales, the latter in both sliding and rolling contact, on a wide variety of surfaces. The lowest obtainable friction coefficients are to be found on elastomeric surfaces, due to the lower contact pressures involved, which lead to less abrasive wear of the adsorbed polymer layer. On hard surfaces, rolling contact shows a much greater effect of the added graft copolymers than does sliding, for similar reasons.

The great advantage of the graft-copolymer approach is that the adsorption is electrostatic and reversible, such that molecules that are removed (intact) by abrasion, can be spontaneously replaced by other molecules from solution. This relies, of course, on the presence of free graft-copolymer molecules in solution. In cases where this is not possible, a more robust surface-binding approach can be obtained via grafting-from methods, which also have significant advantages in terms of maximum molecular weight and surface-grafting density. A wide variety of grafting-from systems has been tested, including poly(methacrylic acid) and poly(acrylamide). A highly practical approach to the fabrication of these brushes has been developed, based on the use of ultraviolet LEDs as a light source in UV controlled radical polymerization via iniferters[6].

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THE MECHANICAL PROPERTIES OF BRUSH-COATED NANOPARTICLES IN A HOMOPOLYMER MATRIX

S.A. Pihan[1], **S.G.J. Emmerling**[1, 2]. **R. Berger**,[1] **J.S. Gutmann**[1, 2]

1 Max-Planck-Institute for Polymer Research, Mainz, Germany
2 Institute of Physical Chemistry, Johannes Gutenberg University, Mainz, Germany
E-mail: Pihan@mpip-mainz.mpg.de

Keywords: *Nanocomposite, Mechanics, Cantilever sensors*

Nanocomposite materials have gained a lot of interest because their ability to tailor existing material properties like elastic modulus or to add new functionalities like electric conductivity [1]. During preparation of nanocomposite materials the central problem is the intrinsic incompatibility between the high energy inorganic filler surfaces (e.g. SiO_2) and the lower energy polymer matrix (e.g. PS). The approach to graft polymer chains to inorganic nanoparticles can drastically enhance the dispersion of particles in a homopolymer matrix. Furthermore the mixture of the brush-coated nanoparticles with different molecular weight homopolymer allows tailoring mechanical properties of the composite material [2].

In our studies we prepared polysilsesquioxane nanoparticles having diameters of 15 to 30 nm [3]. Polysilsesquioxane-synthesis was chosen because it offers the possibility to create very small microgel-particles with a polydispersity down to 0.13 (the polydispersity was calculated by standard deviation divided by the mean square diameter). In a "grafting from" step we used atom transfer radical polymerization (ATRP) to grow poly-ethyl-methyl-acrylate (PEMA) brushes on these microgel-particles yielding well defined PEMA-grafted-microgels (PEMA-g-µgels). We expect that the PEMA brush interface determines the structure of homopolymer surrounding phase significantly. The above mentioned preparation route enabled us to separately control the diameter of the microgel-particles and the length of the polymer brushes (35 - 50 nm).

The radii of individual microgel-particles were investigated by means of non-contact scanning probe microscopy (SPM) and dynamic light scattering (DLS). By analyzing the phase contrast images we were able to distinguish between the core particle and the brush. From the SPM analysis we could determine the size of the core and the surrounding, independently. We found that the calculated brush-length and the core diameter from DLS measurements are significantly smaller compared to our SPM investigations attributed to swelling effects of the core particle and the PEMA brush. To study the miscibility and dispersion of the PEMA-g-µgels in a homopolymer matrix we fabricated macroscopic structures of PEMA-g-µgels by the use of an inkjet-printer. By preparing intersections of the printed structures we were able to investigate textures and structure formation of the PEMA-g-µgels in homopolymer matrix.

Mechanical properties of the above mentioned PEMA-g-µgel system are expected to depend on the core material, grafting density, molecular weight of the grafted polymer and molecular weight of the homopolymer matrix. In order to avoid exhaustive synthesis of PEMA-g-µgels we developed a nanomechanical cantilever sensor method to analyze the mechanical properties of nanogram materials. We deposited materials by inkjet printing of toluene dissolved PEMA-g-µgels dispersed in PEMA homopolymer matrix. Dried structures were then analyzed by investigating the vibration spectra of the nanomechanical cantilever [4].

The analysis of a thin, homogeneous polymer film made by plasma polymerization of norbornene has revealed that the applied nanomechanical method is suitable to determine viscoelastic properties. The Young's modulus derived from cantilever resonance-shift is consistent with complementary measurements. The investigation of thin heterogeneous films made from PEMA-g-µgels and PEMA homopolymer is currently performed.

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(VISCO-)ELASTIC NANO- AND MICROSTRUCTURING OF POLYSTYRENE SURFACES: FROM RIPPLING TO SOLVENT DROPS

Guangfen Li*, Yogesh Karade, Sascha Pihan*, Wilhelm Brünger ***, Andreas Dietzel**, Rüdiger Berger*, Elmar Bonaccurso*, Ramon Pericet-Camara*, Hans-Jürgen Butt*, Karlheinz Graf*,******

* *Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany*
** *Eindhoven University of Technology, Den Dolech 2, 5600 MB Eindhoven, The Netherlands*
*** *Fraunhofer Institute for Silicon Technology, Fraunhoferstrasse 1, D-25524 Itzehoe, Germany*
**** *University of Siegen, Physical Chemistry, Adolf-Reichwein-Str., D-57068 Siegen, Germany*
E-mail: graf@chemie.uni-siegen.de

Keywords: *surface structuring of polymers, rippling, droplet evaporation*

We present two types of polymer surface structuring that are based on the intrinsic surface properties of the polymer. In the first example, surface rippling on ion-irradiated stretched polystyrene (PS) substrates occurs upon heating the sample to the glass transition (Figure 1). The irradiation of the original PS sample leads to cross-linking of a superficial polymer layer with a thickness of ~ 100 nm - 1 µm, depending on the type of ion used. Heating leads to relaxation of the previously stretched sample to its original dimensions, thus forcing the superficial layer to ripple. The (sub-)microscopic ripple distances λ depend on the elastic modulus E_s of the surface layer and on its thickness d. Therefore, E_s can be determined if d and λ are known. We demonstrate this procedure by irradiating the PS surface with different types of ions (He$^+$, Ne$^+$, Ar$^+$) for different periods of times[1]. The ions penetrating the polymer surface primarily leads to breakage of C-H bonds in the polymer which promotes cross-linking. From computer simulations of the ion scattering and E_s the cross-link density can be determined. This way the cross-link density of ion-irradiated PS surfaces can be measured via surface rippling.

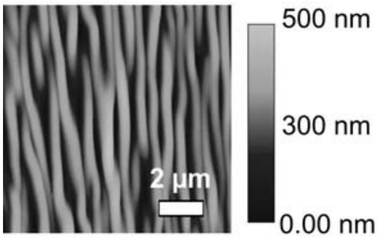

Figure 1 SFM image of a 200% stretched PS substrate after irradiation with 10^{13} Xe$^+$ ions/cm^2 and after annealing at 110 °C for 1 h in vacuum.

In the second example, PS surfaces are locally structured by deposition of liquid microdroplets. If non solvent-droplets as water are deposited on toluene-exposed PS substrates, ring-like concave microstructures are obtained with characteristic rim-heights and depths[2]. Both parameters can be described quantitatively with an elastic theory providing the average elastic modulus of the swollen PS surface. However, longer exposure times to toluene in the order of some minutes reveal a contribution from viscous deformation to surface structuring. If solvent drops are deposited on the original PS surface, the polymer is locally dissolved into the droplet. Additionally, a transport of the dissolved polymer chains from the center to the rim of the droplet is generated by droplet evaporation, an effect known from the formation of coffee-stains. Thus, for medium molar masses of some 100 kDa the polymer accumulates at the rim forming smooth concave surface structures (Figure 2). The resulting surface topography depends on a variety of intrinsic and process parameters. As an example, the influence from the molar mass of the PS will be discussed[3]. For low molar masses, the dissolution of the polymer into the droplet is fast compared to droplet evaporation so that gelation within the droplet occurs. Convex surface structures result. In contrast, at high molar masses of ~ 1 MDa local protrusions occur owing to poor dissolution.

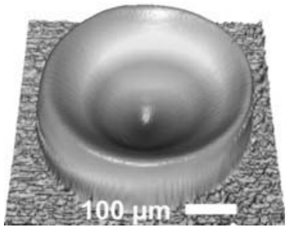

Figure 2 Concave topography in a 210 kDa PS surface after local deposition and evaporation of a toluene drop.

Such concave and convex structures in polymer surfaces can be used as low-cost microlens arrays with tunable focal length.

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SPONTANEOUS GROWTH OF FREE-STANDING CONDUCTING POLYMER THIN FILMS AT AIR/LIQUID INTERFACE

Jian Jin*, **Dong Wang***

* *Suzhou Institute of Nano-tech and Nano-bionics, CAS, Ruoshui Road 398, 215125, Suzhou, China*
E-mail: jjin2009@sinano.ac.cn

Keywords: *conductiong polymer, free-standing films, air/liquid interface*

Conducting polymer films have attracted great interests in many fields due to the emergence of increasingly processable materials with better electrical and physical properties and lower costs.[1,2] The preparation of conducting polymer films is mainly used electrochemical polymerization by depositing the films on electrodes. Therefore, the process is highly dependent on conducting substrates and due to fast polymerization speed during electropolymerization, the obtained films are usually less controllable in film thickness, uniformity, and performance.

Here, a novel strategy for fabrication of free-standing conducting polymer films with controlled thickness from several nanometers to hundreds of nanometers is presented. The films spontaneously grow at air/liquid interface (Figure). In the liquid, conducting monomer is dissolved at a certain concentration. The thickness of the films could be adjusted by changing the concentration of monomer in solution. In addition, asymmetric films with different uniformity of the upper and lower faces are obtained by changing experimental condition. At this case, the two faces exhibit different water wettability. The largest difference of contact angle of the two faces is up to 30ºC. Our work provides a facile, controllable and effective way to fabricate free-standing functional polymer films by using air/liquid interface as reaction field. The approach to attain free-standing conducting polymer films enables the fabrication of electronic devices that are not only more portable but also foldable and flexible.[3-5]

Figure. A) The schematic of free-standing conducting polymer film growing at air/liquid interface. B) The digital image of the film floating on water surface. C) The cross-section SEM image of the film.

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SURFACE FORCES ACROSS POLYMER MELTS

Jijun Wang, Rüdiger Stark, Gexiao Sun, Michael Kappl, Hans-Jürgen Butt

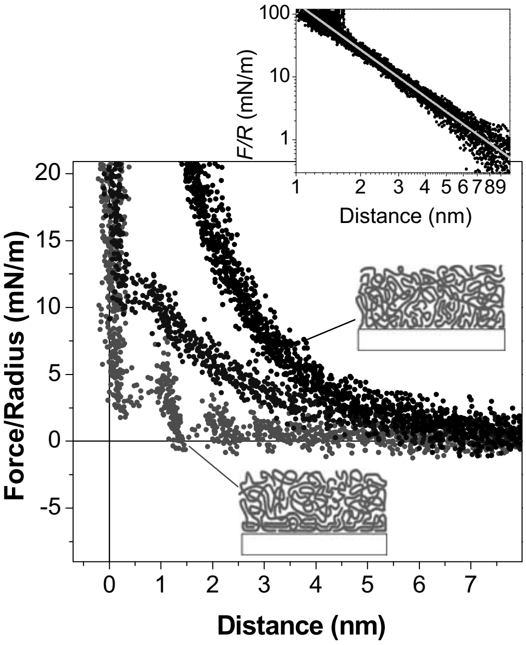
Max Planck Institute for Polymer Research, Ackermannweg 10 55128 Mainz
E-mail: butt@mpip-mainz.mpg.de

Keywords: *AFM, Surface Forces, Nanocomposite*

The structure of a composite material is influenced by the effective force between the filler particles in the polymer melt. Particles are well dispersed when this force is repulsive. If the interaction is attractive aggregates can form. Since the trend is towards using smaller and smaller particles, leading to nano-composite materials with huge internal interfaces, knowledge of the force becomes more and more important. Unlike the situation for aqueous dispersions, our understanding of forces in polymer melts is still rudimentary.

We studied forces across different polymer melts including poly(dimethyl siloxane), poly(ethylmethyl siloxane), and poly(isoprene) with the atomic force microscope (AFM).[1,2] Such experiments are not only important with respect to dispersing particles. A more fundamental interest is in the structure of confined polymers per se. In addition, force measurements provide information on the polymer-solid interface. In addition to monodisperse polymers we also studied mixtures of long and short chains.[3]

To better understand surface forces across polymer melts we measured the force in a melt of polymer chains with a functional end group.[4,5] As surfaces we used self-assembed monolayers (SAMs) of alkyl thiols with different end groups (methyl, amino, and hydroxyl) on gold. The polymer was a hydroxyl-terminated polyisoprene. Results indicate that the hydroxyl group of the polymer binds to the hydroxyl or amino groups of the SAMs. It forms a brush-like structure, which leads to steric repulsion. On amino-terminated SAMs force-versus-distance curves on approach and retraction were monotonically repulsive and reversible. With hydroxyl-terminated SAMs a jump was observed on approach when the load exceeded a certain threshold. On retraction an adhesion had to be overcome. We interpret the jump as a rupture of the polymer layer. It indicates that the kinetics of bond and brush formation is faster on OH-SAMs than on NH_2-SAMs.



Sequences of force curves recorded in PDMS (M_W=18000g/mol) on silicon oxide. Curves were recorded 30 min (red), 4 h (blue), and 20 h (black) after filling the cell with PDMS. Insert: Force curve after 20 h in log-log.

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MECHANICAL PROPERTIES OF MORPHOLOGIES STUDIED BY ATOMIC FORCE MICROSCOPY NANOINDENTATION: POLYMER BRUSHES AND POLYMERIC NANOPHASES

Davide Tranchida, Elena Sperotto, Holger Schönherr

Department of Physical Chemistry - University of Siegen, Adolf-Reichwein-Str. 2, 57076, Siegen, Germany
E-mail: tranchida@chemie.uni-siegen.de

Keywords: *Nanoindentation, Nanophases, Atomic Force Microscopy.*

Peculiar physicochemical properties of polymeric surfaces are responsible for a number of phenomena, such as adhesion, wettability, compatibility, and the ease of modification by surface chemistry. The use of block copolymers (BCPs) and polymer brushes has been exploited in this context to control surface structures with control of functionality on sub-micrometer length scales. In particular, BCPs are widely used to address the coexistence and distribution of nanometer scale domains, as well as to enhance the compatibility in advanced systems as for instance biological molecules, magnetic nanoparticles or ceramic precursors.

Atomic Force Microscope (AFM) nanoindentation has been used to study a large variety of polymeric morphologies.[1] In this work, we show the measurement of mechanical properties of single nanophases developed on poly(styrene)-block-poly(tert-butyl acrylate) (PS-b-PtBA) thin films. The composition and structure of the surfaces, before and after hydrolysis with neat trifluoroacetic, were characterized first. AFM images showed a repeating distance of roughly 100 nm, therefore it was possible to discern the mechanical properties of each phase by limiting the maximum penetration depth under load to ca. 10 nm and by using an AFM tip as indenter, with a radius of curvature at the apex of ca. 7 nm. Moreover, the phases were subjected to surface chemistry, allowing us to change the stiff and glassy PtBA blocks into the soft and rubbery PAA.

By performing nanoindentation at low loads, due to the extremely small volume involved in the stress field, it can be expected that nanoindentations were made on each single nanophase, i.e., locally homogeneous material. In this case, domains with comparable size affect the contact mechanics and result in the two bimodal distributions of the spin-coated sample shown in Figure 1A. Two sharp Gaussian distributions are obtained, centered at 7.0 and 8.9 GPa. The relatively simple shape of this curve can be understood once one recalls the AFM images of the morphology, showing that each phase covered roughly half of this repeating distance. Therefore, the two deconvoluted curves are approximately the same.

Figure 1B reports a set of several different force curves (plots of applied load vs. penetration depth) performed on an anisotropic poly(methyl methacrylate) (PMMA) sample, showing that polymer brushes are stiffer than the isotropic sample. In the debate on the properties of dry brushes, this confirms the results of Urayama et al.[2] Even more so when this qualitative information on compliance of the films is translated into a quantitative estimation of the Young's moduli of the samples. In this case, an elastic modulus of roughly 7.62 GPa is measured for the grafted chains, which should be compared to 5.78 GPa for the spin-coated one.

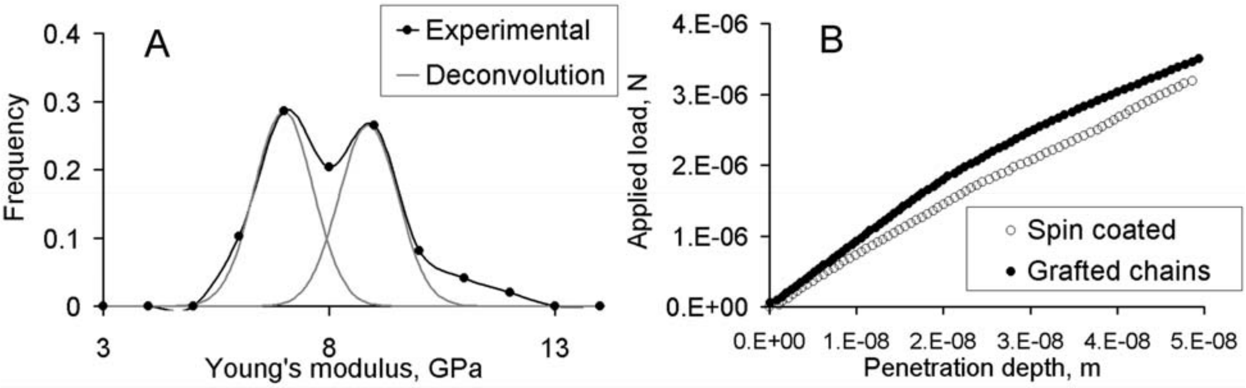

Figure 1. Distribution on Young's moduli for the microphase separated BCP (A). Force curves comparing the mechanical properties of an isotropic PMMA film, and a PMMA polymer brush (B).

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MORPHOLOGY AND OPTICAL PROCESSES IN SILVER NANOPARTICLES/CONJUGATED POLYELECTROLYTE SYSTEMS: APPLICATION TO SERS

S. Kazim[1], M. Prochazka[3], M. Bondarev[2], J.Vohlida[2], and J. Pfleger[1]

[1]Institute of Macromolecular Chemistry, AS CR v.v.i., Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic
[2] Charles University in Prague, Faculty of Sciences, Hlavova 2030, Prague 2, Czech Republic
[3] Charles University in Prague, Faculty of Mathematics and Physics, Ke Karlovu 5, Prague 2, Czech Republic
E-mail address: kazim.samrana@gmail.com

Keywords: *Conjugated polyelectrolyte, Ag nanoparticles, surface-enhanced Raman scattering*

In recent years, noble metal nanoparticles (NPs) have attracted a great deal of attention due to their size dependent optical and electronic properties that predetermine them for potential applications in biosensors, photonic and optoelectronic devices[1]. The resonance interaction of surface plasmons in metal nanoparticles with incident and scattered light gives rise to the surface enhanced Raman scattering of molecules or conjugated polymers that are adsorbed at the NP surface or located in its close proximity, and may affect other electronic process in the polymer as well. It was found that π−conjugated polyelectrolytes (CPEs) provide an interesting environment for metal NPs, which can both influence the morphology of NPs assemblies and bring new electronic properties based on the mutual interaction between plasmons and π-electron conjugated system.

In this work, we report the effect of π-conjugated polyelectrolyte, poly {3-[6-(1-methylimidazolium-3-yl)hexyl] thiophene-2,5-diyl bromide}), P3MIHTBr, prepared by quaternization reaction of poly [3-(6- bromohexyl) thiophene], with 1-methyl-1,3-imidazole, on the morphology and optical properties of Ag sol/P3MIHTBr systems formed by aggregation of silver nanoparticles. The polyelectrolyte concentration was found to have a strong impact on assembling of Ag NPs, and consequently, on the optical processes in the system. Silver hydrosol (average diameter of nanoparticles about 9 nm) was prepared by a simple chemical reduction method using $NaBH_4$ as a reducing agent. Ag sol/P3MIHTBr systems were prepared by adding P3HTIMBr dissolved in DMSO into the silver hydrosol at various concentrations. Upon addition of the polymer to the sol, the optical extinction spectra showed a second SPE band in the long wavelength spectral region that confirms the formation of NPs aggregates. The behavior of the system was explained by an electrostatic interaction of cationic polyelectrolyte with anionic surface of Ag nanoparticles. The electrostatic nature of the NPs stabilization in the colloid and aggregation induced by charge compensation was confirmed by the zeta potential measurements. At low polymer concentration, the surface charge of the NPs is only partially compensated and small but stable aggregates are formed. On the other hand, at high concentration the nanoparticles are spatially isolated by the polymer and no aggregates were observed. Upon optical excitation with appropriate wavelengths (457.9 and 514.5 nm) a well resolved enhanced Raman signal of the polymer was obtained, influenced by both the resonance excitation of the polymeric chromophore (resonance Raman scattering, RRS) and by the plasmon resonance excitation (surface enhanced Raman scattering, SERS), depending on the wavelength of incident light. In SERS, the strong enhancement, assigned to a formation of "hot spots" of a strong optical field localized in aggregates, was dependent on the size and degree of aggregation of the NPs developed at various concentrations of P3HTIMBr. In SERRS spectra observed for higher polymer concentrations, the strong signal originates from the non-aggregated NPs system with a prevalence of the single particle enhancement. The observed quenching of the polymer fluorescence in Ag sol/P3MIHTBr systems, particularly at lower polymer concentrations, points to the efficient energy dumping from the photo-excited conjugated polyelectrolyte to the nanoparticles. It suggests that Ag NPs serve as efficient fluorescence quenchers for π-conjugated polyelectrolytes.

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REAL-TIME CHARACTERISATION OF POLYMER INTERACTIONS USING QUARTZ CRYSTAL MICROBALANCE WITH DISSIPATION MONITORING (QCM-D)

Sofia Svedhem

Dept. of Applied Physics Chalmers University of Technology, Fysikgränd 3, 412 96 Göteborg, Sweden
E-mail: sofia.svedhem@chalmers.se

Keywords: *QCM-D, viscoelastiticy, real-time*

There is an increasing demand of analytical tools for the characterization of interactions of polymers with various surfaces and under different conditions. Monitoring the structural and dynamic changes within these polymeric films as they form, is of critical importance in understanding the behavior of polymers in their environment and optimizing the conditions for desired results. Quartz Crystal Microbalance with Dissipation Monitoring, hereafter referred to as QCM-D, is a real-time technology which monitors the adsorption and conformational changes of polymers or other molecules onto a surface. Extractable parameters are mass, thickness, viscosity and storage modulus. Here we present three studies where QCM-D has been used to obtain information about polymer films, not possible to get with other techniques.

Pluronic polymers[1] adsorb in a brushlike configuration on hydrophobic surfaces and in a pancake configuration on hydrophilic surfaces but the hydrophobicity threshold for the configuration is unknown. QCM-D measurements revealed that Pluronic F-127 adsorbed in a brushlike conformation on surfaces with a water contact angle above 80° as inferred from the thickness, viscosity and elasticity of the adsorbed layer. Additionally QCM-D showed that the concentration of Pluronic F-127 in solution affected only the kinetics of adsorption and not the final layer thickness or conformation of adsorbed Pluronic molecules.

The real-time changes in viscoelasticity of adsorbed poly-lysine and adsorbed histone due to crosslinking by glutaraldehyde, and the corresponding release of associated water was investigated using QCM-D.[2] There is an increasing interest in cross-linking polypeptides and proteins to increase protein stability. Using the Voigt viscoelastic model on the QCM-D data, the mass of the film as well as the changes in viscosity and storage modulus upon crosslinking could be determined. The variation in viscoelastic properties increased substantially after cross-linking presumably due to fluctuation of the randomly cross-linked network structure. An increase in fluctuation of the viscoelastic properties and the loss of entrapped water could be used as a signature of the formation of a cross-linked network and the amount of cross-linking, respectively.

The build-up of a polyelectrolyte multilayer of chitosan and alginate was monitored in the Q-Sense ellipsometry module which allows for simultaneous QCM-D and ellipsometry measurement.[3] Measured by QCM-D, the mass increments for alginate deposition were typically much higher than those for chitosan. Interestingly, the opposite trend was observed for the optical mass: here, the mass increase was slightly higher for chitosan than for alginate. This behavior reflects differences in the solvent content of both layers: upon addition of alginate, less polymeric material adsorbs but much more water is coupled into the film than upon addition of chitosan layers.

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COMPARISON OF MICROSCOPIC AND MACROSCOPIC MECHANICAL PROPERTIES OF SPIDER SILK: EFFECTS OF HYDRATION

Periklis Papadopoulos*, **Roxana Ene***, **Friedrich Kremer***

** Institute for Experimental Physics I – University of Leipzig, Linnéstr. 5, 04103 Leipzig, Germany*
E-mail: papadopoulos@physik.uni-leipzig.de

Keywords: *spider silk, FTIR, mechanical properties*

Spider dragline silk is a biopolymer with exceptional mechanical properties. It is composed of two high-molecular weight proteins, MaSp1 and MaSp2. The alanine-rich blocks form nanocrystals that are interconnected with slightly glycine-rich amorphous chains. Its high toughness is attributed to the breaking of hydrogen bonds in these domains. Recent studies have shown that the amorphous chains are significantly pre-strained and that the degree of pre-strain controls the macroscopic mechanical properties[1,2]. The silk spinning process creates a complicated hierarchical nanostructure and its understanding is important in order to reproduce silk properties in the lab. Even though similar proteins have been synthesized since a long time, attempts to produce spider silk-like fibers have only recently started to give the first promising results, using elaborate procedures[3].

In this study we attempt to determine the interconnection of the nanocrystal and amorphous phases in two states of spider dragline silk, native and supercontracted with water. Infrared spectroscopy is employed to measure crystal stress with a high time resolution, through the shift of main-chain vibration absorption bands[1,2]. The comparison with external stress is carried out while varying mechanical fields are applied to silk. The results show that in both states of silk a serial arrangement between the crystalline and amorphous phase dominates the nanostructure. However, water can break the hydrogen bonds of the amorphous chains and, in combination with hydrophobic effects, it induces the formation of a physical hydrogen-bonded network in the amorphous phase of the supercontracted state. This network increases stiffness, until a stress limit is reached. At higher stress the nanostructure of supercontracted silk is irreversibly transformed to one similar to native. This enables one to make a complete description of the mechanical properties of silk in both states, by taking into account the energy required to break these bonds in the previous structural model that assumed a pre-strain distribution of worm-like amorphous chains[4].

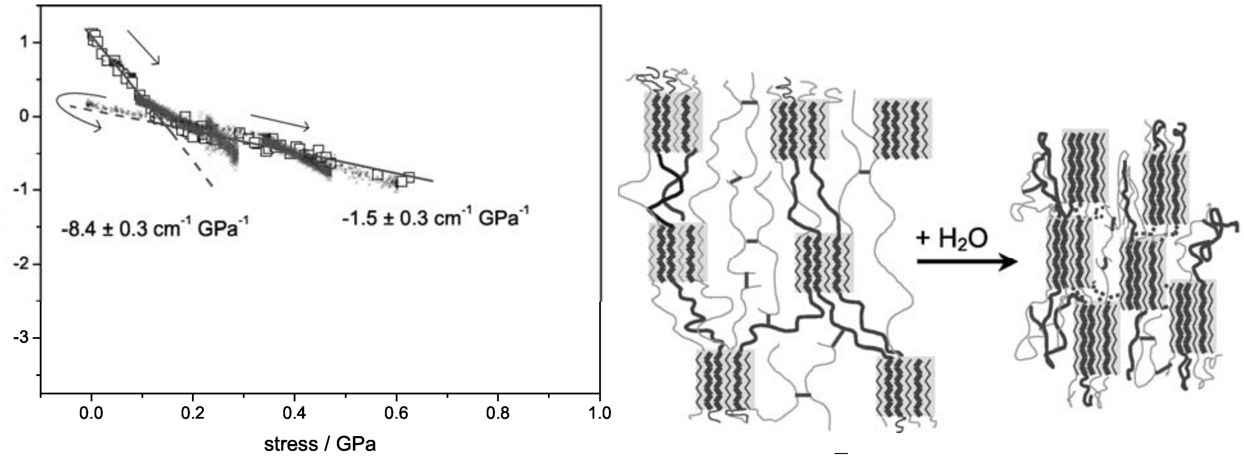

Fig.1: (Left) Comparison of crystal stress (proportional to band shift $\Delta\bar{\nu}$) with external, in supercontracted silk. The irreversible change of the ratio of the stresses after a threshold of ~ 0.2 GPa is exceeded indicates the breaking of hydrogen bonds. (Right) Combined structural model of spider silk. During supercontraction a new hydrogen-bonded network is formed.

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INFLUENCE OF LENGTH SCALE OF HETEROGENEOUS POLYMERS ON MECHANICAL PROPERTIES

Goerg H. Michler

Institute of Physics and Institute of Polymeric Materials – Martin Luther University Halle-Wittenberg, D-06099 Halle/S., E-mail: goerg.michler@physik.uni-halle.de

Keywords: *Nanostructured polymers, mechanical properties, electron microscopy*

The most important properties of many applications of polymers include their mechanical properties. Here, the micromechanical processes of deformation and fracture provide the bridge between structure/morphology and mechanical properties. A shift of interest to smaller and smaller details, from the former µm level to the now increasingly interesting nm level, is currently occurring. This increasing tendency to make structural modifications has also pushed polymer research to improve morphological control through the use of electron microscopy.

Three groups of amorphous and semicrystalline polymers with reduced length scales will be discussed:

- PS/PB blockcopolymers with a multilayered morphology reveal an extreme ductility of the usually brittle PS if the PS layer thicknesses are below a critical size of about 20nm [1].
- Multilayered polymers via coextrusion show, in general, an interesting combination of mechanical and optical properties. In detail, an increase in ductility has been observed if the layer thicknesses are thinner than critical sizes (depending on the type of polymer) [1, 2].
- Polymer nanofibers with a diameter of some 100 nm have been prepared from different polymers using an electrospinning process. By addition of nanoparticles new “nanofiber – nanocomposites” with an extremely fine and homogeneous distribution of the nanoparticles can be realized. The main problem in producing commercial polymer composites with nano-sized filler particles is avoiding particle agglomerates and achieving a good dispersion of the nanoparticles in the polymeric matrix. The advantage of electrospun nanofibers over other techniques is the fine distribution of the nanoparticles. Effects of increased toughness could be observed as consequences of both the nanoscale of the fibers and the size of particles [3].

A first attempt of a joint theoretical explanation of these different experimental effects on the nm-scale will be given in the lecture.

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MICROMECHANICS OF VISCOELASTOPLASTIC RESPONSE OF UNIDIRECTIONAL EPOXY RESIN COMPOSITE.

Kee Yoon Lee*, Sun Kyoung Jeoung, Jae Min Kim*, Hyo Yeon Hwang*, Do Young Kim*, Bum Jae Lee***

** Department of polymer Science and Engineering, Chungnam National University, Dae jeon, South Korea*
*** Korea Automotive Technology Institutem Chonan*
E-mail: kylee@cnu.ac.kr

Keywords*: creep, strain, viscoelastoplastic, viscoelasticity, viscoplasticity*

Polymeric composite materials exhibit viscoelastic as well as viscoplastic behavior with unidirectional continuous fibers. This is the reason why micro-damage accumulate in layers and viscoelastic or plastic stress-strain responses of the matrix. The elasticity was considerably pronounced in the loading axis coinciding or not with the fiber orientation [1] and [2]. On the basis of constitutive equations, the methods for evaluating the rheological properties of material from experimental data were outlined and illustrated for the polymeric composites.

Viscoelastoplastic strains of composites were simulated by using a theoretical integral model with experimental data [3]. In this study, the time-dependent responses of epoxy matrix composites to input loading and unloading were analyzed using creep and strain recovery tests by rheological views of viscoelasticity and viscoplasticity. A general nonlinear constitutive theory for multi-axial loading was started from thermodynamics principles of viscoelastic constitutive equations by Schapery and nonlinear viscoelastoplastic models suggested by Megnis and Varna. They were modified and generalized to describe inelastic behaviors of composites under isothermal creep and strain recovery conditions.

The current model needed the numerical method of least mean square formulation to find out the constants [6]. Calculated results for creep and recovery were compared and reasonably verified with experimental data in Ref [3]. The concepts of this model can show us the basic steps for predicting the creep and recovery properties of the composite materials only from the properties of polymer and fillers [6].

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ENTHALPY RELAXATION IN PC/PMMA MULTILAYERED FILMS FROM MICRO TO NANO SCALE.

K. Arabeche*, L. Delbreilh*, J.-M. Saiter*, G.H. Michler , R. Adhikari***, A. Hiltner****, E. Baer****.**

** LECAP, Institute for Materials Research, Université de Rouen, Faculté des Sciences, Avenue de l'Université BP 12, 76801 Saint Etienne du Rouvray, France.*
***Department of Engineering, Martin-Luther University Halle-Wittenberg, D-06099 Halle, Germany*
****Central Department of Chemistry, Tribhuvan University, Kirtipur, Kathmandu, Nepal*
*****Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106-7202, USA*
E-mail: khadidja22@yahoo.fr

Keywords*: PC/PMMA multilayered films, Enthalpy relaxation, confinement*

The relaxation kinetic of multilayered films PC/PMMA (Bisphenol-A polycarbonate (PC) / atactic polymethyl methacrylate (PMMA)) obtained by multilayer co-extrusion technique [1] is investigated by differential scanning calorimetry (DSC), and compared with the behaviour of PC, PMMA bulk. The average thickness of each layer in this multilayered films range from 16μm to 12nm. The Tool-Narayanaswamy-Moynihan model [2] makes it possible to describe enthalpy relaxation by using the concept of fictive temperature which defines the instantaneous structural state of vitreous material. The aim of this work is to study the apparent enthalpy relaxation Δh^* and fragility index (m) in PC/PMMA multilayered films with thickness reduction. The multilayered films show a lower activation energy and lower fragility in the layer thicknesses thinner than 125nm for PC, while for PMMA these parameters remain constant.

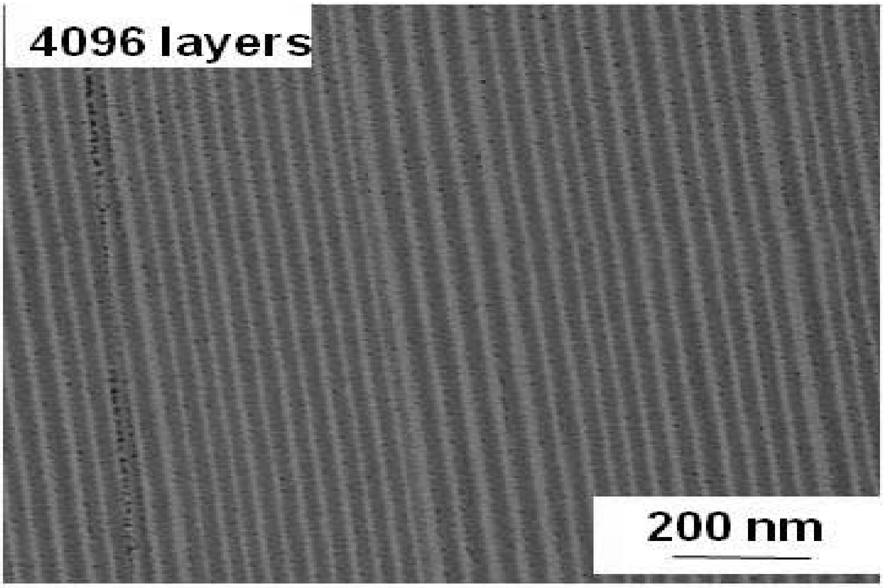

Fig.1 AFM picture of multilayered film with 4096 alternated PC/PMMA layers

These results put in evidence the dependence of parameters like Tg, $\Delta h^*$and m on the morphology of the multilayered films. The reduction of PC parameters with the reduction of layer thickness is associated with a confinement effect produced by conformational changes in the polymer chains. The very different behaviours of PC and PMMA vs. the reduction of layer thickness are a good example of the microstructure influence on the appearance of confinement effects.

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NMR IMAGING OF WATER ABSORPTION BY MULTILAYER COATINGS.

Viktor Baukh*, Henk Huinink*, Bart Erich*, Olaf Adan*, Leo van der Ven**

** Department of Applied Physics, Eindhoven University of Technology, Den Dolech 2, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
*** Akzo Nobel Car Refinishes, P.O. Box 3, 2170 BA Sassenheim, The Netherlands*
E-mail: v.v.baukh@tue.nl

Keywords: *multilayer coatings, water absorption, NMR relaxometry*

Organic coatings are widely used polymeric systems that play an important role in protecting and giving aesthetic appearance to various substrates. To meet needed specifications these systems consist of several layers with distinct properties. The penetration of water into multilayer coatings plays an important role in their performance. Since the presence of water in polymers is coupled with mechanical stress, the water uptake by coatings can be affected by external and internal stresses. Little is known about the effect of stresses on water absorption by multilayer coatings. The total amount of water, which is measured by traditional techniques like gravimetry, is not an appropriate parameter for interpreting the process of water uptake in multilayer coatings. Adequate understanding of the water absorption by multilayer coatings requires information about water distribution in depth as a function of time.
The present study addresses the water uptake by a two layer coating, which consists of waterborne base coat and solvent-borne top coat layers, in the presence of applied external stress. The swelling of the sample and distribution of water was measured in depth by high resolution NMR imaging based on the GARField approach[1], see Figure 1. A model was formulated to interpret the experimental results. The diffusivity of water in the top coat and evolution of driving force for uptake were estimated. The applied stress increased the uptake rate as well as amount of absorbed water and swelling. Further, it was shown with T_2 relaxometry that parts of the polymeric matrix were plasticized during uptake. It can be concluded that high resolution NMR imaging is powerful tool for studying fluid uptake in thin heterogeneous polymeric systems.

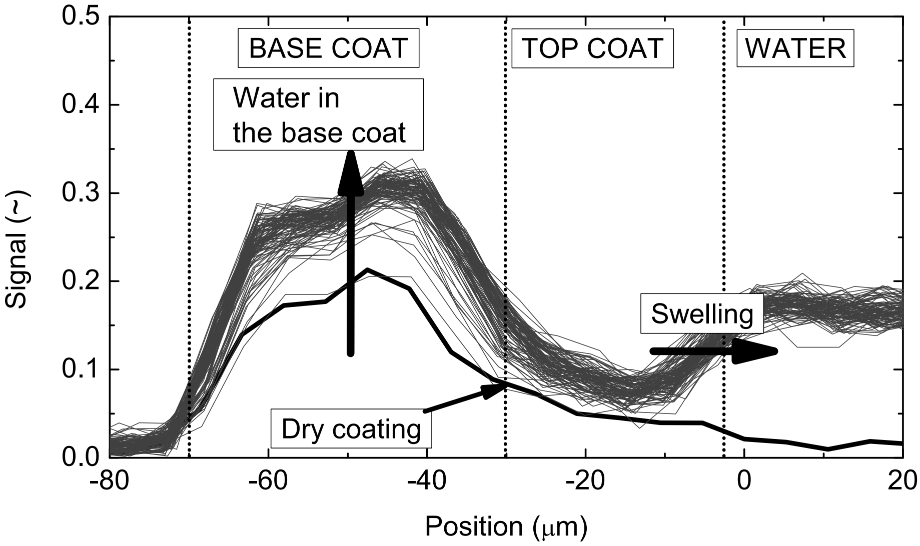

Figure 1. Signal profiles of a two-layered coating during water uptake. The time between two subsequent profiles is 40 minutes. Vertical lines approximately denote interfaces between the base coat, the top coat and water. The bold line represents a signal profile of the dry coating.

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TRANSMISSION LASER WELDING OF POLY(ETHER ETHER KETONE) (PEEK) FOR MEDICAL DEVICE APPLICATIONS AND CHARACTERISATION USING X-RAY TOMOGRAPHIC TECHNIQUES.

Negin Amanat*, Cedric Chaminade, John Grace**, David McKenzie*, Natalie James*****

** School of Physics, University of Sydney, NSW Australia*
*** Raymax Applications, Newport Beach, Sydney NSW Australia*
****Cochlear Limited, Lane Cove, Sydney NSW Australia*
E-mail: n.amanat@usyd.edu.au

Keywords: *PEEK, medical device, transmission laser welding*

Introduction: Thermoplastic use in the medical device industry is rapidly increasing. PEEK has become a highly sought after polymer for a number of medical applications due to its attractive material properties such as high thermal stability, excellent mechanical strength, biocompatibility and excellent resistance to chemical degradation. Medical devices require efficient and effective joining techniques that provide hermetic and strong seals. Transmission laser welding (TLW) is an almost instantaneous polymer joining technique with highly localised heating and therefore minimal effect upon adjacent material and components. Comprehensive characterisation of the joint interface to determine bond quality will provide valuable insight into bond quality.

Aim: The aim of this investigation was to determine the influence of laser process parameters and polymer morphology on the bond quality of transmission laser welded PEEK. X-ray tomography (micro-CT) was investigated as a potential method for enabling three-dimensional visualisation and characterisation of the joint interface.

Methods: PEEK films (amorphous and semi-crystalline) with 250 micron thickness were cut into rectangular strips (35 × 10 mm). Clearweld® was used as the infrared absorbing medium at the joint interface. TLW was used to weld the strips in a lap-joint configuration, with a 10 mm overlap length. Two laser powers (10 and 20 Watts) and five scan speeds (4, 8, 16, 32, 64 mm/s) were investigated for their effect on bond strength for the two morphologies. Micro-CT scans of the weld region were conducted at a resolution of 10 microns. The 2D scan slices were imported into animation software (VGStudio Max) to create 3D models. The joint interface was characterised both qualitatively and quantitatively.

Results: The highest bond strengths were achieved using the two lowest scan speeds of 4 mm/s and 8 mm/s. There was no significant difference between the two laser intensities tested. Overall, the semi-crystalline morphology produced stronger bonds than amorphous for identical parameters. Additionally, a majority of the amorphous bonds failed at the interface, while only a third of semi-crystalline bonds failed interfacially, with the remainder failing through the substrate (bond remaining intact). SEM and X-ray tomography indicated the presence of multiple voids, or bubbles, at the weld interface. These bubbles were a consistent feature for all samples regardless of speed, power or morphology.

Discussion: The significantly lower amorphous PEEK bond strengths, compared with the semi-crystalline PEEK, may be a result of the differing crystallisation kinetics between the two morphologies when heated. It is possible that the amorphous PEEK underwent greater crystallisation during the heating phase, and therefore compromised chain interdiffusion[1]. An interesting finding was the presence of bubbles at the interface, which may be the result of evaporation of water absorbed by the polymer[2]. Micro-CT analysis indicated that between the bubbles, the polymer interface appeared to be homogeneous with no indication of a seam.

Conclusion: Both semi-crystalline and amorphous PEEK can be effectively welded using TLW; stronger bonds were achieved with the semi-crystalline PEEK morphology. Micro-CT was successfully utilised to visualise and assess the 3D reconstruction of the bond region, and to critically investigate the joint interface.

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REVERSIBLE EPOXY NETWORKS WITH PHYSICAL CROSSLINKS BASED ON TAIL-TO-TAIL ASSOCIATIONS OF ALKYL CHAINS

Julieta Puig, Cristina E. Hoppe, Ileana A. Zucchi, Ana Ledo-Suárez, María J. Galante, Roberto J. J. Williams

Institute of Materials Science and Technology, University of Mar del Plata and National Research Council (CONICET),
Av. J. B. Justo 4302, 7600 Mar del Plata, Argentina
E-mail: williams@fi.mdp.edu.ar

Keywords: *nanocomposites, physical crosslinks, reversible networks*.

Linear amphiphilic epoxy polymers synthesized by the polyaddition of diglycidyl ether of bisphenol A (DGEBA) with alkylamines like octylamine (OA), dodecylamine (DA) and hexadecylamine (HA), undergo a physical gelation process through tail-to-tail association of alkyl chains.[1,2] SAXS spectra showed that tail-to-tail associations of alkyl chains were present since the beginning of polymerization and remained in the final materials. Initially, these associations correspond to micelles of the alkylamines dispersed in the solvent (DGEBA). In the course of polymerization micelles are disaggregated as the individual alkylamine chains become part of the linear amphiphilic polymer. However, tail-to-tail associations among alkyl chains attached to the polymer backbone persisted in the final materials. Reactions were followed by rheometry at 100 ºC. For every system, a significant discontinuity in the increase in the storage modulus observed at advanced conversions was assigned to a phase inversion process produced by solvent depletion. By annealing prolonged times at the reaction temperature a cross-over of storage and loss modulus was observed due to the increase in the extent of associations among alkyl chains. Times for physical gelation varied in the order OA < DA < HA. Both DGEBA-DA and DGEBA-HA polymers could be reversibly transformed from gel to liquid states by appropriate heating-cooling cycles; however, the DGEBA-OA polymer showed no thermoreversibility. Physical gels exhibited a high swelling capacity in different solvents (HA > DA > OA).

Amphiphilic gels based on DGEBA-DA were used as dispersion media for a variety of nanoparticles stabilized with alky chains.Synthesis was carried out by two different methods: (a) by immersion of gel slices in previously synthesized NPs dispersions and (b) by impregnation with metallic ions and subsequent thermal reduction of the ions to give NPs (Au y Ag). Photographs of materials obtained using method (a) can be observed in Figure 1.

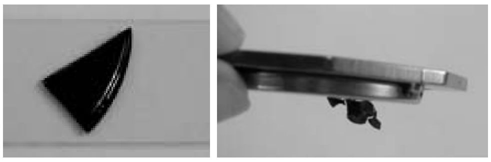

Figure 1. Photographs of nanocomposites obtained by immersion of gels in Au (left) and γ-Fe_2O_3 (right) NPs dispersions (note that magnetic nanocomposite is attracted by the magnet).

Gels infiltrated with gold and silver ions were used to generate NPs "in-situ". The strong color developed after thermal heating the systems for 1 hour at 100ºC, evidenced formation of metal NPs, characterized by typical plasmon absorption bands in the visible range of the spectrum. This effect could be related with the presence of weak reducing functional groups in the polymer (tertiary amines and hydroxyls). Nanocomposites synthesized by methods a) and b) exhibited different properties. Glass transition temperatures (Tg) of nanocomposites prepared by method a) remained unchanged whereas for materials obtained by method (b) Tg values increased from 19.9ºC for the neat matrix to 27.7 ºC for silver and 43.8ºC for gold nanocomposites. Further work, necessary to elucidate the origin of these differences, is currently in progress.

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FUNCTIONAL END-LINKED CONETWORKS BASED ON CLEAVABLE BIFUNCTIONAL INITIATORS: SYNTHESIS BY GTP, ATRP AND RAFT POLYMERIZATION, CHARACTERIZATION AND CLEAVAGE

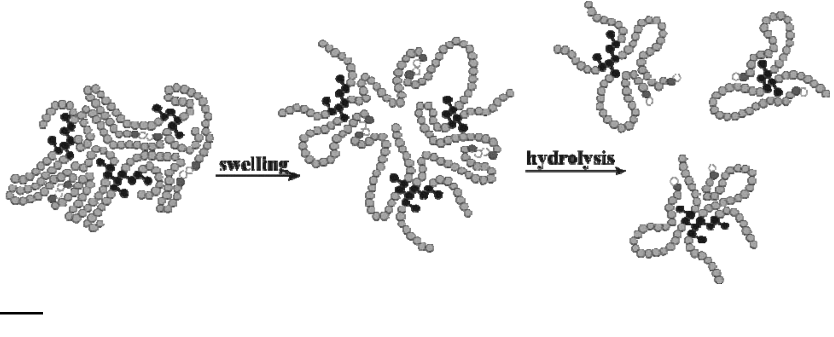
Maria D. Rikkou, Costas S. Patrickios

Department of Chemistry, University of Cyprus, 75 Kallipoleos Avenue, P. O. Box 20537, 1678 Nicosia, Cyprus
E-mail: costasp@ucy.ac.cy

Keywords: *networks, hydrolysis, small-angle neutron scattering.*

The investigation of the properties and exploration of applications of polymer networks have very much progressed during the past 50 years. However, little effort has been devoted to the controlled synthesis of these materials. Most polymer networks available today comprise chains between cross-link points (so-called elastic chains) with broad molecular weight distributions, a result of the simultaneous free radical cross-linking copolymerization of monomer(s) and cross-linker. Availability of better-defined polymer networks may broaden their applications horizon, and would also enable the derivation of accurate structure-property relationships. For the past ten years, our Research Team has been working on the development of well-defined functional polymer networks by the end-linking of ABA triblock copolymers, resulting in materials with elastic chains of narrowly-distributed size and composition, but a broader distribution in the number of arms emanating from each cross-linked core. The network topologies were subsequently expanded to include end-linked star polymers, and, more recently, semisegmented structures. Most syntheses initially involved group transfer polymerization (GTP), a controlled anionic polymerization method best-suited for methacrylates, but were recently extended to include controlled radical polymerization methods, and, in particular, reversible addition-fragmentation chain transfer (RAFT) polymerization and atom transfer radical polymerization (ATRP). Various functionalities were incorporated in these networks, including amphiphilicity (combination of hydrophilic and hydrophobic monomers), ampholyticity (combination of positively with negatively charged monomers), double-hydrophilicity (combination of two different hydrophilic monomers), and degradability. Subsequent network characterization involved measurement of the degrees of swelling in aqueous and organic media, determination of the mechanical properties, and structural characterization using microscopy and scattering techniques.

This lecture will present most recent results on the preparation and characterization of end-linked polymer conetworks combining amphiphilicity and degradability.[1] Degradability was introduced by the use of a cleavable bifunctional initiator bearing two hemiacetal ester groups. Three novel initiators were developed, suited for one of the three controlled polymerization methods used, GTP, ATRP and RAFT polymerization. The bis(hemiacetal ester) cleavable groups in the initiator residues allowed for conetwork site-specific degradation not only in mildly acidic aqueous media, but also in pure water and in lower alcohols, and conetwork conversion to star copolymers. The rate of conetwork degradation depended on polymer architecture and composition. A systematic investigation was performed by following in detail the temporal evolution of the swollen mass of the conetworks in water and methanol. Most interestingly, a particular conetwork presented a maximum in its swelling profile with time, due to simultaneous occurrence of swelling and degradation. A neutron scattering (SANS) study of the conetworks in deuterated water enabled the independent monitoring of conetwork swelling and degradation as the two processes had separate peaks in the SANS profiles, the former of which being related to the self-organization of the hydrophobic blocks within the conetworks, whereas the latter being connected with the correlations among the amphiphilic star block copolymers released in solution during the course of conetwork hydrolysis. A schematic representation of conetwork swelling and degradation to star copolymers is illustrated schematically below.



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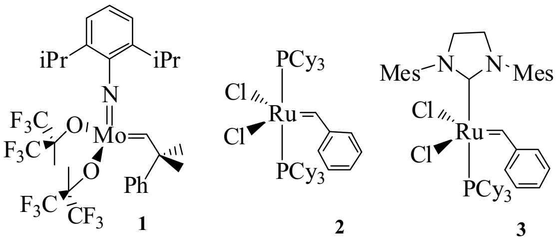
POLY-BiCYCLOPENTADIENE (DCPD): A SPECIALTY THERMOSET WITH A BRIGHT FUTURE

Renata Drozdzak, Gilles Recher, Alexander Daemen

Telene S.A.S, Route d'Arras, 62320 Drocourt-France
E-mail: Renata.Drozdzak@Telene.com

Keywords: *poly(dicyclopentadiene), Ring Opening Metathesis Reaction, Ruthenium catalysts*

Poly(bicyclopentadiene) (poly-DCPD) is obtained through Ring Opening Metathesis Polymerisation (ROMP) of the DCPD monomer formulation. 'ROMP reaction' is a metal carbene catalysed reaction using strained cyclic olefins to produce a wide range of polymers. The driving force is the relief of ring strain. Catalyzed metathesis was discovered in the 1950s by Ziegler. Nevertheless, the mechanism was not understood until Yves Chauvin and co-workers published their metathesis mechanism in 1971 based on a metal alkylidene catalyst initiating the reaction. Many researchers have contributed to the ensuing development of catalysts; however the most efficient and extremely active molybdenum and tungsten catalysts were reported in 1990 by Schrock (**1**, Scheme 1)[1]. In 1995 Grubbs and co-workers reported their new molecularly well-defined ruthenium-carbene complexes (**2**,**3** Scheme 1) which up till now are by far the most tolerant to functional groups and simultaneously compete with the most active Schrock catalysts in catalytic activity[2].



Scheme1. Well defined metathesis catalysts

Today's commercial DCPD resin formulations based on Molybdenum and Tungsten are processed using Reaction Injection Moulding (RIM). In the RIM process two or three monomer streams are brought together in a mixhead and then injected in the mould where the polymerisation takes place. Because of the low viscosity of the monomer streams, the injection pressure is relatively low allowing for lower cost mould materials such as aluminium alloys, nickel shell, or casted kirksite/cast aluminium. The RIM process is especially suitable for the production of large plastic parts.

The formulations based on Ruthenium catalysts are no longer limited to RIM but can be potentially used in a variety of thermoset process such as filament winding, pultrusion, rotomoulding, casting and resin infusion. The robust nature of the Ruthenium catalysts allows using reinforcements such as glass fibre, mineral fibre, foaming agents and many types of fillers.

Poly-DCPD has excellent impact performance, superior chemical resistance, very low water absorption, very low dielectric constant and a high electrical strength. Examples of commercial applications will be presented. Energy required to produce one kilogram of final product as well as the equivalent CO_2 amount produced during its full life cycle, are significantly lower for poly DCPD compared to other materials. The results of a study done by Ecole Nationale Supérieures des Arts et Metiers (ENSAM) will be presented.

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WATER-BASED COATINGS – FILM-FORMATTION AND FILM BUILD-UP

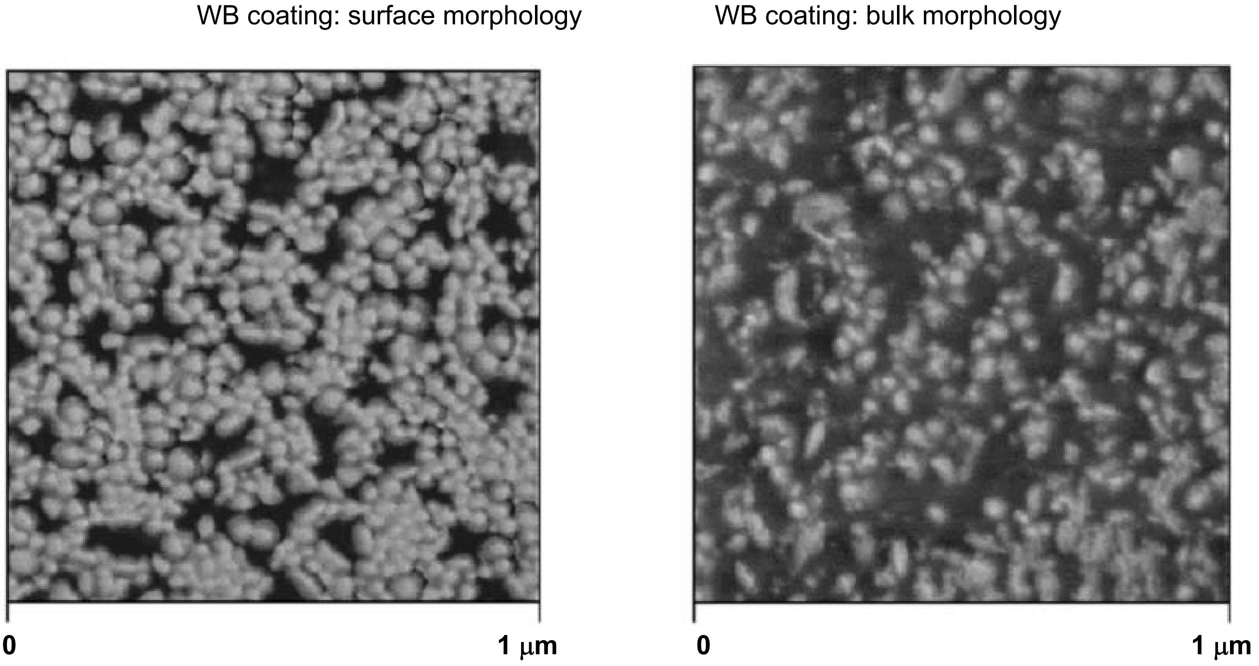
Dorina van Haeringen

DSM NeoResins B.V., P.O. Box 123, 5140 AC Waalwijk, The Netherlands
E-mail: Dorina.Haeringen-van@dsm.com

Keywords: *water-based coatings, morphology, film-formation*

The process of film-formation and film build-up is crucial for the water-based coatings, because it determines to a large extent the coatings properties. In general, the film-formation for aqueous polymer dispersions is much more difficult to control, and more critical than for solvent-based systems. Aqueous dispersions form films by a coalescence process in which the individual polymer particles are forced together as the water evaporates, the particles deform, and eventually interdiffuse. Insufficient levels of coalescence usually have a negative influence on important coating properties like barrier- and mechanical properties. The challenge since the advent of water-based coating technologies has been to develop systems which are film-forming at room temperature and attain a good complex of mechanical properties.

In this study a range of microscopy techniques, and scanning probe microscopy (SPM) in particular, have been used to visualize the film-formation and film build-up in water-based coatings. The film morphologies created by the most widely used technologies for preparation of aqueous dispersions are reviewed. It is shown that within a single coating the level of particle coalescence could be different. Also, to achieve a good general set of properties a complete particle interdiffusion is not always required. Further, various formulation parameters, playing a role in the film build up, such as pigment dispersion/ wetting, additives migration etc are investigated and related to coatings properties.


WB coating: surface morphology
WB coating: bulk morphology

ANALYSIS OF BLOCK COPOLYMERS BY 2D-LC AND ON-LINE COUPLED LC-NMR

Harald Pasch*, Wolf Hiller, Pritish Sinha*, Valentina Mass*****

** University of Stellenbosch, Department of Chemistry and Polymer Science, Private Bag X1, 7602 Stellenbosch, South Africa, E-mail: hpasch@sun.ac.za*
*** Faculty of Chemistry, TU Dortmund, Otto-Hahn-Str. 6, 44227 Dortmund, Germany*
**** German Institute for Polymers, Schlossgartenstr. 6, 64289 Darmstadt, Germany*

Keywords: *block copolymers, LC-NMR, molecular heterogeneity.*

In order to establish a detailed relationship between the molecular characteristics and macroscopic properties of a block copolymer, it is essential to perform a comprehensive analysis to determine its chemical composition distribution (CCD) and molar mass distribution (MMD). Generally, block copolymers are synthesised by sequential monomer addition, in which several factors should be controlled effectively, including the initiation efficiency of the macroinitiator and the molar mass distribution of each block. Standard spectroscopic characterisation methods such as nuclear magnetic resonance spectroscopy (NMR) and Fourier transform infrared spectroscopy (FTIR), cannot differentiate the block copolymer from homopolymer blends. In other words, they cannot determine the existence of unreacted macroinitiator and/or the newly generated homopolymers in the final block copolymer product.

In the present study, the two-dimensional parameter field of the composition and the molar mass distribution of selected block copolymers was studied. Diblock copolymers with different chemical compositions were prepared and analyzed, one set of samples being obtained by standard sequential polymerization while a second set of samples with comparable molar masses and chemical compositions being prepared by coupling reactions. In addition to the analysis of the molar mass distributions and the chemical compositions of the block copolymers, the single blocks were analyzed by interaction chromatography. Molar masses of individual blocks in diblock and triblock copolymers can be measured by various means of liquid interaction chromatography, including liquid chromatography at the critical point of adsorption (LCCC) [1,3]. Operating at critical conditions of one block of the copolymer, this block does not contribute to retention and behaves "chromatographically invisible" [2]. At the same time the other block elutes in the SEC mode and can be quantified accordingly. Subsequently, the block copolymers were analyzed by two-dimensional chromatography where LCCC is used as the first dimension and SEC is used as the second dimension [5].

Since chromatographic methods do not provide information about the microstructure of the monomer units in the block copolymers it was necessary to couple these techniques on-line with spectroscopic techniques such as NMR. The on-line coupling of HPLC and ^{1}H-NMR is a powerful and time saving tool for the analysis of complex mixtures [4,6]. In the study method development has been conducted to us on-flow coupling of LC and NMR. The experimental requirements for both the LC and NMR measurements will be discussed and quantitative information on molar mass, chemical composition and microstructure will be given for selected block copolymers. As compared to bulk analysis the analysis of the different product components provided a much more detailed insight into the molecular complexity of the samples.

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CHARACTERIZATION OF POLYOLEFINS WITH HIGH-TEMPERATURE TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY

Anton Ginzburg, Tibor Macko**, Robert Brüll***

** German Institute for Polymers (Deutsches Kunststoff-Institut), Schlossgartenstr. 6, 64289 Darmstadt, Germany*
*** Dutch Polymer Institute (DPI), PO Box 902, 5600 AX Eindhoven, the Netherlands*
E-mail: AGinzburg@dki.tu-darmstadt.de

Keywords: t*wo-dimensional liquid chromatography, polyolefins.*

Polyolefins are industrially the most produced synthetic polymers. Their industrial production has more as 70 years long history. In 2010, the worldwide production of these polymers is estimated at 130 million tons.[1] Therefore, the synthesis and the characterization of polyolefins has become one of the important areas in polymer research.

Polyolefins are distributed in more than one parameter of molecular heterogeneity (distribution of chemical composition (CCD), molar mass (MMD), tacticity, architecture and end groups). The comprehensive analytical characterization of polyolefins represents a key for understanding structure - property relationships of the final products.

A number of techniques are commonly used in polyolefin analysis. High-temperature size exclusion chromatography (HT-SEC) is the established method for determination of the MMD.[2] TREF and CRYSTAF are non-chromatographic separation techniques that fractionate polymers according to differences in crystallizability. Both techniques require 1-2 days for the corresponding measurements. Moreover, they can only be applied for the characterization of crystalline polyolefins; some types of polyolefins, for example, the functionalized polyolefins with higher concentration of comonomers are, however, amorphous and can thus not be analyzed.

Our group has recently developed the first interactive HPLC systems for polyolefins[3,4] and functionalized polyolefins.[5,6.] Nevertheless, the use of one-dimensional separations does not yield a complete knowledge about chemical heterogeneity, as the complex polymers exhibit several simultaneous dependent distributions.

It is known that two-dimensional liquid chromatography (2D-LC) enables to obtain information about different aspects of molecular heterogeneity of synthetic and biological polymers.[7,8] The use of elevated temperatures (up to 160 °C) is necessary for the dissolution of polyolefins. The conditions for realization of high-temperature 2D-LC of polyolefins have not been published yet. By coupling of the interactive HPLC systems, where the molecules are distinguished with respect to chemical composition, with SEC, where the molecules are separated according to the differences in molar masses (hydrodynamic volume), the full 2D-LC characterization of polyethylene / polypropylene blends and ethylene-vinyl acetate copolymers has been performed for the first time.

The realization of the high-temperature 2D-LC measurements will be described and examples for the 2D-LC separations of commercial samples will be presented.

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THE COUPLING OF LIQUID CHROMATOGRAPHY AT CRITICAL CONDITIONS AND NMR. A NEW TOOL FOR THE CHARACTERIZATION OF POLYMERS

Wolf Hiller*, Harald Pasch, Pritish Sinha**, Mathias Hehn***

**TU Dortmund, Faculty of Chemistry, Otto-Hahn-Str. 6, 44227 Dortmund, Germany*
***University of Stellenbosch, Department of Chemistry and Polymer Science, Private Bag X1, 7602 Matieland, South Africa*
E-mail: wolf.hiller@tu-dortmund.de

Keywords: *online HPLC-NMR, LCCC-NMR, SEC-NMR*

HPLC-NMR is a very powerful tool for the structure elucidation of complex mixtures. However, it is rarely used for polymers. Most papers are related to SEC-NMR. In these cases slow flow rates as well as deuterated solvents are often used.

The lecture will focus on new applications of HPLC-NMR of polymers. In particular, liquid chromatography at the critical point of adsorption will be used to separate different homopolymers and block copolymers. This method is also called liquid chromatography at critical conditions (LCCC). In case of homopolymers, critical conditions are characterited by a status where the different molar masses elute at the same retention volume. As the consequence, LCCC will separate the polymers according to their chemical heterogeneity. The power of LCCC-NMR was demonstrated at polyethylene oxides for the analysis of different end groups[1]. In this case the structure and the length of the end groups could be determined (functionality type distribution (FTD)). Polyethylene oxides were also used to demonstrate the online coupling of 2D-chromatography and NMR. This method combines the separation of the different end groups as well as the molar mass distribution of the polymers.

The main attention of the lecture will be paid to the characterization of copolymers and the microstructure of polymers by coupling of LCCC and NMR.

We have recently shown that LCCC-NMR is the best tool to provide the true chemical composition distribution and the true molar mass distribution of block copolymers. Using critical conditions of one block, this block will be considered as chromatographically invisible. The other block, however, can elute in size exclusion chromatography (SEC) mode under certain circumstances. These conditions allow the separation of existing homopolymer from the copolymer. Therefore, it is possible to determine the true chemical composition as well as the true molar mass of the entire copolymer. PS-b-PMMA block copolymers of different block lengths were analyzed with LCCC-NMR by using solvent mixtures for establishing critical conditions of poly(methyl methacrylate) (PMMA) and polystyrene (PS)[2,3].

The most challenging separation of block copolymers was the development of LCCC methods for analyzing PI-b-PMMA copolymers by using only a single solvent as mobile phase[4]. This method reduces the number of solvent signals which need to be suppressed by ^{1}H-NMR. It also reduces the time significantly to obtain critical conditions. Using LCCC-NMR onflow experiments, the determination of the true chemical composition distribution and the true molar mass distribution could be achieved via a complete analysis of the microstructure distribution during elution. The microstructure of both the PI and the PMMA block was determined during the chromatographic separation.

Recently, we also developed a LCCC method to separate polyisoprenes (PI) according to their microstructure. LCCC-NMR onflow experiments could verify the structure of the isomeric compounds. It was possible to differentiate between 1,2-, 1,4- and 3,4-PI.

For the first time, an online HPLC-^{2}H-NMR experiment was carried out at deuterated block copolymers. The possibilities for the analysis of block copolymers using deuterium NMR as the detector will be presented. Onflow and stop flow data will be shown.

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TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY OF SYNTHETIC POLYMERS

Dušan Berek

Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 84236 Bratislava, Slovakia
E-mail: upoldber@savba.sk

Keywords: *synthetic polymers; liquid chromatography; two-dimensional separations;*

End-use properties of synthetic polymeric materials depend on the molecular characteristics of the composing macromolecules, on their mutual arrangement, and on the nature and amount of additives. Basic molecular characteristics of macromolecules are molar mass, chemical structure (composition) and physical architecture. Without exemption, all molecular characteristics of synthetic polymers exhibit a distribution. Many high-performance synthetic polymers exhibit more than one distribution in their molecular characteristics, these are designated *complex polymers*. Typical examples are various copolymers, many functional, and stereoregular polymers, as well as polymer blends. The mixture of a complex polymer with another macromolecular substance of distinct nature is called *complex polymer system*. Not counting the estimates produced by the rheological measurements, the only quantitative data on molecular characteristics of distributed polymers are generated by the separation methods; the field is at present dominated by liquid chromatography and mass spectrometry. Molar mass distribution of synthetic polymers is most often determined by size exclusion chromatography, SEC, called also gel permeation chromatography. However, SEC separates macromolecules according to their size in solution, which depends not only on molar mass but also on other molecular characteristics of polymers to be characterized. Therefore, it is evident that SEC cannot directly produce exact, quantitative data on molar mass averages and distributions of complex polymers and complex polymer systems. Still, SEC provides valuable information on the *tendencies* of molar mass evolution during polyreactions. As a rule, SEC cannot discriminate polymer species of different nature that possess similar size in solution. Quantitative assessment of minor (<1%) constituents of multicomponent polymers systems with help of SEC is not possible even if their molecular sizes differ substantially. This results from the low sensitivity of the SEC detectors and from the limited both sample capacity and selectivity of the SEC columns. The restricted separation selectivity of SEC prevents identification of undesired macromolecular admixtures in many research and commercial polymeric materials. SEC chromatograms of numerous polymers under study are bell-shaped or exhibit bulges; both these appearances indicate presence of admixtures. To quantitatively characterize complex polymers and complex polymer systems, the exclusion, entropy controlled separation mechanism of SEC is to be combined with one or several interaction, enthalpy driven separation mechanisms. This approach is called coupling of retention mechanisms and the resulting procedures are designated *coupled methods of polymer liquid chromatography*. Still, the coupling of separation mechanisms within one single column is often insufficient for separation of complex polymers. It is necessary to combine two different high performance liquid chromatographic, HPLC procedures executed in two independent chromatographic systems. Such combination is denoted *two-dimensional polymer high performance liquid chromatography*, for short 2D-LC or also LCxLC. The basic rules of 2D-LC of synthetic polymers will be presented in this tutorial together with the analysis of shortages and pitfalls of the existing 2D procedures. The aim is to facilitate the start-up experiments by selection of the appropriate system and to prevent misleading, erroneous results.

INVESTIGATION OF STARCH DEGRADATION BY COMPREHENSIVE SIZE-EXCLUSION CHROMATOGRAPHY

Peter Kilz *

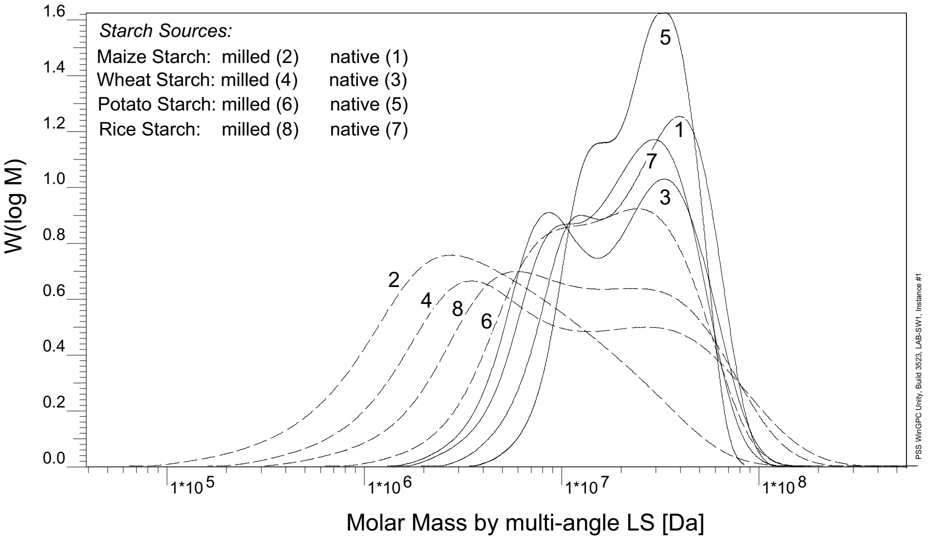
Peter Kilz, PSS GmbH, PO Box 3368, 55023 Mainz, Germany
E-mail: PKilz@polymer.de

Keywords: *size-exclusion chromatography, molecular characterization, degradation*

Molecular characterization of macromolecules by chromatographic methods is important in the elucidation of structure - property - function relationships. Available techniques allow the in-depth characterization of multiple property distributions, e.g. dispersity in chain length, branching frequency and branch length, chemical composition and even constitution. This has been achieved by a combination of fractionation techniques like SEC, LAC, FFF and information-rich detectors e.g. MALLS, viscometry, IR and NMR.
Application of such methods to starches, however, is still not a standard technique for several reasons:

- sample preparation to achieve molecular dissolution is still difficult and not easily reproducible
- starch itself is a highly complex and analytically challenging product
- the correlation of macroscopic properties to structural features is complicated by the complex morphology

Many product properties of starches like sensory behavior, gel formation and gel stability, are affected by processing conditions. Starches modified by dry- and wet-milling formed particle gels in water and may find their application in non-cooked food systems as an alternative to pre-gelatinized, chemically modified starches, maltodextrins and food gums.
The state-of-the-art of advanced SEC characterization of starches using viscometric and light scattering (MALLS) detectors to study the influence of mechanical starch treatment on its molecular characteristics is discussed. Different milling methods were used to modify native starch samples. Molecular characterization of native and milled starches from different natural sources shows that multi-detector SEC can be used efficiently to study degradation by mechanical energy. If sample preparation has been performed properly and proper SEC columns with wide pores and large particles are used, sample recovery is close to 100% and starch molar masses separation covering monomers to several 10 million g/mole are possible.
Comprehensive SEC can be a valuable tool in the exploration of structural changes during starch treatment : gelatinization, grinding, milling chemical modification.Combination of molar mass sensitive detectors allows to elucidate the influence of chemical and/or physical energy on the starch molecule itself.



Results on the structural changes in the starch chains and the position in the molecule where mechnical energy is absorbed will be presented and discussed.

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DEPOLYMERIZATION AND ANTICOAGULANT ACTIVITY OF FUCOIDAN

Soo-Kyung Choi, Byung-Wook Jo

Chemical Engineering Department, Chosun University, Gwang Ju, Republic of Korea
E-mail: bwjo@chosun.ac.kr

Keywords*: fucoidan, depolymerization, antithrombus*

Fucoidan from Fucus vesiculosus has been reported to show anticoagulant activity in vitro and in vivo, and it also was reported that the major antithrombic activity by fucoidan was mediated by heparin cofactor II.[1] Fucoidan also could be beneficial in patients with ischemic disease. Its proangiogenic property enhance in animals neovascularization and angiogenesis, which prevent necrosis of ischemic tissues. However, relatively few studies have explained the biological activity of fucoidans in terms of the molar mass distribution (MWD) and the molecular structure.

Almost all biological studies use a commercially available, crude preparation of sulfated polysaccharides from Fucus vesiculosus rather than a purified fucoidan.

Recently, we depolymerized systematically sulfated α-L-fucans from brown sea-weeds by H_2O_2/ultrasound wave /e-beam irradiation (Figure1). We undertook a systematic analysis of the anticoagulant activity of these depolymerized polysaccharides and took advantage of their wide diversity of regular and repetitive structures to elucidate structure–anticoagulant action relationship. P-selectin is an adhesion receptor expressed on activated platelets and endothelial cells. We have identified the complex formation between P-selectin and the LM-fucoidans. Binding of LM-fucoidan to P-selectin was also analyzed. The fucoidan prevented P-selectin binding to Sialyl Lewis X with an IC50 of 12 nM as compared to 150 nM for HMW fucoidan and 400 nM for heparin.

We also discuss in the present study promising results of hyperplasia inhibition with a LMW fucoidan in stented rabbit arteries. The potent antiproliferative effect on SMCs of LMW fucoidan make it a promising candidate for prevention of in-stent restenosis (Figure 1).

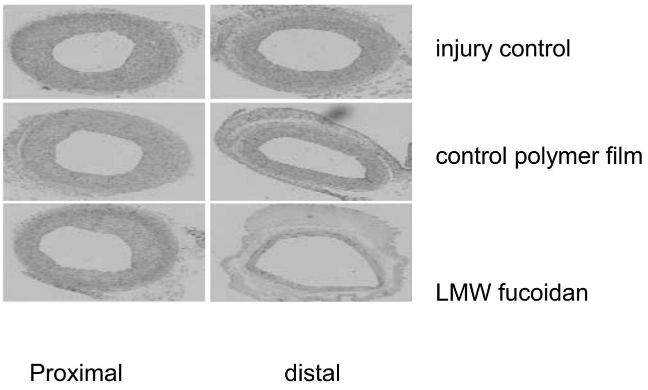

Figure 1. Representative Pathologic Specimens

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HIGH-TEMPERATURE ADSORPTION CHROMATOGRAPHY – A NEW TOOL FOR CHARACTERIZATION OF POLYOLEFINS

Tibor Macko, **Rajesh Chitta)**, **Robert Brüll**

German Institute for Polymers (Deutsches Kunststoff-Institut), Schlossgartenstr. 6, 64289 Darmstadt, Germany
E-mail: TMacko@dki.tu-darmstadt.de

Keywords: *ethylene/alkene copolymers, adsorption.*

Polyolefin materials have been industrially produced for more than 70 years. Temperature Rising Elution Fractionation (TREF), Crystalization Analysis Fractionation (CRYSTAF), differential calorimetry, NMR and FTIR spectroscopy and high-temperature size exclusion chromatography (SEC) are the common techniques for their analytical characterization. High Performance Liquid Chromatography (HPLC), although commonly used for the analysis of many synthetic polymers[1-3], has been not applied for analytical characterization of this class of materials because the corresponding sorbent-solvent systems, which would be suitable for HPLC analysis, were unknown.

Recently we have shown that using selective solvents with high boiling points polyethylene (PE) or polyethylene (PP) may be either eluted in precipitation/dissolution mode[4.5] or adsorbed onto specific zeolites[6,7]. The mentioned HPLC systems based on selective precipitation-dissolution enabled to realize the first separation of PE from PP[4] as well as the separation of ethylene-propylene copolymers[8]. Attempts to desorb PE, PP from the zeolites has been, however, not been successful[9].

A new sorbent – solvent system for HPLC of polyolefins has been identified a recently: A column packed with porous graphite particles (Hypercarb™) enabled to adsorb and to desorb samples of linear polyethylene. Moreover, retention volumes of atactic, syndiotactic, and isotactic polypropylene were also different in this HPLC system. This enabled to separate blends of PE and PP as well as PP according to their tacticity[10,11]. The mentioned chromatographic separation is based on the adsorption of PE, atactic PP or syndiotactic PP from 1-decanol and the following desorption with 1,2,4-trichlorobenzene at temperature as high as 160 °C. This column – mobile phase system enables to separate not only blends of PP and PE but also both ethylene/1-alkene and propene/1-alkene copolymers. The HPLC separation of these copolymers is governed by their chemical composition.

The high-temperature adsorption liquid chromatography represents a new, complimentary technique for analytical characterization of polyolefins. In difference to CRYSTAF or TREF, HPLC enables to separate crystalline as well as amorphous samples. Moreover, the HPLC technique requires less amount of solvents and time, i.e., it has potential to be applied in high throughput environments for the synthesis and analysis of polyolefins.

The lecture will illustrate applications of high-temperature HPLC for the separation of various kinds of polyolefins.

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DETERMINATION OF MOLECULAR PARAMETERS OF POLYACRYLAMIDE SOLUTIONS

Derek Lohmann*, Christoph Johann, Roger Scherrers**, Werner-Michael Kulicke***

*Institut für Technische und Makromolekulare Chemie, Universität Hamburg, Bundesstraße 45, 20146 Hamburg
** Wyatt Technology Europe GmbH, Hochstraße 18, 56307 Dernbach
E-mail: info@wyatt.eu

Keywords: *Polyacrylamide, Molecular Characterisation, Field Flow Fractionation (AF4)*

Native and synthetic polymers exhibit a polydisperse character, expressed by a wide distribution of molar masses and particle sizes. For native polymers (e.g. cellulose, starch) this is a result of differing growth conditions. For synthetic polymers differing reaction conditions impact the growth of polymer chains and thus yield broad molar mass and particle size distributions. To access new fields of application, polymer solution structures of polyacrylamide samples were studied using new techniques and with regard to ageing or conformational changes in solution.

For this investigation, a commercially available sample from Fluka (Fluka PAAm) and a broadly distributed polymer standard from Polymer Standard Service (PSS PAAm) were characterized using size exclusion chromatography (SEC) and asymmetrical flow field-flow fractionation (AF4) hyphenated to a multi-angle light scattering detector (MALS) and a differential refractive index detector (dRI) with regard to their particle size, molar mass and their respective distributions.

For the determination of the intrinsic viscosity and the evaluation of the light scattering measurements (recovery rate) the exact cognition of the polymer concentration is essential. Due to the fact that polymers can show a hygroscopic behaviour, the dry content was determined. Furthermore, viscometric measurements were carried out with varying electrolyte concentrations in order to check for a possible polyelectrolyte effect caused by the presence of ionic side chains.

It could be shown that the intrinsic viscosity does not significantly change over a storage period of seven days. Differing salt concentrations and a lower pH value also had no significant impact on the determined values for the intrinsic viscosity and thus the polymer architecture in solution as well as the calculated molar mass $\mathbf{M_w}$. However, the values for $\mathbf{M_w}$ were significantly lower than those given by the manufacturer. As viscometry is a relative method, a hyphenated assembly of SEC-MALS-dRI was used for further characterization. In agreement with the viscometry measurements, the determined values for M_w deviated from the manufacturers' numbers by 50%. This can be the result of high molar mass components being retained by the guard column or degradation during separation on the columns. Data are depicted in table 1.

Table1: M_w und $<R_G>_z$ from SEC measurements (left), from AF4 measurements (right)

	$M_{w\ detected}$ [g/mol]	$M_{w\ manufacturer}$ [g/mol]	$<R_G>_z$ [nm]	$M_{w\ detected}$ [g/mol]	$M_{w\ manufacturer}$ [g/mol]	$<R_G>_z$ [nm]
PSS PAAm	$2.7 \cdot 10^6$	$5.6 \cdot 10^6$	117	$3.4 \cdot 10^6$	$5.6 \cdot 10^6$	120
Fluka PAAm	$2.6 \cdot 10^6$	$5 - 6 \cdot 10^6$	119	$3.2 \cdot 10^6$	$5\text{-}6 \cdot 10^6$	130

In order to rule this out AF4 fractionation (Eclipse 2, Wyatt Technology Europe, Germany) was carried out in subsequent experiments. A good separation of sample components was achieved. However, the values determined for $\mathbf{M_w}$ and <RG>z are in very good agreement with the values from the SEC and viscometry measurements (see table 2).

In this investigation we prove the absence of aggregates utilizing a hyphenated assembly of AF4-MALS-dRI and therefore to rule out their retention on the guard column. As the values determined with AF4-MALS-dRI differ only insignificantly from those obtained by SEC-MALS-dRI, degradation of the polymer can also be ruled out. It was shown that AF4-MALS-dRI is a fast and reliable method for the determination of molar mass and particle size and is advantageous over SEC-MALS-dRI with regard to shear stability and exclusion of aggregates.

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MOLECULAR CHARACTERIZATION OF UHMW POLYETHYLENE: ASYMMETRIC FLOW FIELD-FLOW FRACTIONATION CONTRA SIZE EXCLUSION CHROMATOGRAPHY

Tino Otte*, **Robert Brüll***, **Tibor Macko***, **Harald Pasch****

** German Institute for Polymers, Address: Schlossgartenstraße 6, 64289 Darmstadt, Germany*
*** University of Stellenbosch, Address: Institute for Polymer Science, Private Bag X1, Matieland 7602, South Africa*
E-mail: totte@dki.tu-darmstadt.de

Keywords: *polyolefin, separation, field-flow fractionation*

For many applications which require particular mechanical strength and chemical inertness, polyolefins with ultra high molar mass (UHMWPO) are used. For example, 2 million people receive artificial knees and hips each year, which are made from UHMWPE. As a rule these polymer materials contain macromolecules with molar masses above 10^6 g/mol. Depending on the polymerization-technique the chain structure of the macromolecules can be linear or branched.[1] The analytical characterization of UHMWPE has several shortages in case of the most often applied analytical methods, e.g. size exclusion chromatography at high temperature (HT-SEC). Shear degradation of macromolecules occurs due to the packed columns and the implemented frits.[2,3,4] Moreover, the presence of large, branched macromolecules leads to an abnormal late elution, which leads to problems in the quantitative evaluation of the SEC chromatograms.
Although AF4 is often applied for separation of large macromolecules and gel particles[5], all corresponding publications, except one[4], describe separations at room or a little elevated temperature. However, the dissolution of UHMWPE requires temperatures as high as 140 – 160 °C.
The asymmetrical flow field-flow fractionation at high temperatures (HT-AF4) was realized on the HT-AF2000 system which was recently developed by Postnova (Landsberg/Lech, Germany). This system is coulpled with the high-temperature chromatograph PL SEC 220 (Polymer Laboratories, part of Varian, Church Stretton, England). The detection was done with a combination of an infrared (IR) and a multi-angle laser light scattering (MALLS) detector. In the AF4-channel no stationary phase is applied. This allows the separation of large macromolecules under very gentle conditions. A ceramic membrane is a part of the AF4 channel. The size-separation is determined by the different diffusion abilities of the macromolecules inside the generated flow field.[5]
We have found out that the dissolution parameters which are used for UHMWPE are substantially influencing the analytical results. The adjustable cross-flow enables to adjust separation selectivity what will be shown especially with regard to the enhanced separation of the high molecular weight species.
By comparing results from high-temperature SEC and high-temperature AF4, the advantages of HT-AF4 over HT-SEC with regard to the above mentioned effects will be demonstrated in this presentation. Finally, some restrictions in polyolefin-separation will be discussed and perspectives for further improvement will be outlined.

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SMALL-MOLECULE DIFFUSION IN SEMICRYSTALLINE POLYMERS AS REVEALED BY COMBINED EXPERIMENTAL AND SIMULATION STUDIES

U.W. Gedde, **M.S. Hedenqvist, A. Mattozzi, F. Nilsson, B. Neway**

Fibre & Polymer Technology, School of Chemical Science & Engineering, Royal Institute of Technology, SE-100 44 Stockholm, Sweden
E-mail: gedde@polymer.kth.se

Keywords*: polyethylene, diffusion, morphology*

The diffusion of *n*-hexane in poly(ethylene-*co*-1-hexene)s with different comonomer contents (0–12 mol%) and crystallinities (15-75 wt.%) has been studied by desorption experiments and analyzing data using the Fickian equations with a concentration dependent diffusivity according to the Cohen-Turnbull-Fujita model.[1] The effect of the impenetrable crystalline phase on the penetrant diffusivity (*D*) is conveniently described by $D=D_a/(\tau\beta)$, where D_a is the diffusivity of the fully amorphous polymer, τ is the geometrical impedance factor and *b* is a factor describing the constraining effect of the crystals on the penetrable non-crystalline phase. Molecular dynamics simulation on fully amorphous systems showed a relatively weak effect of comonomer concentration (degree of hexyl branching) on the penetrant diffusivity; the diffusivity was 3 times lower in the polymer with 12 mol% comonomer than in the linear polymer.[2] For a polymer with 75 wt.% crystallinity the product $\tau\beta$ varied markedly with penetrant concentration (v_{1a}) in the penetrable phase: ca. 1000 (v_{1a}=0) and ca. 10 (v_{1a}=0.15) [3]. The latter limited uptake of penetrant has no effect on the 'gross' crystal morphology and thus not on the geometrical impedance factor. This means that βhas to be strongly dependent on v_{1a}. Data obtained by X-ray scattering, NMR and Raman spectroscopy on samples saturated in *n*-hexane reveal the loosening of the interfacial structure induced by the penetrant, indirectly by the increase in crystal density (reduction of **a** and **b**) and a shift of 1415 cm^{-1} Raman band indicating a restructuration of the crystalline phase that would have not been possible without an increased mobility in the interfacial component and directly by a change in the intensity of the asymmetric X-ray scattering associated with the interfacial component.[3] The geometrical impedance factor has been modelled by mimicking spherulite growth (spherulites were built on the computer using on a Monte Carlo method based on empirical principles from electron microscopy findings) and *t* was obtained as the ratio of the diffusivities of the fully amorphous and semicrystalline systems; the latter were based on on- and off-lattice random walks.[4–6] Briefly, the maximum τobtained from these simulations are of the order of ten, which suggests that β in the systems with v_{1a}=0.15 takes vales close to unity. Off-lattice simulation showed, surprisingly at first sight, that the geometrical impedance factor is insensitive to the ratio of the crystal width and the crystal thickness.[6]

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GAUCHE-TRANS TRANSITIONS IN AMORPHOUS POLYMERS UNDER ANNEALING: LATTICE MODEL AND POLARIZED LIGHT SCATTERING

Masaru Matsuo*, **, Yanling Luo*, Andrzej Galeski***

Department of Apparel and Clothing Science, Faculty of Human Life and Environment - Nara Women's University, Kitauoya higashi-machi Nara 630-8506 Japan
*** School of Chemical Engineering - Dalian University of Technology, Zhongshan Rd. 116012, P.R. China*
**** Polymer Physics Department - Centre of Molecular and Macromolecular Studies, Polish Academy of Science, Sienkiewicza 112 90-363 Lodz, Poland*
E-mail: mm-matsuo@rinku.zaq.ne.jp

Keywords: *density fluctuation, quasi-spinodal decomposition, chain stiffness*

The driving force of density fluctuation in amorphous polymer films during annealing processes was evaluated systematically in terms of thermodynamics on the basis of the logarithmic light intensity as a function of annealing time. The time dependence of $\ell n(I)$ of poly(ethylene terephthalate) (PET) as an example for characterizing an amorphous state was classified into three stages; the first stage (stage I), where $\ell n(I)$ showed insignificant changes with time, the second stage (stage II) where $\ell n(I)$ increased linearly and the third stage (stage III) where the intensity deviated from the linear relationship and tended to level off. The density fluctuation by chain diffusion, termed as quasi-spinodal decomposition, in stage II was analyzed in terms of an increase of trans-conformation of an amorphous chain in stage I. To provide conclusive evidence, the orientation function of chain segments was calculated by using a lattice model that accounts for entropic and energetic characters. The former character is associated with segmental orientation due to the effect of chain stiffness of Kuhn segments characterized by a rod with a relatively large length-to-width ratio *x*, whereas the latter is associated with thermo-tropic systems with anisotropic polarizabilities. By using the theoretical orientation function, uv light scattering patterns were calculated by a new statistical approach, in which the optical axis of a PET chain segment was chosen along the direction perpendicular to the benzene ring. This selection was justified by comparison of the three principal refractive indexes of a PET chain. The calculated patterns provided a clear X-type lobe, when the correlation between optical elements concerning the rotational fluctuation became stronger. The calculated patterns were in a good agreement with the patterns observed in stage III. The series of experimental and theoretical results indicate that the conversion from gauche- to trans-conformation plays an important role when deriving the density fluctuation of amorphous polymer chains associated with the initiation of crystallization. This talk is a summary of refs. [1-2].

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ANALYSIS OF THE AQUEQUACY OF REPRESENTATION OF ENTANGLEMENTS' EFFECTS BY CHAIN LOOPS

José A. Martins[*,**]

** Departamento de Engenharia de Polímeros, Universidade do Minho, Campus de Azurém 4800-058 Guimarães, Portugal*
*** CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal*
E-mail: jamartins@dep.uminho.pt

Keywords: *entanglements, melt elasticity, ordered regions*

It is generally considered that entanglements are a consequence of the fact that polymer chains cannot penetrate each other. In another words, because chains cannot penetrate through each other, they are intertwined, or "entangled". These entanglements survive for some non-negligible time and it is considered that they are responsible for melt elastic properties.

To examine the role of chain intertwining on polymer melt properties, namely their elasticity, the interaction potential energy between a loop and chain at its centre is evaluated. It is considered that this simple geometrical representation adequately describes the role of chain intertwining on polymer melt properties. A detailed discussion is made on the validity of the procedure used to evaluate the interaction potential energy between parallel chain segments and also between a loop and a chain at its centre. It is demonstrated that a simple evaluation procedure in which the additivity of interactions is considered allows the evaluation of this interaction potential energy with an error of 4% only.

It is then demonstrated that the interaction energy between a loop and a chain is or the order of the melt thermal energy, and therefore that the representation of an entanglement by a loop interacting with a chain cannot explain the well known elastic properties of polymer melts. This elasticity and the evaluation of the different contributions to flow activation energy of linear polymer chains are also used to demonstrate that chain loops cannot justify the properties assigned to entanglements. The different possible contributions to flow activation energy are discriminated and a physical meaning is assigned to the activation energy measured in the high temperature flow region. For linear polymer chains in the molten state, only two additive contributions are considered: one results from local and correlated conformational transitions and the other results from short-range ordered regions.

The short-range ordered regions considered have a dynamic character. Their dimensions are estimated from WAXS experimental results of polymer melts at low *q* values,[1] from results of the pair distribution function obtained from molecular dynamic simulations of polymer melts,[2] and from experimental results of flow activation energy. Besides their dimensions, their number and volume fraction is also evaluated, and it is also shown to be in agreement with known experimental results.[3] It is demonstrated that random coil model is an approximate description of polymer melt morphology, but not an exact one. It will be shown that the morphology of polymer melts is consistent up to more than 80% with random coil model.

A new model of melt morphology, of general validity to all macromolecular systems, is proposed. This model is consistent with existing ideas of chain confinement to a tube and of its diffusional movement by reptation. This model explains also the elasticity in polymer melts, and specifically the recently reported experimental results for the low-frequency elasticity in non-entangled polymer melts.[4]

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USE OF DIELETRIC ANALYSIS TO COMPLEMENT MECHANICAL AND RHEOLOGICAL STUDIES NITRILE RUBBER/ACRYLIC RUBBER BLENDS

Micheli Celestino, Bluma Guenther Soares

Instituto de Macromoléculas Professora Eloisa Mano – Universidade Federal do Rio de Janeiro (IMA/UFRJ). Centro de Tecnologia, Bloco J, Ilha do Fundão. Rio de Janeiro, RJ, Brasil, P.O.Box 68525
E-mail: micheli@ima.ufrj.br

Keywords: *rubber blends, thermal analysis, dielectric analysis.*

Rubber blends are being used extensively in numerous applications. A blend can offer a set of properties that can improve the potencial of entering application areas which is not possible neither with the rubbers comprising or the blend. It has been reported that the blend of nitrile (NBR) and acrylic rubber (ACM) can improve oil resistance at high temperature and minimize the oxidative degradation of NBR during service at high temperature [1-3]. The polar nature of the nitrile rubber and acrylic rubber make NBR/ACM blends a very valuable subject to be studied by dielectric analysis (DEA).

In this work three types of equipments were used, namely, Rubber Process Analyzer (RPA 2000), Dynamic Mechanical Analyzer (DMA), and Dieletric Analyzer (DEA) and the aim of this work is complement previously studies on this system using the dielectric analysis technique. This selection was based on the fact that dielectric measurements are extremely sensitive to small changes in material properties mainly at molecular level. An advantage of DEA over other techniques is the possibility to use a wider frequency range. This enables detection of transitions that would not be possible through other techniques. Particularly, DEA complements DMA for characterization of internal motions in polymers [4]

Acrylic rubber (Hycryl) and nitrile rubber (NBR) (33wt% acrylonitrile) was kindly supplied by Petroflex Ind. Com. S.A., Brazil. The NBR/ACM blends in different proportions of NBR/ACM (0:100; 25:75; 50:50; 25:75 and 100:0 wt%) were prepared at room temperature in a two roll mill. The rubbers were compounded for 5 min. Then, the cure system for each rubber component was added and the mixture was performed for an additional time. The cure characteristic of the mixes was determined by using an oscillating disk rheometer (ODR) (Tecnologia Industrial-Argentina), operating at 190°C and 1° arc, following the ASTM D 2084-81 method. The blends were vulcanized up to the optimum curing time in a hydraulic press at 190°C and 15000lb/in^2.

The NBR/ACM blends are immiscible as indicated by scanning electron microscopy, but the DMA showed the absence of two well-defined transitions in NBR/ACM blends suggesting that the transitions of each rubber phases overlapped as a consequence of an increase in the molecular intermixing of both components. The half width values of the tan δ peaks in DMA parameters was a significant broadening of the transition peak of the blends systems, when compared to the pure rubber components. The dielectric analysis showed that NBR/ACM blends presented a decrease in the mobility of the macromolecular chain segments as consequence of an increase in the molecular intermixing of both components, however, this only occurs in mixtures with higher percent of NBR, likes NBR/ACM (75:25 wt%). The storage modulus values of the blends were significantly higher than the pure rubbers in the region below Tg, which indicated strong interactions between the phases, which was also in agreement with the tensile data. The NBR/ACM (75:25 wt%) showed an increase in the minimum and maximum torque when compared with ACM pure. Rheometric data obtained from RPA analyzer show that with increasing amount of ACM in the system the difficulty in the processing of the mixture increases, thus increasing the amount of energy expended during processing.

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STRUCTURAL AND DIELECTRIC PROPERTIES OF CHLORINATED AND NOT CHLORINATED POLY (P-XYLYLENE)

A. Kahouli*,, A. Sylvestre*, F. Jomni**, B. Yangui**, J-F. Laithier***, B. Berge****, J-C. Robert****, N. Garcia****, J. Legrand******

** Grenoble Electrical Engineering Lab. (G2Elab), CNRS, 25 Rue des Martyrs, BP166, 38042 Grenoble, Cedex 9, France*
*** Laboratory for Materials, Organization and Properties (LabMOP), Campus Universitaire-El Manar, 2092 Tunis, Tunisia*
**** Comelec SA, Rue de la Paix 129CH-2301 La Chaux-de-Fonds, Switzerland*
***** Varioptic SA, Bâtiment Tony Garnier, 24A Rue Jean Baldassini, 69007 Lyon, France*
E-mail: alain.sylvestre@grenoble.cnrs.fr

Keywords: dielectric properties, poly (p-xylylene), semi-crystalline polymer

It is known that the chemical, structural as well as the dielectric properties of polymeric films are closely related to molecular chain arrangement, amorphous and crystalline phase fraction, crystallite structure, tacticity, polarity. The dielectric response of polymers under an electric field depends mainly on its polarity. In this report, the real part (ε') and its imaginary counterpart (ε'') of the permittivity of poly-chloro-p-xylylene (parylene-C), poly-dichloro-p-xylylene (parylene-D) and poly-p-xylylene (parylene-N) were studied by dielectric spectroscopy in a wide temperature and frequency range of [20 – 350°C] and [10^{-4} – 10^{6} Hz], respectively. Due to their physical and chemical properties, these polymers are attractive to use in many applications[1]. However, their dielectric properties are not clearly established and knowledge of these properties proves essential today to optimize the devices in which these materials will be integrated.

These films (thickness of a few microns) were deposited at ambient temperature by vapor deposition polymerization (VDP). XRD analysis reveals that the addition of chlorine atoms in the aromatic rings of poly (p-xylylene) displays the migration of the 2θ-peak towards the lower angle of the diffraction pattern and decreases the crystalline phase fraction. The crystallinity ratio decreases from 60% for parylene N to 45% for parylene C and 35% for parylene D. This trend is in relation with the chlorine substitution increase. This trend is attributed to the increasing of the space between the ordered chains due to the larger chlorine atom which can occupy a higher space than the hydrogen. XRD analysis shows that the the distance between to ordered regions is about 5.37 Ǻ for parylene N, 6.39 Ǻ for parylene C and 7.08 Ǻ for parylene D. FTIR spectrum shows that addition of chlorine atoms modifies the position of some bonds. The dispersion phenomenon of the real part of the permittivity of Parylene-C has been attributed to the polar character of these films due to asymmetric structure in the aromatic rings[2]. The dielectric constant of Parylene-N and –D is practically independent of temperature. This last result is in correspondence to the high symmetry of these films. This permittivity increases from 2.65 for parylene N to reach 3.1 for parylene C. Dielectric losses of these parylene families are higher as the microscopic polarization in the system increases (dissipation factor tan(δ) $=2.10^{-4}$ for parylene N and 3.10^{-2} for parylene C). The dielectric response in these three parylenes are compared and discussed as a function of the crystallinity. Since the addition of chlorine atoms in some aromatic sites increases, the glass transition increases (13°C for parylene N, 80°C for parylene C and 100°C for parylene D)as also observed by dielectric spectroscopy (α-relaxation mechanism).

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MICROSTRUCTURAL PARAMETERS AND SURFACE MORPHOLOGY OF 8 MeV ELECTRON IRRADIATED NB_7 BOMBYX MORI SILK FIBERS

Sangappa*, S Asha*, Ganesh Sanjeev, P Parameswara***, R Somashekar*****

** Department of Studies in Physics, Mangalore University, Mangalagangotri – 574 199, Karnataka, India*
***Microtron Center, Mangalore University, Mangalagangotri – 574 199, Karnataka, India*
****Department of Studies in Physics, University of Mysore, Manasagangotri – 570 006, Karnataka, India*
E-mail: syhalabhavi@yahoo.co.in

Keywords: *Fiber, Irradiation, WAXS, microstructural parameters*

When a polymer is subjected to irradiation by ionizing radiation such as gamma rays, x-rays, or accelerated electrons various effects can be expected from the ionizations that occur. The ratio of resultant recombination, cross-linking, and chain scission will vary from polymer to polymer and to some degree from part to part based on the chemical composition and morphology of the polymer, the total radiation dose absorbed, and the rate at which the dose was deposited. Hence in this paper we have reported the crystallinity, microstructural and surface modification in NB_7 silk fibers, induced by electron irradiation. The irradiation process was performed in air at room temperature by use of 8 MeV electron accelerators with the following features. Beam current 20 mA, pulse repetition rate 50 Hz, pulse width 2.2 µs, distance source to sample 30 cm and dose range 0 -100 kGy. The dose delivered to different samples is measured by keeping alanine dosimeter with sample during irradiation. The changes in crystallinity, microstructural parameters and surface morphology in these natural polymer fibers have been studied using wide angle X-ray scattering (WAXS) data and Scanning Electron Microscopy (SEM).

The XRD diffractograms of the fiber samples were recorded using a Rigaku Miniflex-II X-ray diffractometer with Ni filtered, CuKα radiation of wavelength $\lambda = 1.5406$ Å, with a graphite monochromator. The scattered beam was focused on a detector. The samples were scanned in the 2θ range 10-50º with a scanning speed and step size of 1º /min and 0.01º. The morphology of the pure and 8 MeV electron irradiated Bombyx mori silk fiber was observed with a scanning electron microscope (SEM, JSM-6390LV) at 15 kV. All the samples were sputtered with gold. The crystal imperfection parameters such as crystallite size $\langle N \rangle$, lattice strain (g in %) and surface weighted crystallite size (D_s) have been determined by line profile analysis (LPA) using Fourier method of Warren.

Irradiation of polymers mainly causes two important changes. (1) Degradation of the polymer, wherein main chain scission takes place, leading to low molecular weight polymer. (2) Cross-linking of small polymer units leading to the formation of a rigid three-dimensional network, wherein a high molecular weight polymer is produced. Both these effects cause changes in physical and surface properties. Degradation of polymer leads to loss in mechanical strength, whereas cross linking improves the physical properties. It was found that the influence of electron beam irradiation, with increase in radiation dose an increase in degree of cross-linking results increase in modulus and T_g. In the case of many other polymeric materials, ionizing radiation may cross-link them, cuase chain scission or affect their surface. Quite often these effects may occur simultaneously. The final result depends on the nature of the material, on the dosage, dosage rate and energy of the radiation. From the WAXS studies indicates that the crystallite size decreases as irradiation dose increases. From the SEM it is clear that the fracture of the fiber increases as irradiation dose increases. Our results clearly states that changes observed are due to degradation of the fiber sample.

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INDUSTRIAL CONSEQUENCES OF POLYPROPYLENE PHASE MORPHOLOGY

Martin Obadal, **Gottfried Kandioller, Senthil K. Kaliappan, Walter Schaffer, Jens Reussner**

Borealis Polyolefine GmbH, Innotech Operational Support, Advanced Polymer Characterization, St-Peter-Strasse 25, 4020 Linz, Austria
E-mail: martin.obadal@borealisgroup.com

Keywords: *polypropylene, morphology, properties*

Isotactic polypropylene (iPP) is one of the most important industrially used polymers. It is interesting not only commercially but also scientifically. This is based on a rich variety of morphologies arising from crystallization of iPP, an important factor extending its practical use. The term *phase morphology* is rather wide and should be differentiated with respect to a given structural scale. On the supermolecular level, the variation between the crystalline and amorphous phases, resulting mainly from the stereoregularity, can be first considered. In addition at this level (within the crystalline portion), iPP exhibits polymorphic behavior as it crystallizes into four different crystalline modifications, namely monoclinic α, trigonal β, orthorhombic γ and mesomorphic smectic phase[1]. The polymorphism can be readily observed also on the lamellar level. Fig. 1a illustrates the morphology of non-nucleated iPP homopolymer showing a presence of both α and β- phases; on the left side of the figure a typical sheaf-like lamellar morphology of β-phase and crosshatched lamella of α-phase on the right side can be seen. It should be mentioned that the α-phase is in such cases predominant; to obtain higher, even predominant, amounts of β-phase, the use of specific nucleation is essential – such material shows then favorably enhanced toughness and drawability as compared to common α-phase iPP[2,3] and is used also industrially[4]. Another important effect influencing the formation of individual polymorphs comes from crystallization (processing) conditions, mainly temperature and shear gradients proceeding virtually all the time during the polymer processing. As a result highly oriented structures can appear as can be seen in Fig. 1b. The skin (surface layer) of injection moulded iPP then consists of shish-kebab morphologies; although the material is α-phase nucleated the epitaxial overgrowths are obviously composed of β-phase as evident from wide-angle X-ray scattering; a combination of direct and indirect experimental techniques is essential. Finally, back to the expression *phase morphology*, the last case based on the mutual immiscibility of two (or more) individual phases creates a system of two (or more) separated morphologies. Such iPP material called heterophasic or impact copolymer have the iPP matrix while the softer inclusions are based on ethylene-propylene copolymer; impact strength even at low temperature is significantly enhanced[6], see the morphology example in Fig. 1c. The lecture will show several examples of the phase morphology variation in iPP with special attention being paid to the morphology assessment itself highlighting its industrial consequences in terms of post-processing effects and relations to final macroscopic properties.

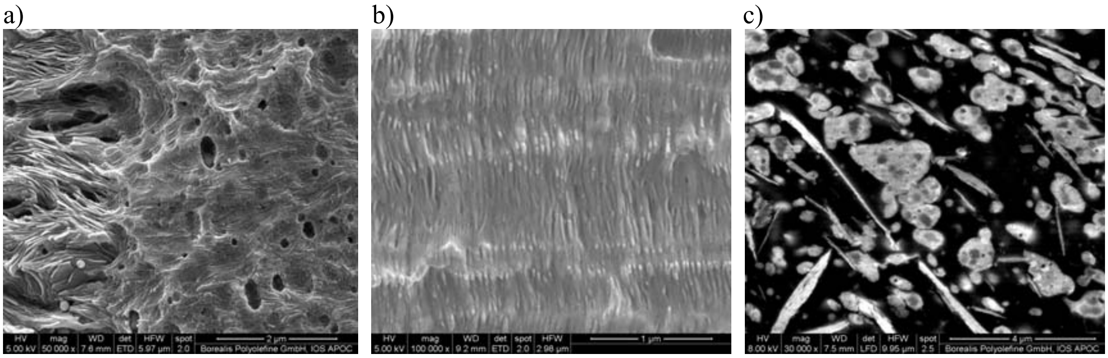

Figure 1. Scanning electron microscopy micrographs : a – non-nucleated homopolymer (Borealis HC300BF), rem.: use zoom too in your browser; b – the skin layer of injection molded iPP (Borealis HD905CF) – both ultra-microtome cuts after permanganate etching; c – the morphology of heterophasic PP after RUO4 staining.

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SOLUTION CRYSTALLIZATION ANALYSIS BY LASER LIGHT SCATTERING (SCALLS). APPLICATION EXAMPLES FOR POLYOLEFINS.

Van Reenen AJ*, Rohwer, EG, Brand, M***

**Department of Chemistry and Polymer Science, University of Stellenbosch, P/Bag X1, Matieland, South Africa*
***Institute for Laser Physics, University of Stellenbosch, P/Bag X1 Matieland, South Africa*
E-mail: ajvr@sun.ac.za

Keywords: *Solution crystallization, Polyolefins.*

We recently reported the use of solution crystallization analysis by laser light scattering (SCALLS) [1,2]. This technique was first described by Shan et al[3], who termed the technique “turbidity fractionation analysis”. During SCALLS analyses, a polyolefin solution is cooled in a controlled fashion and crystallization from solution is followed by measuring the intensity of laser beam passing through the solution (or the intensity of scattered light emanating from the solution) during cooling. During a SCALLS experiment, light is scattered as soon as the crystallite size is large enough to scatter the laser light. In previous papers [1,2] the effect of some experimental parameters and studies on the crystallization of propylene copolymers were reported. SCALLS differs from a technique like Crystaf in that it measures changes directly and quite rapidly and that it affords the opportunity to measure “solution melting” temperatures as well as solution crystallization temperatures. This is quite simply done by heating the crystallized suspension of polymer in a controlled fashion and once again measuring the intensity of scattered light or the intensity of transmitted light as a function of temperature. In both the cooling and heating modes peak temperatures can be obtained by taking the first derivative of the measured intensities. A typical cooling profile is presented in Figure 1

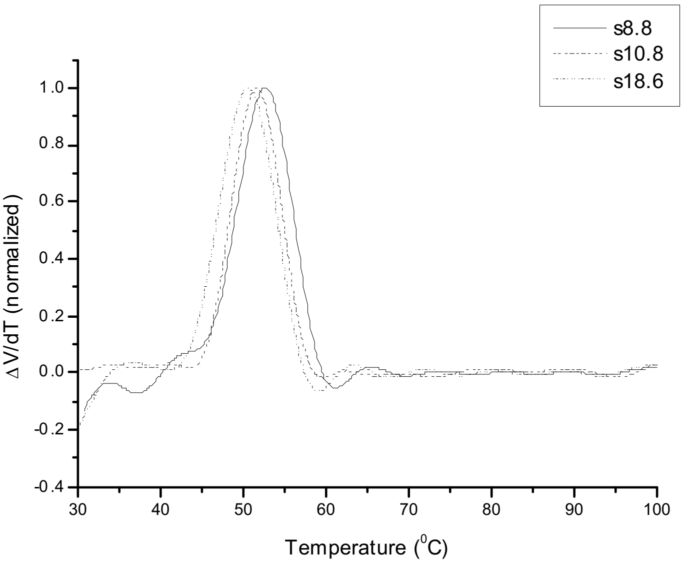

Figure 1. The SCALLS cooling plots for three propylene/1-alkene copolymers

In this paper, we will give examples of the application of this technique, both in the cooling and the heating mode. We will demonstrate that the technique can be used to measure fundamental aspects of crystallization, as well as a useful tool to predict elution temperatures for preparative TREF experiments. The technique can also be used in a similar fashion to analytical TREF to quantify the chemical composition distribution of polyolefins.

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ORIGIN OF MELT MEMORY EFFECT IN POLYMER CRYSTALLIZATION

Weidong Zhang[*,**], **José A. Martins**[*,**]

** Departamento de Engenharia de Polímeros, Universidade do Minho, Campus de Azurém 4800-058 Guimarães, Portugal*
*** CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal*
E-mail: zwd@dep.uminho.pt; jamartins@dep.uminho.pt (corresponding author)

Keywords: *crystallization, origin melt memory, ordered regions*

Reproducibility of repeated crystallization experiments from melts is reached after annealing the melt at a sufficiently high temperature for short time, or at lower temperatures for longer time. It is considered that annealing erases the melt memory. Although the physical origin of melt memory has never been clearly established, it is linked to precursor structures for crystallization.

By applying controlled shear deformations at different melt temperatures and recording the crystallization kinetics in the absence of flow at a constant temperature, we generated the reverse effect, enhancing the crystallization kinetics until it reaches maximum effectiveness in a well defined melt state. It was shown that this state is the steady state,[1] which is also a disentangled state.

Annealing for different time this pre-sheared melt at the same melt temperature at which shearing was previously applied, and cooling further the annealed pre-sheared melt to the same crystallization temperature, one observes the erasing of melt memory effect, which is manifested experimentally by the slowing down of crystallization kinetics. The crystallization kinetics is slowest after relatively long annealing time, when the melt memory effect is erased, which means that the melt is fully relaxed from its previous thermal and mechanical history, and crystallization experiments become reproducible again.

These experiments allowed therefore the identification of two limiting melt states: the fully relaxed melts where crystallization is slowest, and the melts sheared up to a steady state, where crystallization is fastest. Further characterization of the two melt states allowed to conclude the following: ***a)*** melts sheared up to steady state have significantly lower viscosity in limit of zero shear rate than fully relaxed melts; ***b)*** a significant number of constraints is destroyed during the transition from fully relaxed melts to melts sheared up to a steady state, around 1/2 for linear PE and 2/3 for iPP; ***c)*** the repetition time, evaluated at the crossing point between $G'(\omega)$ and $G''(\omega)$ at steady state is 1/3 the repetition time value of fully relaxed melts; ***d)*** the flow activation energy is the same at the two melt states and ***e)*** the morphology of the solid samples, in what concerns specifically the average spherulite size, is independent of the melt state.

Based on this and other experimental results, we concluded that melt memory effect is a pure melt effect. It can be shown that the acceleration in the crystallization recorded for melts sheared up a steady state cannot be ascribed to any effect played by melt impurities (melt temperature and crystallization temperature are exactly the same), to an increase of nucleation density by a pre-shear effect (the final spherulite size is similar), to an increase of supercooling degree by the effect of pressure to drive the melt flow (this increase is too small for explaining the recorded differences in half-crystallization time). Therefore, the acceleration in crystallization kinetics is mainly ascribed to a lower diffusion term of growth rate (for iPP, $\approx 2 \times 10^3$ J/mol lower than that of fully relaxed melt), which is consistent with the experimental verification of lower melt viscosity at steady state, η_o = 0.6 kPa.s (for fully relaxed melt, η_o = 2 kPa.s).

As an additional result, this work presents predictions for dimensions of precursor structures for crystallization, which are consistent with known experimental results. Variation of their dimension with melt temperature and for fully relaxed melts and melts sheared up to a steady state, will also be presented. According to the experimental results obtained, dimensions of precursor structures for crystallization are independent of crystallization temperature. However, they depend on the melt temperature, decreasing by increasing the temperature of the melt. These and other experimental results suggest also the existence of local ordered regions in polymer melts.

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EFFECTS OF RADIATION, IODINIZATION AND IONIZATION ON THE OPTO- ELECTRICAL PROPERTIES OF POLYMER

M. M. Hossain, M. R. Akter, N.K. Zahan, M. R. Alam

Department of Applied Physics & Electronic Engineering University of Rajshahi, Rajshahi, Bangladesh
E-mail: mozaffor_ape@yahoo.com

Keywords: *Transmittance, Reflectance, Conductance.*

Nowadays, polymer materials are widely used in different technologies especially in the field of conducting, electrets properties, encapsulation and nano electronics are the important of them. Among the possible synthetic polymers, polyimide and fluorocarbon(teflon) seem quite promising for the wide application ranging from power apparatus and cable to microelectronics. The commercial grade polyimide(ΠM), fluorocarbon (4MΔ), polyimide-fluorocarbon(ΠMΦ-351) and fluorocarbon-polyimide-fluorocarbon((ΠMΦ-352) sand witch polymer materials of 40, 10 and 50 μm thickness are used for this investigation.

The effects of radiation, iodination and ionization on the optical, dielectric and conducting properties of above mentioned polymers are investigated by measuring the transmittance, reflectance, absorbance, absorption coefficient, extinction coefficient, optical conductivity and electrical properties like dielectric constant and conductance at different frequencies. The values of transmittance slightly increases after radiated by α, β and γ- rays on the other hand the values of reflectance is higher after γ-radiation than the values after α and β radiation. The values of transmittance and reflectance are varies on both side of the polyimide-fluorocarbon polymer sand witch film. It is also observed that the dielectric constant slightly decreases after radiation. Iodinization are also influence the opto-electrical properties of the polymer. It was observed that the transmittance decreases on the other hand reflectance increases with the increase of the iodinization time. Dielectric constant also decreases and conductivity increases after the iodinization. The ionization with $CuSO_4$ electrolyte affects the opto-electrical properties of polymers. Polyimide, fluorocarbon, and fluorocarbon-polyimide-fluorocarbon sand witch materials are shown the identical behaviour on the other hand polyimide-fluorocarbon shows different properties. The glass transition temperature may be arrived after 20 hours of electrolyses due to the electrode heating for polyimide, fluorocarbon and fluorocarbon-polyimide-fluorocarbon materials on the other hand its may be different for polyimide-fluorocarbon polymer film. From the results, it may conclude that the ions are trapped on the surfaces of the bulk of polyimide, fluorocarbon and fluorocarbon-polyimide-fluorocarbons materials on the other hand it may trap across the barrier of fluorocarbon-polyimide sand witch film. The peak arises in the transmittance spectrum of all the above mentioned specimens may due to the presence of C-O group in the polymer. The variation of absorbance after ionization for different duration follows the similar trends as observed in the case of reflectance. The optical conductivity shows peak between 2.5-3.5eV for the polyimide composite specimens but teflon shows different characteristics. Both sides of the polyimide-fluorocarbon polymer sand witch films also shows different characteristics after and before ionization. It was also observed from the results that the dielectric constant is decreasing with increase in frequency during the different time of ionization. The conductance of the all synthetic polymers remarkably enhanced after ionization. The process of ionization also affects on the properties of natural polymers like silk. Ionization enhanced the reflectance of pure silk with $ZnSO_4$ and $Al_2(SO_4)_3$ electrolyte. It was observed that the Zn ions are more active on the silk than the Al ions. Ionization may practically implement for improving the shining properties of natural polymers. Biodegradable polymers are most widely used for drug delivery system. It was also investigated that the bio-degradable polymer coating of the same drug capsule of different trade name shows different opto-electrical properties.

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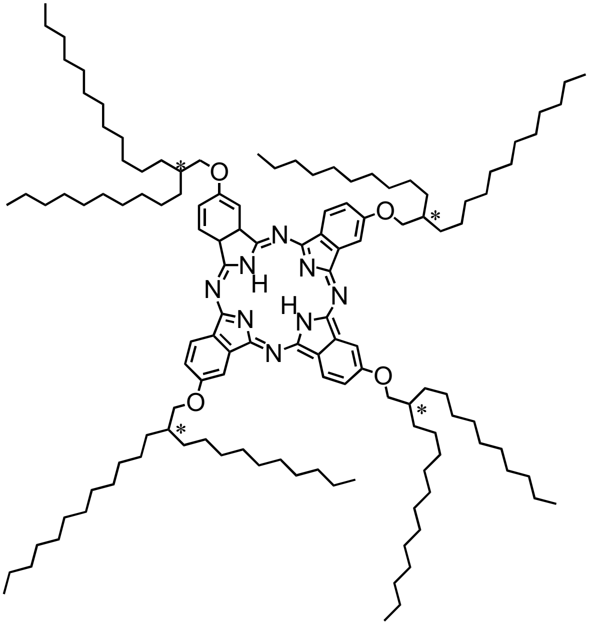
MATERIALS SCIENCE OF DNA

Young-Wan Kwon[1], Chang Hoon Lee[2], Jung-Il Jin[1*], and Yves Henri Geert[3]

[1]Department of Chemistry, Korea University, Seoul 136-701 (Korea)
[2]Department of Polymer science and Engineering, Chosun University, Gwangju 501-759 (Korea)
[3]Laboratoire de Chimie des Polyme`res, UniVersite´ Libre de Bruxelles, CP 206/1 BouleVard du Triomphe, B-1050 Bruxelles (Belgium)
E-mail: jijin@korea.ac.kr

Keywords: *DNA, Discotic LC, Ferromagnetism*

There are still strong controversies and contradictory reports on the electrical properties of DNAs: the claims include from insulators to proximity-induced superconductors. Among many possible reasons for such diversity and less reliability of the reported conductivities of DNAs, controlling the contact between samples and electrodes and the nature of the samples are most important factors to consider. We can mitigate at least the contact problem in the measurement of magnetic properties, which also should be able to shed light on the electromagnetic characteristics of DNAs. The measurements of magnetic properties are not as evasive as the electrical conductivity measurements. Recently we reported magnetic properties of natural and modified DNAs as studied by electron magnetic resonance (EMR) spectroscopy and also by the measurement of magnetic susceptibility using a superconducting quantum interference device (SQUID). In this presentation we would like to make a preliminary report on the magnetic properties studied by EMR and SQUID measurements of natural DNAs and a discotic liquid crystal (DLC) intercalated with iron(III) Phthalocyanine.



2, 9(10),16(17), 23(24)-Tetra(2-decyltetradecyloxy)-phthalocyanine

The discotic liquid crystal was employed as a primitive mimic of DNA because of its capability of forming a stacked morphology. We successfully achieved room-temperature ferromagnetic compositions by intercalating 2,9(10),16(17),23(24)- Tetra(2-decyltetradecyloxy)-phthalocyanine, an organic semiconducting discotic liquid crystal, with low levels of iron(III) phthalocyanine. The compositions exhibit definite magnetic hysteresis loops in the magnetization (M)-magnetic field intensity (H) measurements. Detailed studies of their magnetic properties were conducted by EMR spectroscopy and SQUID measurements.

DENDRIMER BASED FUNCTIONAL NANOTUBES FOR DETECTING DNA HYBRIDIZATION

Chuanliang Feng*, Jean P. Majoral, Wolfgang Knoll*****

** Shanghai Jiaotong University, Dongchuan Road 800, 200240, Shanghai, China*
*** Centre National de la Recherche Scientifique, 205 Route de Narbonne, 31077 Toulouse Cedex 4, France*
**** Austrian Research Centers GmbH, Donau-City-Strasse 1, 1220 Vienna, Austria*
E-mail: clfeng@sjtu.edu.cn

Keywords: *quantum dots, dendrimers, energy transfer*

The functionalization of nanotubes (NTs) is an effective way to design new hybrid materials by coupling the properties of supramolecular building blocks or novel nanostructures to NTs,[1] which have attracted considerable interest as biocatalysts, biosensors, or for bio-separation.[2] One of the novel approaches to functionalize NTs is to integrate quantum dots (QDs) with their promising properties, such as narrow emission bandwidth, photochemical stability, and high quantum yield.[3] However, the strategies reported so far for producing QD modified NTs[4] gave low efficiency of the chemical functionalization or non-uniform assembly of QDs. Therefore, the design of functionalized NTs with multi-functionalities, e.g. equipped with efficient assembly of fluorescent labels, bio-linkers, or surface groups providing enhanced biocompatibility, is key to the successful application of NTs. Here, a strategy for the design and the fabrication of QD/dendrimer composite NTs inside AAO membranes with a pore diameter of 400 nm, a lattice constant of 500 nm and a pore depth of 100 µm is reported (Figure). The arrays of aligned QD/dendrimer composite NTs enabled the detection of DNA hybridisation with significantly enhanced sensitivity. To this end, the high specific surface of the pore walls of the AAO membranes, which amounts to about 70,000 μm^2 per 10 μm^2 membrane surface, is combined with graded band gap architectures for efficient energy transfer to the inner surfaces of the NTs, onto which with single-stranded probe DNA is grafted. Thus, the emission of dye-labeled target DNA can be probed with exceptionally high sensitivity and selectivity after its hybridization to the probe DNA.[5]

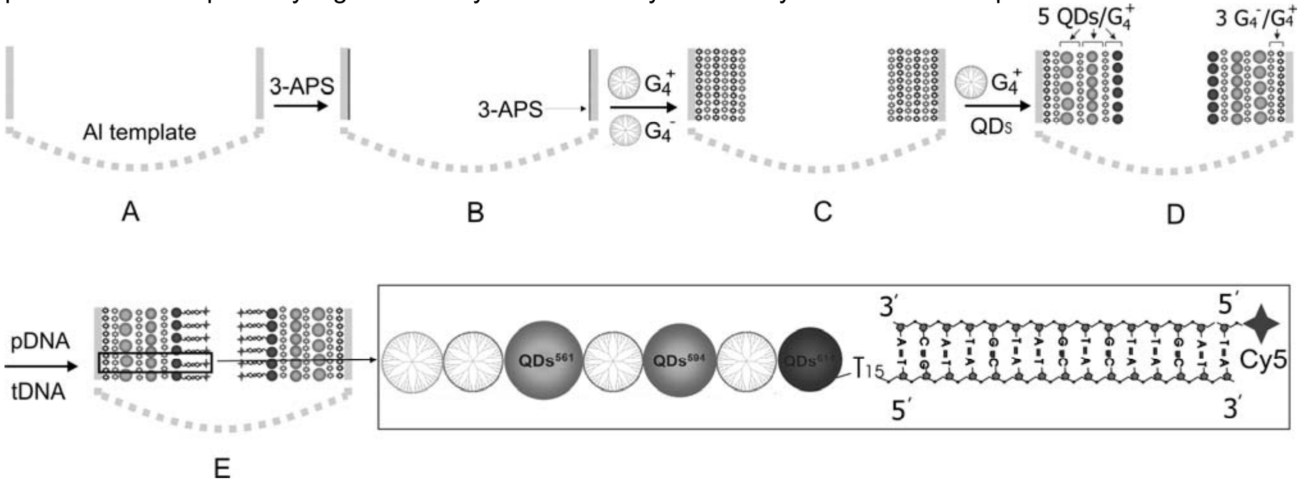


Figure 1. Schematic of ZnCdSe alloy QDs containing nanotubes with a graded band-gap structure prepared by the LBL deposition within porous alumina, followed by DNA immobilization and hybridization inside the nanotubes.

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ELECTRON TRANSFER BETWEEN ENZYMES AND ELECTRODES MEDIATED BY REDOX POLYMER HYDROGELS

Gilbert Nöll*, Federico Tasca, Lo Gorton**, Magdalena Kujawa***, Ilabahen Patel***, Wolfgang Harreither***, Clemens K. Peterbauer***, Roland Ludwig******

** Siegen University, Organic Chemistry, Adolf-Reichwein-Str. 2, 57068 Siegen, Germany.*
*** Department of Analytical Chemistry, Lund University, P. O. Box 124, SE-221 00 Lund, Sweden.*
****Division of Food Biotechnology, Department of Food Sciences and Technology, BOKU-University of Natural Recources and Applied Life Sciences Vienna, Muthgasse 18, A-1190 Wien, Austria.*
***** Research Centre Applied Biocatalysis, Petersgasse 14, A-8010 Graz, Austria*
E-mail: noell@chemie.uni-siegen.de

Keywords: *Redox polymer hydrogels, mediated electron transfer, biofuel cell*

Redox enzymes, which catalyse the oxidation of a specific substrate, can be used for the development of amperometric biosensors and biofuel cells.[1-3] For these applications, the electrons gained from substrate oxidation have to be transferred from the enzyme to the electrode. The Electron transfer (ET) enzyme → electrode is often hampered or not possible at all, because the redox-active moiety of the enzyme is deeply buried inside the enzyme shell. Currently, direct electron transfer (DET) between enzymes and electrodes has been reported only for about 50 out of more than 1060 redox enzymes known today. As an alternative to DET, ET between enzymes and electrodes can be achieved by redox mediators. Redox mediators are small ambiphilic redox-active molecules being able to transfer charge depending on their redox state. A very efficient mode of mediated electron transfer (MET) is achieved when redox enzymes are embedded in a redox polymer hydrogel. Redox polymers contain redox-active molecules/redox mediators linked to an electrochemically inactive polymer backbone in a flexible manner. Up to now, Os redox polymers are most frequently used to "wire" redox enzymes to electrodes.[2-4] As redox centers, Os II/III complexes are applied. These complexes exhibit very stable redox chemistry, and depending on their ligands, the redox potential can by varied over a broad potential range.

In our previous work we have investigated the enzymes cellobiose dehydrogenase (CDH) and pyranose dehydrogenase (PDH) with respect to applications in of amperometric biosensors and biofuel cells.[1, 5, 6] CDHs contain a larger flavin-associated (dehydrogenase) domain and a smaller heme-binding (cytochrome) domain. CDHs oxidize cellobiose, cellodextrins, and lactose at the flavin domain. Depending on their origin they may also oxidize monosaccharids to the corresponding lactones. Especially CDH from the ascomycete *Myriococcum thermophilum* (*Mt*CDH) is of major interest for the construction of biofuel cell anodes due to its ability to oxidize glucose.[6] PDH from *Agaricus meleagris* (*Am*PDH) is a monomeric glycoprotein (7% glycosylation) with a molecular mass of about 66 500 Da, containing one covalently bound FAD as prosthetic group. *Am*PDH catalyzes the oxidation of a large variety of structurally different aldopyranoses including mono-, di-, and oligosaccharides. In contrast to *Mt*CDH, which oxidizes glucose at the C(1) carbon to its corresponding lactone, *Am*PDH is able to oxidize glucose at the C(2) and C(3) gaining up to four electrons from one substrate molecule. We have compared DET and MET using Os redox polymers for different CDHs, and details will be discussed.[7] For *Am*PDH, we have investigated the influence of the Os polymer redox potential with respect to that of the enzyme. Furthermore, we have investigated mixtures of *Am*PDH and *Mt*CDH in an Os redox polymer hydrogel. In principle, the combination of *Am*PDH and *Mt*CDH, leads to an anode, which is able to gain up to six electrons out of one suitable substrate molecule.

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MODIFICATION OF POLYLACTIDE PROPERTIES BY PLASTICIZATION WITH BIODEGRADABLE POLYMERS

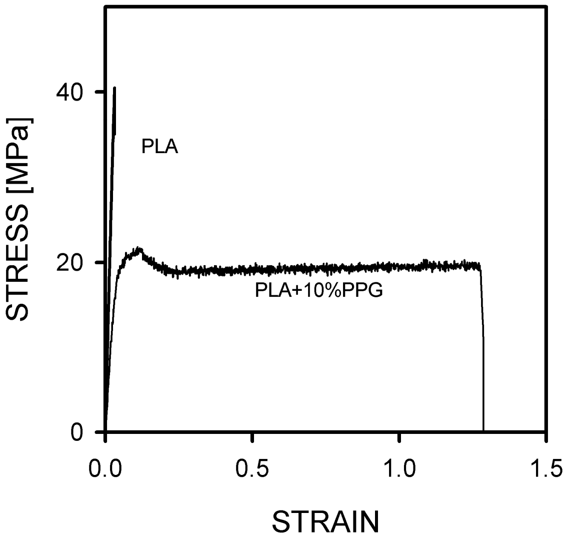
Ewa Piorkowska, **Miroslaw Pluta, Marcin Kowalczyk**

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90 363 Lodz, Sienkiewicza 112, Poland
E-mail: epiorkow@cbmm.lodz.pl

Keywords: *polylactide, plasticization mechanical properties*

Polylactide (PLA) is a biodegradable polymer which can also be produced from annually renewable resources. This fact is responsible for a growing interest in PLA for many applications. Plasticization decreases the glass transition temperature (T_g) and improves toughness of PLA. An upper temperature limit of applicability of an amorphous polymer is determined by its T_g, while that of a semicrystalline polymer by its melting temperature, usually much higher. Thus, the plasticized semicrystalline PLA with improved drawability is an attractive material. Poly(propylene glycol) (PPG) was found to be an efficient plasticizer not only for amorphous but also for semicrystalline PLA[1,2] in contrast to poly(ethylene glycol) (PEG)[3]. However, the blends of PLA and poly(propylene glycol)s were phase separated due to slow crystallization of PLA used in the study.

Our recent research focused on plasticization of PLA with PPG and block copolymers of PPG and PEG. The blends of PLA with various contents of poly(propylene glycol)s and block copolymers of poly(propylene glycol) and poly(ethylene glycol) were prepared and studied. PLA with relatively small content of D-lactide was used to enable faster crystallization. The amorphous films were prepared by compression molding followed by quenching. Structure, thermal and mechanical properties of the blends were characterized. Semicrystalline blends were prepared by cold crystallization and studied as well. It is demonstrated that plasticization and crystallization can lead to ductile semicrystalline PLA, although the effect depends on molecular weight and chemical composition of plasticizer.



Comparison of stress-strain dependencies of PLA and PLA plasticized with 10wt.% of PPG.

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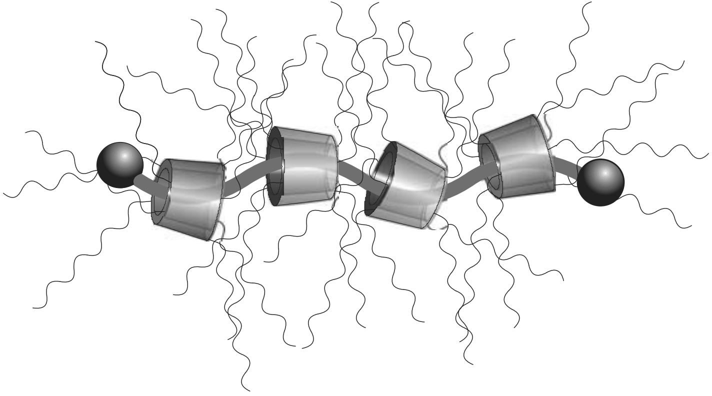
FUNCTIONAL SYSTEMS FROM CYCLODEXTRINS AND POLYMERS

Gerhard Wenz, Christian Teuchert

Saarland University, Campus Saarbrücken, D-66123 Saarbrücken
E-mail: g.wenz@mx.uni-saarland.de

Keywords: *Cyclodextrins, Polymerbrushes, ATRP*

Cyclodextrins (CDs) are doughnut-shaped cyclic oligomers of amylose consisting of 6, 7 or 8 glucose units called α-, β- or γ-CDs, respectively. Cyclodextrins are able to complex both monomeric and polymeric guest molecules in aqueous solution.[1] Cyclodextrins spontaneously thread onto many linear polymers, such as polyethers,[2] polyesters or polysiloxanes in aqueous media due to hydrophobic interactions. Polyrotaxanes were synthesized from the inclusion compound of polyethylene glycol and α-cyclodextrin by blocking the chain ends with bulky naphthalene or anthracene groups.[3] These polyrotaxanes were converted to macroinitiators by esterification of the threaded cyclodextrin rings with bromo-isobutyryl bromide. Atom transfer radical polymerization (ATRP)[4] was started from these macroinitiator to receive polyrotaxane brushes according to the schematic drawing shown below.



The resulting polymer brushes were characterized by NMR spectroscopy, GPC, and AFM. The molecular weights reached about 2,000,000 gmol^{-1}, equivalent to a contur length of about 100 nm. To our surprise, these polymers are thermically unstable. They slowly dissociate yielding the star-shaped polymers and the polymer backbone. Since this dissociation can be controlled by temperature, these new polymers might be potentially useful for the controlled delivery of active substances, such as drugs. In principle, these polyrotaxanes can be prepared with hydrophilic, hydrophobic or block copolymer side chains. Therefore they are applicable in both lipophilic and aqueous environments.

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ALL-POLYMER COMPOSITES

Kinga Jurczuk*, **Andrzej Galeski***, **Ewa Piorkowska****

** Department of Polymer Physics , Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland*
*** Department of Polymer Structure, Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland*
e-mail kinsow@cbmm.lodz.pl

Keywords: *polypropylene, PTFE, nanocomposite*

An ongoing challenge in material science is to design novel polymeric materials with improved properties. This is often achieved by blending with other polymers or by adding filler materials. Fillers with at least one dimension in the nanometer range (so-called nanofillers) have proven to be the best for their dramatic influence on the final properties of the composite material. A promising new system of polypropylene and polytetrafluoroethylene (PTFE) nanofibres was sought. High viscosity polypropylene and PTFE were the raw materials for the nanocomposite. Compositions of PP containing 3-7 wt.% PTFE were prepared by melt mixing. The nanostructure, rheological and mechanical properties were studied. The structure of PP+PTFE nanocomposites were examined using frozen fracture and scanning electron microscopy for the determination of adequate formation of PTFE nanofibers and their distribution. Thickness of PTFE nanofibers around and above 30 nm and their homogeneous dispersion were obtained (see Figure 1).

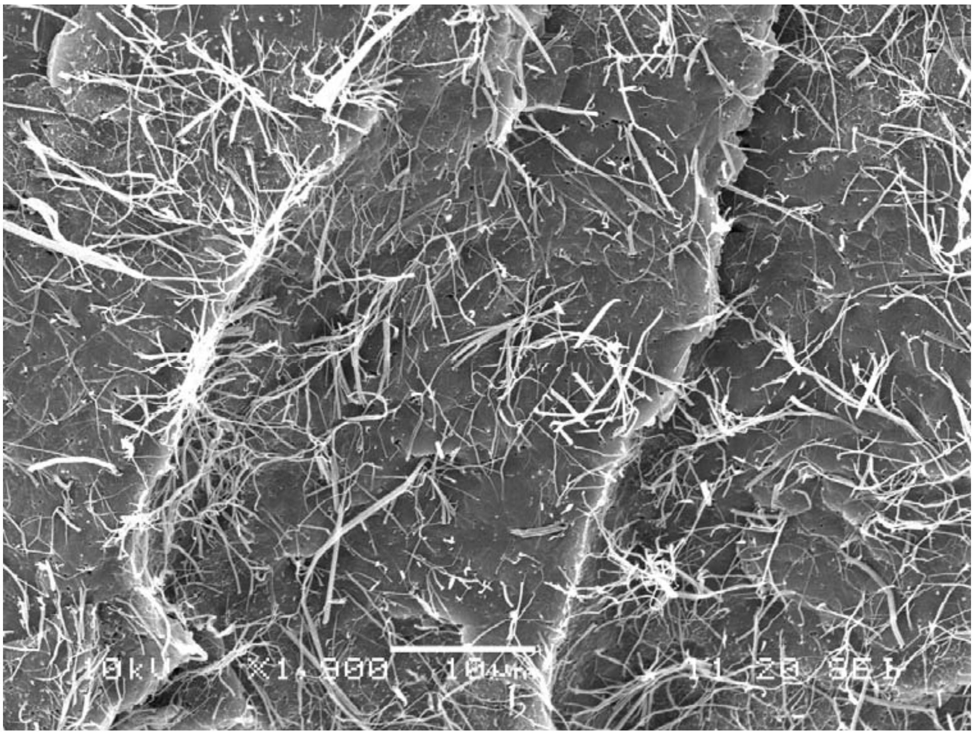

Figure 1. SEM image of the frozen fracture of polypropylene/PTFE 97:3 nanocomposite

The tensile properties and Izod impact strength of injection molded specimens of PP+PTFE blends were determined. Tensile mechanical properties of the composite are slightly improved over plain PP, however, Izod impact strength is significanlty increased. Melt elongation tests were performed using ARES rheometer. The experiments revealed that the melt strength of PP+PTFE nanocomposites is six times higher than for plain PP. Similar results were obtained when PP matrix was changed for polystyrene PS and low-density polyethylene. The melt strength of these blends was three times higher than for plain polymers.

BLACK POLYMERS IN BULK HETEROJUNCTION SOLAR CELLS

Yi Zhou*, **Desta Gedefaw****, **Mats R. Andersson****, **Olle Inganäs***

**Biomolecular and organic electronics, IFM, Linköping University, SE-581 83 Linköping, Sweden.*
***Polymer Technology, Department of Chemical and Biological Engineering, Chalmers University of Technology, Göteborg, Sweden.*
E-mail: yizhou.song@gmail.com

Keywords: *low band-gap polymer, solar energy, energy level, morphology*

Two black polymers, APFO-Black 1 and APFO-Black 2, were synthesized by the Suzuki polymerization reaction. The optical absorptions of the polymers were found to cover the visible region and extend to the near IR region of the electromagnetic radiation. Solar cell devices were made by mixing the polymers as donors and PCBM [60] or PCBM [70] as an acceptor in various mixing ratios. In the best combination, an overall efficiency of around 1% was recorded with APFO-Black 1 while an efficiency of 1.5% was obtained with APFO-Black 2. From electrochemical study the LUMO of APFO-Black 1 was -3.9 eV. The efficiency of the devices fabricated from APFO-Black 1 was not as high as expected based on its absorption spectrum probably due to the low driving force for electron transfer from the polymer to the acceptor. On the other hand the LUMO energy level of APFO-Black 2 (-3.8 eV) is closer to the vacuum level and thus has a better offset from the LUMO of the acceptor due to the electron releasing effect of the alkoxy substituents. Moreover, APFO-Black 2 has revealed a unique absorption spectrum with a peak at 500 nm, which is not observed in APFO-Green 9, enabling the polymer to absorb a larger fraction of the solar irradiance. A better miscibility of APFO-Black 2 with PCBM [60] and PCBM [70] as recorded in the morphology study is presumably due to the polar alkoxy side groups.

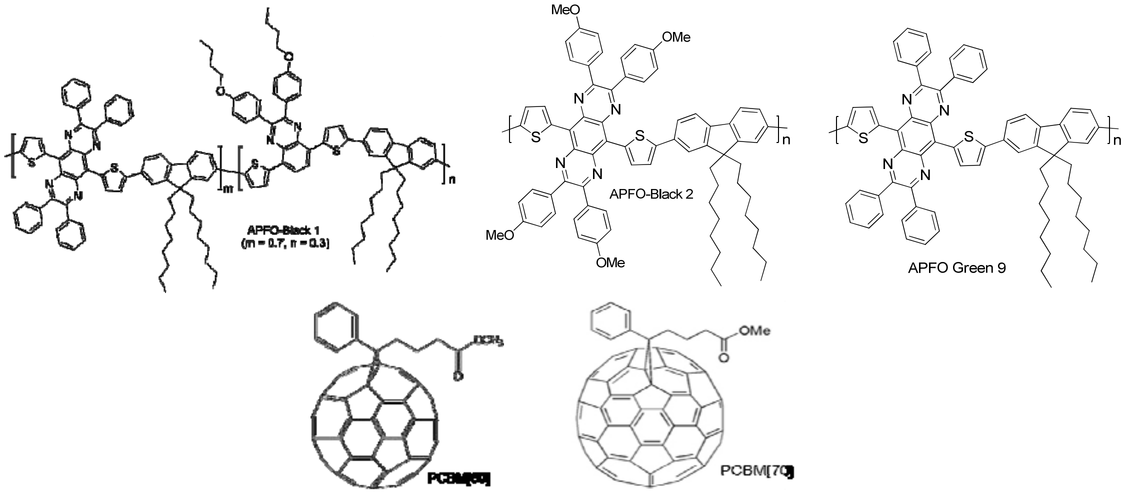

Figure 1 Chemical structures of polymers (electron donor) and PCBM[60], PCBM[70] (electron acceptor) used in solar cells

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GLASS TRANSTION TEMPERATURE BEHAVIOUR AND VISCOELASTIC PROPERTIES OF POLYLACTIDE-CO-GLYCOLIDE/α-TRICALCIUM PHOSPHATE NANOCOMPOSITES

Samuel I. J Wilberforce, **Serena M. Best, Ruth E. Cameron**

Cambridge Centre for Medical Materials, Department of Materials Science and Metallurgy, University of Cambridge, New Museums Site, Pembroke Street, Cambridge CB2 3QZ, UK
E-mail: sijw2@cam.ac.uk

Keywords*: Nanocomposites, polylactide-co-glycolide, glass transition temperature*

Tricalcium phosphate (TCP) was prepared by an aqueous precipitation reaction between Ca $(OH)_2$ and 85 % ortho-H_3PO_4 acid at a molar ratio of 3:2 [1]. The dried TCP powder was transformed to its α-phase via a high temperature calcining process at 1400 °C. A modified solution evaporation (MSE) method via attrition milling [1-2] was employed to break up and disperse varying weight fractions (w_f) of nano α-TCP particles in a 50:50 molar ratio polylactide-co-glycolide (PLGA) prior to intermeshing co-rotating twin screw extrusion and piston injection moulding. Acetone was used as the solvent in the MSE process. The actual w_f of nano α-TCP in the materials was determined by thermogravimetric analysis (TGA). The thermal degradation temperature (TDT) of the materials was also determined from TGA. Field emission scanning electron microscopy (FE-SEM) was employed to determine the fracture surface morphology of the materials. The residue of nano α-TCP, which was left after TGA, was collected for FE-SEM to characterise the particle size distribution of the α-TCP nano-particles. The SEM micrographs of nano α-TCP particles were analysed by image processing and analysis in Java (ImageJ 1.42q/Java 1.6.0_10 [32-bit]) software to determine their particle size distribution. The particle size distribution showed that the α-TCP particles had majority of the particle sizes well within the nano regime (less than 100 nm). Dynamic mechanical thermal analysis (DMTA) was employed to investigate the glass transition temperature (T_g) behaviour and viscoelastic properties of the materials.

The T_g of both extruded and injection moulded (IM) materials dropped by about 16 % and 17 % respectively from the unfilled polymer to nanocomposite with 15.4 % v/v (w_f = 30 % w/w) nano-particle loading. This was thought to be due to the creation of free volume by the weak interfacial bonding between the nano-particles and polymer matrix, facilitating chain mobility. The T_g of other nanocomposites have also been reported to decrease with increasing nano-particle loading [3-4]. However, the T_g increased slightly again at higher loading levels presumably due to an increase in the number of percolating networks, obstructing chain mobility. The T_g and TDT of extruded materials were higher than those of IM materials. It was thought that a good contact was achieved between the nano-particles and polymer matrix via mechanical interlocking [5] during the extrusion process, leading to enhanced T_g and TDT of the extruded materials. Presumably, the use of the intermeshing type twin screw extruder led to the mechanical interlocking effect. These results, thus, suggest that after the MSE process a further mixing process (such as twin screw extrusion) prior to injection moulding may be needed to enhance the properties of the PLGA materials. Within the glassy region, the storage moduli of the IM nanocomposites were higher than the storage modulus of the IM unfilled polymer due to the stiffening effect of the nano-particles. However, the IM nanocomposites showed a lower temperature transition to the leathery region than the IM unfilled polymer presumably due to the creation of free volume by non-adhering nano-particles.

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INTEGRATED APROACHES IN TEMPLATED HYBRID POLYMER MATERIALS

Jochen S. Gutmann*,, Philipp Lellig*,**, Maria C. Lechmann ***

** Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany*
*** Institute for Physical Chemistry, Johannes Gutenberg University, Welderweg 11, D-55099 Mainz, Germany*
E-mail: gutmann@mpip-mainz.mpg.de

Keywords: *Hybrid Materials, Block copolymers, Templates*

Templating of functional oxide materials via block copolymers is a technique that currently progresses towards a mature state[1]. While it is therefore readily possible to obtain nanomaterials from functional oxides with are well defined in terms of their structure, morphology and function, it is furthermore possible to integrate a second function into the (hybrid) material. With this approach even mutually orthogonal functions can be integrated into the same material[2-4].

We have used this integrated templating approach to obtain integrated barrier materials for photo electronic devices as well as functional oxide materials for hybrid solar cells. Doing so, we covered the whole materials science development cycle from chemical synthesis via structural characterization to application. We'll demonstrate why each of these steps is synergistic and how a rational materials design can evolve from basic research.

In the case of hybrid barrier it was possible toy synthesize an amphiphilic polymer which was able to template a titania precursor leading to a network of semiconducting particles. At the same time the nm sized gaps separating the particle network are insulating by a polymer derived ceramic. Using grazing incidence scattering experiments in conjunction with conducting scanning probe experiments we were able to prove the existence of a fractal conductive network. These hybrid barrier layers are alternatives to conventional blocking layers in hybrid/dye sensitized solar cells.[2,3]

The hybrid active layers for solar cell application consist of a specifically synthesized semiconducting, amphiphilic block copolymer. This hole conducting copolymer is used to template titania particles. The resulting one pot synthesis allows for a highly reproducible preparation of active device layers. Current efficiencies can reach up to 0.4% and show a clear dependence on their internal nanostructure.[4]

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GLASS TRANSITION TEMPERATURES OF BINARY SYSTEMS CONTAINING POLYMERS

Witold Brostow*, Ioannis M. Kalogeras, Aglaia Vassilikou-Dova****

**Laboratory of Advanced Polymers & Optimized Materials (LAPOM), Department of Materials Science & Engineering, University of North Texas, 1155 Union Circle #305310, Denton, TX, 76203-5017, USA; **Solid State Physics Section, Department of Physics, University of Athens, Panepistimiopolis, Zografos 157 84, Greece*
E-Mail: brostow@unt.edu

Keywords: *glass transition, binary blends, drug encapsulation*

Glass transition T_g is the most important feature of all non-crystalline materials. In binary polymer-containing systems, fully miscible materials have a single T_g value varying with composition; compatible (partly miscible) systems exhibit 2 composition-dependent transitions; incompatible materials show 2 glass transitions unaffected by the composition. Compatibilizers are in use – their success measured in terms of their effects on T_g values. Glass transition is also pertinent for fundamental understanding of materials behavior [1 – 5].

Given the importance of the problem, several equations representing $T_g(x)$, where x is composition in a binary system, have been developed. However, experimental $T_g(x)$ diagrams are sometimes s-shaped and/or showing both positive and negative deviations from linearity with composition. The extant equations either are not usable in such cases at all, or only with poor results. In this situation we have developed a new equation [6] based on deviations from linearity. The number of parameters needed is a measure of the complexity of the system.

In addition to polymer + polymer blends we are also investigating polymer + drug systems. In medicine polymers are used for drug encapsulation; the success of the encapsulation is reflected in the $T_g(x)$ dependence. Complicated binary $T_g(x)$ diagrams including those with maxima and minima are found. Calculations show that also in the drug encapsulation systems our equation provides reliable results [7].

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CHALLENGES TO POLYMERS FOR ADVANCED CEMENTITIOUS SYSTEMS

Trettin, Reinhard, Wenzel, Thomas, Kowald, Torsten

Institute for Building and Materials Chemistry, University of Siegen Address: Paul-Bonatz-Str. 9-11, 57076, Siegen, Germany,
E-mail: trettin@chemie.uni-siegen.de

Keywords: *Concrete, organic admixtures, superplasticizers, Ultra High Performance Concrete*

The construction industry is one of the most important users of polymers. Progress in the development of new building-materials is therefore connected with new polymers closely. This also applies particularly to new high performance cementitious binding systems. The Ultra-High-Performance Concrete (UHPC) is part of these.

UHPC offers a unique strength and durability[1]. It allows very sustainable filigree and lightweight concrete structures. The high steel-like compressive strength of UHPC only is achieved if the porosity is reduced strongly, i.e. a very dense volume is produced like this of technical ceramic. The strong reduction of the water/cement ratio is one of the most important factors for this. Almost the complete water is chemically bounded and no pores formerly filled with water stay behind the draying of the material. Reactive and not reactive micro and nano particles in addition are used to achieve an optimal packing density of the hardened concrete structure[2].

Without the use of efficient polymeric admixtures such system are not workable. Of particularly importance for the workability are new efficient polycarboxylate polymers[3]. The molecular structure of polycarboxylates are very variable. This means the molecular weight of the polymer, backbone, side chains, ionic strength and the chemical composition. Some of the superplasticizers protect the surface of the cement particles and build a barrier against water. Therefore, the early hydration is retarded and the early development of strength decreased.

A special challenge is the effectiveness of the superplasticizers into presence of micro and nano fillers with extremely high specific surface areas. The aim consists in keeping the amount of the polymers as little as possible to not get any negative influencing of the mechanical properties of the complete system.

The high strength of the UHPC materials is connected to an increasing brittleness represents an additional problem for the product development. To improve the mechanical properties of UHPC carbon nanotubes (CNTs) were incorporated in the cementitious binders[4]. Prior to a successful application of the CNTs some key issues have to be addressed. Firstly, the strong agglomeration of the CNTs due to van der Waals forces has to be mentioned. Secondly, a connection between the CNTs and the binder matrix must be achieved. For the solution of the first problem suitable dispersing agents must be found. These should not influence the properties of the binding system negatively.

In the context of this contribution current research results are presented for the main emphases mentioned above. Investigations are focused on the influencing of the reaction kinetic and the micro and nano structure of the concrete. From the results become conclusions on mechanisms of reactions under special consideration of the polymers derived. The results are discussed also into the state of the current literature.

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POST-IRRADIATION EFFECTS ON NYLON-FIBER REINFORCED CONCRETES

Gonzalo Martínez-Barrera (Dr.),* Enrique Vigueras-Santiago (Dr.),* Carmina Menchaca-Campos (Dr.), Witold Brostow (Prof.)****

** Laboratorio de Investigación y Desarrollo de Materiales Avanzados (LIDMA), Facultad de Química, Universidad Autónoma del Estado de México, Km.12 de la carretera Toluca-Atlacomulco, San Cayetano 50200, Mexico; email: gonzomartinez02@yahoo.com.mx*
*** Centro de Investigación en Ingeniería y Ciencias Aplicadas (CIICAp), Universidad Autónoma del Estado de Morelos, Cuernavaca, Morelos 62210, Mexico.*
**** Laboratory of Advanced Polymers & Optimized Materials (LAPOM), Department of Materials Science and Engineering, University of North Texas, 1150 Union Circle # 305310, Denton, TX 76203-5017, USA.*

Keywords: *polymer concrete, gamma radiation, nylon fibers.*

Concrete is one of the oldest materials used by mankind, a composite *par excellence*. A large variety of methods of improving it have been developed. Several improvements can occur when adding fibers into the Portland cement concrete (PCC). Moreover, the commercial success of polyamides is due to their outstanding properties and economical advantages. Most of them – including Nylon - are used in fiber production [1]. Nylon fibers have been used since early 1980s for secondary temperature-shrinkage reinforcement in shotcrete and concrete [2]. Nylon fibers substantially improve the impact resistance of concrete due to stretching and pull-out of the fibers – phenomena that occur at relatively low loads and result in large strains at failure. Nevertheless, the added fibers have only little effect on tensile or bending strength. Fiber-reinforced concretes (FRCs) have a wider application range than ordinary concretes. Properties of FRCs necessarily depend on the characteristics of the aggregates used [3]. We have studied first effects of gamma radiation on mechanical properties of hydraulic concretes containing Portland cement, silica sand, marble, water and Nylon fibers. Compressive strength and dynamic elasticity modulus are of particular importance. In the second stage we have analyzed the changes in these mechanical properties after storage of our concretes for three years. The long storage results in a 97 % of increment in the compressive strength (Figure 1), and simultaneous lowering by 35 % of the dynamic elastic modulus. We find a larger influence of the Nylon fibers than those of silica sand and marble on mechanical properties of the concretes.

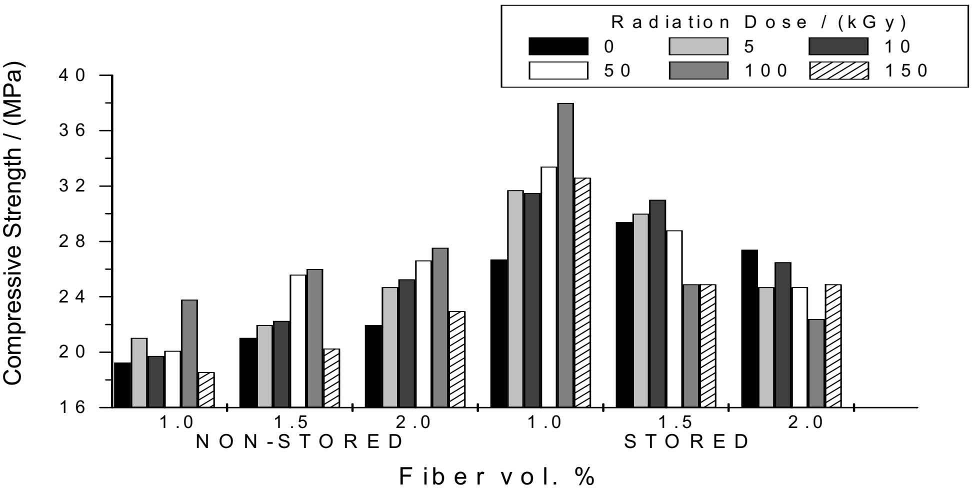

Figure 1. Compressive strength of non-stored and stored concretes, at several irradiation doses.

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FLAME RETARDANTS BASED ON PHOSPHORUS CHEMISTRY FOR THERMOSETS

Mathias Dietz

Clariant GmbH, D-50354 Hurth-Knapsack, Germany,
E-mail: *mathias.dietz@clariant.com*

Keywords: *unsaturated polyester or epoxies, phosphorus containing flame retardants*

Thermoset materials require flame retardants to meet fire protection standards. There is an increasing demand for non-halogen flame retarded composites in particular for construction and mass transportation. In this presentation, examples of phosphorus flame retardants in epoxy and unsaturated polyester will be shown. In highly filled epoxy and unsaturated polyester formulations, it will be shown that phosphorus flame retardants can be used at much lower loadings to achieve the same flammability test result. The benefit of this technology is an opportunity to produce light-weight components with good mechanical properties.

If a flame retarded composite material is selected for an application, the technical property profile and the price/performance ratio are the basis for the design engineer´s decision. The thermoset formulator has a toolbox of options available to produce a commercial flame retardant material. Flame retardants can be either additive or reactive chemicals. An example of an additive flame retardant is ammonium polyphosphate (APP) or aluminium trihydrate (ATH). These additive flame retardants maintain their chemical characteristics within the polymer matrix until they become active upon exposure to high temperatures (e.g.fire).

In the electronics industry the pressure exerted by environmental groups such as Greenpeace to eliminate certain halogen flame retardant chemicals, key consumer electronic OEMs have clearly stated a roadmap toward halogen-free commercial products. Suppliers to these OEMs are now currently offering or developing new halogen free systems for connectors, cables, epoxy laminates for printed circuit boards and other devices. For printed circuit boards the flame retardancy can be attained by the addition of finely divided Exolit® OP 930/935 into an epoxy resin matrix. In that special kind of reinforced epoxy, the new typ of non-halogenated flame retardant can be used without any aluminium hydroxide as further synergist.

The electronics industry is often considered to be technology leader. Whether or not this halogen free trend firmly establishes itself at some future time in other market sectors such as construction or transportation remains to be seen. In recent times, there has been increased interest from formulators for halogen free flame retardants for aerospace, automotive and other industrial sectors.

THERMAL STABILITY AND DEGRADATION KINETIC OF PC/ABS COMPOSITES CONTAINING NANOCLAY AND HALOGEN FREE FLAME RETARDANT

Yousef Jahani*, Elham Feyz*, Masoud Esfandeh*, M. Ghafelehbashi**
** Iran Polymer & Petrochemical Institute, P. O. Box 14965/115, Tehran, Iran,*
*** C.O.R&D Group, Research & Technology Company, National Petrochemical Company, Tehran, Iran*
Email: y.jahani@ippi.ac.ir

Keywords: *PC/ABS nanocomposite, Triphenyl Phosphate (TPP), Activation energy, Thermogravimetric analysis*

Polycarbonate (PC)/Acrylonitrile-Butadiene-Styrene (ABS) blends flame retarded by triphenyl phosphate (TPP), nanoclay and their hybrid have been prepared using direct melt intercalation process in a co-rotating twin-screw extruder. Their morphological properties are characterized by X-ray diffractometry (XRD) and transmission electron microscopy (TEM). The XRD patterns, indicated an intercalated structure. By increasing TPP content the space between the layer of tactoids of nanoclay is increased, as the clay materials are intercalated with triphenyl phosphate [1]. The intercalation of silicate layers are evident in TEM images which confirm the XRD results. The thermal stability of samples was studied by thermogravimetric analysis (TGA), and the kinetic parameters, such as reaction order and activation energy, were determined using various methods such as Kissinger-, Flynn-Wall-Ozawa- and Coats-Redfern (CR) method [2]. The results of the CR-method are summarized in the table.

Table : The kinetic parameters using Coats-Redfern method at 10 °C/min heating rate

Compounds	n (Reaction order)	E_a (kJ/mol)	Correlation coefficient (R)
PC/ABS	n_1=2	E_{a1}=98.2	R_1=0.9908
PC/ABS/2%nano	n_1=1; n_2=3	E_{a1}=149; E_{a2}=161	R_1=0.9661 R_2=0.9849
PC/ABS/10%TPP	n_1=1; n_2=2; n_3=3	E_{a1}=27; E_{a2}=128; E_{a3}=228	R_1=0.9639 R_2=0.9999 R_3=0.9986
PC/ABS/10%TPP/2%nano	n_1=1; n_2=4; n_3=6	E_{a1}=22;E_{a2}=143;E_{a3}=248	R_1=0.9923 R_2=0.9527 R_3=0.9794

The results of kinetic study show that the activation energy order of neat PC/ABS resin and PC/ABS composites with different flame retardants obtained by the Kissinger method, agrees well with those obtained by Coats-Redfern. For the Flynn-Wall-Ozawa method, due to its adoption of the Doyle approximation, the obtained activation energy and its order are very different from the Kissinger and the Coats-Redfern method. In all methods the sample containing the hybrid of TPP/nanoclay has a higher thermal stability and lower flammability.

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POLYISOCYANOPEPTIDE NANOWORMS: STIFF HELICAL POLYMERS AND THEIR APPLICATIONS

Erik Schwartz, Matthijs B. J. Otten, Heather J. Kitto, Matthieu Koepf, Jeroen J. L. M. Cornelissen, Roeland J. M. Nolte, Alan E. Rowan

Institute for Molecules and Materials, Radboud University Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands.
Email: A.Rowan@science.ru.nl

Keywords: *Polyisocyanopeptides, stiff polymers, photovoltaic activity.*

Polyisocyanides have the unusual feature that each main chain carbon atom contains a substituent leading to restricted rotation around the single carbon-carbon bonds and consequently to antropisomerism. This antropisomerism results in a helical conformation of the polymeric backbone, and by changing various parameters an excess of either left-handed (M) or right-handed (P) polymers can be obtained. The well-defined 41 helical conformation (i.e., 4 repeat units per helical turn) is stable only when sterically demanding side-chains are present. Introduction of chiral peptide substituents onto the side chain leads to stable and extremely stiff helical polymers, (with a persistence length of 76 nm), due to the presence of hydrogen bonding interactions between the side chains (see below). Upon polymeric initiation with acid, single polymers wires can be constructed with molecular weights in excess of 50 million Dalton and lengths up to 30,000 nm. The precise arrangement the side-arms of polyisocyanopeptides makes them ideal scaffolds for the organization of dye-molecules over large distances [1].

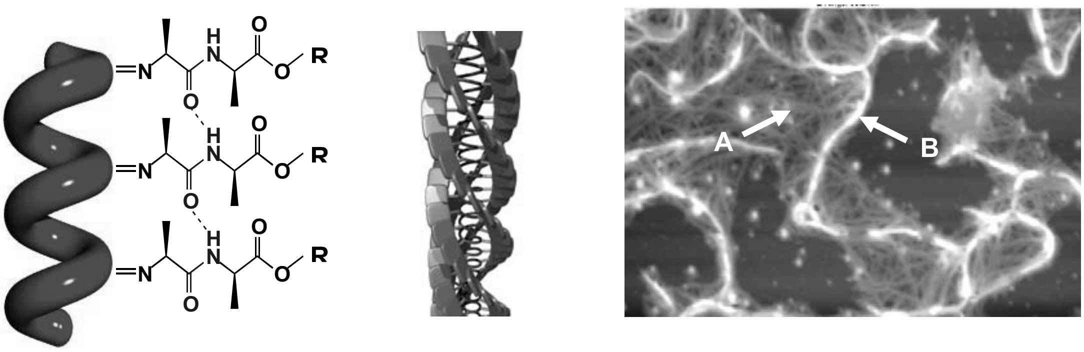

***Figure 1**: a) Schematic representation of the hydrogen bonding β-sheet arrangement in a polyisocyanide helix; b) The proposed 'helter-skelter' like arrangement of the chromophores along the polymer backbone; c) AFM topography image of an ultra-thin blend of P-PDI and P3HT 2D solar cells deposited on native silicon oxide (A =P3HT fibers height 3.5nm; B= PDI fibers height (17±3) nm).*

The polymer backbone allows high control over the spatial location of perylene dyes forming a 'helter-skelter' like ordering (see above middle) which favours long exciton delocalization with lengths of up to 400 Å and highly efficient charge transfer [2]. Solar cells devices composed of these perylene dipetidoisocyanide polymers (PDI) and a regioregular alkylated polythiophene (P3HT) showed a considerable improvement (100 to 1000 fold [3]) with respect to equivalent devices based on perylene crystalline aggregates. This improvement is the result of extremely rapid electron migration possible along the chromophoric polymer wires. Extremely thin 2D photovoltaic cells (<15 nm thick) has been constructed and for the first time the photovoltaic activity between the electron-accepting PDI wires and bundles of electron donating P3HT chains has been visualized on the nanoscale by high resolution Kelvin Probe Force Microscopy [4]. The synthesis, characterization and properties of these unique polymers will be discussed.

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STIMULI RESPONSIVE POLYMERS: EXEMPLIFIED ON SWITCHABLE WINDOWS

Chunye Xu[1, 2]

1. Hefei National Lab. for Physical Sciences at the Microscale, University of Science and Technology of China, 96 Jinzai Road , Hefei, Anhui 230026, P.R. China
2. Electroactive Polymer Laboratory, University of Washington, Seattle, WA 98195, USA
E-mail: cyxu@ustc.edu.cn

Keywords*: switchable (smart) window, electrochromic device (ECD), conducting polymer*

As the economy is growing in the world, energy is being strongly demanded. Commercial buildings in the United States use 18% of the total energy consumption each year. Of this amount, 26% was spent on air-conditioning. Windows make up approximately 13% of wall area in new residences and up to 50% in large office buildings. The Department of Energy estimates that electricity consumption will increase by 45% in the next twenty years and that 2% of all energy used in the United States is “consumed” by residential windows [1]. Because of our limited access to energy on earth, energy efficient devices or energy saving systems are urgently required. A promising technology, developed to face this challenge, is electrochromic, or ’smart’, switchable windows. These windows are capable of controlling the throughput of radiant energy, potentially greatly reducing the amount of electricity consumed in heating and air conditioning by allowing sun in during the winter and blocking it during the summer.

An overview of one the most successful developed switchable windows based on conducting polymers, polythiophene and derivatives, which shows blue color, is presented [2]. In addition, red and green color monomers and devices, a newly designed structure with an organic polymer as active layer and an inorganic carbon, metal or metal oxide working as counter part, and semi-solid electrolyte are developed. Several prototypes were fabricated for different applications in civil, industrial and military fields. Present and future applications for electrochromic window (ECW) that are discussed include large sized architectural and vehicle windows, visual display, camouflage textile and eye protection device [3].

More colors EC monomer developing, monocolor patterning, multicolor patterning, individual sporting, display, architecture window, camouflage textile, battle field use eye protections, etc are under investigation. In addition, self-powered ECW by using solar energy is intensively being developed. The field of ECW is still an emerging one that requires capable and innovative pioneers who will advance the field to develop scientific methods and tools as well as more practical devices that can make human life more comfortable, safer, healthier and longer.

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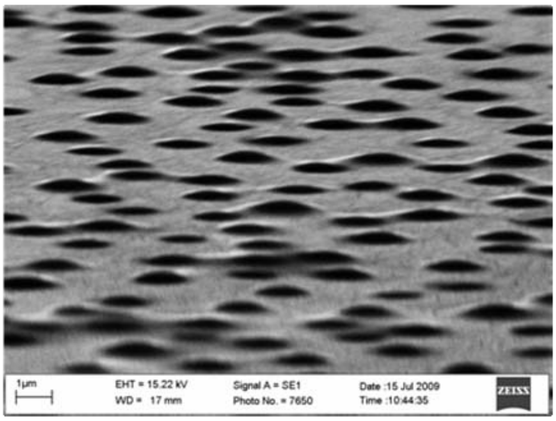
JANUS POLY(N-ISOPROPYLACRYLAMIDE) MICROGELS: ANISOTROPIC BUILDING BLOCKS FOR ADVANCED MATERIALS

Michael J. Serpe *, Courtney D. Sorrell*

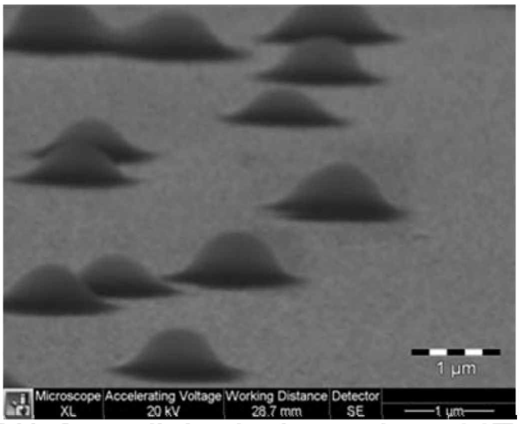
**Department of Chemistry, University of Alberta, Address: 11227 Saskatchewan Dr., Edmonton, Alberta, Canada, T6G 2G2*
E-mail: michael.serpe@ualberta.ca

Keywords: *Janus particles, pNIPAm microgels, Self-assembly.*

Poly(N-isopropylacrylamide) (pNIPAm) is a thermoresponsive polymer, which undergoes a coil to globule transition at ~32 deg C. This results in the transition of the polymer from a hydrophilic to a hydrophobic state, expelling most of its solvating water in the process. Similarly, *materials* composed of pNIPAm undergo this same transition, expelling the majority of their water when raised above this temperature. One very thoroughly studied class of pNIPAm materials are colloidally stable pNIPAm hydrogels (microgels). These materials, which can be synthesized to be 100 nm – 5 mm in diameter, have been shown to be soft below their transition temperature. This softness is manifested as deformation upon attachment to a surface (Figure below). We hypothesize that microgel deformation, upon attachment to a surface, can be controlled by varying the microgel crosslink density (stiffness). By controlling the deformation, we can effectively control the "footprint" of the particle in contact with the surface. Here, pNIPAm microgels, composed of acrylic acid (pNIPAm-co-AAc), were attached to mercaptoethylamine functionalized Au surfaces and dried. Upon drying, the microgels were exposed to 1-Ethyl-3-[3-dimethylaminopropyl]carbodiimide solution, effectively crosslinking the microgel acid groups to the amines on the surface. Following this reaction, the thiol (and microgels) could be electrochemically removed from the surface, resulting in microgels that were half functionalized with thiol. This was confirmed by reacting a maleimide modified fluorophore with the thiol functionalized microgel, followed by fluorescence microscopy. By controlling the microgel footprint, through crosslink density modulation, we were able to change the area of the particle surface which was functionalized with thiol, as confirmed by fluorescence microscopy. We attached various other molecules to the microgel surface, via the thiol group, and studied the resulting microgel assembly properties using electron and fluorescence microscopies. The results show aggregate structures that are dependent on the size, and chemical identity, of the chemical patch.



2% Crosslinked Microgels on MEA Functionalized Au



10% Crosslinked Microgels on MEA Functionalized Au

THERMORESPONSIVE COPOLYMER HYDROGELS BASED ON N-ISOPROPYLACRYLAMIDE AND CATIONIC SURFACTANT MONOMERS

Bernd Tieke, **Tatjana Friedrich**

Universität zu Köln, Department Chemie, Physikalische Chemie, Luxemburger Str. 116, 50939 Köln, Germany
E-mail: tieke@uni-koeln.de

Keywords: NIPAAm copolymers, swelling behaviour, mechanical stability

Poly-N-isopropylacrylamide (P-NIPAAm) hydrogels are known to undergo a reversible phase transition from water soluble to insoluble, if heated to temperatures above 32 °C, the lower critical solution temperature (LCST) of the gel. The phase transition involves clouding of the hydrogel network and expulsion of incorporated water. Reversibility of the transition renders the hydrogels attractive for sensor applications or controlled drug release, for example. Remarkable disadvantages of pure NIPAAm hydrogels are a weak mechanical stability, a slow response to an external stimulus and a poor and not fully reversible swelling behaviour.

Aim of our work[1,2] is to overcome these limitations. For this purpose we copolymerize NIPAAm with cationic polymerizable surfactants (surfmers) in a one-step reaction using gamma irradiation. A chemically and physically cross-linked network structure is formed consisting of blocks of P-NIPAAm and polymerized surfmer, the polymerized micelles acting as additional cross-linking units (Fig. 1).

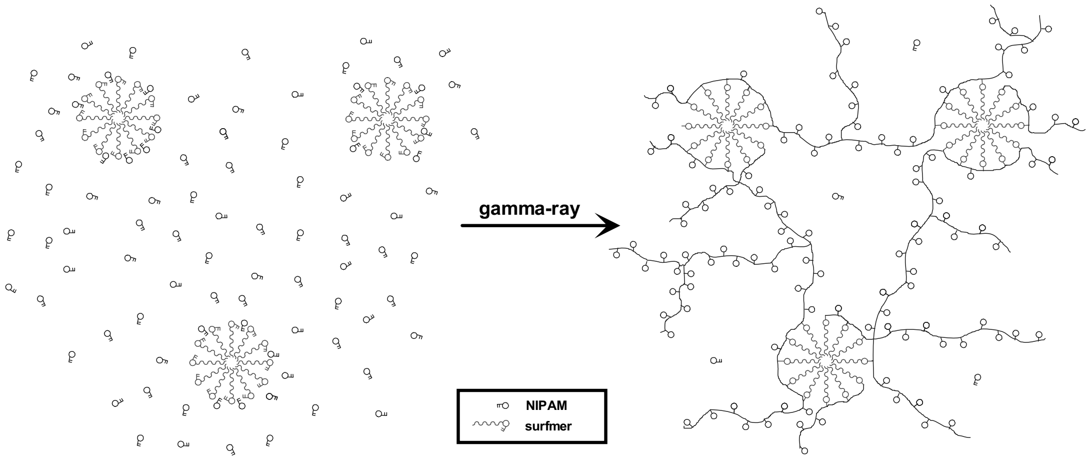


Fig. 1: Structure model of the copolymerisation in aqueous micellar NiPAAm-surfmer-solution.

In our contribution, the phase behaviour of NIPAAm-surfmer comonomer solutions and microemulsions will be characterized. SANS studies of size, shape and dissociation of micelles in monomer solutions and microemulsions with and without NIPAAm will be presented.The influence of the structure of the surfmer and the chemical composition on the mechanical stability of the gel and its thermoresponsive behaviour will be described. The studies indicate that the surfactant-containing hydrogels show increased and fully reversible swelling behaviour as well as an improved mechanical stability. Presence of surfmer also influences the LCST of the hydrogels. Furthermore, the functionalization of the hydrogels via counterion exchange will be described as well as the possibility to use these systems for controlled release.

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MACROPOROUS HYDROGELS BY CRYOGELATION

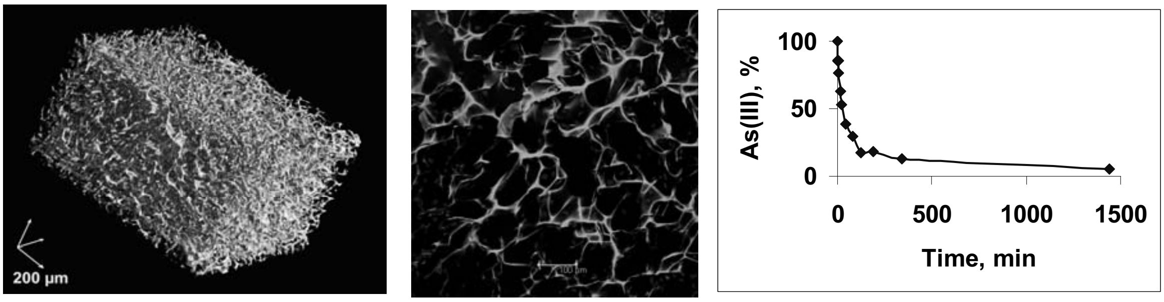
Irina Savina*, **Maria Dainiak****, **Igor Galaev*****, **Sergey Mikhalovsky******, **Ray Whitby***, **Andy Cundy***

** School of Environment and Technology, University of Brighton, Address: Cockcroft Building, Lewes Road, BN2 4GJ, Brighton, UK*
*** Protista Biotechnology AB, Address: IDEON, SE 223 70, Sweden*
**** DSM, Address: P.O. Box 1, 2600 MA Delft, Netherlands*
***** School of Pharmacy and Biomolecular Sciences, University of Brighton, Address: Cockcroft Building, Lewes Road, BN2 4GJ, Brighton, UK*
E-mail: i.n.savina@brighton.ac.uk

Keywords: *macroporous hydrogels, cryogelation, hydrogel pore structure control*

In recent years, there has been increasing interest in the production of macroporous matrices made from hydrophilic polymers. These materials are of potentially widespread utility in the environmental and biomedical fields, as for example separation matrices or cell scaffolds for tissue engineering. The preparation of macroporous hydrogels by cryogelation has recently attracted considerable attention as this process allows production of highly porous matrices with interconnected pore structure.[1-3] At cryogelation the gel forms in a semi-frozen system where most of the solvent is crystallized and monomers, polymer and cross-linkers are concentrated in the small non-frozen regions. Ice crystals formed in the system perform as porogen and pores form in place of the ice crystals after defrosting. The gels produced have a highly heterogeneous structure with large interconnected pores of 1 to 100 µm in size surrounded by thin walls composed of highly concentrated polymer gel. The heterogeneous structure defines a unique combination of gel properties such as high mechanical stability and non-restricted mass-transport of liquid and solutes within the system of interconnected macropores.

Macroporous hydrogels of synthetic, poly-methyl methacrylate hydrogels (HEMA), and biopolymer, gelatine hydrogel were prepared. Macroporous hydrogel morphology was dependent on the monomer and initiator ratio and cryogelation conditions, and was adaptable to the particular application. The porous structure of the hydrogels was assessed by scanning electron microscopy, confocal laser scanning microscopy and micro-computed tomography. Quantitative data on the porosity, pore size and surface area interconnectivity of dried and hydrated hydrogels were obtained using image analysis. HEMA and gelatine macroporous hydrogels were shown to have high potential in tissue engineering as cell scaffolds, particularly for wound regeneration. A HEMA-iron macroporous hydrogel composite was efficient in removing of As(III) from contaminated water.



Figures HEMA macroporous hydrogels, 3-D structure; 2) Dermal fibroblast colonising fibrinogen-gelatine hydrogels; 3) Adsorption of As(III) onto HEMA-iron macroporous hydrogel composite.

Acknowledgments
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THERMO-MECHANICAL EFFECTS OF HYDROLYTIC AGING ON AN ACTIVE POLYMER WITH TRIPLE-SHAPE PROPERTIES

Thorsten Pretsch

BAM Federal Institute for Materials Research and Testing, Address: Unter den Eichen 87, 12205 Berlin, Germany
E-mail: Thorsten.Pretsch@bam.de

Keywords: *Triple-shape polymers, Shape memory polymers, Hydrolytic degradation.*

In the past two decades scientists and engineers have witnessed significant advancements in the exciting field of shape memory polymer (SMP) research. One concrete example is the development of polymers having “triple-shape capabilities”.[1,2] Such triple-shape polymers are functional materials, which add one interesting feature to the property portfolio of conventional (dual-shape) SMPs; it is their ability to move after special thermo-mechanical programming in response to external stimuli like heat from one shape to a second and from that one to a third. Triple-shape polymers could prove to be useful in applications, where two consecutive shape changes are needed. One conceivable application lies in assembly technology, in which step-by-step shape changes for the fastening of two components in difficult to reach places is required. Another promising application could be morphing technology on aircraft.[3] Strong, but steady changes in configuration, i.e. wing geometry in flight at different temperatures, may improve the overall flight performance, making a morphing aircraft skin self-actuating or active.

Thermoplastic elastomers like poly(ester urethanes) are attractive for thermo-mechanical investigations due to their peculiar shape memory properties. Previously, segmented poly(ester urethane) – thitherto known for pronounced “dual-shape capabilities” – has proven to even display “triple-shape functionality” during uniaxial tensile elongation experiments: Gradual heating (–60 °C → 23 °C → 60 °C) of twofold programmed specimens leads first to the transformation from shape (A) to shape (B) and later from shape (B) back to permanent shape (C).[4] One general disadvantage of ester-based polyurethanes is that hydrolytic degradation strongly influences their functionality as recently documented for their “dual-shape capabilities“.[5] Based on these findings, the effects of hydrolytic degradation on the material’s triple-shape properties have been investigated after the immersion of specimens for up to 8 days in water at 80 °C. Subsequently, cyclic thermo-mechanical measurements were conducted. At the beginning, two thermo-mechanical strain storage steps were applied to the material in order to program two temporary shapes. Then, two strain recoveries, during which the material first changed from shape (A) to (B) and later from shape (B) to (C), were thermally induced by gradually heating the material above its two transition temperatures. The hydrolytic degradation behavior of the specimens was analysed with respect to the evolution of figures of merit like shape fixing ability, stress storage capacity and shape recoverability.

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PVC: RESTYLING OF AN OLD POLYMER

Cosimo Carfagna

Institute of Polymer Chemistry and Technology - CNR, Via Campi Flegrei n° 34, 80078 Pozzuoli – Italy
E-mail: carfagna@unina.it

Keywords*: nanofiller, plasticizer, crosslink*

Polyvinyl Chloride (PVC) is one of the oldest and most common plastics in use today, thanks to its easy processability and low cost. As pure resin its properties result very poor and many additives are required during compounding and processing in order to impart the wished properties for the items manufactured by it. PVC finds various applications as rigid resin as well as as plasticized polymer: in both cases wide margin of improvement can be guaranteed with the aim of nanotechnology and of material chemistry.

In the case of rigid PVC, the impact strength increases with increasing filler content and decreasing filler size because the fillers are points where stresses can be relieved in the polymer matrix.

Flexural strength increase with increasing filler content and decreasing filler size because the resin-particles interfaces can act as sites for crack initiation and propagation in regions where tensile stresses arise. Therefore, it is clear that the reinforcing effect of mineral fillers only remains effective if the particulate filler phase and resin matrix phase are bonded together. Young modulus and yielding strength do not decrease with increasing impact strength. The onset temperature of degradation increases with increasing filler content. In air, the nanocomposite presents a delay of weight loss that may arise from the barrier "nanoeffect" due to lower diffusivity of both the volatile thermo-oxidation products to the gas phase and oxygen from the gas phase to the polymer.

In the case of plasticized PVC, plasticizer migration can make useless the materials for some applications because of a general loss of properties. Apart from obvious mechanical damage the main effects observed are related to:

- crazing due to stress, often in combination with a particular environment such as solvent vapour or moisture - so called Environmental Stress Cracking (ESC)
- The pressure applied from plasticizer can cause the polymer fibrils breaking and then the crazes become fractures
- Reduction of flexibility

In order to reduce plasticizer migration, a strategy has been followed acting both on crosslinking PVC and on the nature of plasticizer. The crosslinking has been carried out by means of chemical curing agent during compounding. In order to reduce plasticizer migration, polymers, in the form of linear polyesters and of star-branched polymers have been compounded with pure PVC.[1,2]

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OPEN CELLED THERMOPLASTIC SHEET FOAMS

Gerold Breuer[*], **Zefeng Huang**[*]

TCKT GmbH, Franz-Fritsch-Strasse 11, 4600 Wels, Austria
E-mail: gerold.breuer@tckt.at

Keywords: *open cell foam, thermoplastic, particulate leaching*

In this study, the feasibility of manufacturing open-celled thermoplastic sheet foams was investigated using a particulate leaching method with different organic and inorganic soluble fillers (porogens) to generate the pores. Usually open cell foams have been almost industrially produced from polyurethane thermoset materials, while the manufacturing of porous thermoplastic foams has not been developed extensively. Therefore only few thermoplastic foams with exceptionally high open-cell contents are available[1].
For this study various thermoplastic polymers, like acrylonitrile-butadiene-styrene copolymers (ABS), polypropylene (PP), polyethylene (PE), ethylene vinyl acetate copolymer (EVA) and poly lactic acid (PLA) were chosen. Mixtures of these polymers with porogen contents of 40 % to even 90 % were compounded in a twin screw extruder and pelletized. Sheets of these mixtures were prepared in a moulding process as well as by continuous extrusion. In the following step the sheets were washed with water in order to remove the porogen. The degree of leaching achieved depends on both, filler content and particle size. The time required to completely remove the porogen mainly depends on the solubility and leaching temperature.
With the particulate leaching method open cell foams with several thermoplastic materials have been achieved with densities between 150 and 400 kg/m³. The foam morphology was characterised by means of scanning electron microscopy. The size and interconnection between the pores could be easily controlled by the amount and characteristics (size and shape) of the leachable particles.
Our results show that the particulate leaching method allows the manufacturing of thermoplastic open cell sheet foams at low costs, interesting for numerous industrial applications such as filters, separation membranes, sound insulation panels or artificial bone tissues.

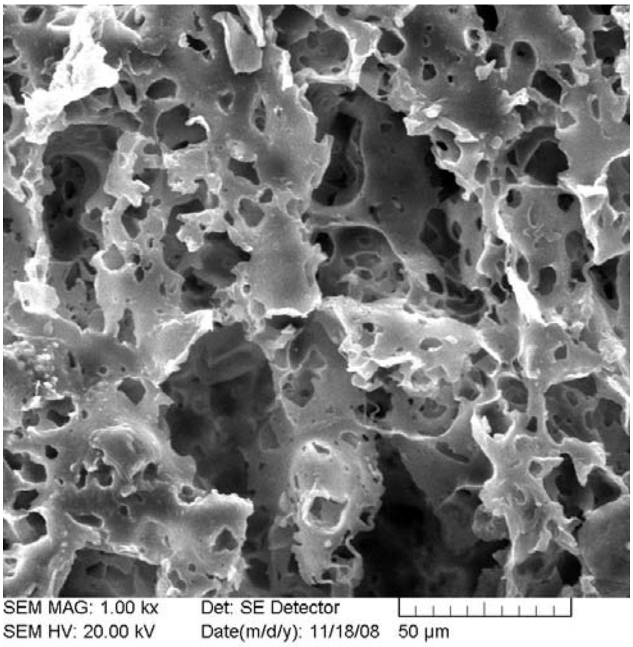

Figure 1: PE based open cell foam

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INFLUENCE OF POLYMER AND SURFACTANT ON THE APHRON-BASED DRILLING FLUIDS CHARACTERISTICS CORRELATING WITH FLUID INVASION CONTROLLING

J. J. F. Cardoso, L. S. Spinelli, E. F. Lucas

Federal University of Rio de Janeiro, Institute of Macromolecules – Horácio Macedo Avenue, 2030, 21941598, Rio de Janeiro-RJ, Brazil
E-mail: spinelli@ima.ufrj.br

Keywords: microbubbles, polymer and invasion controlling.

Problems related to pressure variation in mature oilfields associated with the limitations of conventional drilling fluids have led to discover new fluids. Aphrons fluids are being studied for application in oil well drilling operation. The microbubbles present sizes varying from 10 to 100 µm and a high liquid phase content, so the aphrons are very stable under flow and have colloidal properties that facilitate their transport in pipelines.These fluids consist, basically, of polymer and surfactant, which act as thickening agent and microbubbles producer, respectively. Usually, it can be used with other constituents that function as filtrate controllers, corrosion inhibitors, biocides, lubricants and pH controllers. The specific function of aphrons is to act in the filtrate reduction of oil reservoirs presenting low pressure and depleted zones.

In this work, the aphrons characteristics were evaluated as a function of type and concentration of polymer (xanthan gum and partially hydrolyzed polyacrylamide) and two types of surfactants: anionic (Blue Streak®, sodium dodecyl sulfate-SDS) and nonionic (polyoxide-based copolymer). Such characteristics were correlated with aphrons performance as fluid invasion controller. Polymer concentration was varied from 5.7 to 22.8 g/L, and the surfactant from 2 to 20 g/L. MgO was used as pH controller and glutaraldehyde as biocide. The fluids were produced under pressure of 200 psi using a Fann filter-press and were characterized by optical microscopy (Olympus SZH10 Research Stereo), density and air content. Besides, the viscosity was evaluated by using a Fann 35A viscosimeter and a TA Instruments AR 2000 rheometer, with parallel plates. The fluid invasion control performance test was done using a Petrobras rule N-2607 adapted procedure, in which the fluid was submitted to a pressure differential of 100 psi and forced to pass across a Fann filter with ceramic disc water saturated. The aphrons flow passing by the filter was evaluated in function of time and was correlated with the flow obtained for base fluid.

Despite the aphrons produced with xanthan gum have shown greater viscosity and lower density than those obtained with PHPA, the characterization results (size/size distribution of microbubbles, density, air content and performance) showed that aphrons fluids prepared with SDS, at an optimal concentration, independent of the polymer type, showed better performance and such result is related to relatively higher average diameter and broader size distribution of microbubbles, besides the high air content, in the range evaluated in this study.

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STRUCTURING EDIBLE OILS BY POLYMER GELATION

Tania Dey, Alejandro Marangoni

Department of Food Science, University of Guelph, Guelph, ON N1G 2W1, Canada
E-mail: taniadey@hotmail.com

Keywords: *Polymer Gels, Viscoelasticity and Thermal Analysis*

Structuring oils can offer an alternative towards “bad” fat usage. This can be achieved by enhancing the gelling capability of oils, which in turn also affects the texture, firmness and stability of food products. Our non-aqueous system comprises three components – oil, polymer and surfactant – each having its typical and specific role. While polymers form cross-linked network in gel, surfactants act as a plasticizer and oils behave like a solvent. A wide variety of non-ionic polymers, surfactants and oils were used in this study. Our best chosen polymer was Ethyl Cellulose with different viscosities. Cellulosic gels are known to contain ether-linked polymer strands laterally cross-linked by H-bonding (Physical Gel). Structure-wise the surfactants were varied by choosing different chain-length, head group, unsaturation, side-chains, concentration and hydrophilic lipophilic balance (HLB) values. The edible oils under study had various types of fatty acid content. Based on system composition, soft as well as firm gels were made. Differential Scanning Calorimetry (DSC), Rheometry and Scanning Electron Microscopy (SEM) as well as swelling, binding and infra-red studies were employed to characterize these gels. Clearing temperature was observed to be composition-dependent, whereas gelation temperature was oil-specific. It was interesting to note the existence of an exotherm during gel melting by DSC, which can be attributed to gel re-organization to a more close-packed structure. The nature of the surfactant side chain was found to modify these DSC exotherms. Attempts were made to correlate visco-elastic results of gels with polymer size, surfactant structure and oil composition. Cryo-SEM images offered further insight into the gel structure, particularly mesh-size. Percentage swelling and binding data complemented these results. In general, the interaction was found to be mostly dependent on structure and formulation of the components.

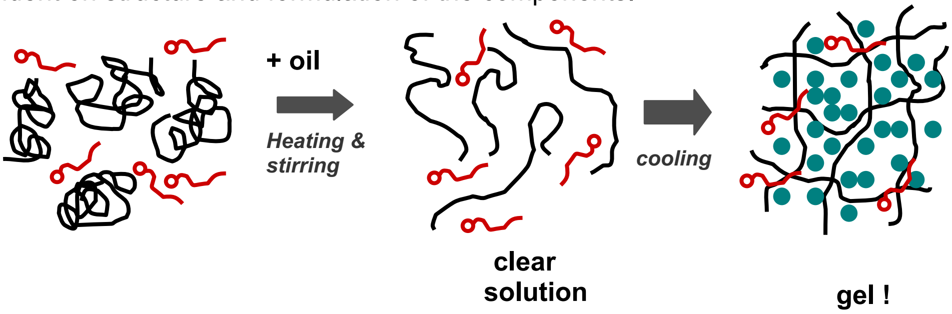

Figure 1: Schematics of Gelation Process

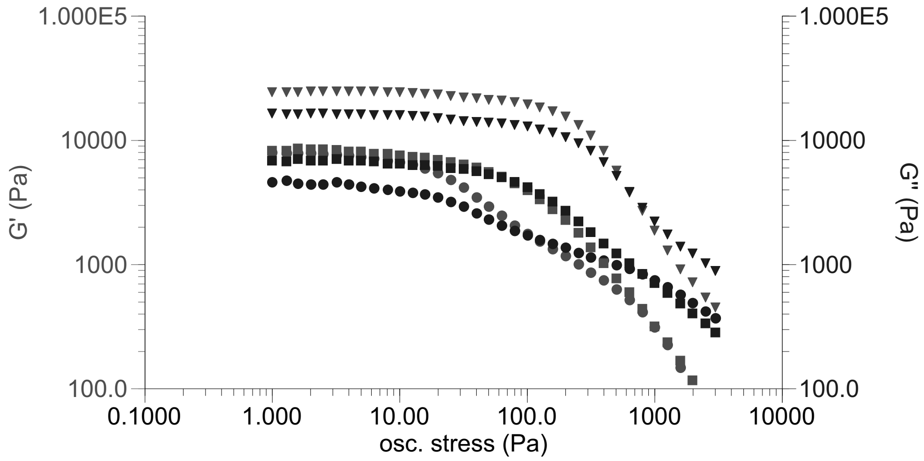

Figure 2: Effect of Polymer on Viscoelastic Properties of Gels [triangle: EC 300, square: EC 22 and circle: EC 10, EC stands for Ethyl Cellulose and the numbers indicate corresponding viscosity in cps]

GLASS TRANSITION AND ENTHALPY RELAXATION IN GLASSY MATERIALS: FROM POLYMERS TO FOOD INDUSTRY

Anais Vuillequez*,, Boulos Youssef*, Jean-Marc Saiter*.**

** LECAP, Institute for Materials Research, Université de Rouen, Faculté des Sciences, Avenue de l'Université BP 12, 76801 Saint Etienne du Rouvray, France.*
*** Nutriset, BP 35, Bois Ricard, 76770 Malaunay, France.*
E-mail: anais.vuillequez@gmail.com

Keywords: *Ageing, glass transition, DSC, Milk powder*

Glass transition is one of the most important little understood phenomena of the physic of condensed matter. This process is characterized by a specific temperature called glass transition temperature (Tg), which depends on the thermal history of the material. The material could be stored in different states: like liquid state (T>Tg) or glassy state (T<Tg). When a material is kept at higher temperature than Tg the like liquid state is reached and dynamic molecular movements are characterized by relaxation mechanisms with a short time constant, while at temperatures lower than Tg the behaviour of the glassy state is characterized by very long time constants.

Some models describe evolution in time of the glassy state. These models have been built for polymeric materials as PET, Epoxide, etc [1,2]. Nevertheless, the same phenomena Tg, relaxation, dynamic molecular movements, *etc* occur for many other materials like sugars (polyoloside, diholoside), protein …

In this work we propose to use the standard model of the relaxation mechanism observed in glassy polymers to other systems such as common food products, in particularly milk powder.

The quality of milk preservation determines the physico-chemical properties of dairy-food products.

The major constituent of milk powder is lactose, which has a Tg of 97-116°C. The presence of other components such as moisture, proteins, fat, mineral and lactic acid can largely affect the physico-chemical behaviour including water absorption, glass transition temperature and crystallization of the milk powders [3].

The aim of the present study is also to investigate the effects of the fat content on the preservation. Three industrial spray-dried dairy powders (skim milk powder (0%MG), whole milk powder (26%MG) and fattened milk powder (50%MG) manufactured for industrial use are characterized. The method used for measuring powder preservation is thermal analysis: differential scanning calorimetry (DSC).

For a given temperature, the molecular relaxation study shows that the more fat content powder of milk, the longer the relaxation time.

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CONTROL OF MACROMOLECULAR ARCHITECTURE OF POLYOLEFINS DURING FUNCTIONALIZATION IN THE MELT

Elisa Passaglia, Serena Coiai, Francesco Ciardelli

ICCOM-CNR-Pisa and Department of Chemistry and Industrial Chemistry ,University of Pisa, 56126 Pisa Italy, E-mail : fciard@dcci.unipi.

Keywords: *free radical, grafting, reactive processing*

Polyolefins are extremely important commodities which can be converted into value-added polymers by post-modification processes. These impart properties like adhesion, dyeability, paintability, wettability, and compatibility, which are not characteristic of the paraffin-like starting materials. Modifications involve the use of free-radicals and are generally carried out at high temperature to reach the necessary fluidity. Therefore functionalization in the melt has to be regarded as non-selective. Cross-linking and degradation set boundaries of the desired grafting reaction and the extent of this last depends on the polyolefin structure and nature of reagents used. The main purpose here is to describe the process in terms of chemical reactions involved, down to the molecular mechanism, and the dependence on the chemical feed in relation to the processing conditions. In order to end up with methodologies able to minimize and control side-reactions thus allowing to maintain original architecture or orient it in an innovative direction[1]. Ethylene polymers, and in particular linear polyethylene (HDPE), is the appropriate polymer for studying the reaction mechanism as well as side reactions due to the simple primary structure. With HDPE it was demonstrated that the process can be driven to a selective grafting without the need of free radical stabilizers and a kinetic equation describing the grafting reaction time evolution can be obtained simply [2]. Examples will show that for various copolymers with more than 50 mol % ethylene units the grafting reaction increases with the increasing concentration of grafting monomer in the feed while degradation and crosslinking can be almost suppressed by proper selection of the monomer/peroxide molar ratio. For polypropylene, as well as for polymers with substituted olefin units and then alternating tertiary carbon atoms, the macroradicals are not stable enough to grant functionalization and to limit side reactions. In these cases the chemistry of the process has to be modified by the use of specific mono- or poly-functional co-agents as macroradical stabilizers[3]. In particular, the chemical cross-linking of PP under dynamic conditions using a peroxide and furan based co-agents, such as butyl 3-(2-furyl) 2-propenoate (BFA) was successfully obtained[4]. Following these evidences PP was functionalized with MAH and peroxide in the presence of BFA obtaining good results in terms of FD and MW.[3,5].Functionalization experiments of propylene based polymers with BFA or BFA/MAH and peroxide were carried out under different feed conditions showing that in the presence of the designed macroradical stabilizer and by optimizing the reagents molar ratios, the reaction becomes stoichiometric with one grafted polar monomer per primary free radical. This allows to increase the functionalization degree up to the values obtained in case of ethylene polymers, by increasing the peroxide/ polymer ratio while maintaining the fixed stoichiometric composition of BFA to peroxide. The modification of co-agent structure was also performed by using tiophene derivatives [6]: in the case of BFA it has be observed that stabilized macroradical can give coupling reaction with formation of new long branched macromolecular architectures during the reactive processing, thus allowing to modify the rheology of the material without substantially altering the number average molecular weight[7]; whereas in the case of the thiophene derivative (BTA) only a partial retaining of polymer chain fragmentation was observed due to the simply reduction of β-scission occurrence.
The results are finally discussed in terms of nonstoichiometric and stoichiometric polyolefin functionalization with evidences demonstrating that these two mechanisms are related to the starting and final macromolecular structure. These results bring about substantial improvement of the general selectivity of the important processes based on the conversion of commodity polyolefins into added value specialties.

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SYNTHESIS, MORPHOLOGY AND ELECTROSPINNING OF POLY(DIMETHYLSILOXANE) BASED COPOLYMERS.

P.E. Mallon*, A.B.E. Abduallah and G. Bayley

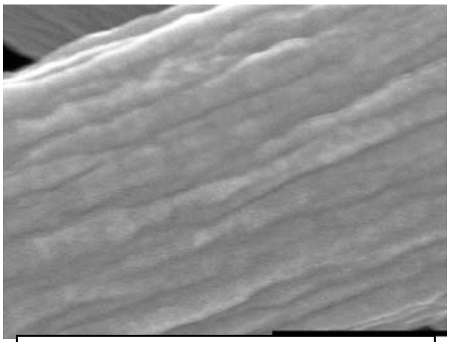
University of Stellenbosch, Department of Chemistry and Polymer Science, Private Bag X1, Matieland 7602
E-mail: pemallon@sun.ac.za

Keywords: *poly(dimethylsiloxane) copolymers, electrospinning, morphology*

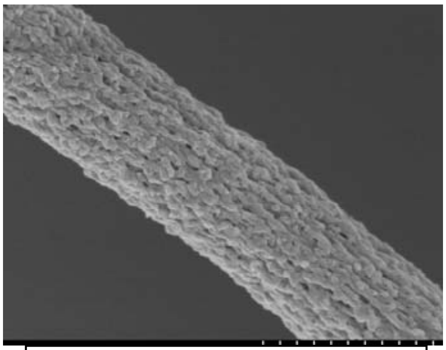
The opposing properties of the components of inorganic-organic hybrid materials means that these materials have nanophase segregated morphologies in the solid state. These types of hybrid materials offer the possibility to combine the unique properties of the individual components into one material. It is possible to control the morphologies of organic-inorganic materials to a certain extent using “living” polymerization methods to produce various block and graft copolymers with well defined and controlled structures [1,2].

The synthesis and characterization of various PDMS based organic-inorganic copolymers will be discussed. These include graft and segmented block copolymers based on polymethylmethacrylate (PMMA), polyacrylonitrile (PAN), polystyrene, and various polyester based PDMS copolymers. The dissimilar nature of the components results in these materials typically having complex morphologies in the solid state as a result of phase segregation. When the polyester component is crystallisable, an even richer variation in morphology can be expected. The chain structure of the copolymer in terms of the distribution of the various segments along the chain and the variation in the composition also has a dramatic impact on the solid state morphology. The morphology of the copolymers is discussed in terms of their analysis by AFM, TEM, positron annihilation lifetime spectroscopy and “off-line” coupled liquid chromatography – AFM and TEM.

It will be shown how the electrospinning technique can be used to produce nanofibers of these copolymers. The inclusion of the PDMS component in the copolymers has a dramatic effect on the nature of the fiber relative to the organic homopolymers. The various factors affecting the nanofiber morphology will be discussed. This will include the effect of the PDMS content of the copolymers on the fiber morphology and porosity. Two examples of the electrospun copolymer fibers are shown in the figure below. Some potential applications of these fibers will be discussed. This includes the possibility for the inclusion of multi wall carbon nanotubes in the electropsun fibers and the use of these fibers as templating materials for the synthesis of porous silicone elastomers.



Surface morphology of electrospun PMMA-g-PDMS



Surface morphology of electrospun PAN-g-PDMS showing porous structure

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DEVELOPMENT AND CHARACTERIZATION OF IN SITU POLYMERIZED NANOCOMPOSITES BASED ON POLYPYRROLE AND POLYANILINE IN THE PRESENCE OF MULTIWALL CARBON NANOTUBES

Md. Moniruzzaman, Chapal Kumar Das

Materials Science Centre, Indian Institute of Technology, Kharagpur, Pin-721302, West Bengal, Índia
E-mail: chapal12@yahoo.co.in

Keywords: *MWCNT, polypyrrole, polyaniline*

Nanocomposites provide large interface areas between the constituent, intermixed phases. It allow significant property improvements with very low loading levels (traditional microparticle additives require much higher loading levels to achieve similar performance), alters chemistry, polymer chain mobility, degree of cure, crystallinity, etc. Carbon nanotubes (CNTs) provide extraordinary stiffness and strength, unique electrical properties, excellent thermal conductivity, high surface area and high chemical stability. Multiwalled carbon nanotubes (MWCNTs)/polypyrrole (PPy) and MWCNTs/polyaniline (PANI) nanocomposites were successfully prepared with both unmodified and amine modified MWCNTs through in situ oxidative polymerization method. The uniform coating of electrically conducting polymers, PPy and PANI were found on to the MWCNTs surfaces and the average diameter is increased than the pure carbon nanotubes which were evident from the Field Emission Scanning Electron Microscopic (FESEM) images and High Resolution Transmission Electron Microscopic (HR-TEM) images. The amine modification is done by ethylenediamine(EDA)/dicyclohexylcarbodiimide(DCC)/THF solution to acid modified MWCNTs (weight ratio of EDA to DCC to MWCNTs = 25:25:1) at room temperature and the acid modification is done by H_2SO_4 and HNO_3 (weight ratio of H_2SO_4 to HNO_3 = 3:1) to pure MWCNTs. The structure of pure and amine modified MWCNT were identified by FTIR spectrum and the peak at 1238 cm^{-1},at 1576 cm^{-1}, at 3258 cm^{-1} and at 2920 cm^{-1} corresponds to the peak of C-N stretching, N-H bending, N-H stretching and C-H stretching respectively for amine modified MWCNT . The capacitance, dielectric constant and conductivity values were measured for the PPy composites containing both unmodified and amine modified MWCNTs by Hioki impedence measurement instrument and found that the values were 100 times greater for the amine modified MWCNTs composite as compared to the unmodified ones. The sample had a circular shape of diameter 13.7mm, thickness 0.93mm and weight 100mg were obtained by dry pressing the composite powdered materials by applying hydraulic pressure of about 6 tons. For unmodified MWCNTs/PPy nanocomposite the specific capacitance, dielectric constant and a. c. conductivity values are 1.87×10^{-4} F/g, 1.34×10^{7} and 1.52 $\times10^{-2}$ S/m respectively and for amine modified MWCNTs/PPy nanocomposite the specific capacitance, dielectric constant and a. c. conductivity values are1.65×10^{-2} F/g, 1.17×10^{9} and 8.24 S/m respectively. Also for unmodified MWCNTs/PANI nanocomposite the specific capacitance, dielectric constant and a. c. conductivity values are 3.21×10^{-5} F/g, 1.78×10^{6} and 1.37 $\times10^{-4}$ S/m respectively and for amine modified MWCNTs/PANI nanocomposite the specific capacitance, dielectric constant and a. c. conductivity values are 5.95×10^{-3} F/g, 4.24×10^{8} and 1.98×10^{-2} S/m respectively. These higher values are due to the porous structure of carbon nanotube which greatly assists the easy passage of the charges from polymer to carbon nanotubes through polymer chains and ultimately accumulation of charge at the porous surface and at the interface of MWCNT and polymer. The thermal stability of amine modified composite is higher than the unmodified composite. This is because of the better affinity between modified MWCNTs and the polymer matrix.

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DROPLET STRUCTURES IN STYRENIC BLOCK COPOLYMER BLENDS AND THEIR NANOCOMPOSITES

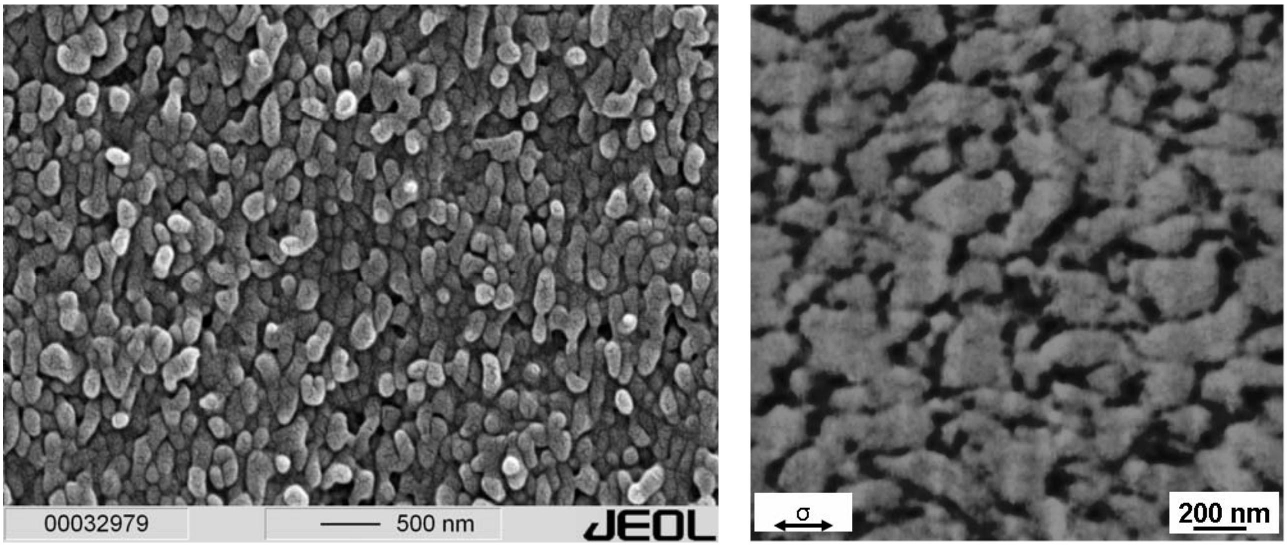
S. Henning*, **R. Adhikari****, **S. Borreck***, **G.H. Michler***

**Institute of Physics, Martin Luther University Halle-Wittenberg, Halle (Saale), Germany*
***Central Department of Chemistry, Tribhuvan University, Kathmandu, Nepal*
E-mail: sven.henning@physik.uni-halle.de

Keywords*: Block copolymers, nanocomposites, morphology, mechanical properties*

Styrene-butadiene block copolymers (SBCs) with polystyrene chains as terminal blocks and lamellar or co-continuous morphologies are a special family of toughened plastics where the glassy polystyrene phase is able to experience pronounced plastic deformation under tensile load. Due to high production costs, however, the block copolymers are seldom used in the pure state. For industrial applications, they are often blended with general purpose polystyrene (GPPS) to reduce cost and tailor optimum stiffness/toughness ratio. Additionally, nanocomposites of such blockcopolymers with alumina nanoparticles of different size and surface modifications were added in different amounts by mixing in solution. In both cases it is crucial to maintain the transparency of the products.

In this work, using scanning and transmission electron microscopy (SEM and TEM), scanning force microscopy (AFM) and tensile testing, we investigate the morphology and the micro-deformation processes in a new kind of highly asymmetric polystyrene/polybutadiene based star block copolymer and its blends with general purpose polystyrene (GPPS) and their nanocomposites. The emphasis has been put on the analysis of blends morphology evolved under various processing conditions and the impact of processing on the micromechanical behaviour of the blends. After mixing with standard polystyrene, these copolymers form typical droplet morphologies (see Fig. 1) under the influence of different processing conditions. The droplet morphologies which were unstable under equilibrium conditions endowed the polymers with surprisingly high toughness. Various parameters responsible for the evolution of the droplet morphology will be discussed and their mechanical properties will be compared with that of lamellar systems.



a) b)

Figure 1: a) SEM micrograph after permanganic etching showing droplet morphology of a blend containing 40 wt.-% GPPS and 60 wt.-% star block copolymer where the rubbery phase is removed by the etching process, b) AFM tapping mode phase contrast image of a deformed sample of the same composition; soft phase is reproduced in darker shades of grey.

MAGNESIUM HYDROXIDE MODIFIED BY 1-N-TETRADECYL-3-CARBOXYMETHYL IMIDAZOLIUM CHOLRIDE AND ITS EFFECTS ON THE PROPERTIES OF LLDPE

Yun-sheng Ding*, **Ping Wang, Long Chen, Sheng-li Chen**

School of Chemical Engineering, Hefei University of Technology, Hefei 230009, China
E-mail : dingys@hfut.edu.cn

Keywords: *Flame retardancy; Magnesium hydroxide; [C_{14}cim]Cl*

In this paper, $Mg(OH)_2$ (MH) was modified by 1-N-tetradecyl-3-carboxymethyl imidazole chloride ([C_{14}cim]Cl), a kind of imidazolium ionic liquid, which was synthesised by our laboratory. And then the modified MH were incorporated into linear low-density polyethylene (LLDPE) by melt-mixing and get the LLDPE/MH-[C_{14}cim]Cl composites. The flame retardance of LLDPE/MH-[C_{14}cim]Cl was tested as standard of UL-94, and the thermally decomposing behavior of composites were characterized by thermogravimetric and differential thermal analysis (TGA), so the tensile and Izod Impact properties of LLDPE/MH-[C_{14}cim]Cl were tested. For comparising, the composites of LLDPE/MH and LLDPE/MH-SA(stearic acid) were prepared and their properties were studied by the same way.

The composite with 50 wt % MH-[C_{14}cim]Cl could be self-extinguished in horizontal burning test and its LOI could reach 31.4%, while the elongation at break of the composite is 40%, and Izod impact strength is 31.3 kJ/m^2. As a contrast, composites of LLDPE/MH and LLDPE/MH-SA could not self-extinguish in horizontal burning test and LOI were not more than 29%, the elongation at break and Izod impact strength were also less than 30% and 21.0 kJ/m^2 respectively. As can be observed in the TGA plots, the decomposition of LLDPE/LQ-MH started at a higher temperature, but more soild residue remaind at 800^{o}C compared with LLDPE/MH and LLDPE/MH-SA (Fig.1).

The [C_{14}cim]Cl could play double roles in the composite. First, it could possesses a good fireretarding synergistic effect to MH in LLDPE matrixs, and second, it also serves as an efficient lubricant and compatibilizer between MH and LLDPE, leading to the great improvement of the processability and mechanical properties, as well as finer dispersion of MH in matrix, thus the flame retardant LLDPE with good comprehensive performance can be obtained.

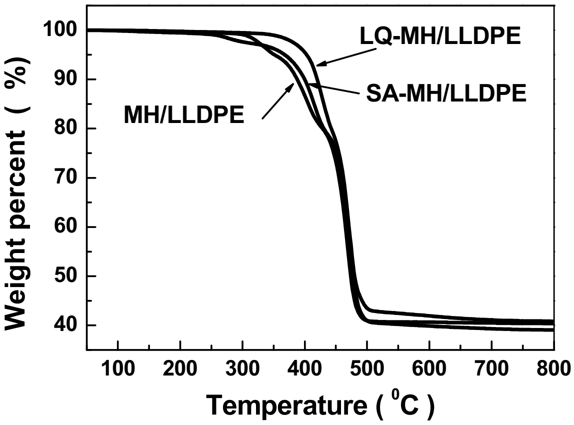


Fig.1 TGA curves of LLDPE/MH, LLDPE/SA-MH and LLDPE/LQ-MH

EFFECT OF INTERFACIAL STRENGTH ON MECHANICAL PROPERTIES OF Al_2O_3/ EPOXY NANOCOMPOSITES

Su Zhao*, Linda S. Schadler, Henrik Hillborg*,#, Tommaso Auletta***

**ABB AB, Corporate Research, 721 78, Västerås, Sweden*
***Department of Materials Science and Engineering and Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York, 12180, USA*
#Royal Institute of Technology, School of Chemical Science and Engineering, Fiber and Polymer Technology, SE- 100 44 Stockholm, Sweden
E-mail: henrik.hillborgl@se.abb.com

Keywords: *epoxy nanocomposite, interfacial strength, alumina oxide nanoparticles*

Polymer nanocomposites are a major force in the design of novel advanced materials suitable for a variety of different applications, such as electrical engineering [1]. Epoxies are widely used as electrical insulation material [1-3]. Micron-sized fillers are usually added to the epoxy resin to form composites with enhanced mechanical, thermal and electrical properties [4]. The limitation of such fillers is that they cause a decrease in ductility [5]. Recently, nano-sized fillers have been shown to increase toughness, modulus, and ductility simultaneously [5-7].The toughening mechanisms and fatigue crack propagation behavior operating in Al_2O_3/ epoxy nanocomposites with either strong or weak interfaces between particles and matrix have been investigated [8,9]. The strong interface was achieved by surface silanization of the nanoparticles, whereas the untreated nanoparticles led to a weak interface (Fig. 1). It was shown that the surface-treated Al_2O_3/epoxy nanocomposite exhibited a significant increase in ductility (39 % at 3 vol.% particle loading). A significant improvement in fatigue crack propagation resistance was observed for both nanocomposites. The crack arresting mechanisms included particle matrix debonding and plastic void growth for both nanocomposites. Additionally, in the nanocomposites with a stronger interface, a significant plastic deformation of the matrix around the well-bonded nanoparticles contributed as well.

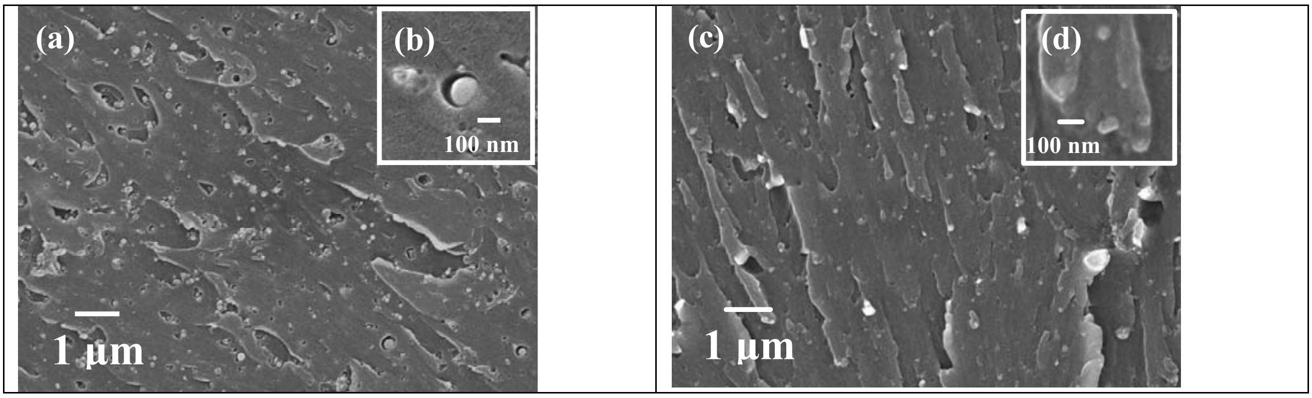


Figure 1. Scanning Electron Micrographs showing the nanoparticle dispersion in an epoxy resin. (a-b) 3 vol. % of untreated-Al_2O_3, and (c-d) 3 vol. % of silanized-Al_2O_3 .

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ANOMALOUS ENHANCEMENT OF THERMAL CONDUCTIVITY OF POLY VINYL ALCOHOL

R.R.Yadav*, Giridhar Mishra*, J. Philip, S. Uma****

**Physics Department, University of Allahabad, Allahabad-211 002, India*
***STIC, Cochin University of Science and Technology, Cochin-682022, Kerala, India*
E-mail: rryadav1@rediffmail.com

Keywords: *Thermal conductivity, nanoparticles suspension, Poly vinyl alcohol*

A PVA colloidal solution having suspended gold nanoparticles (nanofluid) has been developed using a chemical reaction. Colloidal solutions of representative concentrations of 0.1, 0.2, 0.5 and 1.0wt% Au-nanoparticles contents in the primary solutions are used to study the modified ultrasonic attenuation, ultrasonic velocity, thermal diffusivity and thermal conductivity in PVA polymer molecules on incorporating the Au nanoparticles. Average size of Au nanoparticles could be varied in the range 4-10 nm. XRD and TEM measurements were made to determine the crystal structure and size of the nanoparticles. The XRD patterns of Au-samples show that the samples are single phase and no other distinct diffraction peak, except the characteristic peaks of cubic phase Au were found. The diffraction peaks are broad suggesting that the samples consist of very small particles. Particles size calculated using Scherer's formula were well consistent with the average particle diameter obtained from the TEM images. The TEM images reveal that the gold nanoparticles are spherical in shape with sizes around 4 nm and clusters with size distribution between 4-10 nm. The gold nanoparticles are well dispersed in colloidal solution as evinced by TEM images. Also the selected area electron diffraction pattern (SAED) and HRTEM image for 0.1 and 0.2 wt% Au-np-PVA are taken. The SAED patterns are revealing the crystalline structure of the Au metal nanoparticles in PVA. The whole microscopic images reveal that the Au metal nanoparticles could be obtained in PVA matrix even in the absence of protective agent. UV-Visible spectroscopic measurements are made to determine the optical absorption in the nanofluid. In the case of 0.1 wt% Au-np-PVA, the UV-Visible spectrum shows a strong absorption peak at 538 nm due to the plasmon oscillation modes of conduction electrons in the colloidal nanoparticles-liquid suspensions. Photoacoustic method has been used to determine thermal diffusivity at different temperatures. Thermal conductivity as a function of temperature has been determined using thermal diffusivity and differential scanning calorimetric heat capacity (DSC) data in the range of temperature from 5^0C to 50 ^{0}C. A maximum thermal conductivity 4.308 W/mK has been found at 300K following the maximum thermal diffusivity $20.35\text{x}10^{-8}$ m^2/sec at the same temperature. The thermal conductivity increases 20 times on 0.2 wt% nanoparticles inclusion at ambient temperature. An ultrasonic attenuation mechanism has been developed to predict the thermal conductivity enhancement at different temperatures. It is observed that for 0.2 wt% Au-np-PVA, ultrasonic velocity characteristic minimum occurs at 30 ^{0}C having symmetrical temperature dependent curve. Also there is a characteristic maximum of ultrasonic attenuation at 28 ^{0}C for the same sample. The calculated value of the ultrasonic attenuation in the Au-np-PVA sample (0.2 wt% Au-np) at 300K following the S. Biwa model for scattering loss including the ultrasonic attenuation due to nanoparticles and thermoelastic loss comes to be $\alpha = 124.96\text{x}10^{-3}$ Np/cm. The observed attenuation in our experiment for the sample is $\alpha = 152.08\text{x}10^{-3}$. Source of excess ultrasonic attenuation is the anomalous enhancement of thermal conductivity of the sample due to 0.2 wt% Au-np suspension in PVA as the attenuation due to thermoelastic mechanism (dissipative type of loss) is directly proportional to the thermal conductivity of the samples. Brownian motion of the particles for the interaction/convection is justified by the FTIR results of the like materials Ag-np-PVA solution. A possible theoretical model based on the Brownian motion induced convection effect has been proposed for the theoretical explanation of the anomalous thermal conductivity enhancement. Viscoelastic behaviour of the nanofluid at ambient temperature is suggested on the analysis of anomalous decrease of the ultrasonic velocity at the ambient temperature due to 0.2 wt% nanoparticles suspension in PVA. The critical temperature for the anomalous enhancement of the thermal conductivity is about 30^0C which is near the human body temperature in some cases. Therefore the material may be important in medical applications.

FUNCTIONAL POLYMERS TO REMOVE IONS IN CONJUNCTION WITH MEMBRANES

Bernabé L. Rivas

Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile,
E-mail: BRIVAS@UDEC.CL

Keywords*: Functional polymers, membranes, pollutant ions.*

Water-soluble polymer-ion interactions take place in a homogeneous medium. To face the problem of separation of ions bound to the polymer and non-bound, one of the most promising techniques used is the application of separation methods based on membrane process (1-2). Membrane filtration easily allows this separation by means of a method known as *liquid-phase polymer-based retention (LPR)* technique.

The ion retention properties are investigated by LPR technique (washing and enrichment methods). The first is a batch-like method where a solution containing the polymer and the metal ions to be separated is placed in the ultrafiltration cell at a given pH and ionic strength. Interactions of metal cations: Co(II), Ni(II), Ca(II), Mg(II), Pb(II), Cd(II), Zn(II), and Cu(II), and As(V) as anionic species with water-soluble polymers were studied at different pH and filtration factor, Z.

It is useful to quantify the separation process by plotting the retention of the metal species versus filtration factor. The filtration factor (Z) is defined as the volume ratio of filtrate (V_f) versus cell volume (V_o). Retention (R) is defined for any species as the fraction per unit of the species under study remaining in the cell during filtration.

The metal ion retention ability of a water-soluble polymer depends strongly on the pH. As the pH increases the metal ion retention increases. It is due to at higher pH, the majority of carboxylic acid groups are non-protonated. Therefore, the carboxylate group is more available to bind metal ions. Particularly at pH>5 which is above to the pKa value for an acrylic acid. The interactions between the polymer and the metal ions are mainly due to electrostatic forces and to formation of coordinating bonds. Other weak interactions may appear such as trapping metal ions in the bulk of the polymer phase. Respect to the removal of metal ions, at higher pH, as pH 5 and pH 7, increased the ability to bind metal ions and there is not an important decrease of the retention as Z increases. That means that the sulfonic/sulfonate-metal ion interaction is strong. The polymer-metal ion interaction may be intramolecular, intermolecular or both. As(V) species are removed by polymers containing ammonium groups. The highest retention ability was observed at higher pH (6 and 8). The retention of arsenic occurs basically through the exchange of the counter ion of the polycation and the anionic species of the arsenic. For that it is necessary that the functional water-soluble polymers contain ammonium salt groups to remove arsenate species. It is possible remove by employing LPR in combination with catalytical electro-oxidation (EO). As(III) is electro-oxidized to As(V) and removed by LPR technique.

In addition, water-soluble polymers containing carboxylic acid and sulfonic acid groups showed a high affinity for metal ions. It depends on the structure of the polymers and on the pH, and filtration factor, Z. The functional polymer group-metal ion interaction would occur through different mechanisms. For carboxylate groups this should be a complexing process and for sulfonic acid groups it should be an electrostatic process.

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MICRO AND NANOSTRUCTURED EPOXY RESIN BASED POLYMER BLENDS

Sabu Thomas*

** Centre for Nanoscience and Nanotechnology, Mahatma Gandhi University, Address: Priyadarshini Hills, Kottayam, Kerala, India - 686 560.*
E-mail: sabupolymer@yahoo.com, sabuchathukulam@yahoo.co.uk

Keywords: epoxy resin, block copolymer, nanomorphologies

Epoxy based blends have generated a lot of interest recently due to their increasing commercial importance. Epoxy resin is often blended with rubbers and thermoplastics to generate micro morphologies for the better impact performance [1]. We have very recently shown the viscoelastic phase separation operating in Epoxy/SAN and Epoxy/ABS systems leading to micro and nano sub inclusions [2,3]. Recently, nanostructured blends based on epoxy resin/block copolymers systems have appeared in literature [4]. These nanostructured blends have the potential to show super toughness. In the proposed talk, miscibility, phase separation, morphology, mechanical and viscoelastic properties of a series of epoxy based blends will be discussed. The block copolymer composition and molecular weight are the controlling factors in deciding the nature of the morphology (spherical, wormlike and vescicular). The block copolymer used in our study is styrene-block-butadiene-block-styrene triblock copolymer. The phase separation, gelation and vitrifcation will be investigated detail. Since both styrene and butadiene block are immiscible in epoxy resin, thus results in phase separation in macroscopic length scale. So the epoxidation of block copolymer using hydrogen peroxide is done at different time to obtain the different epoxidation degree. The epoxidation degree of epoxidised block copolymer is confirmed by FTIR and ^{1}HNMR studies. It can be seen that as the epoxidation degree increases the miscibility of the block copolymer in epoxy resin also increases and a good miscibility or transparency is found at highest epoxidation degree. The initially miscible block will phase separate into nanoscale morphologies and there occurs a reaction induced microphase separation. Techniques such as SEM, TEM, OM, laser light scattering, rheology will be made use of for the characterization of the morphologies. Cure kinetics studies by DSC analysis show that there is a delay in cure occured by the addition of block copolymer. There is a slight decrease in T_g values as observed for the cured blends with increasing epoxidation degree due to the plasticisation effect of block copolymer in epoxy resin. Finally the role of the nano and micromorphologies on the mechanical and viscoelastic properties will be disused.

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CARBON NANOTUBE FILLED ELECTROSPUN POLYACRLONITRILE-GRAFT-POLY(DIMETHYLSILOXANE) FIBERS FOR SILICONE ELASTOMERS COMPOSITES

G. Bayley*, **P. E. Mallon***, **M. S. Hedenqvist** **

**Department of Chemistry and Polymer Science, University of Stellenbosch, Private Bag X1, 7602 Matieland, South Africa*
***School of Chemical Science and Engineering, Royal Institute of Technology (KTH), SE-100 44 Stockholm, Sweden*
E-mail: bayley@sun.ac.za

Keywords: *Electrospinning, Nanocomposites, Multi-walled Carbon Nanotubes*

Nanocomposites have received considerable interest in the last few years. These materials consist of nano-metric scaled fillers dispersed in a continuous polymer matrix. Benefits of these types of materials include enhanced physical properties for the bulk material as well as the possible introduction of new functional properties. One of the main problems facing the production of nanocomposites is the agglomeration of the nano-fillers, which can lead to poorer material performance. A common means to aid dispersion is by the introduction of functional groups on the filler surface. In this work we aimed to enhance the properties of crosslinked poly(dimethylsiloxane) (PDMS) elastomeric films, by the introduction of reinforcing nanofibres. The electrospinning[1] technique was employed in the fiber production. Novel graft copolymers of polyacrylonitrile-graft-poly(dimethylsiloxane) (PAN-g-PDMS) were synthesised with varying PDMS content and molecular weight. A technique was developed whereby these graft copolymers were electrospun and the resultant fibers dispersed in the silicone films in two ways; as non woven mats and as aligned fibers. PAN suits this type of reinforcement application due to its good mechanical properties. To further enhance the physical properties of the silicone films, multi-walled carbon nanotubes (MWCNT's) were included in the fibres. It is widely known that MWCNT's do not disperse well in silicone due to a lack of interaction with this matrix. A facile method for the inclusion of well dispersed MWCNT's in the silicone matrix by making use of the electrospinning technique is presented. The mechanical properties of the composites show dramatic improvements relative to the unfilled silicone elastomer. Figure 1(a) below shows the stress-strain curve for various composites. The improved mechanical properties are attributed to yielding and "pull-out" of the fibres during the tensile testing. Figure 1(b) shows the tensile fractured surface illustrating the fiber "pull-out" and yielding. Besides the increase in bulk physical properties, MWCNT's have the added advantage of introducing new functional properties to the composites. The conductive nature of MWCNT's allows the preparation of fully flexible conductive silicone composites.

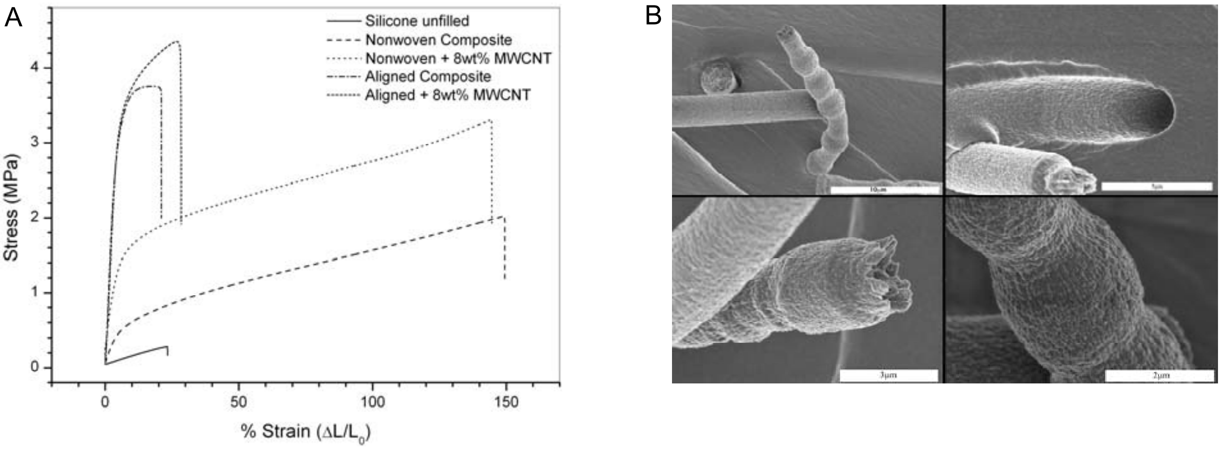

Figure 1: Stress-strain curves (A) for the various silicone composites and SEM images (B) of the composite fracture surface showing fiber pullout and yielding.

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MAGNETORHEOLOGICAL POLYMERIC MAGNETIC COMPOSITE MATERIALS

Fei Fei Fang, Bong Jun Park, Hyoung Jin Choi*

** Department of Polymer Science and Engineering, Inha University, Incheon 402-751, Korea*
E-mail: hjchoi@inha.ac.kr

Keywords: *Magnetorheological fluid, Magnetic particle, Composite, Rheology*

Magnetorheological (MR) suspensions along with electrorheological (ER) fluids have been regarded as intelligent materials for various electromechanical device applications with a large and tunable increase in shear viscosity under an external magnetic field [1, 2]. When the magnetic field is imposed, its rheological properties vary by showing a characteristic fibrillation, with strings of the particles oriented along the magnetic field direction. Carbonyl iron (CI) particles are known to be superior candidate of MR fluids due to the high saturation magnetization and appropriate particle size, however, they have severe sedimentation problem due to the large mismatch of the particle density to the carrier oil. Therefore, our efforts on improving MR characteristics of the magnetic particles along with their rheological analysis will be focused. Coating the surface of CI particles producing favourable core-shell structure along with apparently decreased density for synthesized composite particles with PMMA, PS, PVB, and PANI via either solvent casting or conventional in-situ dispersion polymerization [3, 4] will be covered in addition to carbon nanotube (CNT) coating [5] and double wrapping process with polymeric shell (PMMA, PANI, and PS) and CNT layers. Magnetite (Fe_3O_4) has also attracted much attention due to the relative low density compared with CI particles. However, it is very difficult to assemble and maintain nano-sized iron oxide particles dispersion for MR fluid application because of their serious aggregation problem. Thus, various polymeric systems of PVB, PS, PMMA, and some conducting polymers (PPy, PANI) have been employed to fabricated Fe_3O_4/polymer composites via various polymerization methods. Especially, CNT was also adopted to load some magnetite nano-particles which also exhibited good MR behaviors. The synthesis process is shown in figure 1. MR characterizations are investigated via rotational and oscillation mode tests. Yield stress and flow curve are examined based on model equations which are analogous to ER fluids.

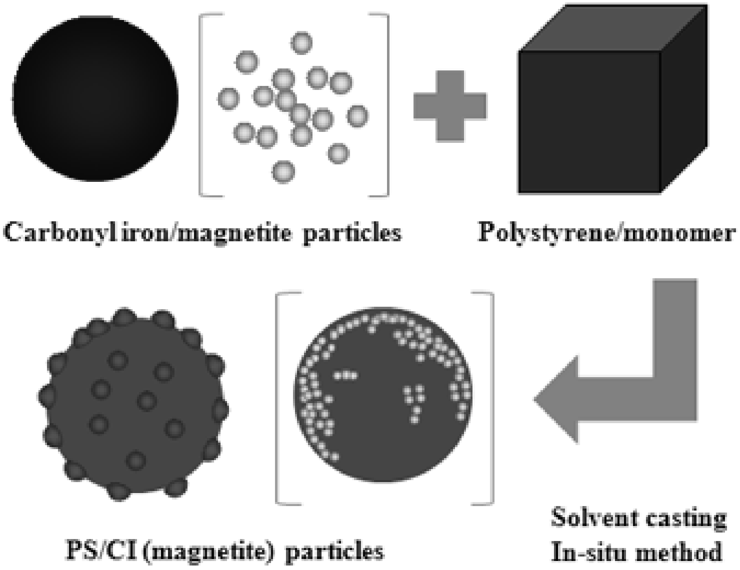

Figure 1 Synthesis process of polymer/magnetic composite particles.

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THE EFFECT OF PROCESSING CONDITIONS ON THE MORPHOLOGY, MECHANICAL AND ELECTRICAL PROPERTIES OF $BaTiO_3$-POLYMER COMPOSITES.

Sara Dalle Vacche*, Yves Leterrier*, Véronique Michaud*, Dragan Damjanovic, Jan-Anders E. Månson***

** Laboratoire de Technologie des Composites et Polymères – Ecole Polytechnique Fédérale de Lausanne, Address: Station 12, 1015 Lausanne, Switzerland*
*** Ceramics Laboratory – Ecole Polytechnique Fédérale de Lausanne, Address: Station 12, 1015 Lausanne, Switzerland*
E-mail: sara.dallevacche@epfl.ch

Keywords: *Ferroelectric composites, Thermomechanical properties, Electrical properties.*

Ferroelectric ceramic – polymer composites have a unique mix of electrical and mechanical properties. Piezoelectric and pyroelectric activity, a wide range of dielectric constants and high breakdown strength are combined with mechanical flexibility, formability and low acoustic impedance. Furthermore their properties may be tailored by the judicious choice of the polymeric matrix and ceramic filler, of their volume fraction, and of the type of connectivity, making these materials very attractive for applications as embedded capacitors, sensors and actuators. Composites with 0-3 connectivity, i.e. a continuous polymer matrix filled with a ceramic phase discontinuous in all directions, are particularly interesting because of their relative ease of fabrication and processing. The functionality of these composite materials is mostly due to the dielectric, ferroelectric and piezoelectric properties of the ceramic phase, which therefore often needs to constitute more than 50% in volume. On the other hand the possibility of integrating these composites as embedded devices in host structures, which are often polymer based, or using them as efficient actuators depends greatly on their thermomechanical properties. Most of the studies on ferroelectric ceramic-polymer composites, however, focus on their electrical properties, and relatively few systematic studies on their thermal and mechanical behaviour have been published so far. Furthermore the ceramic volume fractions considered are often much lower than those used in most applications [1, 2], studies of highly filled composites mainly being limited to lead-based ferroelectric materials [3].

In the present study 0-3 $BaTiO_3$ – polymer composites were prepared, containing up to 60% volume fraction of ceramic phase. $BaTiO_3$ was chosen as the ceramic filler as it is a common piezoelectric material with high dielectric constant, having the additional benefit from an environmental point of view of being lead-free. For the matrix, a low viscosity epoxy resin and a polyvinylidene fluoride based polymer were chosen. The first is a thermoset resin commonly used for several applications, and the second is a thermoplastic semicrystalline polymer which displays piezoelectric activity. A common route for achieving very high loading of ceramic filler is the use of solvents to reduce the viscosity during processing. However, as the materials prepared via the solvent route were found to have poor mechanical properties, attributed to the presence of residual solvent, most of the effort focused on obtaining high ceramic volume fractions via a solvent free process.

The thermomechanical, dielectric, ferroelectric and piezoelectric properties of the obtained composites were investigated, and discussed in the light of the properties of the basic components, the processing route and the resulting morphology. X-ray diffraction was carried out to determine the crystal structure of the $BaTiO_3$ in the pure powder and in the composites, confirming that processing did not alter the crystallographic structure of the ceramic phase. Scanning electron microscope observation of fracture surfaces of the composites evidenced that a satisfactorily homogeneous dispersion of $BaTiO_3$ in the matrix could be obtained, although aggregates with diameter of some micrometers and some porosity were detected. The thermal and mechanical behaviour of the composites was studied by differential scanning calorimetry and dynamic mechanical analysis. The glass transition temperature was found not to significantly depend on the amount of filler, while both the storage and loss moduli increased upon addition of $BaTiO_3$. Furthermore, all the composites displayed a region of linear stress-strain behaviour smaller than the pure matrices. Finally, experimental results also evidenced the possibility to obtain low leakage current and high breakdown voltage.

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STUDIES ON MORPHOLOGY AND CONDUCTIVITY OF POLY (N-METHYL) ANILINE NANOPARTICLES PREPARED IN NONSTIRRED REACTION MEDIUM.

Chabukswar V.V.*, Navnath K.Dhomase*, Sanjay V. Bhavsar*, K.C.Mohite, V.B.Gaikwad***, Bahule, B.B.***

** Department of Chemistry, Nowrosjee Wadia College (Affiliated to University of Pune) 19, Bund Garden Road, V. K. Joag Path Pune-411001. INDIA -*
***School of energy studies, Dept. of physics, University of Pune*
****K.T.H.M. College, Nashik*
E-Mail" vvchabukswar@gmail.com

Keywords*: Poly (N-Methyl aniline), conductivity, morphology*

Polyaniline has elicited the most interest due to its wide range of conductivity, unique redox tunability, good environment stability, low cost, ease of synthesis and promising application in many fields. But intractability i.e. infusibility and insolubility is the main factors that affects the application of polyaniline. Dispersing of polyaniline is the most effective approach to solve this problem. We have studied and worked on synthesis of dispersible polyaniline and its results by some novel methods which are described here. Poly (N-Methyl) aniline nanoparticles with controllable morphology and sizes especially well oriented arrays were prepared by just removing a routine operation, stirring, from conventional method of synthesis and using acrylic acid as a soft template [1]. Chemical oxidative polymerization of N-Methyl aniline was carried out in two different reaction condition 'with and without stirring' [2] using an organic acid (DL-Tartaric Acid) as dopant [3], ammonium per sulphate (APS) as oxidant and acrylic acid as soft template. The effect of stirring on morphology of polymer has been studied. It is found that polymer formed in non stirring experiment predominantly produce highly dispersible, smooth nanoparticles with controllable morphology and sizes [4]. These nanoparticles are having large surface area and thereby high conductivity of polymer. Mechanism for generation of well dispersed and smooth nanoparticles is supported by homogeneous nucleation of polymer nanoparticles in non stirred experiment and role of acrylic acid as soft template. It was observed that product formed in 2 hours was having good properties than formed in 48 hours. In case of experiment where reaction mixture was stirred at 1000 RPM exactly opposite results were obtained. In this case comparatively coral-like, granular and uncontrolled polymer particles were formed. Mechanical stirring induces heterogeneous nucleation [5] and forced newly formed particles to collide on each other and triggers aggregation [6] of particles. These coral like granular particles are having comparatively small surface area and less conductivity. Conductivity measurement, UV- visible, XRD and FTIR spectroscopy were performed to characterize the product. The synthesized product was used as sensor for ammonia. We believe that this new method can be used to synthesize highly conductive polymers in minimum time and bulk quantity. Processabililty problem of many polymers can be solved by using this technique

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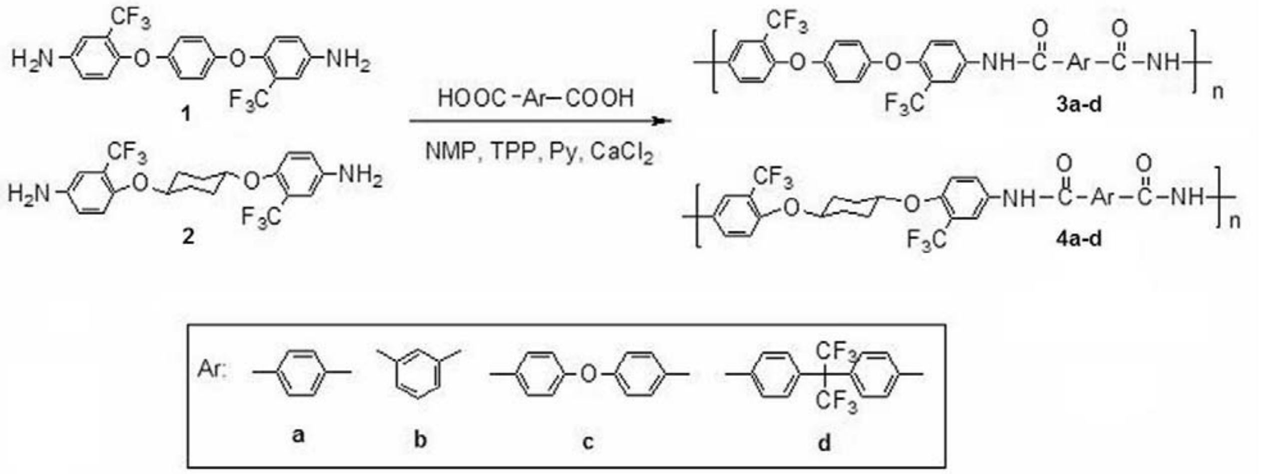
HIGHLY ORGANOSOLUBLE AND TRANSPARENT POLYAMIDES CONTAINING TRIFLUOROMETHYL PENDANT GROUPS

Penghui Li, Chenyi Wang, Guang Li, Jianming Jiang
State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, China
E-mail: lig@dhu.edu.cn

Keywords: *soluble polyamide, optical transparency, trifluoromethyl group*

According to the phosphorylation technique [1-4], two series of aromatic polyamides (PA **3a-d** and **4a-d**) were synthesized from the CF_3-containing diamines **1** and **2**, respectively, with various aromatic dicarboxylic acids (Scheme 1). The polyamidation was carried out via solution polycondensation using triphenyl phosphite (TPP) and pyridine (Py) as condensing agents in the N-Methyl-2-pyrrolidone (NMP) solution containing dissolved $CaCl_2$. All the polycondensation reactions proceeded readily in a homogenous solution, and the polyamides were obtained in high yields and moderately high inherent viscosities (0.55-1.29 dl/g). The structures of these polymers were confirmed by FT-IR, ^{1}H-NMR and elementary analysis. Wide-angle X-ray diffraction measurements revealed that the polyamides were amorphous nature.



Scheme 1 Synthesis of aromatic polyamides **3a-d** and **4a-d**.

Unlike the commercial polyamide (Kevlar or Nomex), most of the obtained polyamides could be quickly soluble in NMP, DMAc, DMF, DMSO and THF at room temperature, and the maximum dissolvability even exceeded more than 10 wt%. The excellent solubility of these polyamides might be determined by the specifically designed structures through incorporation of the bulky pendant trifluoromethyl groups and ether linkages in macromolecules chains, which could decrease the packing densities and intermolecular interactions of macromolecular chains, thereby enhancing their solubility. All the obtained polyamides could be readily processed into flexible, tough and nearly colourless films by casting of their solutions, and the UV cut-off wavelength ($\lambda_{cut\text{-}off}$) of these films were in the range of 326~364 nm. Their tensile strengths and initial modulus could be in the range of 54~101 MPa and 1.6~1.9 GPa respectively. These polyamide films also revealed low dielectric constants (2.15~2.93 at 1 MHz) and low water absorptions (1.96%~2.84%). Moreover, These polyamides exhibited high glass transition temperatures (T_g) in the range of 202-244°C and good thermal stability with 10% weight loss temperatures between 340 to 464 °C in nitrogen atmosphere. Compared with PA **3a-d**, PA **4a-d** displayed better solubility and lower T_g values.

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SYNTHESIS AND CHARACTERIZATION OF OLIGO AND POLYTHIOPHENES WITH THIOPHENE SIDE CHAINS

Geeta Saini , **Josemon Jacob***

Centre for Polymer Science and Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016 INDIA
E-mail: : saini.geeta18@gmail.com

Keywords: *Tetrathiophenes, hexathiophenes, polythiophenes.*

Polythiophenes constitute one of the most widely studied classes of conjugated polymers for applications in field-effect transistors and solar cells because of their ease of synthesis and desirable electrical and optical properties.[1] The type and nature of the substitutents used to induce solubility greatly influence the morphology and band gap in these materials. Although several approaches has been described in literature to tune the band gap, the concept of using thiophene based solubilising groups on the thiophene main chain has not been explored so far. It is anticipated that introduction of alkyl thiophene side chains will show improved charge transport compared to their alkyl counterparts. Here, we report on the synthesis and characterization of thiophene based oligomers and polymers bearing alkylsubstituted thiophenes as solubilising groups and investigation into their physical properties.
A series of tetrathiophenes with alkyl thiophene side chains in the H-H (T1), H-T (T2) and T-T (T3) substitution pattern were synthesized and characterized by ^{1}H-NMR, ^{13}C-NMR and in two cases, by X-ray crystallography. The nature of the linkages is found to have a profound impact on the observed band gap both in the oligomers and polymers. The synthesis was achieved by simple transition metal catalyzed cross coupling methodology and usually proceeds in high yield. The UV results show that for best conjugation, H-T and T-T substitution is preferable which is also supported by X-ray crystallographic data. Also, a series of six polythiophenes with 3,4-(dialkyl thiophene) substituents were prepared by Yamamoto-type polymerization using nickel(0) reagent and by oxidative polymerization using iron(III) chloride.[2-3] All compounds were obtained in high purity and shows good solubility in common organic solvents. The synthesized polymers show absorption maxima between 450-484 nm ($CHCl_3$) in solution which is comparable to regioregular Poly(3-alkylthiophene)s and 150 nm red shifted compared to 3,4-disubstituted polythiophenes.

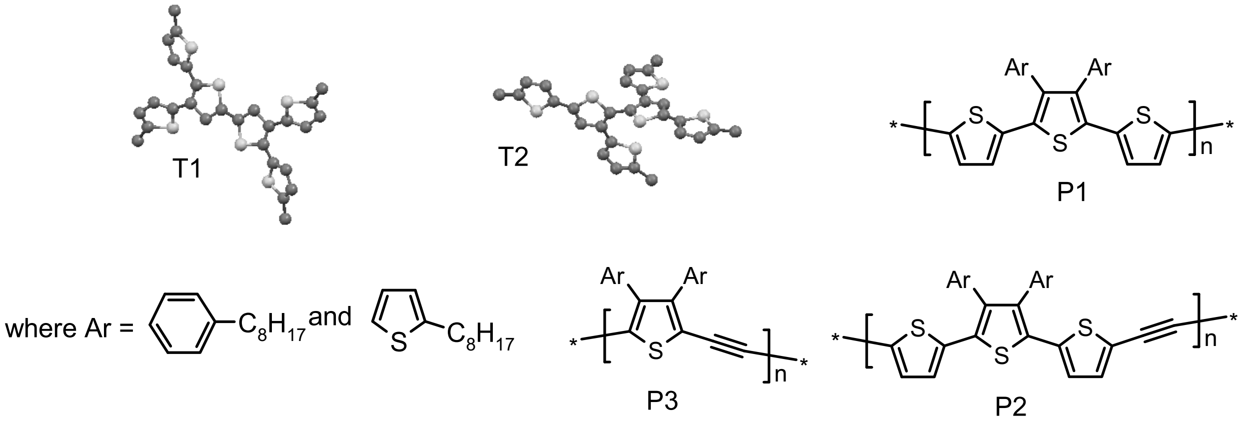

Chart 1: Structures of Polymers P1, P2 and P3 and Crystal Structures of Tetramers T1 (H-H) and T2 (T-T)

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A NEW NATURAL POLYMERIC CATALYST BASED ON STARCH FOR KNOEVENAGEL CONDENSATION

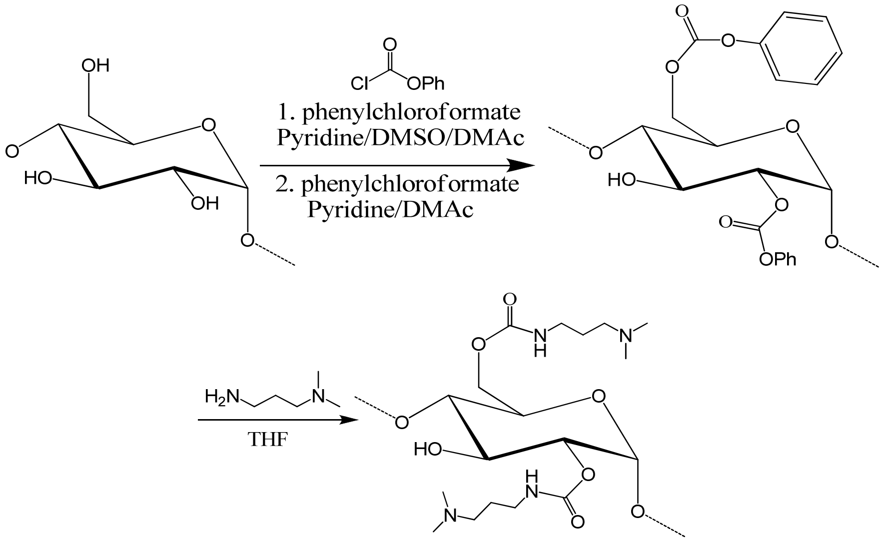
A.Pourjavadi*, N. Nikoosersht*, F. Seidi*

**Polymer Research Laboratory, Department of Chemistry, Sharif University of Technology, P.O. Box: 11365-9516, Tehran, Iran.*
E-mail:na.nikoosersht@gmail.com

Keywords: *Knoevenagel condensation, starch, polymeric catalyst, aldehyde*

The Knoevenagel condensation [1] is one of the most important bond forming reactions which has been used in the synthesis of numerous intermediates and end-products for pharmaceuticals [2].This reaction can be catalyzed by amines [3] and some catalyst polymers [4], [5].

In the present work, a new natural catalyst based on starch synthesized by our group has been utilized to catalyze Knoevenagel condensation (Scheme 1). This catalyst has been prepared according to the following pattern:



Scheme 1. The synthetic route for a catalyst based on starch.

This catalyst basically is a polyamine, which has been characterized with the different methods such as GPC, ^{13}C-NMR, and ^{1}H-NMR-spectroscopy. The GPC experiments show molecular weights around 45000 for the synthesized catalysts. In this work, the different aromatic aldehydes were reacted with various donors, namely, diethyl malonate, malononitrile in the several procedures such as solvent free, in water and various organic solvent, for exampe, THF, methanol, and ethyl acetate. The products worked up were with best yield in THF, solvent free and water, respectively. As this polymeric catalyst can be dissolved in water, and also be used in solvent free condensation, it is a suitable candidate for green chemistry.

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NOVEL SYNTHETIC METHODOLOGY OF 1,2,3-TRIAZOLE-EMBEDDED COPOLYETHER POLYOL BY AZIDE- ALKYNE CLICK CHEMISTRY

Bum-Jae Lee, Kwon-Young Jung, Sun-Duk Ko, Ki-Yoon Lee

Department of Fine Chemical Engineering & Applied Chemistry, Chungnam National University,
Address : 220 Gung-dong, Yuseong-gu, Daejon, Korea, 305-764
E-mail : bjlee@cnu.ac.kr

***Keywords**: Click Chemistry, 1,2,3-triazole-embedded copolyether polyol, 1,2,3-triazolyl polyurethane.*

1,2,3-Triazole-embedded polyether polyols were synthesized using Cu(I)-catalyzed 1,3-dipolar cycloaddition[1] between the Glycidyl Azido (co)Polymer(GAP) and various alkynes involving phenyl acetylene, 1-pentyne, 3-bytyn-2-one at various temperatures. The GAP was converted easily with aromatic alkynes and aliphatic alkyne in high yield (>95%) in the presence of triethylamine(TEA) at room temperature in CH_2Cl_2/H_2O(1/1). But in the click chemistry with acetyl alkyne, it was found that azide-acylalkyne reaction was proceeded slowly even in high yield(>94%), in which TEA was not effective on this reaction rate and conversion.

Controlled synthesis of 1,2,3-triazolyl poly(GAP-co-THF)s having high viscous liquid phase were performed by this click reaction between poly(GAP-co-THF)([GAP]/[THF] = 1/1) and 1-pentyne at [azide]/[alkyne]/[$CuSO_4.5H_2O$]/[Na ascorbate]/[TEA] = 1/1/0.1/0.5/1 without any noticed change of polyol difunctionality. The poly(GAP-co-THF) was converted to 1,2,3-triazolyl poly(GAP-co-THF) in more than 95% yield within 6 hrs in CH_2Cl_2/H_2O(1 / 1), 2hrs in DMSO or DMF @ room temperature. The controlled poly(GAP-co-THF) was obtained by the S_N2 reaction of NaN_3 in DMF @ 100°C for 12 hrs with poly(ECH-co-THF), which was synthesized by cationic ring-opening polymerization of epichlorohydrin and THF using 1,4-butandiol/BF_3THF via activated monomer mechanism process.[2] The structure of synthesized 1,2,3-triazole-embedded copolyether polyols has been characterized by ^{1}H-NMR, ^{13}C-NMR, FTIR and GPC.

These 1,2,3-triazole-embedded polyols were applied to polyurethane cured with diisocyanate(IPDI) to investigate the cure properties and mechanical properties. These novel 1,2,3-triazole-embedded polyurethanes can be the promising new energetic binder for the improved castable explosives and propellants compared to GAP[3].

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EFFECT OF CELLULOSE NANOFIBER ADDITION TO A SEGMENTED POLYURETHANE WITH SHAPE MEMORY PROPERTIES

María Luján Auad*, Tara Richardson*, Norma Marcovich, Mirta I. Aranguren****

** Department of Textile Fibers, Auburn University, USA*
***INTEMA- Facultad de Ingeniería, Universidad Nacional de Mar del Plata, Argentina*
E-mail: marangur@fi.mdp.edu.ar

Keywords: *cellulose nanofibers, shape memory behavior, nanocomposite films.*

The effect of the addition of cellulose nanofibers to a synthesized segmented polyurethane (SPU) presenting shape memory properties was investigated. Shape memory polymers are materials capable of storing a deformed shape and self-recovering their original one as a response to an external stimulus, which in the present study corresponds to the heating of the sample above a "switch" temperature.

The polyurethane (PU) was synthesized in solution of dimethylformamide (DMF) using the usual technique of two step -synthesis, with toluene-diisocyanate (TDI), polytetramethylene-glycol (Mn=2900 g/mol) as the source of the soft segments domain and butanediol as chain extender. The cellulose nanofibers (CNF) were obtained by acid hydrolysis of microcrystalline cellulose (Avicel PH-101, FMC BioPolymer, U.S.A.) in concentrated sulfuric acid aqueous solution.[1] The nanocrystals obtained were washed, freeze dryed and re-dispersed in DMF. Previous studies carried out in our laboratories showed that incorporation of the CNF during the synthesis of the PU lead to covalent bonding between polymer and nanofibers with the consequent loss of the shape memory properties of the materials, an unwanted result.[2] Thus, the CNF were incorporated into the PU after completing the synthesis. Films of the neat PU and cellulose nanofiber composites were prepared by solution/suspension casting.

The resulting nanocomposites were rubbery elastic films that were tested to study their thermal, dynamic-mechanical and mechanical behavior, as well as their shape memory response.

The cellulose nanofiber concentration at the percolation threshold was determined from the rheological response of molten samples with different concentrations of cellulose (Figure 1) and it was found at ~0.93 wt.% of nanofibers.

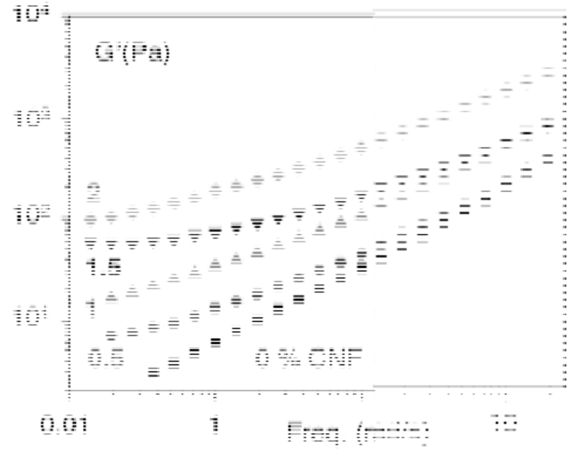

Figure 1. Freq. sweep of nanocomposite films.

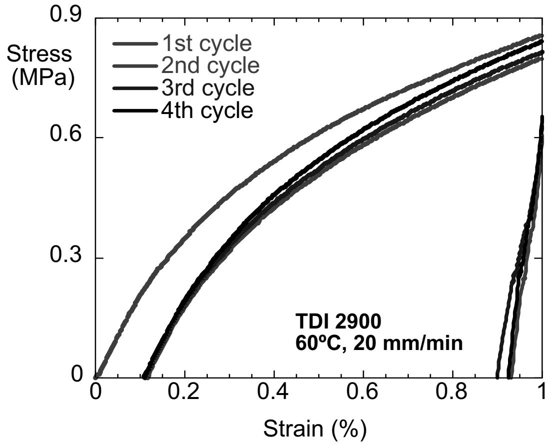

Figure 2. Thermal-tensile test cycling of PU

The shape memory capabilities of the nanocomposites were evaluated from the responses to thermal - mechanical cycling the samples under tensile requirements.[3] All the composites showed shape memory behavior with little differences with respect to the neat SPU (Figure 2).

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HIGH PERFORMANCE THERMALLY CURABLE POLYURETHANES CONTANING BENZOXAZINE OR NAPHTHOXAZINE GROUPS IN THE MAIN CHAIN

H. Yeganeh*, S. Mehdipour-Ataei, S. Jamshidi, A. Jangi

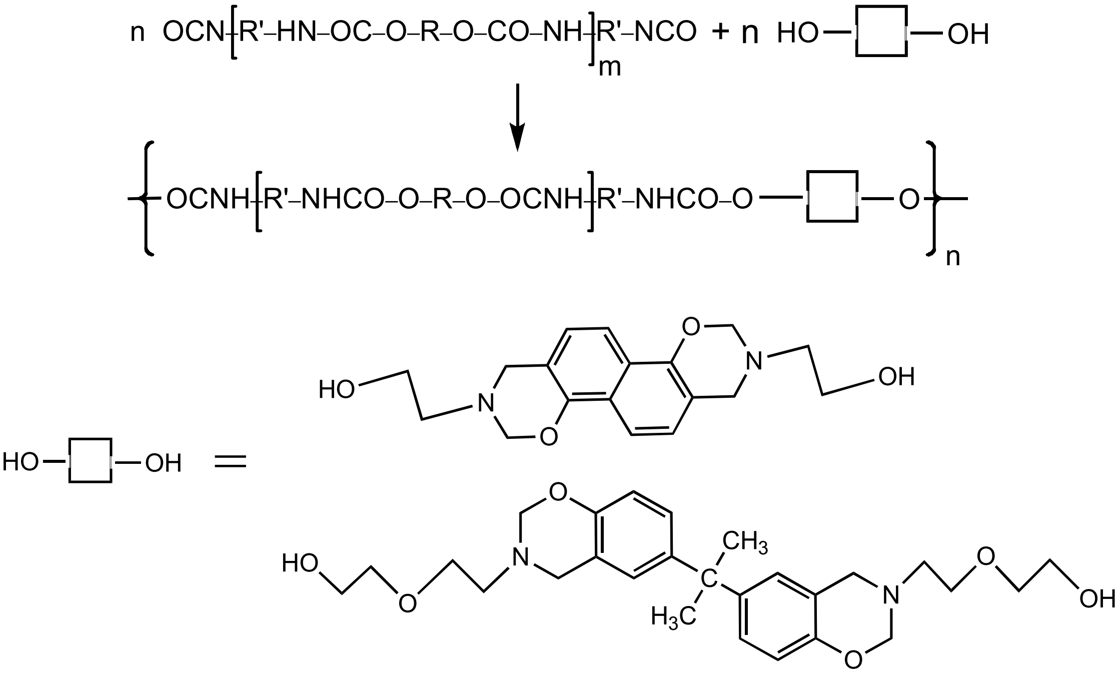
Polyurethane Department, Iran Polymer and Petrochemical Institute, PO Box: 14965/115, Tehran, Iran
E- mail: s.jamshidi@email.com

Keywords: *polyurethanes; polyoxazines; thermal stability*

Contrary to excellent thermal, electrical and chemical properties of polyoxazines, they suffer from high brittleness[1]. Also, despite attractive mechanical properties, low service temperature and low dielectric strength are some of shortcomings of polyurethanes for electrical insulation applications. For broadening the application windows of these materials and taking advantages of each class, their combination through a novel synthetic method is considered in this work.

Processable thermoplastic poly(urethane-benzoxazine)s and poly(urethane-naphthoxazine)s were prepared successfully via chain extension reaction of NCO-terminated urethane prepolymers with a benzoxazine or naphthoxazine diol. Under optimized thermal treatment, ring opening polymerization of oxazine moieties occurred and crosslinked networks obtained. Thermal, mechanical and electrical properties of prepared networks were evaluated and correlated to their structures. The results were compared with preistine polyurethanes and polyoxazines.

Due to good elongation property, significant enhancement in decomposition temperature, and high value of dielectric strength in comparison to neat polyurethanes, these newly developed materials can find potential applicability as high performance electrical insulators with service temperature higher than related unmodified polyurethanes.



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PREPARATION AND CHARACTERIZATION OF NOVEL SOLUBLE THERMALLY STABLE PYRIDINE-BASED POLYIMIDES CONTAINING AMIDE AND ETHER UNITS

Elahe Gharekhani*, Shahram Mehdipour-Ataei, Masoud Taghi-Ganji*****

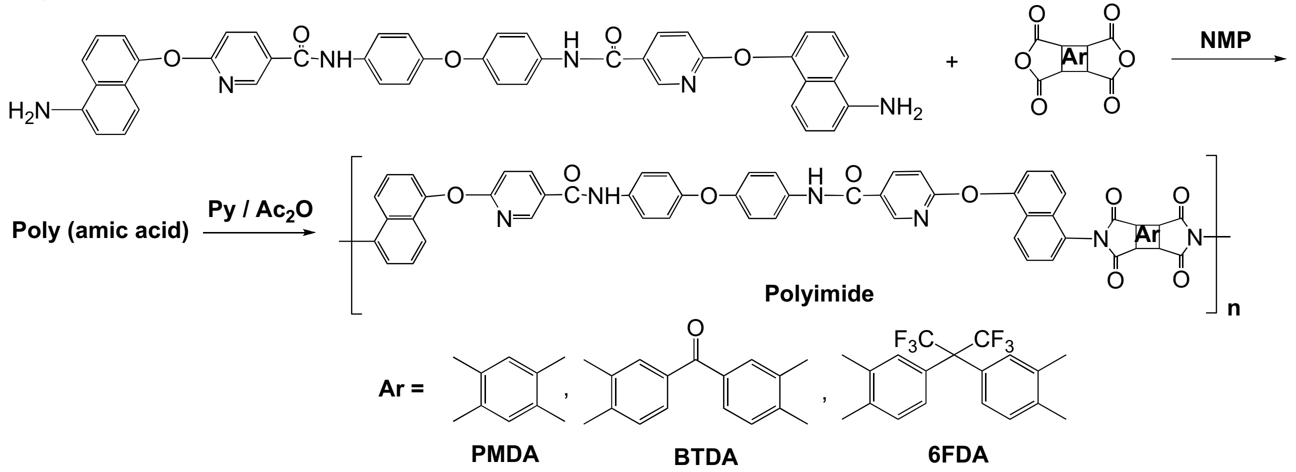
** Department of Chemistry, Islamic Azad University, Saveh Branch, Iran*
E-mail: e.gharekhani@yahoo.com
***Iran Polymer and Petrochemical Institute, P O. Box 14965/115, Tehran, Iran*
**** Department of Chemistry, Islamic Azad University, North Tehran Branch, Tehran, Iran*

Keywords: *polyimide; thermally stable; polycondensation*

Aromatic polyimides are well accepted as high performance polymers and they are well as high temperature resistant materials[1]. Polyimide materials are noted for their high thermal stability, solvent resistance, excellent insulating integrity, good mechanical strength, excellent dimensional stability, low coefficient of friction, high dielectric strength, low dielectric constant, low out gassing, and resistance to creep and wear[2]. However, they are generally insoluble and infusible. Almost all of the polyimides synthesized for the purpose of high temperature properties are difficult to process owing to their generally low solubility and high melting or glass transition temperatures. For balancing of the thermal stability and the processability numerous methods to obtain polyimides with chemically modified chain structures have been introduced. The most important methods include incorporation of hinge atoms or kink units or flexible spacer units either into the dianhydride fragment or diamine fragment or both[3,4].

Preparation of novel types of polyimides with specific properties was considered. In this way a new diamine was prepared by two consecutive reactions. Reaction of 4,4'-oxydianiline with 6-chloronicotinoyl chloride resulted in preparation of a dichloro diamide compound (DCDA) which was reacted with 5-amino-1-naphthol to afford the new diamine with specific structural features.

Polycondensation reaction of the diamine with various aromatic dianhydrides using two-step method yielded polyimides.



All the precursor, diamine (monomer), and polyimides were fully characterized using conventional methods and the physical and thermal properties of the polyimides including solution viscosity, thermal stability, thermal behavior, solubility, and crystallinity were investigated. Presence of flexible ether groups, pyridine polar parts, and bulky naphthyl units from one side and introduction of amide units and fully aromatic structures from the other side resulted in preparation of polyimides with improved solubility and high thermal stability. Therefore, the opposition of thermal stability versus solubility was effectively improved by designing of such a diamine and related polyimides.

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EFFECT OF TWO KINDS OF IONIC LIQUIDS ON THE KINETICS OF METHYL METHYLACRYLATE MICROEMULSION POLYMERIZATION

Yun-sheng Ding* , **Jingjing Lu, Wanggao Feng**

** School of Chemical Engineering, Hefei University of Technology, Hefei 230009, China*
▪ *E-mail: dingys@hfut.edu.cn*

Keywords*: microemulsion polymerization; imidazolium ionic liquid; methyl methylacrylate*

Microemulsion polymerization of methyl methylacrylate (MMA) was conducted in the presence of ionic liquids including 1-n-tetradecyl-3-methylimidazolium bromide([C_{14}mim]Br) and 1, 4-Bis (3-tetradecylimidazolium-1-yl) butane bromide, a kind of gemini ionic liquid, respectively. The microemulsion polymerization was conducted under the ionic liquids and ammonium persulfate as emulsifier and initiator respectively without co-emulsifier. After polymerization, the resulted latex particle size was studied by Malvern 2000 light scattering spectrophotometer. Meanwhile, the number-average molecular weight (Mn) and the molecular weight distribution (Mw/Mn) of PMMA were measured by a Waters 1515 gel permeation chromatography (GPC) equipped with microstyragel columns (10^3, 10^4 , 10^5Å) and Waters RI detector at 40°C, tetrahydrofuran (THF) was used as eluent at a flow rate of 0.3mL/min. Molecular weights were calculated based on monodispersed polystyrene standards (1mg/mL in THF).

We obtained the stable, bluish monodisperse microlatices with average particle diameter ranging from 17 to 60 nm, depending on the ionic liquids concentration and methyl methylacrylate content in microemulsion polymerization. The datum of the conversion–time curves with dilatometric method showed that polymerization apparent kinetics of MMA was directly correlated with the structure of imidazolium ionic liquid, MMA microemulsion polymerization rate(Rp) of gemini system ionic liquid was significantly higher than [C_{14}mim]Br system with the same mole of ionic liquids in initial stage of whole polymerization process(Fig.1). Tetradecyl trimethyl ammonium bromide (TTAB) and gemini surfactant of the alkanedyl-l,4-bis(dimethylalkylammonium bromide)type(m-s-m) with m being 16 and s being 4 used as surfactants were also involved for comparison.

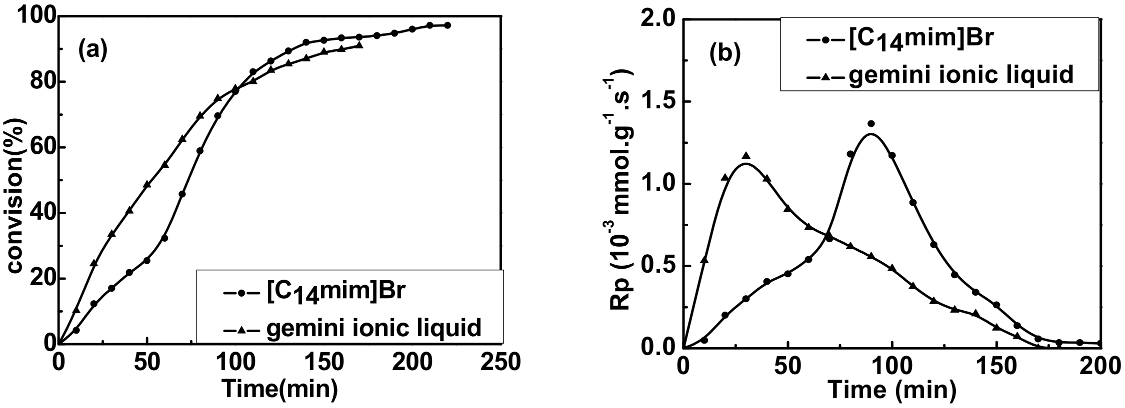

Fig.1. (a) Conversion versus time curves for the polymerization in MMA microemulsion with different ionic liquids (b) Polymerization rate versus time for the same samples shown in (a)

CHARACTERIZATION OF AMPHIPHILIC POLYMERS OF COMPLEX ARCHITECTURE USING DIFFERENT LIQUID CHROMATOGRAPHY MODES

Shazia Abrar, Bernd Trathnigg

Central Polymer lab, Institute of Chemistry, Karl-Franzens University of Graz, Heinrichstraße 28, A-8010 Graz, Austria
E-mail: shazia.abrar@edu.uni-graz.at

Keywords*: Amphiphilic star shaped polymers, characterization, Liquid chromatography.*

Amphiphilic molecules having complex architecture show very different elution behaviour as compared to the homopolymers and simple block copolymers [1, 2]. Some commercial polysorbates have very complex composition that is a mixture of different functionalities as has been characterized by SEC and different High performance liquid chromatography modes [3]. Star shaped and branched polymers with different length, number and functionality of the arms and nature of the core have been characterized using different modes of liquid chromatography; offline and online two-dimensional.

For offline two dimension separations; Reverse phase separations have been carried out in the Prodigy ODS3 column. Different ester functionalities were fractionated using fraction collector and then further analysed by Normal phase separation condition on Water Spherisorb column. Mobile phase composition conditions were optimised on the columns used for separation. For online two dimension separations: 1_{st} dimension separation mode is normal phase liquid adsorption chromatography on Spherisorb 5µ Silica and 2nd dimension separation mode is liquid chromatography under critical conditions [4]. The solvents (acetone, methanol and water, all HPLC grade) were purchased from Roth (Karlsruhe, Germany). Samples that were analyzed are the ethoxylates esters of Glycerol, Trimethyl propane, neopentyl glycol and some commercial polysorbates samples.

Functionalities of complex polymeric samples were studied under critical condition of the repeating units. Elution behaviour of different esters having similar hydrophilic repeating units but different central core have been determined. Liquid Adsorption Chromatography under critical conditions of the repeating hydrophilic units gives a very nice separations of different ester functionalities. The effect of central adsorbing block on the elution of esters with same repeating units was determined. For the samples with smaller number of hydrophilic units, a complete separation of esters according to the length of their hydrophilic block was obtained. For the star shaped polymers having different length of the arms but overall same number of the hydrophilic units, a separation according to the symmetry was also observed. The separated fractionalities were then further analysed for the detailed study of their structure. Comparison of offline and online two dimensional characterization approaches and study of the elution behaviour under various separation conditions has been made. A complete picture of the polymers architecture has been obtained successfully.

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DETERMINATION OF CHEMICAL COMPOSITION DISTRIBUTION OF ETHYLENE-METHYLMETHACRYLATE AND ETHYLENE-BUTYLACRYLATE COPOLYMERS BY CRYSTAF AND HIGH-TEMPERATURE HPLC

Rajesh Chitta*, Vincent Monteil, Etienne Grau**, Christophe Boisson**, Robert Brüll*, Tibor Macko***

**German Institute for Polymers (Deutsches Kunststoff-Institut), Schlossgartenstr. 6, 64289 Darmstadt, Germany*
***Laboratoire de Chimie et Procédés de Polymérisation, Bâtiment 308F, 43, Bd du 11 Novembre 1918, B.P. 2077, 69616 Villeurbanne Cedex, France*
E-mail: RChitta@dki.tu-darmstadt.de

Keywords: *ethylene-butyl acrylate; ethylene-methyl methacrylate; high temperature liquid chromatography (HT-HPLC).*

The knowledge of chemical heterogeneity and chemical composition distribution are crucial to establish structure property relationships. The CCD of functionalized polyolefines is routinely analyzed by Temperature Rising Elution Fractionation (TREF) or Crystallization Analysis Fractionation (CRYSTAF) techniques.[1-3] In both the separation is based on the crystallization of the macromolecules from a hot solution, so copolymers with low crystallinity or amorphous in nature can not be characterized by these techniques. Moreover, these techniques are very time consuming. With the aim to obtain additional information, fractions prepared by preparative TREF are analysed by DSC, NMR and FTIR spectroscopy. Distribution of the chemical composition along the molar mass axis may by obtained by coupling SEC-FTIR.[4]

High-performance liquid chromatography (HPLC) is an important tool for the fast separation of complex polymers with regard to chemical composition.[5,6] The majority of published HPLC methods are conducted at operating temperatures of up to 60°C. These temperatures are too low for the dissolution of many types of polyolefins, which require at least 120 °C for dissolution due to their semicrystalline nature. Recently several high-temperature HPLC systems for the analysis of copolymers composed of ethylene and polar comonomers were developed by our group.[7-11] It was shown that semi crystalline as well as amorphous functionalized polyolefins could be analysed with the high-temperature adsorption liquid chromatography. The HPLC separation is governed by the chemical composition of the copolymers.

We have analysed a series of ethylene-methylmethacrylate and ethylene-butylacrylate copolymers by both high-temperature HPLC and conventional techniques, such as DSC and CRYSTAF and the obtained results were compared.

It was found that only some of the samples could be analysed by CRYSTAF or DSC, as majority of the samples were amorphous. On the other hand, exclusively, HPLC technique was able to characterize all the samples irrespective of crystallinity and also revealed presence of homopolymers in some polymer samples as well as the chemical heterogeneity of the copolymers. The results demonstrate advantages and importance of HPLC to meet the requirements of new and improved analytical techniques for the characterization of chemical composition distribution of new tailor-made polyolefins.

The results from conventional analytical techniques as well as from HPLC analytical system will be presented in the poster.

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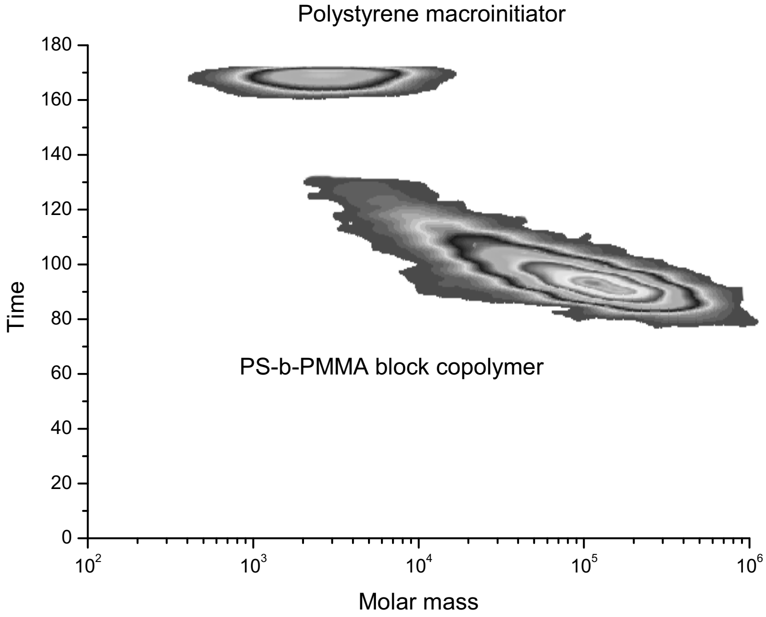
2-D CHROMATOGRAPHIC ANALYSIS OF POLYSTYENE-BLOCK-POLY(METHYLMETHACRYLATE) COPOLYMERS SYNTHESIZED USING BORANE CHEMISTRY

Wael K. Elhrari,* Peter E. Mallon*

**Department of Chemistry and Polymer Science, University of Stellenbosch, Private Bag X1, Matieland, 7602, South Africa*
E-mail: wael@sun.ac.za

Keywords: *block copolymers, 2D chromatography, 9-borabicyclo[3.3.1]nonane (9-BBN).*

A novel route to prepare polystyrene block methylmethacrylate copolymers (PS-b-PMMA) is described. The polystyrene segment is prepared by living anionic polymerization techniques [1] and the methylmethacrylate segment is prepared via free radical autoxidation of a borane agent attached to the styrene chain [2]. The chemistry involves a transformation of the anionic polymerization process to borane chemistry by firstly producing polystyrene with chain end unsaturated alkyl functional groups prepared using a *n*-butyllithium, initiator and termination with allylchlorodimethylsilane. Secondly, the unsaturated macroinitiator end was hydroborated by 9-borabicyclo[3.3.1]nonane (9-BBN) to produce a borane terminated PS. Thirdly, the borane group at the chain end was selectively oxidized and converted to polymeric radicals in the presence of methylmethacrylate which then initiated radical polymerization to produce block copolymers. Several block copolymers with different methyl methacrylate block lengths were synthesis. The autoxidation reaction of hydroboranated styrene macromonomer was initiated by injecting controlled amounts of dry (O_2). High or low mols of O_2 injected in the reaction mixture will spoil the reaction and no block formation occurs. The overall mols% O_2 added was kept to less than the mols% of 9-BBN.The produce copolymers were characterized using several chromatographic techniques include LC-CC (liquid chromatography under critical conditions) for both segments and two-dimensional chromatography with LCCC in the first dimension and SEC in the second. The results show that block formation was successful with most polystyrene chains undergoing block formation.



2D-LC contour plots for block the copolymer. First dimension: critical conditions for PS; second dimension: SEC. the compositions of eluents at the critical condition were 51.7/48.3 (ACN/THF) vol%. The stationary phase used was symmetry C18 5μm and nucleosil C18 columns.

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CHROMATOGRAPHIC SEPARATION OF COPOLYMERS ACCORDING TO THEIR TACTICITY

Tibor Macko*, **Francesco Cutillo****, **Vincenzo Busico****, **Robert Brüll***

** German Institute for Polymers (Deutsches Kunststoff-Institut), Schlossgartenstr. 6, 64289 Darmstadt, Germany*
***Laboratory of Stereoselective Polymerizations, „Paolo Corradini" Department of Chemistry, Federico II University of Naples, Via Cintia - Complesso di Monte S. Angelo - 80126 Napoli, Italy*
E-mail: TMacko@dki.tu-darmstadt.de; francesco.cutillo@unina.it

Keywords: *tacticity, polypropylene, adsorption.*

It is known that liquid chromatography enables to separate stereoregular polymers according to their tacticity. Inagaki and co-workers were the first to report the separation of polymethyl methacrylate according to tacticity by thin layer chromatography.[1] Berek et al. have separated polymethyl methacrylate[2,3] and polyethyl methacrylate[4,5] according to tacticity using liquid chromatography at critical conditions. Similar separations have also been realized by temperature gradient interaction chromatography by the group of Chang.[6]

Although tacticity play a substantial role in polypropylene and other polyolefins, corresponding HPLC methods separating according this parameter were missing. CRYSTAF[7] and precipitation-dissolution of polypropylene in different solvents and at different temperatures[8] lead to a partial separation of polyolefins according to their tacticity.

Measurements of several groups[9,10] led to conclusion that long chain n-alkanes are strongly and preferentially adsorbed onto the graphite basal plane as a consequence of strong lateral interactions between long-chain molecules adsorbed side-by-side on the flat graphite surface. Taking this conclusion into account, we have tested porous graphite as adsorbent for polyolefins. It was found that atactic and syndiotactic polypropylene are strongly adsorbed on graphite from 1-decanol at temperature as high as 160 ^{o}C, while isotactic polypropylene is not retained at all.[11,12] Moreover, linear polyethylene is also fully adsorbed. Polypropylene contains methyl groups in different steric positions and these methyl groups prevent the polypropylene chains to form closely packed layers on the planar surface of graphite because of steric hindrance. Therefore polypropylene with different tacticity show quantitatively different adsorption behaviour from polyethylene on graphite.

The high-temperature gradient adsorption liquid chromatography represents a novel approach for the separation of polyolefins. The basis of this method is adsorption and desorption of polyolefins at high temperature. In this work we will describe application of adsorption HPLC on separation of various stereoregular copolymers. Samples of polypropylene with various tacticity as well as syndiotactic / isotactic polypropylene copolymers have been analysed by high-temperature gradient HPLC. A correlation between the elution volumes and the average values of tacticity obtained with NMR spectroscopy has been found.

Acknowledgements

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SEPARATION OF POLYETHYLENE AND POLYPROPYLENE WITH HIGH-TEMPERATURE LIQUID CHROMATOGRAPHY

Rajesh Chitta*, Tibor Macko*, Robert Brüll*, Yongmei Wang, Anton Ginzburg***

** German Institute for Polymers (Deutsches Kunststoff-Institut), Schlossgartenstr. 6, 64289 Darmstadt, Germany*
** * Department of Chemistry, University of Memphis, Memphis, 38154 TN, USA*
E-mail: RChitta@dki.tu-darmstadt.de

Keywords: *polyethylene, polypropylene, adsorption.*

Application of HPLC techniques for the characterization of chemical composition distribution (CCD) of polyolefin materials could not only speed up their analysis but also information about amorphous part of polyolefin samples could be obtained. As it is known the most used techniques for determination of CCD of polyolefins are TREF and CRYSTAF. Both techniques are based on crystallization, i.e., amorphous samples are not selectively separated.

Only very few sorbent-solvent systems are known until today, where precipitation or adsorption of polyolefins in a HPLC column at temperatures above 100 °C has been observed. Such chromatographic systems have been only recently applied for separation of blends composed of polyethylene and polypropylene[1-5] or ethylene-propylene copolymers[6,7].

With the aim to find additional HPLC systems for separation of polyolefins, we have tested several solvents as both the sample solvent and the mobile phase in combination with several sorbents. Polystyrene/divinylbenzene (PS/DVB) particles, PS/DVB with chemically bonded octadecyl groups, porous graphite, zirconium oxide covered with carbon and oligo(dimethylsiloxane) modified silica gel were used as the column packing. Polyethylene and polypropylene eluted without retention (in size exclusion chromatography mode) in many polar mobile phases. We have found, however, that use of some polar liquids as the mobile phase leads to a pronounced partial or full retention of polyethylene and polypropylene in specific HPLC columns. The polymers could be eluted from the column packings after change of the mobile phase using a linear gradient starting from the tested solvent and ending with pure 1,2,4-trichlorobenzene. Sample dissolving, injector and column oven temperature were in between 140 and 160 ^{o}C.

The elution behaviour of the polymer standards in the described chromatographic systems will be illustrated in this poster. Several new solvent-sorbent systems, which enable adsorption and the following desorption of polyethylene and polypropylene were identified. It will be shown that some sorbent-solvent systems possess different selectivity: For example, while isotactic polypropylene is retained in one system, it is not retained in another system. This is of interest in practical applications of HPLC analysis of polyolefins.

Acknowledgement
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CHARACTERISATION OF BLENDS OF POLYISOPRENE BY ON-LINE HYPHENATION OF CRITICAL CHROMATOGRAPHY AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Pritish Sinha*,* , Wolf Hiller**, Harald Pasch *,*****

**Deutsches Kunststoff Institut, Schlossgartenstr 6, 64289 Darmstadt, Germany*
***Technische Universität Dortmund, Otto-Hahn-Strasse 6, 44227 Dortmund, Germany*
**** University of Stellenbosch, Institute for Polymer Science, Private Bag X1, Matieland, 7602, South Africa*
E-mail: hpasch@sun.ac.za

Keywords: *HPLC-NMR, polyisoprene blends, microstructure analysis*

On-line coupling of HPLC-NMR is a powerful tool for the analysis of complex polymer mixtures. SEC-NMR was used for the analysis of poly(methyl methacrylate) and block copolymers of poly[(methyl methacrylate)-co-(butyl methacrylate)] according to their chemical composition [1-2]. We have recently published the application of liquid chromatography at critical conditions (LCCC) with NMR for the complete characterisation of PS-*b*-PMMA copolymers and the blends of homopolymers of both PS and PMMA by operating at the critical conditions of both PS [3] and PMMA [4].

Blends of 1,4-polyisoprene and 3,4-polyisoprene were analysed by on-line hyphenation of liquid chromatography at critical conditions and ^{1}H-NMR. Chromatography at critical conditions was established for 1,4-polyisoprene by using MEK-cyclohexane solvent composition of (90-10). At this solvent composition 1,4-PI samples elute at the same retention volume whereas the 3,4-PI samples show size exclusion chromatography behaviour in which the 3,4-PI samples with higher molar mass elute earlier followed by samples of lower molar masses as shown in the Figure below. At these critical conditions a complete separation into the blend components was achieved. Using NMR as detector the microstructure of polyisoprene was identified and quantified.

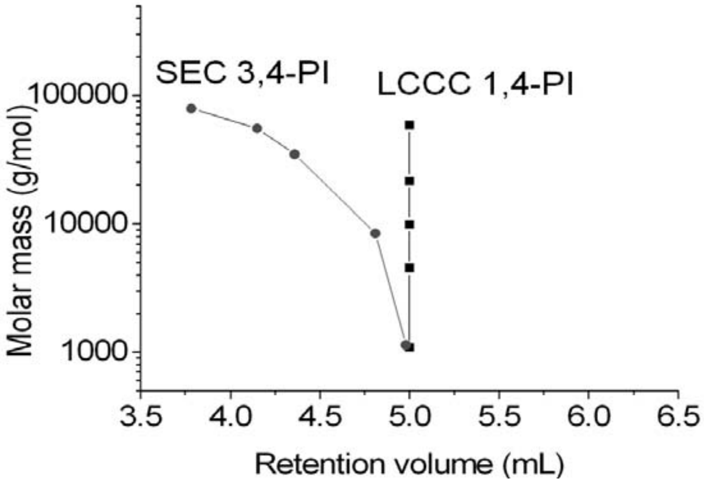

Fig.1: Critical conditions of 1,4-PI and size exclusion chromatography behaviour of 3,4-PI showing molar mass versus retention volume at a mobile phase composition of MEK-cyclohexane ■ = 90:10, ● **=** 90:10

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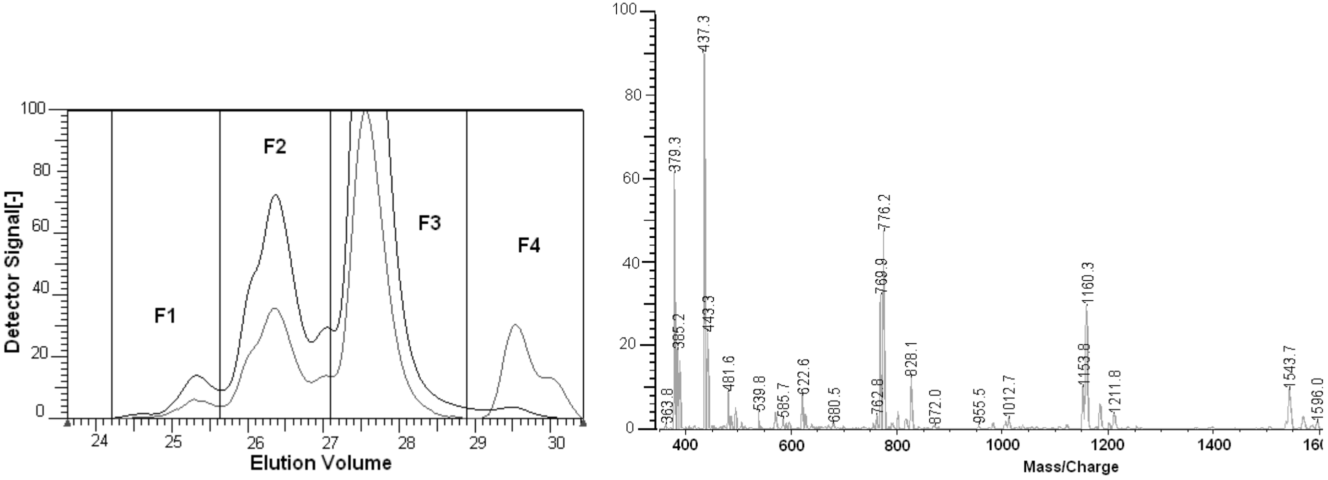
THE COMBINATON OF LIQUID CHROMATOGRAPHY AND MASS SPECTROMETRY TECHNIQUES FOR THE CHARACTERIZATION OF ALIPHATIC POLYESTERS

Nadine O. Pretorius[1], **James B. McLeary**[2], **Harald Pasch**[1]

1. UNESCO associated Centre for Macromolecules and Materials, Department of Chemistry and Polymer Science, University of Stellenbosch, Private Bag X1, 7602 Matieland, South Africa
2. Freeworld Coatings Research Centre
E-mail: jmcleary@sun.ac.za;

Keywords: *Polyesters, HPLC, MALDI-TOF MS*

Complex polymers are distributed with respect to chain length (molar mass), chemical composition, functionality and molecular topology [1] thus polymer properties are very frequently determined not only by one of these distributions but by the correlation of two or more distributions. Aliphatic polyesters are industrially implemented in high performance coatings, paints and varnishes, however it is typically difficult to correlate the resulting properties with the synthesis parameters as these polymers vary in reactivity and application properties. Due to the stepwise polymerization mechanism, it is often assumed that the synthesis of copolyesters by direct polyesterification will lead to randomized products. The formation of cyclic products by intramolecular reactions of hydroxylic (OH) and carboxylic (COOH, acid) functional groups, including side-reactions such as transesterification, alcoholysis, ester-ester interchange allow even further randomization, enabling a highly complex system. Polyesters exhibit functionality type distributions and branching distributions in addition to the molar mass distribution. The functionality type distribution influences the reactivity of the system while branching affects the flow properties. Thus the properties are determined by not only one but by the correlation of two/more distributions. The different methods of polymer chromatography are useful tools for analyzing the molecular distributions, in combination with sophisticated spectroscopic techniques (FTIR, NMR, MS) the molecular heterogeneity of complex polymer can be fully described [2]. The present study entails method development of interaction chromatography and its combination with the mentioned analytical techniques to facilitate the analysis of the various distributions obtained during the synthesis of model condensation polymers. Two simple aliphatic polyesters, which serve as building blocks for the more complex industrial variety, were investigated. Sample batches included polyesters synthesized from Phthalic and Maleic Anhydride respectively, in combination with propylene glycol, with varying percentages of monomer incorporation. SEC, HPLC and its combination via off-line coupling to MALDI-TOF MS revealed the presence of several distributions of varying functionality type and molar mass at different intervals throughout the polymerization reaction. Only the combination of the different coupling techniques provided the opportunity of more in-depth analysis of structure-property relationships.



Size-exclusion Chromatogram of a poly(propylene o-phthalate and the MALDI-tof MS of F3 (fraction three).

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SOLUTION CRYSTALLIZATION ANALYSIS BY LASER LIGHT SCATTERING (SCALLS)

Margaretha Brand*, Albert van Reenen*, Eric Rohwer**

** Department of Chemistry and Polymer Science, University of Stellenbosch, South Africa*
***Laser Physics Institute, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa*
E-mail: maggie@sun.ac.za

Keywords*: solution crystallization, laser light scattering, polyolefins*

Understanding polymers and their behaviour is very important for academics and industry. Various techniques for characterizing polyolefins do exist. Based on the work done by Shan[1] et al we built an instrument to study polymers in solution during heating and cooling cycles directly. SCALLS has proved to give detailed information about the crystallization and dissolution/melting of the polymer depending on the type of temperature cycle used. Molecular weight effects on the crystallization of polyolefins have been studied with interesting results[2]. Information is obtained directly by use of lasers and thus more detail and in certain cases better resolution compared to traditional techniques with longer analysis time[3]. For the first time the solution melting temperature of polyolefins was measured and some fundamental studies have led from this including looking at the applicability of the Flory-Huggins equation in predicting the crystallization behaviour of polyolefins in solution. The Flory-Huggins equation for the free energy of mixing can be used to describe the thermodynamic equilibrium of a polymer solution assuming the solution is homogenous; i.e. there is a uniform distribution of solvent and polymer segments[4,5].

According to the work of Mandelkern[6] and Anantawaraskul et al[7] the Flory-Huggins equation can be re-written as $\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u} \frac{V_u}{V_1}\left(\nu_1 - \chi_1 \nu_1^2\right)$. In the past, the crystallization temperature was substituted for the pure polymer (T_c^0) and the crystallization temperature for the polymer in the presence of solvent (T_c) for the corresponding melting temperatures. Brüll et[8] al illustrated that as the comonomer content affects the crystallizability (and melting temperature), plotting: $\frac{1}{T_c} - \frac{1}{T_c^0}$ vs $\frac{1}{\text{Comonomer content}}$ should result in a straight line. It occurred to us that having the ability to directly measure the solution melting temperature by SCALLS, we could test if the assumptions made with respect to using the Flory-Huggins equation for copolymers holds true. We therefore decided to evaluate a similar series of copolymers using SCALLS and to plot $\frac{1}{T_m} - \frac{1}{T_m^0}$ against $\frac{1}{\Delta H_u}$, or against the inverse of the comonomer concentration. It was found that using the solution melting temperature as originally intended a power curve relationship is obtained. From this we can deduce that the amount of comonomer affects the solubility of the polymer in a non-linear way.

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STUDY OF TERTIARY CRYSTALLIZATION PROCESS AND MORPHOLOGY IN LLDPE AND HDPE

Triinu Poltimäe*, **Elvira Tarasova***, **Andres Krumme***, **Arja Lehtinen****, **Anti Viikna***

** Department of Polymer Materials - Tallinn University of Technology, Address: Ehitajate tee 5, 19086 Tallinn, Estonia, E-mail: triinu.poltimae@ttu.ee*
*** Borealis Polymers OY, P.O. Box 330, FIN-06101, Porvoo, Finland, E-mail: lehtinen.arja@elisanet.fi*

Keywords: *polyolefins, fractions, crystallization.*

The non-isothermal and isothermal crystallization behavior of Ziegler-Natta (ZN) and single site (SS) based ethylene/1-butene and ethylene/1-hexene copolymers (named as linear low density polyethylenes, LLDPE, in general) as well as high density polyethylene (HDPE) and their molar mass (MM) and compositional fractions has been studied by differential scanning calorimetry (DSC). It was observed in non-isothermal DSC scans that for molar mass fractions with MM larger than 10 kg/mol in addition to the dominant high-temperature crystallization peak (HTCP) and low temperature crystallization peak (LTCP), a very-low temperature crystallization peak (VLTCP) is present at temperatures in between 60-75°C. Such peak is absent for the lowest MM fractions. The remarkable fact is the absence of melting peak in DSC endotherms directly corresponding to VLTCP.

The partial crystallinity and peak temperatures, obtained from VLTCP, increase with MM and level off at MM around 60-100 kg/mol. At the same time the crystallinity of HTCP decreases with MM that involves a molecular correlation between the primary and secondary crystallization processes. It was found that the crystallinity as related to the area of the VLTCP is catalyst type dependent, and is higher for the SS catalyst compared to the ZN. Within the same type of catalyst (ZN) the VLTCP crystallinity is larger for LLDPE than for HDPE. Peak temperature of VLTCP linearly decreases with increasing comonomer content while the VLTCP crystallinity practically does not change with comonomer content.

Because there is a clear correlation of both peaks (HTCP and VLTCP) with molar mass, it is implicit that these exotherms (especially the VLTCP) are also a consequence of melt topology; in other words, entanglements. Then, the key to the presence of this VLTCP exotherm will not be only the sequence distribution caused by the comonomer, but also the melt topology that restricts the crystallization after a primary nucleation and further (usually spherulitic) growth in most semicrystalline polymers [1]. The increase in VLTCP crystallinity with MM leads us to suggest that inter-crystalline links are responsible for the formation of the VLTCP. During crystallization numerous tie molecules are formed especially at rather large supercooling. These tie molecules can aggregate locally to form inter-crystalline links (named us as bundles) [2].

From the annealing experiments used to predict the morphology of studied fractions it was suggested that studied copolymers along with lamellar crystals contains some portions of bundled-like crystallites. The fractions of SS sample were also studied by hot-stage microscopy to obtain the crystallization kinetics. The morphological evolution of fractions with MM is presented.

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ISOTHERMAL CRYSTALLIZATION OF POLYMERS BY DEPOLARIZED LIGHT INTENSITY. POSSIBILITIES AND LIMITATIONS.

Pawel Sajkiewicz*, Beata Misztal-Faraj, Arkadiusz Gradys

Institute of Fundamental Technological Research, Polish Academy of Sciences, Pawinskiego 5B, 02-106 Warsaw, Poland
email: psajk@ippt.gov.pl

Keywords: *Crystallization, light depolarization intensity, polymers*

As yet, the measurements of depolarized light intensity were based on the single crystal formula assuming direct proportionality between depolarization ratio and degree of crystallinity. It has been shown recently [1, 2] that this traditional way of interpretation is incorrect. According to Ziabicki et al. [1, 2], depolarization ratio, *J*, of the system of stacks containing parallel birefringent plates randomly oriented in the sample plane, is a non-linear function of the product of the degree of crystallinity, *x*, function of average crystal dimensions, *d*, and optical birefringence of crystal, Δn_c. Degree of crystallinity, *x*, is given by:

$$x \cong \frac{-\ln(1-J)}{\sin^2\left(\frac{\pi\ \Delta n_c\ d}{\lambda}\right)} \cdot \frac{d}{B}$$

where B is sample thickness and λ - wavelength of the incident light.

Our paper is focused on testing of the light depolarization technique (LDT) for the analysis of kinetics of phase transition using our new setup and the new method of data interpretation. Our setup [3] allows direct, on-line recording of depolarization ratio instead of intensity of separate components, parallel and perpendicular, as it is performed in common apparatus. Isothermal crystallization of poly(vinylidene fluoride), isotactic poly(propylene), and high density poly(ethylene) was investigated. In addition to LDT, wide- and small angle X-ray scattering (WAXS, SAXS) and differential scanning calorimetry (DSC) experiments were performed. SAXS measurements allowed determination of crystal thickness during isothermal crystallization while WAXS and DSC results provided us with crystallinity for comparison with LDT results.

The results show that the use of our new setup with direct registration of depolarized light intensity together with the new model for data interpretation provides potential opportunity for quantitative analysis of kinetics of crystallization. The advantage of LDT relies on a lack of inertia effects existing in some methods like calorimetry as well as on high sampling rate. There are however several limitations of the applicability of this method. It can be applied to systems having optically isotropic amorphous matrix. The second problem is that determination of crystallinity from LDT needs in general supplementary measurements of crystal thickness and crystal birefringence by other methods. This is particularly the case of isothermal crystallization at relatively low temperatures where the crystals are not only thinner but can posses relatively low birefringence due to high concentration of defects. Comparison of depolarization results with WAXS and DSC crystallinity, indicate that LDT can be practically applied for crystallization at relatively high temperatures. In such case, it is sufficient to use as birefringence of real crystals theoretical values of crystal intrinsic birefringence and constant (final) value of crystal thickness for particular temperature, making the whole procedure relatively simple. Application of constant crystal thickness for the whole process of isothermal crystallization will result in small error in crystallinity determination at the beginning of crystallization.

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SEMI-CRYSTALLINE STUDY AND DIELECTRIC PROPERTIES OF LOW-K POLY-TETRAFLUORO-P-XYLYLENE (VT-4) FOR MICROELECTRONIC APPLICATIONS

A. Kahouli*,, A. Sylvestre*, F. Jomni**, B. Yangui**, J-F. Laithier***, B. Berge****, J-C. Robert****, N. Garcia****, J.Legrand******

** Grenoble Electrical Engineering Lab. (G2Elab), CNRS, 25 Rue des Martyrs, BP166, 38042 Grenoble, Cedex 9, France*
*** Laboratory for Materials, Organization and Properties (LabMOP), Campus Universitaire-El Manar, 2092 Tunis, Tunisia*
**** Comelec SA, Rue de la Paix 129CH-2301 La Chaux-de-Fonds, Switzerland*
***** Varioptic SA, Bâtiment Tony Garnier, 24A Rue Jean Baldassini, 69007 Lyon, France*
E-mail: alain.sylvestre@grenoble.cnrs.fr

Keywords*: parylene-F, dielectric properties, low-k dielectric interconnect*

Poly(tetrafluoro-p-xylylene) or parylene-F, also called parylene-VT4, is a linear organic polymer consisting of four aromatic fluor atoms and two methyl groups. The chemical structure of VT-4, which is the following one ($[-(-H_2C-C_6F_4-CH_2-)-]_n$), shows that these films are non-polar due to the high symmetry of this material. This polymer has been deposited in thin film at room temperature by vapor deposition polymerization (VDP). XRD-patterns show that the as-deposited VT-4 films are semi-crystalline (55% with grain size = 90 Å) and composed of the hexagonal β-crystalline phase (d_{hkl} = 4.89 Å). Low relative permittivity (*k* ~ 2.2) and high thermal stability up to 450°C[1] makes the VT4 to constitute an interesting material to compete with porous low-*k* for dielectric interconnects. Changes in the dielectric constant and losses with frequency and temperature are of interest to predict reliability and optimize the device in which this material will be integrated.

In our study, dielectric spectroscopy measurements were recorded in the frequency range 0.1 – 10^6 Hz and in a large interval of temperature 20 – 400°C.

From room temperature to the glass transition T_g = 60°C, VT-4 presents a large peak attributed to the β-relaxation, which takes place over five decades observed in the variation of dissipation factor according to frequency.

In the temperature range 60°C – 100°C, the full width at half maximum (FWHM) of this peak decreases and the amplitude increases as the temperature goes up until 100°C. In order to understand phenomena responsible for this last trend, different thermal protocols have been carried out. Results emphasize that the peak occurring at 80°C has irreversible character. The trends of dielectric permittivity and the dissipation factor according to the temperature show that parylene-VT4 presents a transition in the dielectric properties. This transition is not corroborated to XRD analysis which reveals no phase transition in the structure after the application of thermal protocols. So, this process is probably attributed to an electrode effect due to ionic conduction in the polymer or a diffusion of some oligomers. This last assumption seems reasonable. Indeed, FEG microscopy performed on these materials show the presence of some 'agglomerate free chains' at the surface of parylene-VT4. These 'agglomerate free chains' could consist of oligomers. Activation energy calculated for this relaxation process is about 3 eV. This value is conventional for interfacial effects due to monomers or oligomeric species.

Finally, a last relaxation peak observed at low frequency and high temperature (>350°C) has been attributed to a Maxwell-Wagner-Sillars (MWS) relaxation induced by the trapping of F^- ions at the amorphous – crystalline interfaces. This MWS effect is clearly identified by the electric modulus *M* formalism. The maximum frequency of the imaginary part of the electric modulus (*M''*) obeys an Arrhenius-type law with activation energy of about 1.6 eV.

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CHARACTERIZATION OF POLYSULFONAMIDE IN DILUTE SOLUTION BY LASER LIGHT SCATTERING

Ye Chen, Wantao Wu, Yumei Zhang*, Huaping Wang

State Key Laboratory for Modification of Fiber Materials.-Donghua University, Address: 2999, North Renming Road, Songjiang Area, Shanghai, 201620 China
E-mail: tedchancy@mail.dhu.edu.cn, zhangym@dhu.edu.cn

Keywords: *polysulfonamide, laser light scattering, random coil, molecular weight*

Polysulfonamide (PSA) copolymer, due to its excellent flame retardancy and good mechanical performance, has been commercialized to manufacture fibers as a trade name of TANLON by Shanghai Tanlon Fiber Co., Ltd. The fibers are widely used as protective textiles, filters, insulation materials, and also applied to aerospace engineering and munitions industries. PSA exhibties good solubility and spinnability in some polar organic solvents, which also faciliates its manufacture. However, the phsicochemical propertes of PSA in the organic solvent have not been reported. Up to now, the characterization of PSA in solution is limited to the measurement of the molecular weight, which was usually determined by the intrinsic viscosity.

Herein, the solution behaviors of poly(3,3'-diphenylsulphone terephthalamide) in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were firstly studied by laser light scattering (LLS), both static light scattering (SLS) and dynamic light scattering (DLS). From SLS measurment, the radius of gyration R_g, the molecular weight M_w and the second virial coefficient A_2 were obtained. The positive values of A_2 indicate that both DMSO and DMF are good solvents for PSA. The persistence length ρ, calculated from the Benoit-Doty equation, was 3.9 nm in DMSO and 4.8 nm in DMF, suggesting that PSA was flexible chains in these solvents. From DLS measurement, the hydrodynamic radius R_h of PSA in DMF and DMSO were obtained. And the value of R_g/R_h is about 1.8 both in DMF and DMSO, which indicated that single PSA chain was in random coil conformation.[1]

Furthermore, we combined the LLS results with GPC results, intrinsic viscosity, as well as the DP degree calculated from conversion of polymerization, and established a systematic molecular weight characterization of this polymer. Besides, we combined LLS and molecular dynamic simulation, and illustrated the conformation of this macromolecule in dilute solution. The length of the repeat unit of poly(3,3'-diphenylsulphone terephthalamide) chain was calculated to be l = 1.628 nm from compute simulation. Then combining the persistence length obtained from LLS results, the characteristic ratio C_∞ was calculated about 4.8 for PSA in DMSO while 5.8 in DMF which also indicated PSA was flexible chains. If the assumption of a freely rotating chain of PSA in solvents was given, the rotation angle could be obtained. And the value was about 135^o in DMSO and 130^o in DMF. The chemical defects and/or twists as well as an inherent torsional flexibility can reduce the chain stiffness.[2] We proposed that though the benzene rings are the main structure in PSA backbone, the existence of amide group, carbon-carbon single bond, carbon-sulfide linkage in backbone make the internal rotation of molecule easier, and the PSA chains twist at a definited rotation angle in dilute solution.

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CHARACTERIZATION OF POLYELECTROLYTE COMPLEXES OF OPPOSITELY CHARGED POLYMETHACRYLATE COPOLYMERS PREPARED IN METHANOL.

Akpa, Paul Achile*,**Okore,Vicent Chima****, **Attama, Anthony Amaechi****

Department of Pharmaceutics, Faculty of Pharmaceutical Sciences, University of Nigeria, Nsukka.I 410001, Enugu State.Nigeria.
E-mail: paul.akpa@unn.edu.ng

Keywords: *Characterization, Polyelectrolyte complexes, Polymethacrylates.*

Traditionally, polyelectrolyte complexes are synthesized in aqueous systems and the preparation and characterization of these complexes in organic solvents have not been studied extensively(1). Two oppositely charged polymethacrylate copolymers namely EUDRAGIT® E 100 which is a cationic copolymer based on dimethylaminoethyl methacrylate and neutral methacrylic esters and EUDRAGIT L100-55 which contains an anionic copolymer based on methacrylic cid and ethyl acrylate, were brought together in an appriopiate vessel to interact (2).These copolymers are widely used as coatings and matrix forming materials in the pharmaceutical industry(3).

Polyelectrolyte complexes of these copolymers were prepared by mixing solutions of the individual copolymers in methanol and collecting the precipitate produced after allowing for a sustained interaction between the copolymers for a duration of one hour at room temperature. The white precipitate produced at the end of the reaction which is deemed to be the interpolyelectrolyte complex formed as a consequence of the reaction between the copolymers. It was subjected to turbidimetric analysis with a view to ascertaining the stoichiometry of the interpolymer interaction. Evaluation of the FT-IR spectra as well as elementary analysis provided further proof of the formation of a 1 :1 polyelectrolyte complex. Further evaluation of physicochemical properties of the novel interpolyelectrolyte complex included assessment of films of blends of the two copolymers under study. UV spectrophotometric evaluation of complimentary solutions of the two sample polymers indicated the extent of turbidity of the solutions of the two copolymers. Particle size analysis was carried out by means of image analysis. The response of the complex to heating was studied by means of differential scanning calorimetry (DSC).The films were found to be insoluble in water, ethanol, and a broad range of other common solvents. The DSC studies indicated that the glass transition temperature of the complex produced varies from the values obtained for the individual copolymers as well as the physical blend of the two polymers. Finally, it may be posited that the combination of the two oppositely charged copolymers culminates in the formation of a 1:1 polyelectrolyte complex which could be a novel material to be subjected to wide ranging studies to ascertain its utility in applications.

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X-RAY INVESTIGATIONS OF SEMICRYSTALLINE POLY(3-HEXYLTHIOPHENE) THIN FILMS

S. Grigorian, S. Joshi*, D.Tiwari , L. Grodd and U. Pietsch

Solid State Physics. – University of Siegen, Walter-Flex-Str 3, 57068 Siegen, Germany
**currently at University of Bayreuth*
E-mail: grigorian@physik.uni-siegen.de

Keywords: *P3HT, GID, OFETs.*

Charge carrier mobility is one of the decisive parameters of organic field-effect transistors (OFETs) which determines the overall performance of any silicon based devices. One of the promising candidates for OFETs is regioregular poly(3-hexylthiophene) (P3HT), which has been explored extensively in recent years [1]. Low (LMW) and high molecular (HMW) weight P3HTs have also been shown to provide a significant effect on ordering and transport properties [2,3]. In the last years surface sensitive x-ray techniques emerged to a versatile and frequently used techniques in the field of thin films and patterned nanostructures and have been applied for structural and morphological investigations of P3HT films. Combination of x-ray reflectivity and grazing incidence diffraction, especially, grazing incidence in- and out-of-plane geometries allow to probe the ordering and structural properties in the lateral directions of the film as well as along the normal to the thin film surface [3,4]. The mobility of the polymer films strongly depends on the structural properties, anisotropy and degree of crystallinity of these films. Previous studies have shown a complicated behaviour of the charge carrier mobility: the charge carrier mobility in the LMV-fraction is despite of the higher crystallinity a few orders of magnitude smaller then in the HMW fraction. Moreover, our recent investigations allow to conclude that amorphous matrix rather then crystalline nanodomains is dominating and strongly influence on mobility of the charge carrier [3,4]. Furthermore, temperature and thickness dependent studies have shown a complicated nature without uniform expansion or compression: inter-layer distances increase with temperature while intra-layer distances have shown the opposite behaviour. The melting temperature was found to depend on the thickness of the active P3HT layer, indicating a strong substrate-layer interaction.

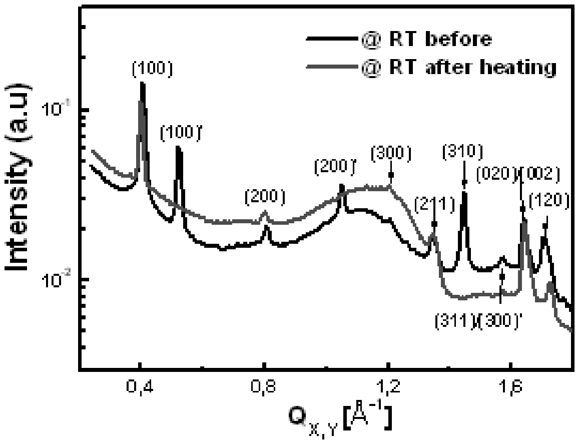

Figure 1. Room temperature in-plane grazing incidence diffraction profiles of LMW P3HT films before (black) and after (red) annealing at 100°C.

Additionally, correlation of the structural and electrical properties of the P3HT films under applied electrical field will be discussed. First findings reveal that the (020) peak associated with in-plane π-π-distances is stronger affected by an applied electrical field in comparison to the out-of-plane (h00) peaks, which are related to the inter-layer lattice spacings along the alkyl side chains. These investigations show partly reversible changes of the crystalline structure and are supposed to be dependent on the crystallographic directions.

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INNATE CONFINEMENT EFFECTS AS A ROUTE TO CONFINED SPACE CRYSTALLISATION

N. Sanandaji*, B. Neway*, Y. Li, L. Eriksson***, P.-E. Werner***, C. J. Hawker**, M. S. Hedenqvist*, U. W. Gedde***

** Fibre and Polymer Technology, Royal Institute of Technology, SE-100 44 Stockholm, Sweden.*
*** Materials Research Laboratory, University of California Santa Barbara, 93106-5121 Santa Barbara, California, USA.*
**** Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, Svante Arrhenius väg 12, 106 91 Stockholm, Sweden.*
E-Mail: nimas@kth.se

Keywords: *PCL, confined space crystallisation, metastable phases*

In this work, an in-depth analysis of crystalline characteristics has been performed for a unique set of strictly monodisperse poly-ε-caprolactone (PCL) oligomers. The molecules have different sets of end groups with various degrees of bulkiness and hydrogen bonding potential, affecting their aptitude to pack in ordered crystal structures. The oligomers also have different numbers of repeating units (n = 2-64), affecting the degree to which end groups influence overall molecular characteristics. The presence of bulky end groups leads to an innate confinement effect on crystallisation which in turn makes it possible to utilize the set of PCL oligomers to study confined space crystallisation. Confined space crystallisation is explored as a route to gain further understanding about the early metastable phases in crystal formation. The monodisperse nature of the samples made it possible to collect very precise small-angle and wide-angle X-ray scattering data (SAXS and WAXS) as well as calorimetric data. Computer modeling studies were performed to support experimental findings. It was shown that end groups strongly affected crystallisation features for the shorter oligomers ($n \leq 8$) but to a lesser extend for the longer oligomers ($n \geq 16$). The presence of a bulky end group at one end of an oligomer could inhibit the formation of hydrogen bonds on the other end. Short oligomers (n = 8) with OH-end groups exhibited novel packing characteristics. At one isothermal crystallisation temperature the molecules exhibited not only lamellar ordering but also an additional, likely rectangular or slanted, ordering. The sample was packed in a unique structure with molecular chains lying parallel but not aligned head to head with each other. At a higher crystallisation temperature the molecules packed in a double layered structure and at an even higher temperature in a typical non-folded but tilted single-molecular layer pattern. Unit cell determination was performed for a short oligomer with two bulky end groups, showing the existence of a tetragonal unit cell with different dimensions than the orthorhombic unit cells previously reported for linear PCL without end groups. To gain greater insight into the earliest stages of molecular packing, in situ WAXS measurements were performed using a synchrotron radiation beam and measuring data each 12 s whilst very slowly going from melt to isothermal crystallisation. It was shown that the crystal unit cell was distorted during the first minutes of slow crystallisation, which might either represent a metastable phase or else a highly distorted orthorhombic phase.

MODELLING THE PERMITTIVITY OF ANISOTROPIC COMPOSITES

Fritjof Nilsson, **Ulf W. Gedde, Mikael S. Hedenqvist**

** Fibre & Polymer Technology, School of Chemical Science & Engineering, Royal Institute of Technology, SE-100 44 Stockholm, Sweden*
E-mail: fritjofn@kth.se

Keywords: *Anisotropic composites, computer simulations, dielectric materials*

The purpose of this study was to develop and evaluate effective media models for anisotropic two- and multiphase materials, like composites and semi-crystalline polymers. The main aim was to find effective ways to predetermine the permittivity of dielectric (insulating) nano-composites. However, due to the similarities between the equations of electrostatics, diffusion and heat transfer, our three new models constructed for predicting electrostatic geometry effects for anisotropic insulators have a much wider applicability than the title indicates. The three simulation methods are briefly described below.

(1) For approximately periodical insulating materials a finite element model based on a "smallest repeating box" strategy was developed in order to mimic frameworks with fibres, crystals, clay particles, lamellar layers, foams and spheroids. The volume fraction of particles could be varied between 0 and nearly 100%. With the introduction of parameters for relative aspect ratios, overlap, packing density and rotations, the model became very flexible while still maintaining its simplicity, allowing for a wide range of applications without the need of supercomputers.

(2) Primary intended as a part of a multi-scale model for semi-crystalline polymers, a finite element composite model with oriented, randomly positioned particles of different shapes was also constructed.

(3) An analytical formula for approximating the effective permittivity of two- or three-component insulators with brick-shaped inclusions was derived. For a wide range of volume fractions, permittivity ratios and packing conditions, it gave solutions very close to corresponding finite element simulation data for lamellae, much closer than all other analytical formulas found in the literature. Simulation results for layered silicates (mica) were found to be in good agreement with literature data. It was noticed that the effect of water or air inside the composite had a major impact on the composite permittivity.

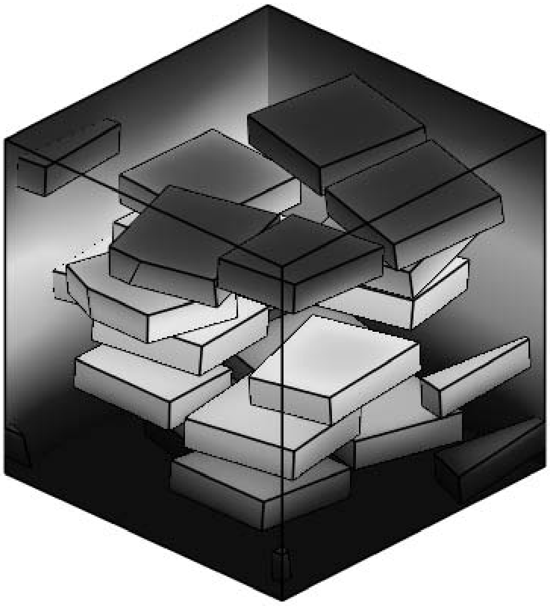

Figure 1. A modelled composite consisting of brick-shaped inclusions surrounded by a polymer matrix.

CHARACTERISATION AND AGEING OF FLUOROPOLYMER BINDERS FOR POLYMER BONDED EXPLOSIVES (PBX'S)

Louise Byers

AWE, Aldermaston, Reading, Berkshire, UK, RG7 4PR
E-mail: louise.byers@awe.co.uk

Keywords: *fluoropolymer thermal ageing*

Polymer bonded explosives (PBX's) contain an explosive filler (typically >90%) surrounded by a polymer binder which increases the mechanical strength and reduces the shock sensitivity of the explosive[1]. Current research includes investigating the use of fluoropolymer binders with the explosive triaminotrinitrobenzene (TATB) to form an insensitive high explosive (IHE). The fluoropolymers were chosen based on their excellent thermal stability and high density. As part of this research, it is necessary to be able to fully characterise these candidate binders and understand their long term stability through the use of thermal ageing trials. This is important for fluoropolymers as the degree of crystallinity has been known to change over time during ageing[2]. The results of a six month ageing trial in which several fluoropolymer binders were stored at 60°C and then analysed using DSC, TGA, XRD, DMA and uniaxial tensile tests, are discussed.

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PREPARATION AND CHARACTERIZATION OF THERMALLY STABLE LAYERED SILICATES FOR USE IN POLYMER BASED NANOCOMPOSITES

Wissam Abdallah*, **Ülkü Yilmazer****

** Polymer Laboratory, Chemical Engineering Department – Middle East Technical University, 06531 Ankara, Turkey*
*** Chemical Engineering Department – Middle East technical University, 06531 Ankara, Turkey*
Email: w.k.abdallah@hotmail.com

Keywords*: Thermal Stability, Layered Silicate, Polymer Nanocomposites*

The addition of a small amount of clay to a polymer may produce a nanocomposite with enhanced properties relative to those of the virgin polymer. In particular, the mechanical properties, fire retardancy, heat distortion temperature and permeability show improvement, enabling the use of nanocomposites in applications such as packaging, automotive, barrier film, and so on. The present study is aimed at investigating the purification and modification of organically modified montmorillonites (organoclays) by organic salts and their subsequent effects on the thermal stability (thermogravimetry and differential scanning caliroemtry), morphological (X-ray diffractometry, Scanning electron microscopy, Transmission electron microscopy) and mechanical (tensile, Impact) properties of polymer/clay nanocomposites. The clays mined from Resadiye (Tokat/Turkey) were purified by sedimentation, and then used in the synthesis of five organoclays by replacing the interlayer inorganic sodium cations with two phosphonium and three imidazolium surfactant cations. 2wt % of the organoclays were then used in the production of Amorphous poly (ethylene terephthalate) (PET) based nanocomposites by extrusion with the help of 5 wt% of elastomeric compatibilizer.

The onset decomposition temperature (2 wt. % loss) of the clays increased from 299°C up to 523°C upon purification. The modified organoclays exhibited a maximum onset decomposition temperature of 370°C with imidazolium salts and 289°C with phosphonium ones. The thermal properties of organoclays are apparently related to the nature of the surfactants and their arrangement in the interlayer space of montmorillonite. While phosphonium salts improved the thermal stability slightly for the composites, imidazolium ionic liquids made a difference in the onset decomposition temperature from 397°C rather than 385°C for pure PET.

XRD analyses of purified clays assured removal of inorganic minerals and resulted in higher cation exchange capacity. The basal spacing of the two phosphonium-modified clays is 2.6 nm and 1.8 nm, and that of the purified bentonite is 1.1 nm, indicating a monolayer arrangement of quaternary phosphonium ions in the interlayer space, while the values between 1.35 nm and 1.45 nm for imidazolium-montmorillonite indicates a more compact structure. These results were also parallel to PET composites produced.

The mechanical properties of the nanocomposites were higher in comparison to the virgin polymer. The tensile strength and young’s modulus revealed a maximum of 58 MPa and 2,065 MPa respectively for binary imidazolium-composites with clays only, and 50.8 MPa and 1,822 MPa for ternary composites with clays and elastomer, from a value of 47 MPa and 1,750 MPa for the pure polymer. Phosphonium-modified clay composites revealed a lower improvement than those modified with imidazolium ones. The elongation at break increased from 4% for the virgin polymer to a maximum of 209% for imidazolium composites and 96% for phosphonium composites. The impact strength at break of PET increased from 2.9 kJ/m^2 to a maximum of 4.7 kJ/m^2 and 6.0 kJ/m^2 for phosponium and imidazolium composites respectively.

THE DEPENDENCE OF SOUND VELOCITY IN POLYPROPYLENE CONTAINING VARYING PROPORTIONS OF NANO-FILLERS AND BINDER

Basem Alsawy*, Elaine Brown, Kirill Horoshenkov, John Sweeney

The IRC Polymer Process Engineering Laboratory, University of Bradford, Bradford, West Yorkshire, BD7 1DP, United Kingdom
E-mail: A.B.H.Alsawy@Bradford.ac.uk

Keywords: *Ultrasound, Polypropylene, Nano-composites*

An ultrasound technique was developed to characterise both injection moulded and extruded polypropylene samples containing varying proportions of nano-clays (0-5%) and binder (0-9%). More specifically, the polypropylene used was grade PPH 5042 supplied by Total Petrochemicals. The nano-clay silicate material was Closite 15A® supplied by Southern Clay Products, and the compatibiliser that was used to bind the material together was PPMA Fusabond P M613-05. The method of examination incorporated the use of a data acquisition system that was used to compute the sound velocity and attenuation, to a high degree of accuracy, in each material that was tested. This system involved the use of a standard Olympus-Panametrics Model 5800 computer-controlled pulser connected to various high frequency transducers ranging in frequency from 2.25MHz to 20MHz (also made by Olympus-Panametrics). This pulser was connected to a Tektronix 2004B digital oscilloscope, which was connected to a computer having all the necessary data processing software. From the results obtained, the general observed trend is that the velocity of sound decreases with increased concentration of filler. As well as this, the velocity of sound varies within each sample according to the position along the sample which is being tested. In addition to this, the sound velocity generally increases with increased frequency for each sample under examination. These findings can be explained in terms of the molecular structure of the material and also the matrix involving the filler as well as the compounding technique used to produce this material. The proportion of compatibiliser/binder also has an effect as it provides better molecular bonding in the structure, however too much binder starts to have an adverse effect due to excessive molecular exfoliation. In addition to sound speed and attenuation measurements, tensile tests and density measurements were also carried out in order to determine whether sound velocity in the material relied on these parameters. This gave rise to a negative correlation which may be explained in terms of the dispersion of sound waves in the polymer matrix due to the presence of nano-particles. To validate the results obtained from the system used, the polymer samples were tested at the same frequencies using a standalone Olympus-Panametrics thickness gauge (25DL Plus), and both sets of results were extremely similar. Finally, we conclude that this method has proven to be extremely reliable in producing accurate results for sound velocity and attenuation in polymer samples, and provided an explanation as to how these parameters relate to the physical and molecular properties of the material.

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STUDY OF THE DISPERSITY OF POLYMERS NANOCOMPOSITE FILLER USING DIELECTRIC PROPERTIES

Serg Bourbigot*, Mikle Delichatsios, Igor Chmutin***, Vjacheslav Meriakri****, Mikle Parkhomenko****, Natali Ryvkina***, Svetlana von Gratowski****,**

**Laboratoire des Procédés d'Elaboration de Revêtements Fonctionnels, Ecole Nationale Supérieure de Chimie de Lille, BP 90108 59652 Villeneuve d'Ascq Cedex – France,*
***University of Ulster, FireSERT, School of Built Environment, UU, FIRESERT (block 27) BT37 0QB Newtonabbey Great Britan(GB),*
****Concern Nanoindustry, B. Tatarskaya, 38, Moscow 113184, Russia,*
***** Kotel'nikov Institute of Radioengineering and Electronics Russian Academy of Sciences. Fryazino Branch, Vvedenski sq.1, Fryazino, Moscow region, 141190 Russia,*
E-mail: meriakri@ms.ire.rssi.ru

Keywords: *polymer nanocomposite, dielectric properties, monodispersity.*

INTRODUCTION Dielectric properties of polymers are of great interest because of fundamental value and applications. From fundamental point dielectric properties gives important information about molecular motion and relaxation processes. Polymer nanocomposites have many practical advantages like the more easy preparation of products with needed properties and hence reducing of the manufacturing cost. Polymer composites with carbon nanotubes (CNT) and nanoclay have recently been investigated for improved electrical conductivity, optical devices, high strength composites, fire retardant properties of polymers. Study of dielectric properties gives very important information about structure and these physical properties and retardant possibility of polymer nanocomposites.

MATERIALS, METHODS Seven samples of nanocomposites based on Nylon 6 and poly(lactic acid), PLA, as a matrix and multiwalled carbon nanotubes CNT, two organo-clays Southern Clay: Cloisite 20A (polar) and Cloisite 30B (non polar) as nanofillers were investigated. For determination in the millimetre wave length ranges of complex refractive index of lossy materials where it is impossible to measure transmission coefficient of material layer, two new methods were used. These methods do not require phase of reflected wave measurement with help complicated and expensive Vector Network Analyzers. These methods based on or module of reflection coefficient from material surface measurement in waveguides of different cross section, or on measurement of reflection coefficient module from structure: an additional plate – material under test and frequency of reflection module minimum.

In the frequency range from 4 to 10 GHz measurements were realized with help usual waveguide resonator method. In the frequency range from 10 kHz to 1 MHz was used method based on the measurement of the capacitance of local areas in a nanocomposite. For measurement of the real and imaginary parts of the complex permittivity setup includes high-precision broadband dielectric spectrometer BDS-40 (Novocontrol). Also electric conductivity was measured.

RESULTS The measurements carried out have shown that the best parameter to describe the nonuniformity of the distribution of nanoparticles in polymer matrices is the imaginary part of the permittivity in the microwave band. This parameter depends both on the distribution of the nanoparticles and on to what extent individual nanotubes are stretched. In good samples it varies in wide limits for small variations of the concentration of nanoparticles.

CONCLUSIONS Here we present application of dielectric spectroscopy for control the uniformity of retardant nanoparticles distribution in polymer nanocomposite. We have worked out three methods for determining the dispersity of nano fillers in a polymer matrix: (1) a low-frequency method based on the measurement of the capacitance of local areas in a nanonocomposite, (2) a microwave resonator method, (3) a millimetre wave reflection method. It was shown that all these methods or one of them allow to determine heterogeneity of the distribution of Fire Retardant nanoparticles in a polymer matrix in both cases of: 1) lossy fillers (carbon nanotubes) and 2) low loss fillers (nanoclay).

INFLUENCE OF SPHERICAL AND PLATELET NANOPARTICLE CONTENT AND PROCESSING PARAMETERS ON MECHANICAL BEHAVIOUR OF POLYPROPYLENE COMPOSITES.

Karol Bula*, **Teofil Jesionowski****, **Jolanta Janik*****

** Institute of Materials Technology - Technical University of Poznan, Piotrowo 3 Street, Zip: 61-138, Poznan, Poland*
***Institute of Chemical Technology and Engineering - Technical University of Poznan, M. Sklodowskiej-Curie 2 Sq., 60-965 Poznan, Poland*
****Polymer Instituite - Technical University of Szczecin, Pulaskiego 10 Street, 70-322 Szczecin, Poland*
E-mail: Karol.Bula@put.poznan.pl

Keywords: *thermoplastic composites,anisotropic fillers, mechanical parameters.*

Mechanical and thermal properties of polymers are generally improved by the addition of inorganic fillers. The properties of polymer-mineral reinforced composites are determined by the component properties (particle shape, surface area, surface chemistry, polymer structure) and as well as by the processing method and processing conditions [1,2]. Final characteristics of the composites are also influenced by the microstructure and filler oritntation formed during injection molding. Faster injection speed promote higher shear rate and may cause changes in filler dispersion and particle orientation. The knowledge of the relation between the filler morphology and injection parameters e.g. speed, is an important in explanation of its mechanical and thermal properties. In this study the influence of filler particles shape and injection molding conditions, by means of injection speed on composites properties of amorphous silica and oMMT with isotactic polypropylene was determined. Composites of isotactic polypropylene (iPP) with various SiO_2 and oMMT content were prepared by melt compounding using maleic anhydride grafted polypropylene (PP-*g*-MAH) as a compatibilizer. The composites containing 0.5, 1, 3 and 5% by wt. of inorganic particles were melt-blended in a co-rotating twin screw extruder. The extrudates were injection molded into dumbbell-shaped specimens using an ENGEL 80/25 HLS injection molding machine, at the mold temperature of 30 °C. The injection speed was set as 50 mm/s and 110mm/s. For tensile test bar preparation the double cavity mould was applied (see fig. 1).

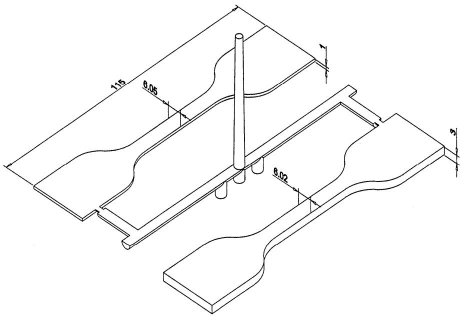

Figure 1. Schematic view of tensile specimes (1mm and 3mm of thickness) with the sprue and flow channel configuration.

The cavities had the same injection flow length but different thickness: 1mm and 3 mm. Tensile strength, yield stress, Young's modulus and elongation at break of PP/PP-*g*-MAH/SiO_2 and PP/PP-*g*-MAH/oMMT-composites were mainly discussed versus the processing conditions: injection speed and the sample thickness. Performed mechanical test proved that the addition of inorganic particles leads to sharp increase in stiffness and tensile strength for composites compared to unfilled polypropylene. The most pronounced increase in mechanical properties was regarded to Young's modulus and was observed for samples with 1mm of thickness in both systems with spherical silica as well as with organically modified montmorillonite.

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MECHANICAL PROPERTIES OF NBR/ACM BLENDS. EFFECT OF NANOFILLER

Micheli Celestino*, **Bluma Guenther Soares ***

[*] Instituto de Macromoléculas Professora Eloisa Mano – Universidade Federal do Rio de Janeiro (IMA/UFRJ). Centro de Tecnologia, Bloco J, Ilha do Fundão. Rio de Janeiro, RJ, Brasil, P.O.Box 68525
E-mail: micheli@ima.ufrj.br

Keywords: *nanocomposite, rubber, mechanical properties.*

Recently, NBR/ACM blends have attracted significant attention due to their outstanding mechanical properties, solvent resistance and thermal stability [1]. However, these properties can improved by incorporation of the clay in blend [2]. Polymer-clay nanocomposites are a rapidly developing class of composites, wich is defined as a molecular composite of polymer and organophilic silicate layers of clay mineral. The dispersion of small amount of clay in the polymer matrix can impart radical improvement in mechanical properties, solvent resistance, ionic conductivity, flammability resistance, gas barrier properties, and biodegradability of polymers [2]. The polymer/clay nanocomposites can generally be prepared by common methods such as in situ polymerization, solution and melt mixing [3].

Acrylic rubber (ACM) (Hycryl) and Nitrile rubber (NBR) was kindly supplied by Petroflex Ind. Com. S.A., Brazil. Montmorillonite modified (Southern Clay Products) with cationic exchange capacity (CEC) of 95 meq/100g was used in this work. In the first method, the blends with clay were prepared in an open two-roll laboratory mixing mill at room temperature. In the second method, the rubber was first dissolved in toluene. The MMT20A was dispersed in toluene for 24h. The required amount of the clay dispersion was poured into rubber solution and the mixture was agitated for 4 h. This solution was precipitate in methanol and dried in a vacuum for 3 days. Subsequently the compounding ingredients for vulcanization were mixed with this in an open two-roll mill at room temperature. All the blends were vulcanized up to the optimum curing time in a hydraulic press at 190^{o}C and 15000 lb/in^{2}.Tensile-strain experiments were performed by means of an Instron 5564 testing machine at room temperature with speed of 200 mm/min, following DIN procedure 53504. The samples were conditioned at 21^{o}C and 53% of air humidity for 24 hours before the testing. The swelling measurements were utilized to determine the crosslinking density of the studies of NBR/ACM. The structure of the dispersed silicate layer in the composite was studied by XRD. The Figure 1 shows the diffraction peak of MMT-20A pure and the blends. The diffraction peak of MMT-pure in 2 theta = 3,5º (d001 = 25,24 Ǻ). In the order hand, for all sample the former peak is quite totally absent and the latter is very poorly defined, evidencing the high proportion of exfoliated platelets or small clay aggregates constituted of a very small number of platelets. This trend indicates the efficiency of intercalation of blend. In all samples, the properties improved with increasing amounts of clay in the mixture.

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SEMI-QUANTITATIVE EVALUATION OF THE INTERACTIONS BETWEEN MULTIWALL CARBON NANOTUBES AND POLYMER MELTS

Vera S. Cruz,[*,**] **José A. Martins**,[*,**] **M. C. Paiva**[*,***]

** Departamento de Engenharia de Polímeros, Universidade do Minho, Campus de Azurém 4800-058 Guimarães, Portugal; ** CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal*
**** IPC, Universidade do Minho, 4800-058 Guimarães, Portugal*
E-mail: jamartins@dep.uminho.pt

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Understanding, at a molecular level, the interactions between carbon nanotubes and polymers melts is a difficult problem with strong technological relevance. It is known that nanotubes act as nucleating agents enhancing crystallization kinetics, which implies the existence of physical interactions between nanotubes and the polymer chains. It was shown by time-resolved FTIR spectroscopy that nanotubes surfaces induce conformational ordering of polymer chains.[1] As a result of this induced ordering, polymer chains lay flat-on on the nanotube surface resulting in the development of nanocrystals which enhance strongly the crystallization kinetics.[2]

It is known that the physical interactions responsible for this induced conformational ordering are van-der-Waals interactions, but there is no model available to provide an estimation of the dimensions of these surface-induced ordered regions as a function of the polymer chemical structure and melt temperature.

Composites of nanotubes and polymer melts of amorphous and semicrystalline polymers indicate common features in small amplitude oscillatory shear flow experiments: a significant increase in the $G'(\omega)$ value with the increase in the nanocomposite concentration,[3] associated with the manifestation of elasticity at low oscillation frequencies, and the apparent increase in the flow activation energy with the nanocomposite concentration.[4] These two last features indicate the universality in the nature of the interactions between polymer melts and carbon nanotubes, regardless the polymer tacticity.

More specifically, polymer chains of semicrystalline and amorphous polymer melts interact with the nanotubes surfaces by van-der-Waals interactions. The increase in the elastic behavior observed by increasing the concentration of nanotubes is explained only if relatively strong interactions develop at the nanotube surface. Since van-der-Waals interactions are additive, strong interactions between polymer chains and nanotubes surface imply the development of ordered clusters of chain segments at the interface.

With the aim of understanding and quantifying the interactions at the interfaces between nanotubes and polymer melts, we present in this work a set of thermal analysis and rheological experiments performed with atactic polystyrene and MWCNT with concentrations from 1%wt up to 15%wt. The thermal analysis experiments performed in a temperature range between 40 ºC and 200 ºC indicate that MWCNT-PS composites have higher specific heat capacities than the pure polymer, which is also higher than that of MWCNT that is comparable to the heat capacity of high temperature pyrolitic graphite. A detailed discussion of these unexpected results will be postponed to another work.

Here we will focus the discussion on the different values obtained for the flow activation energy and the increase in $G'(\omega)$ above the value of $G''(\omega)$ for nanotubes concentrations higher than 5%wt. Since this increase in $G'(\omega)$ at the terminal flow region is observed in all experimentally accessible frequency scale, the experimental evaluation of the longest relaxation time for the nanocomposites melts becomes a difficult, or even impossible, task. According to all theories of melt relaxation in the linear viscoelastic regime, the longest relaxation time is evaluated at the reciprocal of the frequency at which $G'(\omega)$ and $G''(\omega)$ intersect. The semi-quantitative, and approximate, estimation of the dimensions of surface-induced ordered regions is made by assigning a physical meaning to the flow activation energy of the pure polymer and by estimating the magnitude of the van-der-Waals interactions between the nanotubes and polymer chains.

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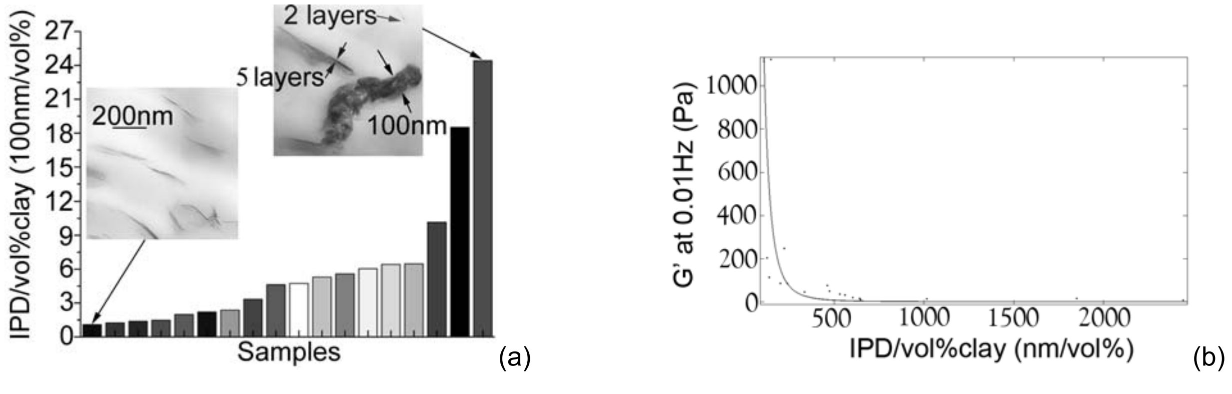
EFFECTS OF COMPOSITION AND PROCESSING CONDITIONS ON CLAY DISPERSION IN POLYPROPYLENE NANOCOMPOSITES

Shaobo Xie*, Eileen Harkin-Jones*, Yucai Shen*, Rund Abu-Zurayk*, Peter Hornsby*, Marion McAfee*, Tony McNally*, Raj Patel, Hadj Benkreira**, Phil Coates****

** School of Mechanical and Aerospace Engineering, Queen's University Belfast, Belfast BT9 5AH, UK*
*** School of Engineering, Design & Technology, Bradford University, Bradford, West Yorkshire BD7 1DP, UK*
E-mail: shaoboxie@gmail.com

Keywords: *Clay; Dispersion; Nanocomposites.*

Melt intercalation appears to be by far the most common method for the preparation of polymer/clay nanocomposites industrially. Processing parameters such as temperature, residence time and shear stress may be expected to have significant effects on the structures and properties of resulting nanocomposites. The clay dispersions obtained kinetically by the processing conditions should be also thermodynamically favored, which requires the total change in free energy, $\Delta F=\Delta E-T\Delta S<0$, where polymer-clay interactions and temperature (T) are crucial.[1] Polypropylene (PP)/clay nanocomposites have been widely investigated, however there are few reports studying the effects of both thermodynamic and dynamic factors on ultimate dispersion. In the present work, a systematic study based on a Design of Experiments (DoE) methodology has been done, taking account of the effects of composition and processing factors on clay dispersion in PP matrices. A maleated PP, MAPP, was used as a compatibilizer. 18 samples were prepared in a mini-mixer where 6 factors were varied including screw speed, residence time, temperature, clay loading, MAPP loading and the matrix MFI. Clay dispersion was quantitatively characterized by XRD, TEM, optical microscopy (OM) and rheology. As well as clay layer separation (d_{001}) and low-frequency plateau G' at 0.01Hz two further parameters, degree of dispersion and interparticle distance per unit volume of clay (IPD/vol%clay),[2] obtained from TEM and OM observations were utilized as the response. Figure 1(a) shows IPD/vol%clay of the prepared nanocomposites, the lower value indicating the better dispersion. This is the first study on the quantitative characterization of clay dispersion in polymer matrix over the whole range of particle size, since polymer/clay nanocomposite usually exhibits the coexistence of tactoids of different thicknesses and micron-size agglomerates. Figure 1(b) shows the correlation between G' at 0.01Hz and IPD/vol%clay, indicating the rationality of this methodology. DoE analysis revealed temperature to be the most significant processing factor in the control of clay dispersion with lower processing temperature favoring better clay dispersion. This may indicate that the diffusion of the polymer chains inside the silicate galleries[3] is not the control step for the intercalation/exfoliation of clay.



(a) (b)

Figure 1: (a) IPD/vol%clay of the whole samples. The inserted TEM images show the dispersion states of the selected samples. (b) The correlation between G' at 0.01Hz and IPD/vol%clay.

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TRIBOLOGIC AND BIOACTIVITY STUDIES OF SULPHONATED POLYETHER ETHER KETONE/NANO HYDROXY APATITE COMPOSITES

K. Aravind*, D. Sangeetha*

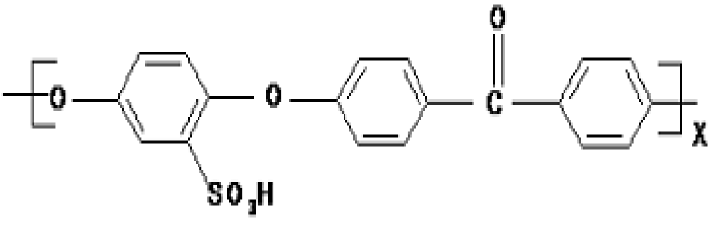
**Department of Chemistry, College of Engineering, Anna University Chennai, Chennai – 25, India*
E-mail: aravindbhat29@gmail.com, sangeetha@annauniv.edu

Keywords*: Tribology, triboelectricity and bioactivity*

Poly ether ether ketone (PEEK) possesses favourable properties for application in medicine. It has so far been used specifically in orthopedics as a hard tissue replacement material. However, it lacks bioactivity and is not biodegradable thus limiting its application in medicine. It is found that sulfonation of PEEK (SPEEK) and introduction of nano hydroxyapatite (nHA) addresses these drawbacks. Though, by sulfonating, there is improved bioactivity, its mechanical property is found to drastically decrease. Yet, SPEEK has the potential for application in soft tissue and resorbable orthopedic prosthesis as well as in the area of implantable drug delivery device and tissue engineering applications. Hence, in this work we have fabricated SPEEK/nHA composite membranes by two methods (i) casting and (ii) electrospinning and their properties with respect to tribology and bioactivity were studied and compared.

Materials and methods: PEEK was sulfonated using sulfuric acid to obtain SPEEK and the degree of sulfonaion was determined by CHNS elemental analysis. In the first method, SPEEK/nHA composites were fabricated by solvent evaporation and were molded in to the desired thickness using hot press. In the second method, nano-composite membranes of SPEEK/nHA were obtained after optimizing the conditions of electrospinning. Both the membranes were subjected to various analyses as follows. The composites were characterized using FTIR and XRD to confirm the interaction between nHA and SPEEK. The SEM pictures of the samples obtained by electrospinning showed clearly the nanofibres and the pores present between them. The nHA was also visualized to be uniformly distributed through out the composite membranes. The stability of the prepared composites were tested by immersing the samples in simulated body fluids and estimating the leaching out of the nHA after continuous stirring for 24 hours. It was found that both the membranes obtained by the two methods were equally stable. The composites containing nanofibres exhibited better tribologic properties which was determined using a Pin on Disc Tribometer. The tensile property of the samples was tested using Universal Testing Machine and compared with pure SPEEK films. The bioactivity studies carried out by immersing the samples in simulated body fluid for 48 hours showed that the samples of the SPEEK nanofibre composite exhibited more dense HA deposition when their surface was analyzed through SEM.

The results of the study indicated that the nanofibre SPEEK/nHA composites exhibited superior tribologic and bioactive characteristics when compared to the cast composite membrane. The composites showed promising results for application in controlled drug delivery and tissue engineering.



Sulfonated Polyether ether ketone

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SYNTHESIS AND SELF-ASSEMBLY OF NEW COMB-LIKE MALEIC ANHYDRIDE COPOLYMERS FOR FABRICATION OF SILVER NANOPARTICLES WITH VERY NARROW PARTICLE SIZE DISTRIBUTION

Olena Kudina*, Olga Budishevska*, Andriy Voronov, Ananiy Kohut**, Stanislav Voronov***
**Lviv National Polytechnic University, Address: St. Bandery Str., 13, 79013, Lviv, Ukraine*
***North Dakota State University, Address: Dept. 2760, P.O. Box 6050, Fargo, ND 58108-6050, USA*
E-mail: okudina@gmail.com

Keywords: *amphiphilic copolymers, self-assembly, nanoreactors*

There is a great interest in designing and manipulation of supramolecular nanostructured materials fabricated in processes of molecular (macromolecular) self-assembly in solutions . Comb-like amphiphilic copolymers represent the class of macromolecules which are able to self-assemble and form nanostructured functional polymer materials .

Common methods of synthesis of comb-like copolymers are challenging because of the necessity to synthesize alternate macromolecules. The synthesis of new amphiphilic comb-like copolymers via polymer-analogous reactions of maleic anhydride copolymers is therefore considered as a research tool to regulate the density of grafting[1]. The proposed synthetic approach of comb-like polymer synthesis consists of two stages. In the first stage α-olefines (or alkylmethacrylates) and maleic anhydride undergo radical polymerization to form alternating binary copolymers. In the second stage, binary copolymers are reacted with monomethyl polyethyleneglycols ethers by polymer-analog reactions. The structure of synthesized polymers was confirmed by FTIR, ^{1}H NMR spectroscopy and GPC.

Synthesized comb-like copolymers are soluble both in polar and non-polar media. The macromolecules form micelles in dilute aqueous and organic solutions, thus confirming the surface activity of synthesized macromolecules. The self-assembly of the miclelles and further formation of micellar aggregates (amphiphilic nanostructures) by increasing polymer concentration has been observed in DLS measurements both in polar and non-polar solvents.

The self-assembled polymeric structures of the comb-like copolymers have been used as nanoreactors for the synthesis of silver nanoparticles. Concentrated solutions of amphiphilic invertible polymers, containing polyoxyethylene fragments and able to form self-assembled nanostructures are known[2] for reducing Ag^+ to metallic silver after adding silver precursors ($[Ag(NH_3)_2]OH$, $AgNO_3$). In concentrated (10-50% w/w) benzene solutions of copolymer dodecene-co(maleic anhydride)–co-methoxypolyethylene oxymaleate (DDC-MA-$PEGME_{350}$) silver nanoparticles with diameter about 30 nm were synthesized. Intriguingly, that silver nanoparticles of very narrow particles size distribution have been fabricated using a broad range of various concentrations of comb-like polymeric nanoreactors. The intensity of absorption on the UV-vis spectra is increasing with the increasing polymer concentration in solutions indicating the increase of silver nanoparticles concentration. The UV-vis measurements, which have been confirmed by TEM (Fig. 1a), prove the results of UV-vis measurements.

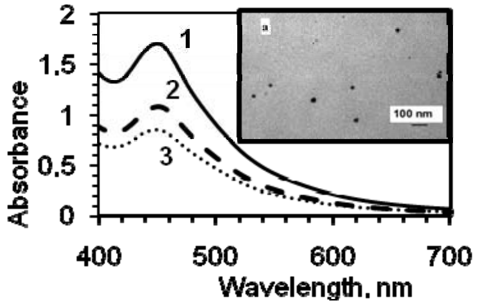

Fig. 1 UV-vis spectra of colloid silver in concentrated benzene solutions DDC-MA-$PEGME_{350}$ (1-50, 2-25, 3-10%), a – TEM image of silver nanoparticles.

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INFLUENCE OF ANIONIC GUESTS INTERCALATED IN LAYERED DOUBLE HYDROXIDE HOST ON MORPHOLOGY AND THERMAL PROPERTIES OF LDPE BASED NANOCOMPOSITES.

Nattaya Muksing*, Serena Coiai, Elisa Passaglia**, Rathanawan Magaraphan***

**Polymer Processing and Polymer Nanomaterials research Unit, Center for Petroleum, Petrochemicals, and Advanced Materials, The Petroleum and Petrochemical college, Chulalongkorn University, Bangkok 10330, Thailand.*
***CNR-ICCOM Pisa Section, Department of Chemistry and Industrial Chemistry, University of Pisa, Via Risorgimento 35, 56126, Pisa, Italy.*
E-mail: Rathnawan.K@chula.ac.th

Keywords: Anionic surfactants, layered double hydroxide, Low density polyethylene, Nanocomposites.

Intercalation of organic guest species into layered inorganic solids is a way of creating ordered inorganic–organic assemblies with desirable physical and chemical properties. Layered double hydroxides (LDHs) have been considered not only as traditional heterogeneous catalyst but also as a new emerging class of layered nanofillers for the preparation of polymer/layered crystal nanocomposites. Due to their highly tunable properties, various anionic guest species can be introduced between the layers in order to functionalize LDHs further or to modify the properties of LDHs. i.e. causing the expansion of the interlayer distance and making the compatible with the organic polymers.

In this work, the synthesis and characterizations of intercalated guest species (sulfate surfactants) having different alkyl chain lengths (n_c = 8, 12, and 20) were carried out. The evidences of anionic guests intercalated layered host structure on the morphological and thermal properties were characterized by a combination of X-ray diffraction (XRD), Fourier transform infrared (FTIR), scanning electron microscopy (SEM), and thermogravimetry (TGA). Subsequently, low density polyethylene (LDPE) nanocomposites with various organomodified LDHs were prepared via melt-compounding using polyethylene grafted maleic anhydride (PE-g-MAH) as a compatibilizer. The morphological and thermal properties of such nanocomposites were studied with highlight on the effect of nanolayered dispersion in the polymer matrix.

The successful intercalation of anionic guests into LDH layered host was evident by an increase of the basal spacing (d_{003}). It was observed that the size of the anionic guests as well as the organic–inorganic interactions played an important role for the difference in morphology. For example, an aggregated structure and more roughness of surface was evident when the n_c = 8 (Fig. 1b) compared to the pristine one (Fig.1a). The well-stacked of hexagonal particles with connecting to each others was evident when the n_c = 12 (Fig. 1c) When the n_c = 20, the irregular hexagonal plate-like particles with uneven surface and unsharped edges (Fig.1d) was appeared. The obtained nanocomposites established partially exfoliated/intercalated mixed morphology in which their extent of exfoliation/intercalation depended not only on the guest's structures but also the interactions within the layers. Either exfoliated or intercalated structure was preferable when the number of alkyl chain length is larger (≥ 12). The TGA profiles for the nanocomposites exhibited a faster charring process and greater thermal stability above 400 ^oC and remarkable increase in the degradation temperature about 20–33 ^oC higher than that of pure matrix. The addition of organomodified LDHs also enhanced the storage modulus and the relative glass transition (β relaxation) temperature of the nanocomposites.

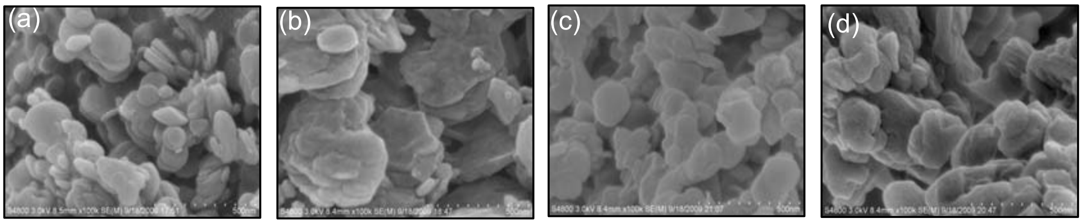

Fig. 1 SEM micrographs of (a) LDH-NO_3, (b) LDH-C8, (c) LDH-C12, and (d) LDH-C20.

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SYNTHESIS AND ULTRASONIC CHARACTERIZATION OF COPPER NANOPARTICLE-POLYVINYL ALCOHOL NANOFLUIDS

Giridhar Mishra*, **R.R. Yadav**

Ultrasonics NDE Lab., Physics Department – University of Allahabad, Allahabad-211002, India
E-mail: giridharmishra@rediffmail.com

Keywords: *Copper nanoparticles, Nanoluid, Ultrasonic properties, TEM, Thermal properties.*

This study investigates the ultrasonic properties of copper (Cu) nanoparticles dispersed in polyvinyl alcohol (PVA). The colloidal solutions of dispersed copper metal nanoparticles with different concentrations have been developed using a novel chemical method. Nanofluids containing copper metal nanoparticles so-prepared were characterized by UV-Visible spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The formation of Cu metal nanoparticles is monitored by UV-Visible spectroscopy. The colloidal solution shows strong visible light absorption at 580 nm. This occurs due to the interaction of small metal particles with an external electromagnetic field, induced by light, resulting in coherent oscillation of the conduction (free) electrons on the surface, called the surface plasmon resonance. The sharp absorption peak indicated narrow size distribution of Cu metal nanoparticles in PVA. The UV-Visible spectrum suggests that Cu salts have been reduced by PVA. The XRD analysis of the nanofluids has confirmed the formation of Cu nanoparticles in the solution. XRD results reveal that the nanoparticles are crystalline. The size of the crystalline nanoparticles (grain size) was also determined by means of the Scherrer formula. All the peaks on the XRD pattern can be indexed to that of pure copper metal. The peaks are corresponding to the 111,200,220 and 311 planes respectively. The Cu-nanoparticles occur in the usual cubic crystal structure (F_{m3m} space group). TEM images of the colloidal solution show well-dispersed non-agglomerated spherical particles having 10-20 nm diameters in the polymer solution. The selected area electron diffraction pattern (SAED) patterns of Cu metal nanoparticles in PVA shows the crystalline structure of Cu metal nanoparticles. Particle size calculated using the Scherrer formula were well consistent with the average particle diameter obtained from TEM images. Measurements of ultrasonic velocity and ultrasonic attenuation in the prepared samples were made as function of temperature and concentration of the copper nanoparticles in the PVA. The variation of ultrasonic velocity with temperature is almost same for all concentrations of Cu metal nanoparticles. Temperature dependent ultrasonic attenuation has different maxima and minima for different concentration of the Cu-nanoparticles suspended in PVA. Maximum attenuation appears in 0.5 wt% Cu nanoparticles-suspended in PVA. The wave attenuation in these composites is a complex process where the viscoelastic loss and the scattering loss coexist. It is also important to recognize that the relative contributions of these loss mechanisms may change not only depending on the acoustic properties of the constituent (matrix and particles) but also according to the particle size, particle concentration and the frequency of interest [1]. One important fact is to be noted that the characteristic behaviour of the ultrasonic attenuation in the Cu-PVA nanofluid is not found in any of the individual components of the composite. Addition of small amount of nanoparticles in fluids shows anomalous change in thermal behaviour of nanoparticles-liquid suspensions. One fascinating feature of nanofluids is that they have anomalously high thermal conductivities at very low nanoparticles concentrations. The experimental results were modelled to establish the ultrasonic mechanism to extract the useful information about the nanofluid. Our ultrasonic investigation accounts for the enhancement in the thermal conductivity of the colloidal solutions. The predictions based on our study are in good agreement with the available experimental and theoretical data about the thermal conductivity of the nanofluids[2,3]. Thus we can propose that the Brownian motion of the metal-nanoparticles in nanofluids produces convection like effects at the nanoscale [3].

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LONG-TERM PERFORMANCE OF POLYMER NANOCOMPOSITES

Sohail Nawaz*, **Patricia Nordell ***, **Bruska Azhdar***, **Henrik Hillborg****, **Ulf W. Gedde***

** Fibre & Polymer Technology, School of Chemical Science & Engineering, Royal Institute of Technology, SE-100 44 Stockholm, Sweden*
*** Also at ABB AB, Corporate Research, SE-721 78, Västerås, Sweden*
E-mail: sohailn@kth.se

Keywords*: poly(ethylene-co-butylacrylate), aluminium oxide nanoparticles, long-term performance*

The long-term performance of composites based on poly(ethylene-*co*-butylacrylate) copolymer with two different weight fractions of butylacrylate (27 wt.% and 8 wt.%) and two types of Al_2O_3 nanoparticles (nanoamur and nanodur) were studied. The nanoparticles were either uncoated or functionalized using octyl- or amine-terminated silane. The composites also contained 0.2 wt.% of Irganox 1010, a hindered phenolic antioxidant. The samples were aged in air at 90°C. The concentration of antioxidant in the aged samples was analyzed by differential scanning calorimetry (assessment of OIT) and confocal Raman spectroscopy. The virgin (unaged) samples showed remarkable differences in OIT. The samples with uncoated nanoparticles showed very low OIT values suggesting that most of the antioxidant had adsorbed onto the nanoparticles. This effect was most pronounced for the nanoparticles with largest surface area (according to nitrogen absorption measurements) and the highest concentration of hydroxyl groups on the nanoparticle surfaces. The samples with coated nanoparticles showed higher OIT (effect strongest for the nanoparticles coated with octyl-terminated silane), which indicate that the coating largely prohibited adsorption. The loss of stability with increasing ageing time followed essentially the same kinetics independent of filler concentration and filler coating type suggesting that the antioxidant migration is not strongly influenced by the presence of the nanoparticles. The results suggest that the sites at the nanoparticle surfaces initially available for adsorption are already occupied by the adsorbed antioxidant molecules. Ongoing research are focussed on several issues, among them the possibility that adsorbed antioxidant molecules can enter the polymer matrix phase, i.e. the nanoparticles with adsorbed antioxidant could be source for slow release of stabilizer to the polymer matrix.

STRUCTURE, MORPHOLOGY AND BIODEGRADABILITY OF POLY (ε-CAPROLACTONE) BASED NANOCOMPOSITES

Ramesh Neppalli, Valerio Causin, Carla Marega, Roberta Saini, Antonio Marigo

Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, 35131 Padova, Italy
E-mail: ramesh.neppalli@unipd.it

Keywords: *polycaprolactone, montmorillonite, composites*

Almost all synthetic commodities, such as polyolefins, polyamides, etc. have been investigated for the preparation of nanocomposites. Because of environmental concerns and the need for high end products and for niche applications, increasing attention is being posed on biodegradable materials such as starch, cellulose, polylactides, polycaprolactone or blends of such biodegradable polymers. The main disadvantage of such polymers is their poor physical mechanical performance, but many properties of such materials can be improved through appropriate composite and blending formulations.[1]

In this study, biodegradable polycaprolactone (PCL)/organo-modified clay nanocomposites were prepared by solvent casting, employing different amounts of organoclay and polymer matrices differing by average molecular weight. Nanocomposites having intercalated structures were obtained. Nanocomposites were characterised using wide angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS) methods. Negligible variations in the degree of crystallinity as a function of clay content were detected by WAXD. SAXS was more effective in studying the role of clay in shaping the morphology of the materials. SAXS results showed that the lamellar morphology of low molecular weight matrices are more affected by the presence of clay, than high molecular weight matrices. For example, the thickness of crystalline lamellae increased in low molecular weight polymer nanocomposites with increasing clay amount, but this effect was much smaller in the case of nanocomposites with a high molecular weight matrix.

Differential scanning calorimetry (DSC) was used to understand crystallization behaviour of nanocomposites prepared. The crystallization temperature decreased by adding the clay to polymer matrix, i.e. an inhibiting effect on crystallization due to clay was observed. Analogous results were obtained with the other molecular weights. This effect is reverse to what has been frequently reported i.e. clay normally acts as a nucleating agent. Another very unusual result refers to the tensile properties of the samples. The composites retained the modulus of the PCL matrix. It is noteworthy, though, that large increases in the strain at yield and strain at break were obtained. In other words, addition of clay does not influence their stiffness, but greatly enhances its ductility. This behaviour is highly infrequent in nanocomposites.

Biodegradation studies were carried out with respect to time; the influence of structure on the degradation of nanocomposites were studied by WAXD. The biodegradability of the PCL/clay nanocomposites was evaluated by burying specimens in organic compost. After exposing to biodegradation, the degree of crystallinity increased in all samples, meaning that by aging the less ordered portion of the sample was preferentially degraded. This effect was more evident in nanocomposites with 1% of clay with both molecular weights of PCL. Biodegradation rate was reduced with the addition of clay to polymer, coherently with the observed increase in the lamellar thickness brought about by this filler. Biodegradation is in fact favoured by a less crystalline structure.

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CHARACTERIZATION OF CLAY-DIMETHACRYLATE COMPOSITES OBTAINED BY *IN-SITU* PHOTOPOLYMERIZATION

Tatiana Batista, Isabel C. Rigoli, Carla C. S. Cavalheiro, Miguel G. Neumann

Instituto de Química de São Carlos, Universidade de São Paulo, Caixa Postal 780, 13560-970 São Carlos SP, Brazil
E-mail: neumann@iqsc.usp.br

Keywords: *clay-polymer composites, photopolymerization, cross-linking*

Composites of triethynleneglycol dimethacrylate/Bis-GMA [2,2-bis(p-2'-hydroxy-3'-methacryloyloxypropoxy-phenyl)propane] copolymers with a surfactant-modified clay (35-45 wt% dimethyldialkylamine C14-C18 on SWy-1) were prepared by in situ photopolymerization. Photopolymerization kinetics as a function of clay loading (0.5-10 wt%) were determined by ATR-FTIR spectroscopy. The composites were characterized by DRX and SEM. Figure 1 shows the degree of conversion of copolymers with different clay loadings, which was determined from the ratio between the absorption peak areas of the aliphatic C=C band (~1635 cm^{-1}) and the aromatic carbon-carbon band (~1608 cm^{-1}) before (A^*) and after (A) irradiation. [1,2]

$$DC(\%) = 100 - \left\{ \frac{A^*(1635)}{A(1635)} \times \frac{A(1608)}{A^*(1608)} \right\} \times 100$$

It can be seen that the degree of conversion of the composite ranges from 43 to 51 %, when the clay loading increases.

X-ray diffraction (XRD) was used to identify intercalated structures and determine the interlayer space. Figure 2 shows XRD scans for organic clay (SWy org), the pure copolymer TB and the polymer/clay composites (TB/SWy). The organic clay shows a peak at $2\theta = 5.1°$, which corresponds to a basal spacing of 1.73 nm and the pure copolymer presents a peak at $2\theta = 18°$, which is characteristic of polymers. For the 0.5 % composite the peak attributed to the d_{001} distance is not observed, indicating that the copolymer incorporated in the interlayer of the clay promoted its delamination. SEM images show that the composites with low clay loading are homogeneous, indicating an efficient dispersion of the clay in the monomers before polymerization. The diffractogram for the composite with higher clay loading still presents the peak corresponding to the d_{001} distance, suggesting the presence of tactoids, possibly due to a less efficient delamination under these conditions because of the lower proportion of monomers in the system.

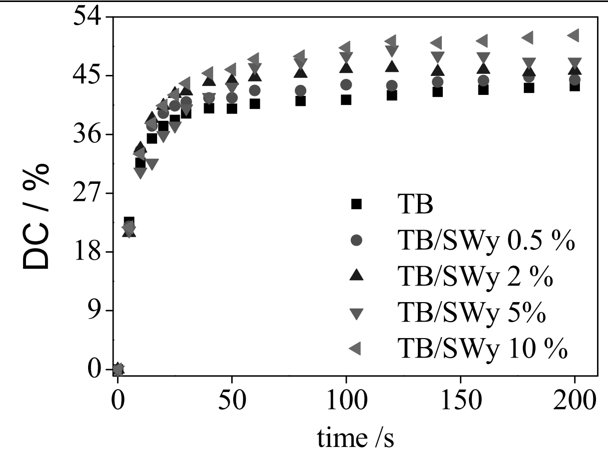

Figure 1. Degree of conversion of the composite at different clay loadings as a function of irradiation time.

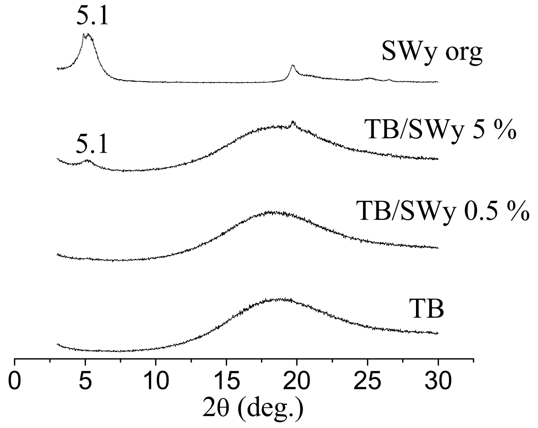

Figure 2. X-ray diffractograms of organic clay SWy org, the composites TB/SWy and pure polymer TB.

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STUDY THE CURE KINETICS OF BUTYL RUBBER/CLAY NANOCOMPOSITES

Mehdi Razzaghi Kashani, Arezoo Sepehri

Polymer Physics and Mechanics lab – Chemical Engineering Department, Tarbiat Modares University, Jalal Al-ahmad Street, Tehran, 14117-13116 Iran
E-mail: Arezoo_sepehri@yahoo.com

Keywords: *Butyl Rubber nanocomposites, Cure kinetics, Autocatalytic model*

Cure kinetics of butyl rubber (IIR)/organo-clay (Cloisite 25A) nanocomposites, prepared by melt mixing process, were investigated by Oscillating Disk Rheometer (ODR). For characterizing of the nanocomposites' structure, X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were employed. In XRD results, the shift in (001) peak reveals the intercalation of rubber into clay platelets for all nanocomposites with no sign of full exfoliation but increase in clay content may cause the appearance of a peak with higher 2θ which show more fraction of organo clay with decreased distance of interlayer. SEM results were in agreement with XRD patterns and showed a higher number of layered silicate agglomerations in highly filled compounds.
Rheometric results show a marked increase in both scorch and optimum cure time due to the barrier effect of clay in the rubbery matrix against diffusion of curing material to reach cross linking sites on rubber chains. For evaluation of kinetic parameters with a series of mathematic expressions, different types of data, due to the experimental instrument, can be employed. In this study data of torque versus time was obtained from ODR rheometer under isothermal condition, which is used to evaluate kinetic parameters. The degree of cure (conversion) at a time, t, is defined as

$$\alpha = \frac{M_t - M_0}{M_\infty - M_0} \qquad (1)$$

Where, M_0, M_t, M_h are the torque values at the time zero, at a given time of curing, and at the end of curing respectively. The model of autocatalytic reaction equation, as given below, can be used for the cure kinetics characterization of butyl/clay nanocomposites due to the time of maximum reaction rate which occurs at the time greater than t=0,

$$\frac{d\alpha}{dt} = k(T)\alpha^m(1-\alpha)^n \qquad (2)$$

Where k is the rate constant, which obeys an Arrhenius temperature dependency and m and n are reaction orders that are dependent on temperature. The parameters k, n and m can be determined using eq. (2). A nonlinear regression was used and the results in table 1, show a close agreement with experimental results which indicate the suitability of autocatalytic model for cure behaviour of these nanocomposites**.**

Table 1. Vulcanization kinetic parameters of butyl and its nanocomposites

property	t_c(°C)	0-Phr	4-25A	12-25A	24-25A	12-Na+
k	150	0.1363	0.1678	0.1174	-	0.1323
	160	0.2331	0.2185	0.1721	0.1725	0.2258
	170	0.4232	0.4036	0.3821	-	0.4172
	180	0.7324	0.7619	0.7458	-	0.6177
m	150	0.5766	0.5499	0.5365	-	0.6049
	160	0.5806	0.5806	0.5126	0.5250	0.5702
	170	0.6601	0.6064	0.6032	-	0.6619
	180	0.7188	0.6859	0.6641	-	0.6604
n	150	1.4121	1.4183	1.4824	-	1.4118
	160	1.4194	1.4500	1.4874	1.4750	1.4298
	170	1.3394	1.3969	1.3958	-	1.3314
	180	1.2786	1.3141	1.3347	-	1.3355

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INORGANIC NANO AND MICRO FILLERS IN PP/PA COMPOSITES: PROCESSING/MORPHOLOGY/PROPERTY RELATIONSHIPS.

Roza Tchoudakov*, Moshe Narkis*, Arnon Siegmann**

** - Technion - Israel Institute of Technology, Department of Chemical Engineering, Haifa, 32000, Israel,;*
*** - Technion – Israel Institute of Technology, Department of Materials Engineering, Haifa, 32000, Israel,*
E-mail: ceroza@tx.technion.ac.il

Keywords*: polymer composite, morphology, inorganic nano- micro-filler*

The presented study deals with polymer composites based on two immiscible polymers containing two types of fillers, micron-sized and inorganic nano-sized, added simultaneously to the blends during melt mixing. Polypropylene PP as the matrix (QB; MFI= 0.27, Carmel Olefins, Israel), and copolyamide CoPA (Ny66-6, T_m=220°C, Nilit, Israel) as the minor phase were melt mixed together with titanium oxide TiO_2 nano-powders of 200nm or 20nm (TiO_2^f) primary particle size as the nano-filler, along with mica, or talc, or wollastonite as the micron-sized filler. It is shown that such materials are characterized by a segregated structure where fillers, micron-size and nano-size are attracted to the PA phase. The micron-size filler particles are enveloped by the PA phase and TiO_2 particles are mainly located upon the PA phase surface and partly within it. The sequence of ingredient incorporation into the melting equipment has a significant influence on the morphology of the composite. When both fillers are premixed with PP and PA was subsequently added, the composites are characterized by a finer structure, with finer micron-size filler dispersion and a very fine dispersion of the nano-particles upon the PA particles surface – Figure 1. No agglomerates of the nano-sized fillers are seen in the two step melt mixing composites. Mechanical properties of the studied materials are significantly influenced by the addition of the two fillers – Figure 2. Some of the studied composites demonstrate unusual enhancement of elongation at break and Izod impact energy.

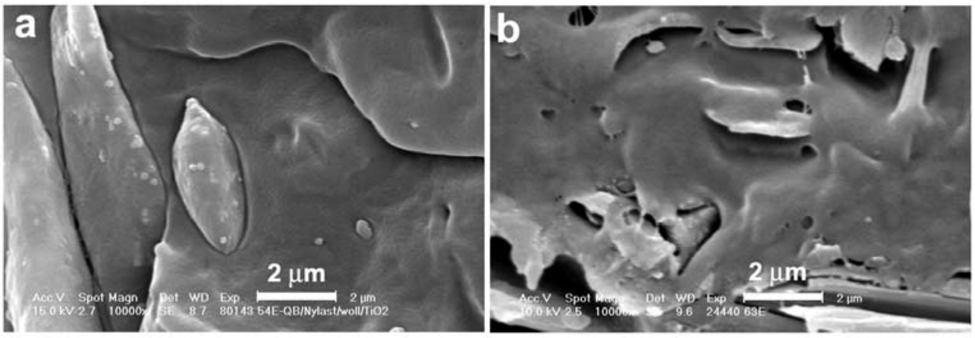

Figure 1. Freeze-fractured surfaces of the PP/Ny/wollastonite composite with TiO_2: (a) 200 nm, (b) 20 nm.

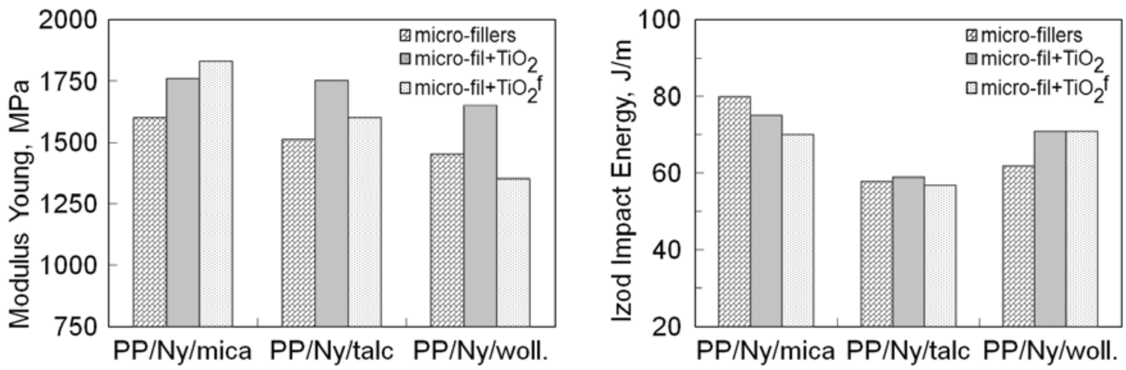

Figure 2. Mechanical properties of the composites produced by the two steps method**.**

PHYSICAL AND MECHANICAL PROPERTIES OF LDPE/ORG-MMT NANOCOMPOSITES PREPARED BY MELT INTERCALATION METHOD

Hossain Nazoksast, Yadolla Teimoori

Polymer Engineering Lab. – University of Amirkabir, Address: Hafez Street, 424, POBo:15875-4413, Tehran, Iran
E-mail: yadi_1626@yahoo.com

Keywords: *Nanocomposite, Melt intercalation, Polyethylene, Compatibilizer, Properties.*

Polyethylene/ organo-montmorillonite clay (org-MMT) nanocomposites were prepared utilizing PP-g-MA as a compatibilizer by melt intercalation method. In order to increase the miscibility of polyethylene (PE) with nanoparticle's surface at first, a primary master-batch consisting of compatibilizer and org-MMT was prepared; then this compound was melt intercalated with PE to synthesis the PE/org-MMT nanocomposites. The effect of amount of the nanoparticle on nanocomposite's structure and properties has been investigated. In this work LDPE/clay nanocomposite film was successfully synthesized, the specimens of nanocomposite demonstrated improved physical and mechanical properties rather than the pure matrix. The XRD results showed that the interlayer distance of nanoparticle layers increased and a partially intercalated structure was obtained by melt intercalation method. The DSC data demonstrated that the melting temperature has slowly increased and crystallinity has slightly decreased. Consequently, we can claim that the thermal properties of LDPE/clay nanocomposites did not considerably change with clay content. A rise in the mechanical properties such as yield stress and modulus was observed by a tension test ; by addition of 5% clay the tensile strength increased about 7%, the tensile modulus enhanced about 35% and the yield stress increased about 16% in comparison with the pure LDPE.

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EFFECT OF ORGANOPHILIC MONTMORILLONITE AND ACRYLIC COPOLYMERS ON NANOSTRUCTURE AND PROPERTIES OF EPOXY RESIN NETWORKS

Adriana Silva*, Soraia Zaioncz*, Karim Dahmouche, Bluma Soares***

** Macromolecular Institute, Federal University of Rio de Janeiro (UFRJ), P.O Box 21945-970, Rio de Janeiro-RJ, Brazil*
*** University of Zona Oeste (UEZO), Rio de Janeiro, Brazil*
E-mail: adrianadosanjos@ima.ufrj.br

Keywords: *Epoxy resin; copolymer, organophilic clay; nanocomposite.*

The use of epoxy resin in high performance structural materials is common practice, particularly in the matrices for advanced composites for the aerospace industry. However, the major drawback of these materials is that in the cured state they are brittle [1]. Polymer/layered silicate nanocomposites based on layered smectite clays as the reinforcing part of the matrix often improve toughness and mechanical properties [2,3]. The present paper discusses the effect of incorporation of clay on the degree of intercalation and properties of epoxy-clay nanocomposites.

The aim of the present work is to synthesize nanocomposites of the epoxy resin modified with acrylic polymers and organophilic montmorillonite (Cloisite 30B). 2-Ethylhexyl acrylate-methyl methacrylate copolymers (10 phr) were prereacted with epoxy resin (100 phr) using at 80ºC for 2h. A little amount of acrylic acid was also introduced as the third monomer reaction between the carboxyl groups of the acrylic copolymer and the oxirane rings of the epoxy matrix. After organophilic clay (2.5 phr) was stirring for 25 min. Then, a stoichiometric amount of hardener triethylene tetramine (TETA) was added.

The SAXS patterns of epoxy composites for all samples show two peaks located around 1.5 nm^{-1} and 3.8 nm^{-1}, confirming the existence of non-exfoliated clay aggregates or tactoids, which were not detected by XRD. Through SAXS curves was observed to increase the intensity of the peak with the composition of clay. This result is consistent, that increase in clay content induces a lower MMT dispersion in composites.

The dispersion of clay in epoxy resin result a slight decrease of storage modulus (Figure 1). This behavior can be attributed to the presence of tactoids, which involves reducing the efficiency of clay as reinforcing agent of the matrix. On the order hand, all the composites showed displacement of tan delta peak for higher temperature (Figure 2). This effect can be attributed to the decrease of segmental mobility of the matrix, due to the presence of clay, leading to an increase in Tg. Furthermore the addition of clay in epoxy systems increased the thermal stability as observed by the increase in degradation temperature.

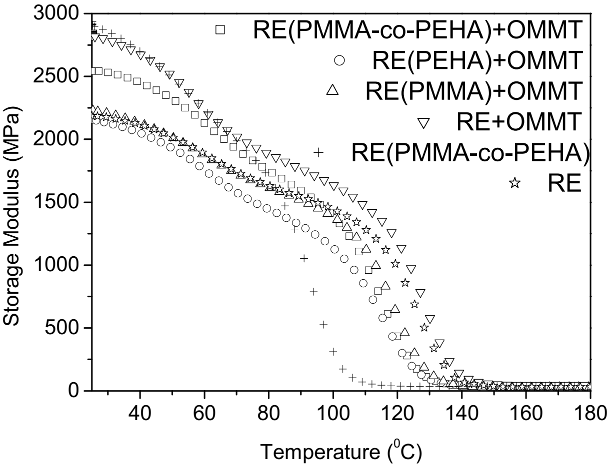

Figure 1. Storage Modulus of epoxy networks.

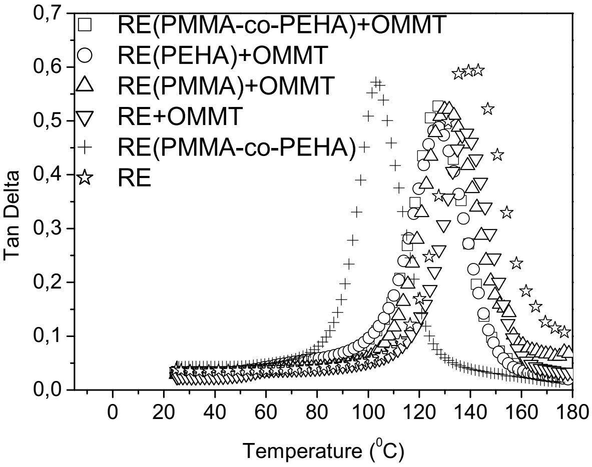

Figure 2. Damping of epoxy networks.

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COMPATIBILIZER LOCALIZATION IN FULLY EXFOLIATED POLYPROPYLENE/CLAY NANOCOMPOSITES

Marcin Zarod, **Andrzej Galeski**

Department of Polymer Physics , Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland
e-mail marzar@cbmm.lodz.pl

Keywords: *polypropylene, nanoclay, nanocomposite*

Polypropylene/ nanoclay nanocomposites were prepared by two-step extrusion with preparation of the masterbatch. The composition was optimized with regard to the composition and the ratio of nanoclay/compatibiliser. The preparation of the masterbatch was elaborated to ensure an efficient covering of of nanoclay platelets with the compatibiliser[1-3]. Further compounding was optimized by varying processing parameters until full exfoliation of nanoclay platelets was achieved. The criterion was the loss of any periodicity in XRD pattern that was checked by examination of ultrathin sections in transmission electron microscope. Compatibiliser/nanoclay interface was enhanced by OsO_4 staining. in polypropylene nanocomposites has been revealed by TEM images. Nanocomposites with different compatibiliser amount were prepared by two-step extrusion and examined. It was evident that up to the ratio of compatibilizer/nanoclay 4:1 the compatibilizer is located preferentially on the surfaces of nanoclay platelets and none was found in the bulk of polypropylene (see Figures 1a and 1b).

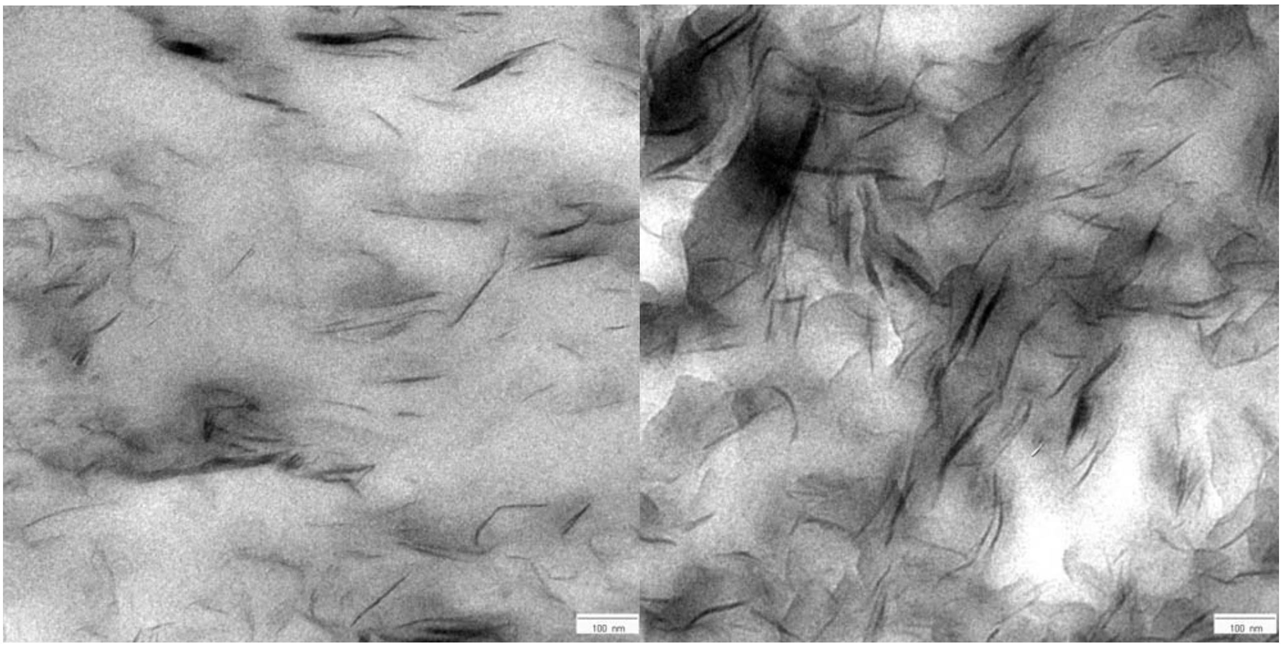

Figure 1: TEM images of ultrathin sections of polypropylene nanocomposites: a. unstained, b. stained with OsO_4 .

The thickness of the compatibiliser layer adhering to nanoclay platelets differs depending on the compatibiliser concentration, exfoliation of clay and polypropylene type.

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THERMAL PROPERTIES OF ISOTACTIC POLYPROPYLENE COMPOSITES FILLED WITH NANO- AND MICROPARTICLES

Ruijuan Zhou*, Thomas Burkhart

Institut für Verbundwerkstoffe GmbH, Technische Universität Kaiserslautern
Erwin-Schrödinger-Str., 67663, Kaiserslautern, Germany
E-mail: Ruijuan.zhou@ivw.uni-kl.de

Keywords: characterization, iPP composites

In recent years, many studies have shown improvement in mechanical properties of polypropylene by incorporation of inorganic fillers[1, 2]. The objective of this work is to evaluate the influence of nano and microparticles having the similar surface nature (hydrophilic) on thermal behaviors of isotactic polypropylene (iPP). For that purpose, iPP (Moplen® HP400H, LyondellBasell) composites filled with 5 wt.% nanosilica (Aerosil® 90: 20 nm) as well as micro-alumina (Dispal® N7-80: 40 μm) were prepared by melt blending in a Brabender kneading chamber and then characterized by using scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and polarized light microscopy (PLM).

The SEM micrographs show that the nanoparticles are well dispersed in matrix, whereas the microparticles form some large agglomerates indicating a much poorer dispersion state. The DSC results show that the incorporation of 5 wt.% particles does not significantly increase the melting temperature of iPP in composites (about 168 °C). However, the crystallization temperature (Tc) and the crystallinity degree (Xc) of iPP composites are clearly improved compared to pure iPP, particularly in the case of iPP/microparticle composite (Tc from 112 °C of pure iPP to 120 °C and Xc from 44% to 47%). This result can be attributed to a heterogeneous nucleation effect induced by particles. The lower the crystallinity (spherulite density), the larger the spherulite growth is. This is proven by related PLM analysis. Moreover, the nanoparticle filled composite shows better developed α-crystalline structure than microparticle filled composite. In the case of thermal stability at high temperatures, both particles show a similar reinforcing effect due to the same particle content in matrix, indicated by much lower decomposition rates of both composites in comparison with pure iPP. The remaining weight fraction of composites after TGA tests keeps nearly constant at 5 wt.%, as expected.

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TEMPERATURE DEPENDENT MECHANICAL BEHAVIOR OF POLYVINYLIDENE FLUORIDE

Viviane Gonçalez*, **Marysilvia F. Costa****, **Ilson Paranhos Pasqualino***

** Departamento de Engenharia Naval e Oceânica– Universidade Federal do Rio de Janeiro UFRJ/ COPPE – Centro de Tecnologia, Bloco I, Cidade Universitária, Ilha do Fundão, 21945-970, Rio de Janeiro, RJ, Brazil*
***Departamento de Engenharia Metalúrgica e de Materiais - Universidade Federal do Rio de Janeiro UFRJ/ COPPE – Centro de Tecnologia, Bloco F, Cidade Universitária, Ilha do Fundão, 21945-970, Rio de Janeiro, RJ, Brazil*
Email: viviane@lts.coppe.ufrj.br

Keywords: *polyvinylidene fluoride, viscoelasticity, mechanical behavior, relaxation, numeric simulation.*

Polyvinylidene Fluoride (PVDF) is a semi-crystalline thermoplastic that has four different crystalline structures (α, β, γ and δ) [1]. The most common structure is the α and it is possible through this to get the other structures using heat treatment or mechanical. The β is responsible for piezoelectric and pyroelectric properties and the phased corresponds to the polar α [2]. However, if the α polar phase that has attracted recent interest due to the high potential in structural applications, such as in the offshore industry where this polymer is used as a barrier pressure in flexible pipes used in the exploitation and transportation of oil, or inshore as material for reliner pipeline transport of fluids [3,4]. Structural Applications of PVDF are relatively recent. It is known that chemical bonds between the fluorine and carbon are responsible for their high mechanical and chemical resistance. Because of this these materials are chemically inert in solvents and various environments such as oil and water. They will also have greater resistance to high temperatures in relation to polyamides and the polyethylene. PVDF and all polymers are materials dependent on time and frequency [5], thus it is important to study the viscoelastic behavior to assess the lifetime of a polymeric structure. For this reason we chose to study the viscoelasticity of PVDF through relaxation tests at different temperatures (25, 55, 70 and 90°C) and initial strains (5 and 10%). The thermal characterization of PVDF as received was made by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The behavior of stress-strain and relaxation of PVDF with temperature was investigated (25, 55, 70 and 90°C). There was a decrease in elastic modulus with increasing temperature: 1008, 520, 337 and 285 MPa to 25, 55, 70 e 90ºC respectively and 5% initial strain, although the reduction was not linear with increasing temperature. The decrease in modulus with increasing test temperature is due to mobility of the amorphous chains. The crystalline region remains unchanged since the glass transition temperature of PVDF is higher than the temperatures used in the tests. The increase in temperature contributes to the mobility of amorphous chains, causing the structure to deform more easily and its mechanical performance is compromised. The decrease in relaxation module (G (t)) was also obtained with increasing temperature, 670, 377, 275, 185 MPa to 5% initial strain and 742, 545, 339, 224 MPa to 10% of initial strain in 25, 55, 70 and 90ºC respectively. It was observed that samples deformed up to 10% showed a more drastic reduction in the module compared to samples deformed up to 5% regardless of temperature. This behavior is related to conformational changes of groups or segments of the polymer chain, resulting from rotations around the chemical bonds that occur with increasing temperature. The increase in temperature contributes to the mobility of polymer chains, thus decreasing the relaxation module. Through the analysis of X-ray diffraction (XRD) revealed that the structure did not change after relaxation tests regardless of test temperature, 51, 56, 54 and 59% of cristalinity to 5% of initial strain and 25, 55, 70 and 90ºC respectively. It was observed 57% of cristalinity degree to sample as received. Experimental results were used to validate the numerical model (ABAQUS) developed where good correlation with the experimental results were observed.

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MECHANICAL AND FLAME RETARDING PROPERTIES OF POLYSTYRENE FOAM CONTAINING SOLID SURFACE MATERIALS

Yoo Sung Choi*, **Hwang Woo Jo,**** **Soo-Kyung Choi***, **Byung Wook Jo***

** Dept. of Chemical & Biochemical Engineering, Chosun University,*
*** Dept. of Polymer science and Engineering, Chosun University*
375 Seosuk-dong Gwangju 501-759, Republic of Korea
E-mail: usung12@naver.com

Keywords*: GPPS, flame retardant, inorganic wastes*

Solid surface materials, so called articial marble (AM) are manufactured from polymeric materials. Granules may also be added to enhance the color effects. Solid surface materials are non-porous and homogeneous, with the same composition throughout the thickness of the solid surface material. They are capable of being repaired, renewed to the original finish and fabricated into continuous surfaces with inconspicuous seams.

The polymeric resin materials used for producing solid surface materials are 1) filled acrylic polymers, 2) filled polyester polymers and 3) filled acrylic-polyester blend. The filler most often used is Alumina Trihydrate (ATH). AM consists of various materials such as PMMA, ATH, alumina and silica etc. The ATH can be used for improving flame retarding properties of polymeric composites because ATH absorbs the heat(470kcal/kg) and lowers smoke emitting at the fire atmosphere.

E-beam cured blends of GPPS (general purpose polystyrene foam) with inorganic wastes such as AM and surface treated fly ash (FA. Photo1)has been of great interest in improving the mechanical properties of the blends. E-beam irradiation leads effective cross-linking of GPPS with inorganic wastes which show no macro phase separation between GPPS and the inorganic materials. . It gives much shorter curing time, low shrinkage, improved performance and elimination of hazardous cross-linking agent etc. Emitted fractions (v/v) of smoke fumes in GPPS with inorganic wastes in ppm at different temperatures were as follows,
Carbon monoxide 10(300°C), 40(400°C), 60(500°C), 95(600°C)
Other aromatic compounds fractions 10(400°C) 30(500°C), 10(600°C) and no hydrogen compounds

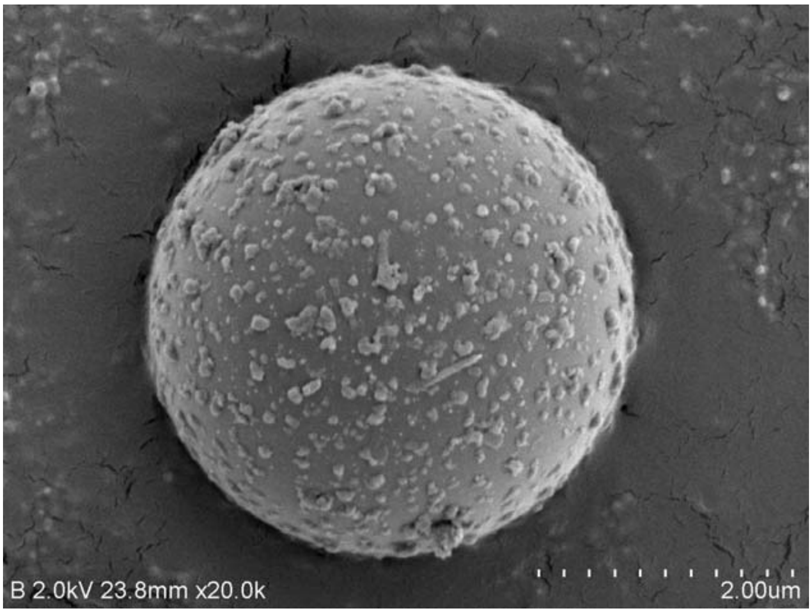

Photo1. Fly-ash surface treated by poly(ethylene vinyl acetate)

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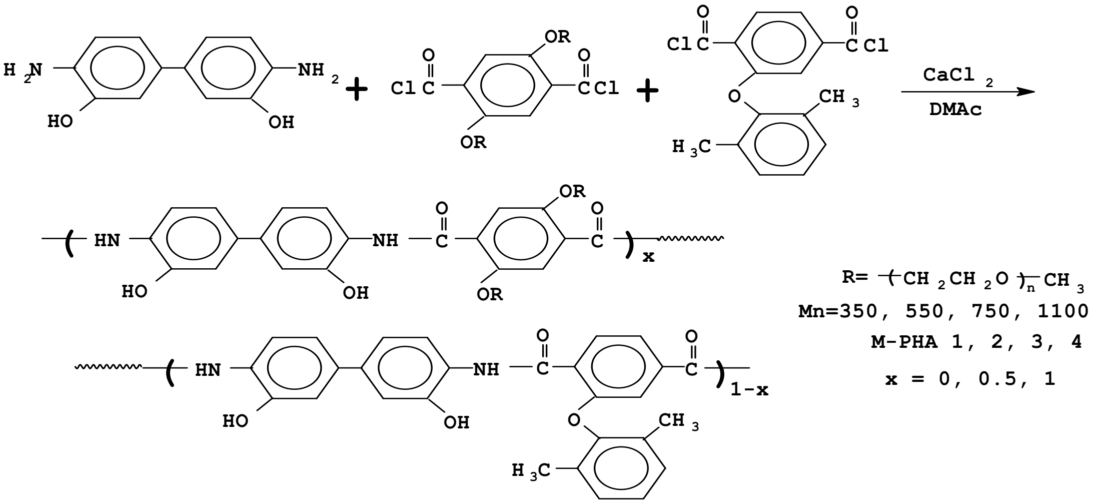
FLAME RETARDANT AROMATIC POLY(HYDROXY AMIDE)s

Jae Kon Choi[1], Hwang Woo Jo[1], Duyoung Wee[1], Byung Wook Jo[2]

[1]*Dept. of Polymer science and Engineering,*
[2]*Dept. of Chemical & Biochemical Engineering, Chosun University,*
375 Seosuk-dong Gwangju 501-759, Republic of Korea
E-mail: bwjo@chosun.ac.kr

Keywords: *aromatic PHA, flame retardant, cyclization*

Aromatic polybenzoxazoles (PBOs) are a class of heterocyclic polymers that have excellent thermal stability, high mechanical properties, good environmental resistance, and superior hydrolytic stability. Highmodulus fibers can be produced by the spinning of liquid-crystalline solutions of rod-like aromatic PBOs in sulfuric acid or polyphosphoric acid. However, the PBOs are too much tough to process in conventional ways. It's necessary to modify the chemical structure of their precursor compounds. Aromatic polyhydroxyamides (PHAs) having poly(ethylene glycol)methyl ether (MPEG) group and/or ether linkages in the polymer main chain were synthesized by solution polycondensation at low temperature (Scheme 1). PHAs were studied by FT-IR, ^{1}H-NMR, DSC, TGA, XRD, Dynamic Mechanical Analyzer (DMA), Universal Testing Machine (UTM) and Limiting Oxygen Index (LOI). The inherent viscosities of the PHAs measured at 35 °C in DMAC solution were in the range of 0.68~1.49 dL/g. Solubility of PHAs was soluble or partially soluble in Tetrahydrofuran (THF) and Trifluoroacetic acid (TFA), and pyridine as well as aprotic solvents, but the PBOs were nearly insoluble in a variety of solvents. PHAs were converted to polybenzoxazoles (PBOs) by thermal cyclization reaction, and endothermic peak by thermal cyclization was observed in the range of 210~350 °C. The 40% weight loss temperature of the PHAs showed in the range of 414~777 °C and PBOs except for PBO 1 showed in the range of 424~628 °C. Char of PHAs and PBOs showed high values in the range of 24~56% and 35~64% respectively. Wide-angle X-ray scattering patterns of the PHAs showed in the range of 21.58~29.48 Å. Storage modulus of PHAs was decreased as increasing chain of MPEG, and showed about 110 MPa. Initial modulus and Tensile strength of the PHAs were showed in the ranges of 0.12~0.22 GPa, and 2.24~3.43 MPa, as they were increased with increasing mole ratio of quinoxaline . The LOI values of PHAs showed in the range of 39~41.2, as they were increased with increasing mole ratio of quinoxaline.



Scheme 1

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A STUDY ON STRUCTURAL, MECHANICAL AND THERMAL PROPERTIES OF POLYMER COMPOSITES OF POLYVINYL ALCOHOL WITH INORGANIC SALTS

Gulfam Nasar, M Saleem Khan, Uzma Khalil

National Center of Excellence in Physical Chemistry, Polymer Lab, Peshawar University, Peshawar, Pakistan
E-mail: gulfamnasar@yahoo.com

Keywords: *PVA, Composites, Polymer*

Polymer composites have gained the attention of scientists and researchers all over the world. During the recent years lot of research has been conducted in search for more handy and cheaper materials. Polymer composites are adding a great deal to material that is more durable and useful as compared to the conventional material[1] Mechanical and thermal properties of composite materials greatly depend on the nature, proportion and compatibility of the components of the composite materials[2]. The presence of any second phase (disperse phase as polymer or filler) in a polymer matrix (disperse media) affects the mechanical properties of the mixture (blends or composites) depending on the relative concentration of the two phases, nature of the disperse phase, surface characteristics, distribution of one phase in another, domain size and shape, adhesion between two phases, size of the particles, surface area and degree of compatibility, in particular. In this paper we have tried to find relationships of these properties *i. e.* thermal conductivity, tensile strength and Young's Modulus of the composite material. Two systems were selected; poly(vinyl alcohol)/ Sodium sulphate composite, and poly(vinyl alcohol)/ Lithium sulphate composite. Various concentrations of these salts were added to poly(vinyl alcohol), using triply distilled water as solvent. Films were cast, dried at room temperature and were subjected to mechanical, structural and thermal characterization. Thermal conductivity was determined at room temperature using Quick thermal conductivity meter. Polyethylene, silicon and quartz were used as reference[3]. It was found out that the thermal conductivity of both the systems is highly dependent of the nature and the concentration of added salt in the polymeric composite. Thermal conductivity of the poly(vinyl alcohol)/sodium sulphate composite, and poly (vinyl alcohol)/lithium sulphate composite decreased with concentration of the salts in the polymer composite. These composites were also analyzed for their structure and the properties exhibited were explained on the bases of their structure. Similar trends were observed in mechanical properties of these composites, *e.g.* tensile strength, elongation at break and Young's Modulus.

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EVALUATION OF CHEMICAL AND MECHANICAL RESISTANCE OF SPHERICAL POLY(METHYL METHACRYLATE-*CO*-VINYLACETATE) PARTICLES WITH VARIED COMPOSITION

Renata V. Pires, Hélida V. P. Vieira, Elizabete F. Lucas

Federal University of Rio de Janeiro, Institute of Macromolecules
Av. Horácio Macedo, 2030 – Ilha do Fundão, 21941-598. Rio de Janeiro, Brazil.
E-mail: repires@ima.ufrj.br

Keywords: *Suspension polymerization, poly(vinyl acetate),chemical resistance*

Some industrial processes require filling in voids with diameters of about 100 μm. Polymeric resin particles can be used to fill in these spaces, even though they need to be removed at the end of the process. In this work, we synthesized spherical resin particles by suspension polymerization. Benzoyl peroxide was used as initiator at a concentration of 1% in relation to the total monomer mass. The concentrations of the monomers and suspension agent in relation to the aqueous phase were 40 and 1.25%, respectively. The reactions were performed at 80 ºC for 4 hours. The methyl methacrylate/vinyl acetate (MMA/VAc) ratio was varied in the range of 100/0 to 10/90. The resins were characterized regarding composition (by ^{13}C-NMR), bead size distribution (by passing the beads through sieves), morphology (by optical microscopy), glass transition temperature (by DSC) and acid resistance. The VAc content in the copolymer composition was lower than that in the feed due to the solubility difference between monomers. In general, the particle sizes were in the range of ~50 to ~400 μm, with a greater concentration in the range from 150 to 355 μm. The optical micrographs showed that all beads were spherical, due to the polymerization process used. As expected, the glass transition temperatures varied in function of the MMA/VAc proportion, confirming the more rubbery character of the spheres containing higher vinyl acetate content. For this reason, they could be more efficient for filling in voids. The resistance to acids was evaluated by exposing the resins to 1.0 molar hydrochloric acid for 72 hours, and then observing them under an optical microscope for comparison against micrographs of the resins that was not exposed. The resins had undergone a significant decrease in size. The greatest variation occurred for the particles containing the highest MMA content. As increasing the VAc content in the copolymer, it becomes necessary to use a more concentrated acid. This size reduction confirms that these resins can easily be removed from the system by the action of acid. The compression resistance is being evaluated in columns filled with the polymer material submitted to a pressure of about 15 psi. The beads will be analyzed by optical microscopic in order to observe the changes in shape as a function of composition and pressure.

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WATER VAPOR TRANSPORT IN LIQUID CRYSTALLINE THERMOSETS

Lei Nie, Patrick Fairclough, Anthony J. Ryan

Department of Chemistry.-University of Sheffield, Address: Daiton Building, Western Bank, S10 1DH, Sheffield, UK).
E-mail: chp07ln@sheffield.ac.uk

Keywords: Liquid crystalline thermoset, Water barrier, Water vapor permeability.

Liquid crystalline thermoset (LCT) is a special liquid crystalline material which has unique characteristics of both liquid crystals and high performance thermosets. In the LCT, the molecules are arranged on one or two dimensional or positional regularity; and unlike liquid crystalline polymers, the molecules are crosslinked by covalent bond to form a three-dimensional network. Therefore, the regularity and 3D network gave them excellent mechanical properties. For most engineering polymers or thermosets, the variable real life environments during the service would have great influence on their performance. The long-term properties of the LCT depend on the interaction of the LCT with the environmental conditions such as the temperature or moisture. Within those conditions, the water absorption in the thermosets has predominant detrimental effects on their long-term mechanical properties. Many researchers have reported the synthesis, characterization, mechanical properties, thermal properties of LCT, and moisture sorption of conventional epoxies.[1,2] However, the mechanism of interaction between water and liquid crystalline thermosets remains unclear. In our research, 4, 4'-diglycidyloxy-α-methylstilbene (DOMS) has been prepared as the liquid crystalline epoxy.[3] Several different crosslinkers, e.g. sulfanilamide (SAA), sebacic acid (SBA), 4, 4'-diaminodiphenylmethane (DDM) and 2, 4-diaminotoluene (DAT), have been tried to make different kinds of liquid crystalline or non-liquid crystalline thermosets. And their inner structures and thermal properties have been characterized by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and wide angle X-ray scattering (WAXS). The smectic structure in the DOMS/SAA system has been proved by both experimental and theoretical results. Because of the efficient chain packing of the smectic mesophase of the liquid crystalline epoxy, the 3D network of the LC structure exhibits high barrier properties to moisture transport than the conventional epoxy network.[4,5] The permeability of LC thermosets obtained by the dynamic vapor sorption (DVS) tests is much lower than conventional epoxy resin (2.7 times lower at 85 while 3.9 times lower at 65).The relationship between the permeability and inner structure of LCT has been established. Dynamic mechanical analysis (DMA) was also employed to analyze the sub-T_g transitions of the liquid crystalline thermosets, which might have effect on the performances in the DVS test.

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WATER UPTAKE AND MECHANICAL RESPONSE OF THIN NYLON FILMS – AN NMR IMAGING STUDY

Nico Reuvers*, **Henk Huinink***, **Bart Erich****, **Olaf Adan ****

**Department of Applied Physics, Technical University Eindhoven, P.O. Box 513, 5600MB Eindhoven, The Netherlands,*
***TNO Built Environment and Geosciences, P.O. Box 49, 2600 AA Delft, The Netherlands*
E-mail: n.j.w.reuvers@tue.nl

Keywords: *Nylon, NMR, water uptake*

The variety of applications of nylons (or polyamides) leads to the interest to study fluid uptake processes. Either used as an engineering plastic, high strength fiber or packaging material, fluid uptake will affect the mechanical properties of nylon. For a better understanding of the relation between mechanical behavior of thin films and moisture uptake these processes are studied using NMR imaging. Using NMR both water distribution and sample deformation are measured. Nylon (PA6) films are pasted on glass plates and a tube filled with water is set on top of this plate to do the experiments. The nylon films are made by hot-pressing nylon pellets at a temperature of 280 ºC.
On the nylon films uptake and drying experiments are performed using both H_2O and D_2O. The water distribution in depth (1D) is imaged using the so-called GARField approach[1]. Samples saturated at a certain relative humidity, ranging from 0 to 100 percent, are used to calibrate the NMR signal. This calibration allows us to obtain spatial information about the amount of water per unit mass of nylon. During the water uptake process three stages can be identified (as shown in the figure). These three stages go together with the bending of the glass plate underneath the sample. Water first weakens and swells the upper part of the nylon layer leading to a upward bending of the middle of the glass plate. Then during a second stage water ingresses further towards the bottom of the sample while the middle of the glass plate moves downwards indicating shrinkage and/or stress relaxation. The third part of the uptake process is only observed as a mechanical response of the glass plate.

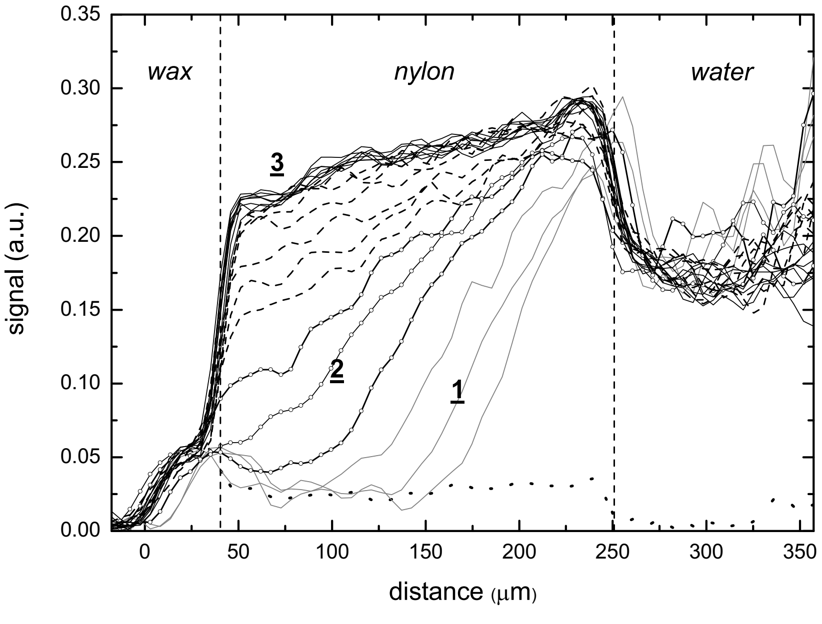

Figure 1. NMR hydrogen profiles measured during water ingress every 34 minutes in a nylon film. In this figure a position correction is applied to correct for the mechanical response. The left part of the figure corresponds to the glass/wax substrate and the right part of the figure shows the water that is placed on top of the nylon film.

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EXPERIMENTAL EVALUATION OF FLOW ACTIVATION VOLUME FROM STEP-SHEAR EXPERIMENTS

Sara R. S. Sampaio*,** **Weidong Zhang***,** **José A. Martins***,**, **Andrzej Galeski*****

** Departamento de Engenharia de Polímeros, Universidade do Minho, Campus de Azurém 4800-058 Guimarães, Portugal;*
*** CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal*
**** Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland*
E-mail: jamartins@dep.uminho.pt (corresponding author)

Keywords: *tube model, flow activation volume, Mz molecular weight*

In the viscoelastic linear regime the following combination of mechanisms were considered to explain the stress relaxation of a tube deformed during an idealized rapid "step" deformation: chain reptation, primitive path (or contour length) fluctuations, Rouse modes inside the tube and (thermal) constraint release (CR). This last relaxation process may be viewed in the following way: reptation of the test chain releases constraints in the matrix chains and vice-versa, so that this mutual CR accelerates the melt relaxation. A simple CR model is the double reptation for which the longest relaxation time is half the relaxation time in the absence of this CR relaxation mechanism. Of specific interest to this work are CR models considering the increase in the tube diameter, also called dynamic tube dilation (DTD), as an additional possible relaxation mechanism. The Graessely parameter, defined as $Gr = M_L M_e^2 / M_S$ (where M_L and M_S are the molecular weights of the long and short chains, respectively and M_e is the molecular weight between entanglements) is used to ascertain, whether or not, the relaxation of long chains in binary blend of long and short chains proceeds by DTD. It was considered that when $G_R > 0.1$ diffusivity of long chains begins to be affected by the short chains, *i.e.* by tube dilation.

For fast flows, in the viscoelastic non-linear regime, two additional tube relaxation mechanisms are considered. Under flow chains stretch relaxing by retraction, which originates an additional release of constraints, the convective CR, a mechanism similar to the thermal CR, but in this case originated by flow. Since at steady state chains are no longer stretching, the convective release of constraints imposed by the matrix chains on the test chain should proceed at a rate proportional to the flow rate.

We evaluate in this work from experimental results the flow activation volume in a polydisperse sample of isotactic polypropylene (M_n = 24388 g/mol, M_w = 150596 g/mol, M_z = 488609 g/mol), Graessley parameter Gr =1.05 (with M_e = 5500 g/mol). It was evaluated as $V^* = k_B T \ln(\dot{\gamma}_1/\dot{\gamma}_2)/(\tau_1 - \tau_2)$, where $\dot{\gamma}_1$ and $\dot{\gamma}_2$ are two different constant shear rate values at which a material at a temperature T is sheared; τ_1 and τ_2 are corresponding shear stress values evaluated at the yield point (maximum value in a stress-time or stress-strain curve). This flow activation volume (V_R^*) is equal to the volume of a tube confining the longest chains in the melt, those of M_z molecular weight, which is equal to $\pi\sqrt{M_e} \cdot M_z \cdot l_k^3 / 4M_k^{3/2}$, where M_e is the molecular weight between entanglements and M_k is the molecular weight of the Kuhn monomer.

A higher value of flow activation volume was evaluated at steady state by step shear experiments – V_{Sh}^*, which is approximately twice the value of V_R^*. In this last evaluation, τ_1 and τ_2 are the shear stress values at steady state at different constant shear rates. As shown in a previous work,[1] a significant entanglement loss occurs in polymer melts from the yield point up to the steady state. For iPP it was found that only 1/3 of the initial constraints survive at steady state, which means that, at steady state, $M_{e,sh} \cong 3M_e$. The diameter of this tube is $\sqrt{3}$ wider that the diameter of the tube in a relaxed melt and $V_{Sh}^* \cong \sqrt{3}\ V_R^*$, which is also the volume of a tube confining the chains with the same M_z molecular weight.

These results demonstrate that flow occurs only when the largest chains in the melt start to move, that the time-scale for this movement is dictated by reptation, and that, as shown also in a previous work,[1] the different relaxation mechanisms for explaining the relaxation in polymer melts have to be reanalysed.

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NANOSCALE ORDERING BETWEEN POLYROTAXANES

José Joaquín Atencia*,, Rüdiger Berger*, Berna Serrano**, Javier Pozuelo****

** Max-Planck-Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany*
***Materials Science and Engineering and Chemistry Engineering Department, Escuela Politécnica Superior, Carlos III de Madrid University, Avda. de la Universidad 30, 28911 Leganés, Spain*
E-mail: jatencia@ing.uc3m.es

Keywords: *Polyrotaxanes, Scanning Force Microscope, Epoxy Resin*

Recent development in rigid macromolecules, like inclusion complexes based in polymers and cyclodextrins (CD), called polyrotaxanes (PR), can be used like one-dimensional nanofillers in epoxy resin to improve thermal and mechanical properties [1]. CD are (1-4) α-linked cyclic oligomers of glucopyranose having a singular toroidal shape. Thus the size of the inner cavity and its relative apolar inner surface of these CD, are able to form inclusion complexes with polymers [2]. Pseudopolyrotaxanes, based on poly(ethylene glycol) (PEG) and α-CD (ciclodextrin with 6 glucopyranose units), have been synthesized. Formation of these inclusion complexes lead to precipitation of the product from aqueous solution of the CD. Dethreading of pseudopolyrotaxanes can be avoided by using a bulky end-groups, e.g. 1-naphthol.

The structure of a polymeric nanocomposite is defined by segregation, agglomeration and ordination of the nanofillers in the epoxy resin. It is mandatory to study the nanofillers aggregation per se for understanding the interaction. Then their behaviour in the epoxy resin can be better predicted. In many cases the nanofiller/nanofiller interactions lead to an agglomeration and in consequence a bad miscibility in the epoxy resin. One method for improving this miscibility is to do a chemical modification on the PR. In this study, phenylisocyanate has been used as modifier of the PR`s surface. Using the latter a hydrophobic character was obtained. In order to investigate the interactions between hydrophilic and hydrophobic PR, scanning force microscopy (SFM) was performed on drop casted films in air [3]. We found that there is a significant difference in agglomeration behaviour between hydrophilics and hydrophobic PR (*Figure 1*). In the case of the hydrophobic PR a drop cast solution of dimethylformamide onto mica lead to fiber like aggregation (*Figure 1, right side*). The fiber type aggregation was attributed to the hydrophobic interaction of the phenylisocyanate groups. To verify the role of the hydrophobic chemical modification a film was prepared on a hydrophobic substrate, i.e. HOPG. On HOPG no fiber like aggregation was observed. Thus the hydrophobic interaction of the PR to the HOPG substrate dominates and influences the aggregation. Furthermore the dependence on the concentration of PR on mica substrate was investigated. Based in our investigations a model is proposed for understanding the behaviour of the PR in a polymer nanocomposite. Finally the different miscibility of PR hydrophilic and hydrophobic with different percentages, in two system, epoxy resin and polyaminomethylsyloxane, has been investigated. With these results we propose a model for the behaviour the polyrotaxanes in epoxy resin with different polarity.

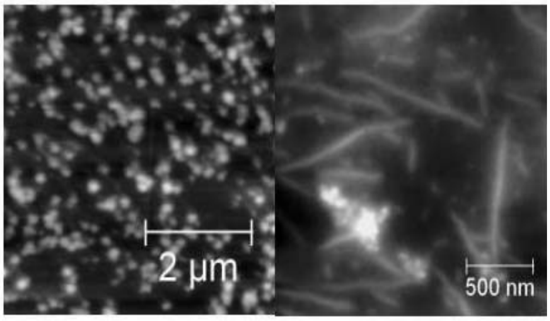

Figure 1. Agglomerates of PR Hydrophilic (Left) and Fibbers of PR Hydrophobic (Right**)**

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METAL-LIGAND COORDINATION INDUCED SELF-ASSEMBLY OF BOLAAMPHIPHILES BEARING BIPYRIMIDINE

Bo Song*, Guanglu Wu*, Zhiqiang Wang*, Xi Zhang*, Mario Smet, Wim Dehaen****

** Key Lab of Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China*
*** Department of Chemistry, Katholieke Universiteit Leuven,Celestijnenlaan 200F box 2404, B-3001 Leuven, Belgium*
E-mail: bo.song@uni-siegen.de

Keywords: *self-assembly, bolaamphiphile, metal-ligand coordination*

Self-assembly of amphiphilic molecules is a simple yet efficient bottom-up way of fabricating nanostructured materials, which have potential practical applications as soft matters or in mimicking biomineralization processes. To fabricate stable and also controllable self-assemblies, the strong supramolecular interaction metal-ligand coordination interaction is introduced in bolaamphiphiles. The study demonstrated that the new molecule bpym-8 itself can form spherical aggregates in aqueous solution by self-assembly. And after coordinating with Cu (II), the spherical structures are induced into clustered aggregates (Figure 1). It is noted that the assembly of bpym-8 can be reversibly converted back by removing the Cu(II) ion from the coordination. This study presents a new type of bolaamphiphile that is able to coordinate with metal ions, which may provide a new clue in fabricating reversibly tunable supramolecular nanomaterials.

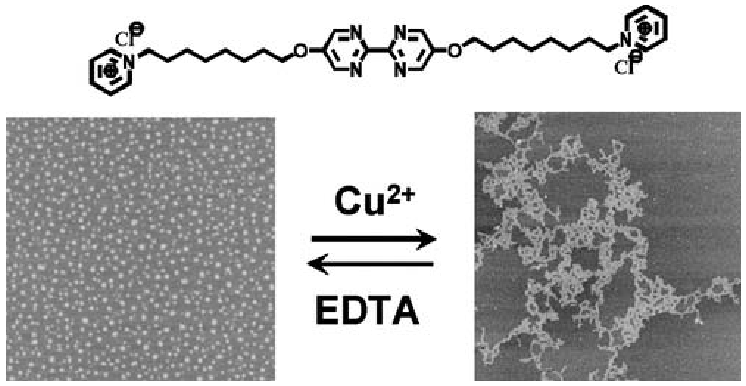

Figure 1 The molecular structure of bpym-8 and its reversibly tuned morphology change

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SYNTHESIS AND CHARACTERIZATION OF DI(ETHYLENE GLYCOL) METHYLETHER METHACRYLATE-BASED POLYMER BRUSHES

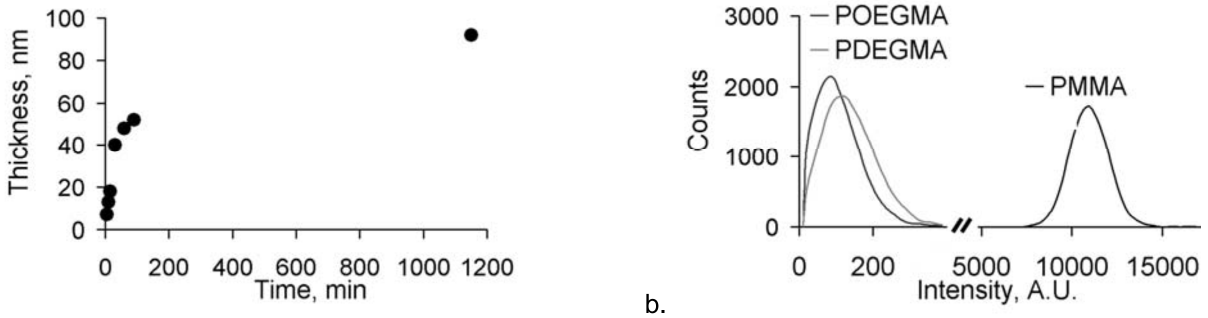
Elena Sperotto, Davide Tranchida, Holger Schönherr

Department of Physical Chemistry - University of Siegen, Address: Adolf-Reichwein-Str. 2, 57076, Siegen, Germany
E-mail: sperotto@chemie.uni-siegen.de

Keywords: polymer brushes, protein resistant surfaces, ATRP

Protein resistant or "non-fouling" surfaces have recently attracted growing interest because of the increasing number of their biomedical and biotechnological applications.[1] Recent research on new methodologies to fabricate 'non-fouling' surfaces pointed towards polymer brushes as a versatile and robust way for surface modification, with a wide range of mechanical and chemical properties. In particular, poly(ethylene glycol) (PEG) brushes showed their resistance to protein adsorption and cell adhesion; recent examples of other types of PEG-based brushes also show this characteristic.[2] One of the most used synthetic techniques is atom transfer radical polymerization (ATRP) since it offers a unique means for the design and synthesis of the polymer brushes, which are therefore easily controlled in their thickness, grafting density, roughness.

In this work, we report on the synthesis of poly(diethylene glycol methylether methacrylate) (PDEGMA) brushes on gold surface via ATRP, and in particular we compare them to the well-know and widely used POEGMA (poly-oligoethyleneglycolmethylether methacrylate) brushes.[3] The ATRP initiator is immobilized on the gold surface via different techniques, such as self-assembled monolayer formation from a solution and absorption *via* micro-contact printing (µCP). Both routes allowed to achieve polymer brushes with identical thickness under the same polymerization conditions, indicating a similar grafting density. The kinetic profile (increase of film thickness vs. time) of the polymerization at room temperature was followed by *in situ* Surface Plasmon Spectroscopy and *ex situ* Atomic Force Microscopy imaging. The profile did not show a saturation behavior and no plateau was reached, at least till 20 hours of reaction, when the film thickness corresponded to 92 nm. The synthetic protocol allowed good control on the film thickness and roughness, therefore pointing to homogeneity of the grafted chains. It is worth to mention that, compared to POEGMA, PDEGMA shows faster kinetic and allowed us to obtain thicker films. A first test for non-specific protein resistance was performed using fluorescent-labelled Albumin, detected *via* confocal laser scanning fluorescence microscope, and the PDEGMA surface showed comparable resistance to the POEGMA brushes. However, it was observed that nanomechanical properties of DEGMA are considerable different when compared to POEGMA. This results, taking into account the influence of films mechanical properties on cell-surface interactions,[4] suggest PDEGMA as a new alternative to POEGMA.



a. b.

Figure 1. a) Kinetic plot of brush thickness vs. time of polymerization for DEGMA brushes; b) Intensity measured by confocal laser scanning microscope after exposure to fluorescent-labelled protein solution.

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FABRICATION AND CHARACTERIZATION OF BLOCK COPOLYMER-BASED BIOINTERFACES BY GRAFTING-TO APPROACHES

Ekram Wassel, **Sina Ghassemi**, **Holger Schönherr***

Physical Chemistry, Universität Siegen, Adolf-Reichwein-Str. 2, 57076 Siegen, Germany
E-mail: wassel@chemie.uni-siegen.de

Keywords: *Polymer biointerfaces, block copolymer films.*

In the context of advanced materials and tailored interfaces for application in the areas of (bio)sensors and biologically oriented research involving biointerfaces, structured and functionalized thin films received increasing attention in recent years. The chemistry and surface engineering involved in the fabrication of (bio)sensor surfaces possess very similar requirements as those used for the generation of biointerfaces to experimentally address and interrogate *e.g.* cell-surface interactions. In addition to a sophisticated and optimized surface chemistry to facilitate efficient and controllable bioconjugation and to implement the function of suppressing non-specific adsorption of proteins, these requirements include compatibility with micro- and nanopatterning and -structuring methodologies and the control of mechanical properties.

To address these needs, we previously introduced thin spin-coated films of polystyrene-*block*-poly(*tert*-butyl acrylate) (PS-*b*-P*t*BA) on various substrates as versatile, robust reactive platform for the immobilization of (bio)molecules for the fabrication of tailored biointerfaces [1-4]. The selective deprotection of the *tert*-butyl-ester groups in the P*t*BA skin layer by hydrolysis under acidic conditions or by thermolysis [2], the activation with *N*-hydroxysuccinimide and the subsequent derivatization with amino functionalized (bio)molecules were reported. In addition, biochemically and topographically micro- and nanostructured films were prepared [1,3] and the interaction with cells was studied [4]. In the current study the specificity of analyte binding of this biointerface platform was significantly expanded by implementing the well-established streptavidin - biotin complexation. α, ω-Biotin-amine end-functionalized poly(ethylene glycol) (PEG), immobilized covalently on active ester modified PS-*b*-P*t*BA films render the films reactive towards strepavidin. Based on contact angle, FTIR spectroscopy and AFM data, it was shown that the polymer films were efficiently modified. The complexation of a biotin-tagged dye was quantitatively determined by confocal fluorescence microscopy and surface plasmon resonance measurements. The surface coverage of the immobilized dye as a function of dye concentration in solution was found to be consistent with a high affinity-type adsorption isotherm.

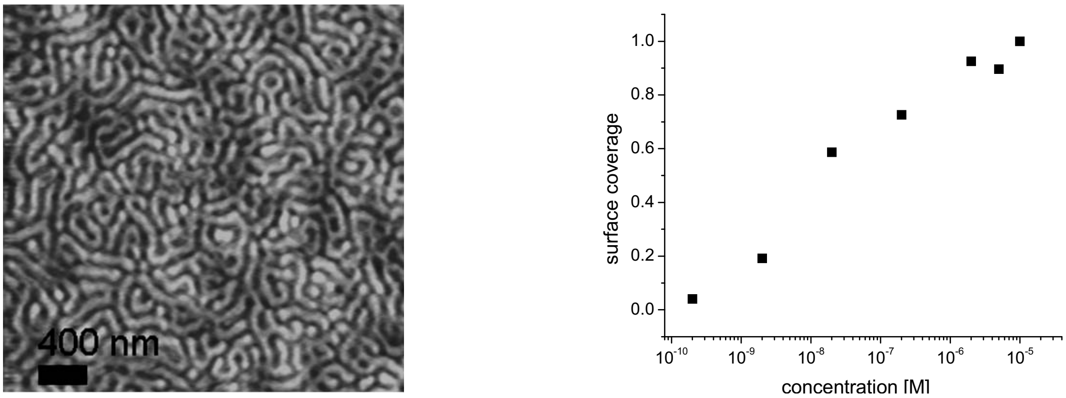

Figure 1 (a) AFM topography image of block copolymer morphology. (b) Surface coverage of the selectively immobilized dye as a function of dye concentration in solution.

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IDENTIFICATION OF SPECIES FORMED AND THEIR MIGRATION TO AN AQUEOUS PHASE FROM A LOW MOLAR MASS HYDROCARBON ANALOGUE OF PE EXPOSED TO CHLORINATED WATER

Wenbin Yu*, **Bruska Azhdar***, **Ulf W. Gedde***

** Fibre and Polymer Technology, School of Chemical Science and Engineering, Royal Institute of Technology, SE- 10044 Stockholm, Sweden*
E-mail: wenbiny@kth.se

Keywords: polyolefins; Antioxidants; Chlorinated water media

Chlorine is added to potable water as disinfectant. However, chlorine, as a strong oxidizer, may degrade water distribution piping, which is commonly made from polyethylene. Pressure testing, in which plastic water pipe is exposed to continuous flowing water containing chlorine under constant internal pressure[1], is expensive and complicated to control reaction due to requirement of constant pH and chlorine concentration. A new method[2] was developed to assess the protecting efficiency of phenolic antioxidants in polyolefins. A liquid hydrocarbon analogue, squalane, is used in this method and antioxidants are dissolved in it. The water phase which contains 10 ppm of either Cl_2 or ClO_2 (pH = 6.8), is heated up to 70°C with intense stirring to make sure the oil phase, squalane mixed with antioxidants, well dispersed in water phase. A comparison experiment was performed in which the aqueous phase was HPLC quality water. The rate of phenolic antioxidants consumed by highly oxidising chlorinated species was assessed during typically five hours. DSC was employed to determine the oxidation induction time (OIT), i.e. indirectly the concentration of phenolic antioxidant in the squalane phase. GC/MS was used to identify the species formed in the experiment. Solid phase micro-extraction (SPME) was used in water phase to identify low concentration degraded species. It was shown that the time to consume the phenolic antioxidant (Irganox 1010) in chlorine water and chlorine dioxide water is much shorter than that in pure water. Degraded products from squalane and antioxidants could be found in both the squalane phase and in the aqueous phase. When the antioxidant system was depleted, squalane was oxidized by chlorinated species present in the aqueous phase.

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FUNCTIONALIZATION OF BAMBOO AND SISAL FLOURS IN IONIC LIQUIDS

N. L. Bhandari*, R. Adhikari*, W. Mormann **, G. H. Michler***

** Central Department of Chemistry, Tribhuvan University, Kathmandu, Nepal*
*** Laboratory of Macromolecular Chemistry, University of Siegen, Germany*
**** Institute of Physics, Martin Luther University Halle - Wittenberg, Germany*
E-mail: nepalpolymer@yahoo.com

Keywords*: Bamboo flour, IR Spectroscopy, Cellulose Fibers.*

Cellulose fibers are produced by nature, have highly crystalline texture and high aspect ratio and possess amazingly high strength due to parallel arrangement of macromolecular chains in the microfibrils. By virtue of their low density, easy availability and biodegradability, the cellulose fibers are becoming popular as fillers for several commodity plastics for design of biomedical materials. The aim of this work is to study the functionalization of cellulosic materials present in crude bamboo and sisal fibers flour in ionic liquids (ILs). The samples used for the chemical treatment were powders of two different bamboos (Bamboo I, local name: Tama Bans and Bamboo II; local name Taru Bans) and sisal fibers collected from Kathmandu valley. The commercial micro crystalline cellulose (Avicel PH 101) was used for the purpose of comparison. The powders of bamboos and sisal were prepared by mechanical grinding of dry shoots and fibers. The flours were subjected to silylation and acetylation reactions using hexamethyldisilazane (HMDS) and acetic-anhydride, respectively as reagents in ILs media. The changes in fiber morphology were studied by scanning electron microscopy (SEM). The results so far obtained indicate that crude flours of bamboos and sisal can be functioinalized to a significant degree. The microscopic structures of the treated fibers remain unchanged (see Fig. 1).

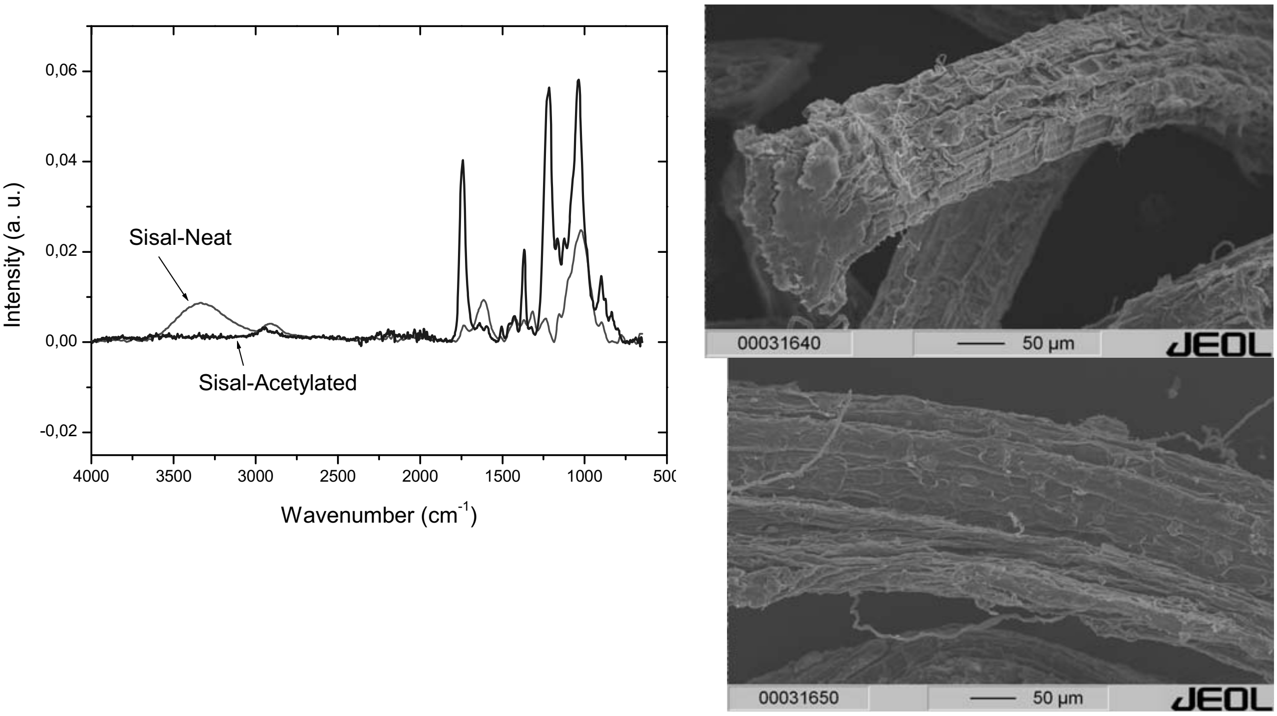


Figure 1. Left: IR spectra of sisal fiber before and after acetylation in IL; right: SEM micrographs of sisal fiber without (top) and after (bottom) acetylation reaction

THERMAL AND MORPHOLOGICAL BEHAVIOR OF POLYPROPYLENE/WOOD FLOUR COMPOSITES

R. Adhikari*, N. L. Bhandari*, L. H. Hai *, S. Henning****, H.- J. Radusch ***, G. H. Michler****, J. M. Saiter*******

* *Central Department of Chemistry, Tribhuvan University, Kathmandu, Nepal*
** *Department of Chemical Sciences, University of Padova, Padova, Italy*
*** *Centre for Engineering Science, Martin Luther University Halle-Wittenberg, Germany*
**** *Institute of Physics, Martin Luther University Halle-Wittenberg, Germany*
***** *Institute of Materials, University of Rouen, Rouen, France*
E-mail: nepalpolymer@yahoo.com

Keywords: Wood Polymer Composite, Electron Microscopy, Tensile properties

In recent years , the environmental concerns associated with synthetic fibers and uncertainties in oil prices have triggered the research interest on the suitability of natural fibers (which primarily comprises cellulose) as reinforcing fillers in various classes of plastics. The mechanical properties of these fibers are dependent on the cellulose content in the fibre, the degree of polymerisation of the cellulose etc. The fibers with higher cellulose content and higher degree of polymerisation are found to exhibit higher tensile strength and modulus. Due to their strongly hydrophilic nature of the cellulose molecules, generally, the surface modification of the natural fibers is an essential part of introducing them into the polymer matrix. In this work, we perform the comparative studies on the thermal and morphological behavior of compression molded polypropylene (PP)/wood flour (WF) composites using wood flours of different origins. The WFs used in this work were the byproducts of the carpentries. The comparison has been made on the basis of results obtained from thermogravimetric analysis (TGA), differential calorimetry (DSC), scanning electron microscopy (SEM; see for instance Fig. 1) and tensile testing. It has been demonstrated that the addition of 5 wt.-% of maleic anhydride grafted polypropylene has a significant effect on the morphological and thermomechanical behavior of the composites. Although, microscopic examinations revealed no significant differences in the morphology of the compatibilized composites containing wood flours of different origins, a remarkable shift in the thermal degradation behavior was observed.

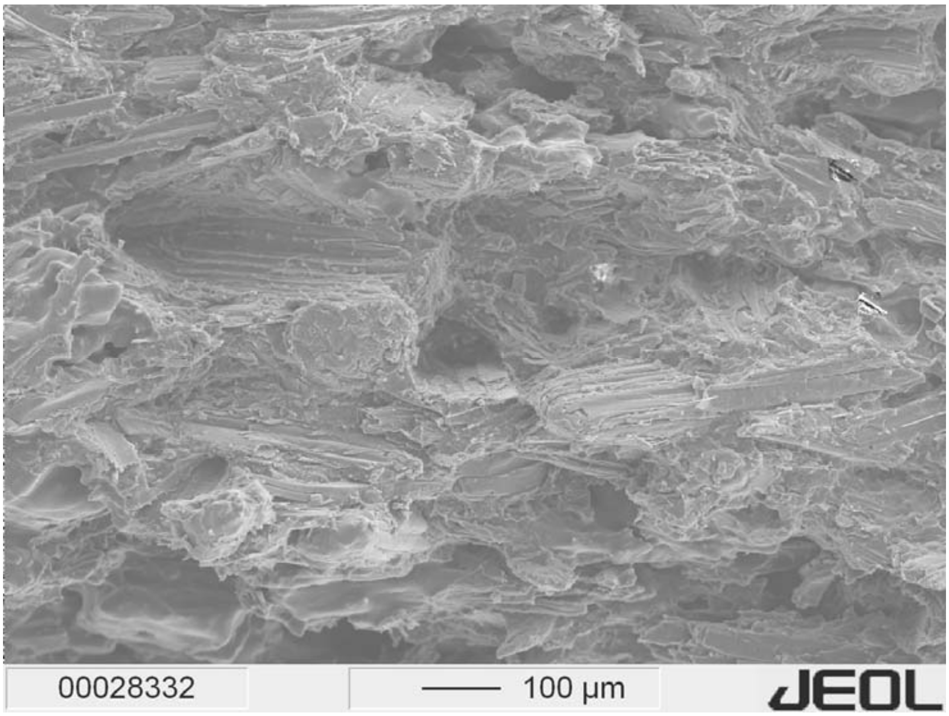


Figure 1. SEM micrograph of a composite comprising 60 wt.-% wood flour in polypropylene

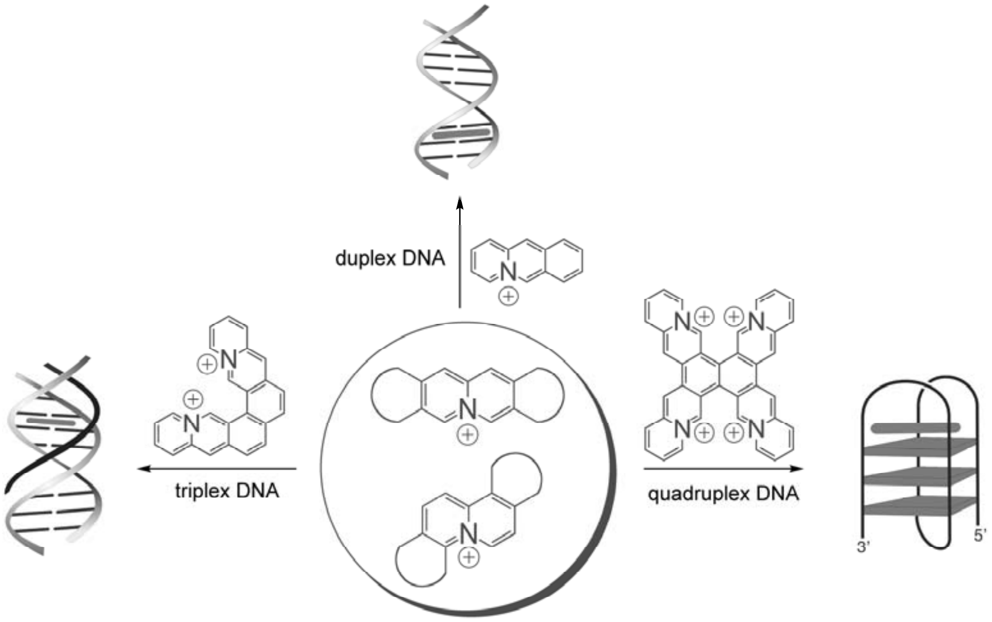
SELECTIVE ASSOCIATION OF AZONIAPOLYCYCLIC LIGANDS WITH DNA – INTERCALATION INTO DUPLEX, TRIPLEX AND QUADRUPLEX POLYNUCLEOTIDE STRUCTURES

Katharina Jäger, Heiko Ihmels, Sandra Uebach

University of Siegen – Organische Chemie II, Adolf-Reichwein-Strasse 2, 57076 Siegen, Germany
E-mail: jaeger@chemie.uni-siegen.de

Keywords: *polynucleotides, DNA intercalators, polyaromatic heterocycles.*

Polyaromatic heterocyclic systems represent attractive targets as functional materials.[1] Specifically, heterocyclic polyaromatic cations with a quaternary nitrogen atom represent versatile sources for the design of water-soluble materials, e.g. for DNA recognition through π–π interactions with the stacked nucleic bases.[2] Such an association of organic ligands with nucleic acids is a significant process in biology and in medicine,[3] because it usually induces a significant change of the polynucleotide structure and may have a fundamental influence on the physiological function of the nucleic acid. Along these lines, annelated derivatives of the quinolizinium ion represent a particularly interesting class of cationic heteroaromatic compounds.[4] For example, the azoniaaromatic structure is found in DNA-targeting alkaloids such as coralyne, berberine and sempervirine and thus constitutes a promising lead structure for drug design. With the long-term goal to establish annelated quinolizinium derivatives as versatile platform for the design of DNA-binding ligands, we studied the DNA-binding properties of quinolizinium derivatives.[5] Herein we demonstrate the significant influence of structural parameters, namely the shape and substitution pattern of the ligand, on the binding affinity and the binding selectivity of DNA-intercalating cationic hetarenes, specifically towards different polynucleotides such as triplex- and quadruplex DNA (Scheme 1).



Scheme 1

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EFFECT OF ADDING CASSAVA STARCH ON PROPERTIES OF BIODEGRADABLE POLYHYDROXY BUTYRATE-HYDROXYVALERATE BLENDS PREPARED BY MELT PROCESSING

Phasawat Chaiwutthinan *, Monchai Tajan, Yosita Rudeekit***, Thanawadee Leejarkpai******

**Polymer research unit - National Metal and Materials Technology Center (MTEC), 114 Thailand Science Park, Phahonyothin Rd., Klong 1, Klong Luang, Phathumthani 12120, Thailand*
E-mail: phasawc@mtec.or.th

Keywords: *polyhydroxy butyrate-hydroxyvalerate, cassava starch, melt processing*

Poly(hydroxybutyrate-hydroxyvalerate) (PHB-HV) is a bio-polyester, produced by microorganism and can be completely digested by microorganisms to carbon dioxide, water and biomass. However PHB-HV is not widely used because of its high cost as compared to synthetic plastics. Starch is attractive material due to its low price. The addition of starch to PHB-HV not only reduces the cost but also leads to a completely biodegradable material with desired physical properties. This work, blends of PHB-HV with cassava starch were prepared by extrusion compounding with a co-rotating twin screw extruder in different ratio of 100/0, 90/10, 80/20, 70/30, 60/40, and 50/50. A temperature profile ranging between 140-170^{0}C was set along the screw barrel. The blends were determined by tensile testing, Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and biodegradable testing in composting condition. The variation in mechanical properties, thermal properties, chemical structure, morphology, and biodegradability for different proportions of PHB-HV/starch are discussed. The result showed that the tensile strength and Young's modulus decreased gradually as the content of starch increased. The tensile strength and the modulus of PHB-HV/starch blend (50/50) was 82% and 73% of pure PHB-HV, respectively. In addition, PHB-HV/starch blends with starch content up to 50% were more flexible than pure PHB-HV. FT-IR was used to study the chemical interactions between PHB-HV and starch, as starch has hydroxy groups on the backbone, while PHB-HV has carbonyl groups, along its main chain. The result could be concluded that no chemical interactions between PHB-HV and cassava starch. The DSC data revealed that PHB-HV/starch blends had a single glass transition temperature for all proportion of the components. The glass transition temperature values of blends were lower than that of pure PHB-HV. The T_g values of blends were in the range of 1.5-2.0^{0}C. Moreover, the melting temperature peak of blends were shifted toward lower temperature as the starch content in the blend increased. The thermal stability was determined by TGA. The TGA curve of PHB-HV/starch blends exhibited three degradation steps: at around 100^{0}C, between 180 and 290 ^{0}C and above 290^{0}C. For blends with starch content 10-50%, the temperature at the maximum rate of weight loss was about 10^{0}C higher than that of pure PHB-HV. The residue obtained after the thermal degradation of blends varied according to starch content. The amount of residue obtained was increased from 2.67 to 12.77% of the initial mass for blends with 10-50% starch, respectively. The morphology of PHB-HV/starch was investigated by scanning electron microscopy. For PHB-HV blends with the starch contents less than 30%, the starch were well dispersed throughout the matrix, while at the higher starch contents, the starch were presented as agglomerates. The formation of these agglomerates contributed to slightly poor mechanical properties. Both PHB-HV and PHB-HV/starch blend were found to be biodegraded under composting condition.

CHARACTERISATION, PROPERTIES AND BIODEGRADATION OF CASSAVA STARCH AND POLY(BUTYLENE ADIPATE-CO-TEREPHTHALATE) BLENDS

Monchai Tajan*, Phasawat Chaiwutthinan, Yosita Rudeekit***, Thanawadee Leejarkpai******

** Polymers Chemistry Lab. – National Metal and Materials Technology Center (MTEC), Address: 114 Thailand Science Park, Phahonyothin Rd., Klong 1, Klong Luang, Pathumthani 12120, Thailand*
E-mail: monchait@mtec.or.th

Keywords: *Cassava starch, Biodegradable copolyester, Biodegradation*

Poly (butylene adipate-co-terephthalate) (PBAT) is a synthetic biodegradable copolyester with many properties, including biodegradability, melt processability, good thermal and mechanical properties. At the same time, cassava starch is the most abundant natural biopolymer in Thailand. Their blends give interesting materials for industrial packaging application due to improved cost competitiveness and biodegradability as starch content increases. However, our understanding in the role of starch as biodegradable filler in the blends is not clear. In this work, we studied the effects of starch content on the properties of the extrudated polymer, the blends were melt compounded using a co-rotating twin screw extruder. The concentration of starch in the blend was varied from 10% to 70% by weight. The blends were characterised by means of fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), wide-angle X-ray diffraction (WAXD), melt flow index (MFI), capillary rheometry, scanning electron microscopy (SEM) and mechanical properties measurement. Each the blend showed a small broad melting endotherm at around 120°C due to the low crystallinity of the copolyester. The glass transition, melting and crystallization temperature of the blends were invariant with starch content when compared to the copolyester. However, the addition of starch increased the thermal resistance of these blend. There is a discrepancy between the crystallinity index values obtained from WAXD and DSC measurements, but both methods seem to represent the variation of polymer crystallinity with increasing starch content quite well. The MFI values of the blend increased with starch content. The higher MFI could be attributed to the better interface between starch and the copolyester. The result is in conformity with the more serious shear-thinning tendency of starch/copolyester melts. The rheological data indicated that the introduction of starch improved the processability of the blends. The original copolyester exhibited the highest tensile strength, which decreased with increasing starch content. However, it is interesting to note that 50% starch content exhibits a modulus higher than that of the copolyester. Blend morphology indicated that the unmelted phase of starch becomes finer as starch content increased. Therefore, a higher starch content led to greater melting of the starch granules. Moreover, 70% starch content, a continuous phase between starch and the biodegradable copolyester is exists. The FTIR spectra showed frequency shifts (3 - 7 cm^{-1}) to be definitive evidence of intermolecular interaction in the blends and also supported the results of SEM analyses of starch/PBAT blends. Also, the biological degradation behaviors of the blends under controlled composting conditions according to ISO 14855-99 were investigated with regard to the degree of degradation. Monitoring result showed that 50% starch by weight was biodegraded to 73.31% within a period of 120 days of composting. These results demonstrated that the biodegradable starch/copolyester blends have the performance useful for packaging and film applications.

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PREPARATION AND APPLICATION OF LOW MOLECULAR WEIGHT ALGINATES

Soo-Kyung Choi, Yoo Sung Choi, Byung Wook Jo

Dept. of Chemical & Biochemical Engineering, Chosun University, 375 Seosuk-dong Gwangju 501-759, Republic of Korea
E-mail:bwjo@chosun.ac.kr

Keywords: aromatic PHA, flame retardant, cyclization

Alginate has been used as food stabilizer, gelling agent, encapsulation material for drug, plant growth stimulator, wound dressing material and drug delivery system. However, high molecular weight alginate limits its application in specific fields caused by its high viscosity and poor solubility in water. Polysaccharides such as alginate and fucoidan can be degraded in several ways, such as chemical, enzymatic, and irradiation methods. The common disadvantages of these methods are the low recovery, difficulties to remove chemical agents and high processing cost .

In this presentation hydrogen peroxide was used for producing low molecular weight sodium/silver alginate(LMSoA/LMSiA) under e-beam irradiation or sonication in a controlled way.

Hydrogen peroxide, a strong oxidizing agent can be easily decomposed and produces radicals spontaneously. Oxidation reaction with hydrogen peroxide under e-beam irradiation was found to be much more effective in lowering the molecular weight of sodium alginates compared with any methods we have checked. Sonication is also useful method to degrade high molecular weight sodium alginates and also to increase the depolymerization rate effectively. The results were as follows:

The M.W. of the polysaccharides can be controlled effectively by controlling energy intensity, irradiation dose amounts of H_2O_2 used in depolymerization process. The molecular weight of depolymerized alginates was investigated with the GPC-MALLS and intrinsic viscosities. The ***K*** and ***a*** parameters of the MHSS-equation,and the depolymerization rate constant were calculated from the measurements.

Though the particles of the LMSoA/LMSiA (depolymerized alginates) and LMF were aggregated to produce clustered aggregates, we could prepare depolymerized Ag-alginate about 100 nm in size by using ultra-sound waves. Antibacterial effects of the LMSA and LMF were considerably higher than the original high M.W. polysaccharides, they showed, for example, about 350 ppm of MIC value with high antibacterial characteristics in E. coli, Staphylococcus and Propionibacterium acnes

The original raw materials did not show any cytotoxicity, on the other hand the depolymerized polysaccharides showed cytotoxicity for several animal cells by MTT test.

The antibacterial cosmetics were prepared from the LMSoA, LMSiA and/or LMF on the basis of their physical properties and cytoxicity.

HYDROPHOBIZATION OF NANOFIBRILLATED CELLULOSE

Ulla Hippi, Kuisma Littunen, Jukka Seppälä

Polymer Technology Research Group - Aalto University School of Science and Technology, Address: Kemistintie 1, 02150 Espoo, Finland
E-mail: ulla.hippi@tkk.fi

Keywords: *nanofibrillated cellulose, hydrophobization, grafting from*

Maintenance of nanodispersions is a key aspect in processing and compatibilizing of nanocomposites. Cellulose fibrils bind very willingly to each other, which makes it difficult to first separate them and further to maintain the nanostructure during processing. Redispersion of dried nanofibrillated cellulose is a challenge due to high interactive forces, large contact area and entanglements. If hydrocarbon chains are linked onto surface of nanofibrillated cellulose, its tendency to aggregate may be dramatically changed.

In this paper we present two methods to add hydrophobic chains onto nanofibrillated cellulose and characterization of the resulted products. Short hydrocarbon chains have been added through anhydride reaction with cellulose, and polymeric chains by grafting from nanofibrillated cellulose surface with butyl acrylate or glycidyl methacrylate by redox initiated free radical polymerization.

Chemical structure of the products was characterized with FTIR and solid-state ^{13}C NMR. Chemical modifications changed the materials behavior with water droplet compared to the neat dried nanofibrillated cellulose, as can be seen in Figure 1. Nano-scale structure of the products was characterized with AFM and is shown in Figure 2. Fibrillar structure was preserved well in both modifications although some aggregation was also observed. Polymeric coating on the fibril surface was easily visible.

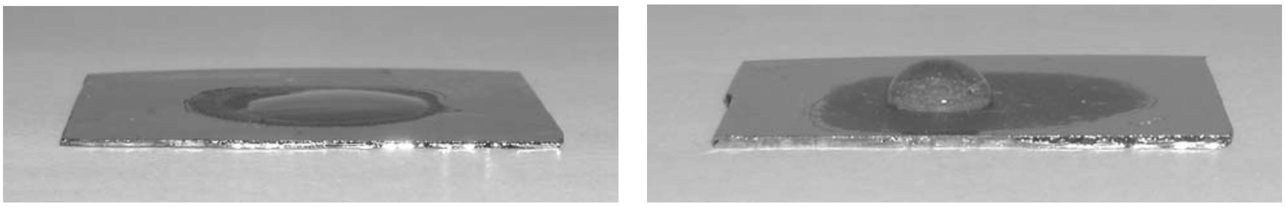

Figure 1. Contact angle with water of unmodified (left) and hydrophobized (right) nanofibrillated cellulose.

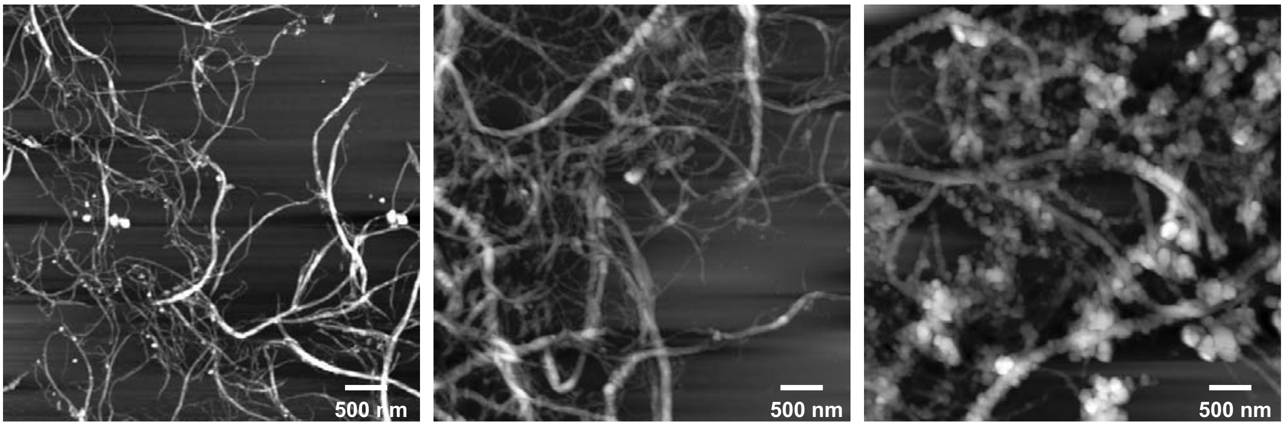

Figure 2. AFM micrographs of unmodified nanofibrillated cellulose (left) and nanofibrillated cellulose grafted with short (middle) and long hydrocarbon chains (right).

EFFECT OF CRYSTALLIZATION ON THE HEAT RESISTANT PROPERTY IN BAMBOO-FIBER / TALC / PLA COMPOSITES

Qing-Feng Shi, **Hai-Yan Mou, Wei-Hong Guo**

Polymer Alloy Lab- School of Materials Science and Engineering- East China University of Science and Technology
Address: Mei Long Road, NO.130, Shanghai, China, 200237
E-mail: sqf3690@126.com

Keywords: *Polylactic (PLA); Transcrystallization; Fiber; Heat-resistant-temperature; Composites*

In this paper, polylactic (PLA) composites have been prepared with bamboo fiber and Talc by melt blending in HAAKE mixer. When BF or Talc added, the improvement in heat resistant temperature of PLA composite was about 10 °C after the simple heat treatment (put samples in 120 °C for 30 min). And, the heat resistant temperature has nearly no changes in pure PLA after the same treatment. However, with the same heat treatment, PLA composites have a great improvement in heat resistant temperature after bamboo fiber and Talc both added. When 20 wt % BF and 20 wt % Talc has been added, the heat resistant temperature of PLA composites was about 30 °C improvement at 1.8Mpa loading. And the heat resistant temperature of PLA composites was above 100 °C with 20 wt % BF and 5 wt % Talc both added at 0.45 Mpa loading. As a conclusion, after the simple heat treatment, the heat resistant temperature of PLA composite samples reaches the using temperature of dunnage in daily life.

PLA composites have been investigated by Fourier Transformation Infrared Spectra (FT-IR), Scanning Electron Microscope (SEM), Thermogravimetry (TGA), X-Ray Diffraction (XRD) and Polarizing Microscope (POM) in researching the reasons on great improvement of PLA composites after the heat treatment. There was no obvious chemical reaction before and after the heat treatment in PLA composites with BF and Talc both added through the FT-IR spectrum. And, XRD test has the same results that there were no crystal type changes in PLA composites with BF and Talc both added when the sample has been heat treated. After TGA testing, the degradation temperature of PLA composites has nearly the same values before and after the heat treatment. Interestingly, after the heat treatment, there was transcrystallization in the PLA composites with bamboo fiber and Talc both added by POM observing. However, the transcrystallization could not been observed in the PLA composites which only BF or Talc added. Therefore, the great improvement of heat resistant temperature is probable attributed to the formation of transcrystallization in the PLA composites after the heat treatment. And the probable mechanism in formation of transcrystallization has been shown at the end of this paper.

Finally, the effect in formation of transcrystallization, such as crystallization temperature, diameter of fiber has been investigated simply by POM. In the high crystallization temperature, the growth of spherulite was slow, the growth of transcrystallization was more perfect and the transcrystallization preferred to grow around the large diameter of bamboo fiber. Of course, in the low crystallization temperature, there was the opposite phenomenon. Details of researching on the effect in transcrystallization and the mechanical properties of PLA composites with transcrystallization have been planned in our future work.

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USE OF SISAL FIBER MODIFIED WITH MERCAPTO GROUPS ON REACTIVE COMPATIBILIZATION OF THERMOPLASTIC ELASTOMER VULCANIZED

Alex S. Sirqueira*, Matheus M. Cossa, Renan G. Maciel*, Monica C. Vieira***

** Centro Universitario Estadual da Zona Oeste – UEZO, Av. Manuel Caldeira de Alvarenga 1203, 23070200, Campo Grande, Rio de Janeiro, Brasil.*
*** Universidade Federal do Rio de Janeiro, Instituto de Macromoléculas, Av. Brigadeiro Trompowsky s/n, Ilha do Fundão, Rio de Janeiro, Brasil.*
E-mail: alexsirqueira@uezo.rj.gov.br

Keywords: *Sisal fiber, Compatibilization, mechanical properties, thermoplastic elastomer,*

The interest in the use of natural fibers in polymeric composite materials has increased significantly. Brazil has a great potential to contribute with different natural fibers due the large green area. The use of natural fibers in composites can help the local industries to development new ecological strategies to improve the production of fibers and theirs plantation. The new materials with natural fiber can be competitive with the other reforcing agents, like fillers due the low cost. The Brazilian sisal fibers studied have exhibited mechanical and thermal properties within the range in the literature and were suitable for use in polymer composites. In this paper were investigated the use of sisal fiber (*Agave sisalana*) in thermoplastic elastomer vulcanized (TPV). The TPVs are obtained by the mechanical blends between thermoplastics and elastomers. Only elastomeric phase are cured by specific curing agent like sulfur, peroxide and resin, it happens during the mix in a internal mixer or extruder, this process is called Dynamic Vulcanization. To improve the adhesion between polymer and fiber many researchers modified the fiber surface with acetate groups. We modified the fiber with mercapto groups, which can react with the double bonds present in the elastomer phase.

Sisal fibers were cut in small pieces (10 mm), washed in hot water for 3 hours to remove organic material. After that the fibers were reacted with NaOH for 4 h at 40 °C. The reaction modified were conducted in the presence of thioglicolic acid for 3 hour at 40 °C.

Design experiments (2^2) were used to optimize the answer in the end variable (tensile strength, elongation at break and hardness). The formulation of TPV were PP (40phr), SBR (60 phr), peroxide (variable) and sisal fiber (variable). The TPV were produced in an internal mixer (Haake) at 190°C for 6 minutes. All the polymer components were added at the same time, after 2 minutes fibers were added. The last component added was peroxide. The samples for mechanical properties were obtained in a Battenfeld injection, at 240°C in the barrel and 40°C in the mold.

The tensile strength was proportionally increased as the fiber amount. The TPV with modified fiber exhibited higher tensile strength as compared the TPV without sisal modified. This behavior can be explained by the reactions between the mercapto groups and the insaturation in SBR phases. The SEM figures confirm that hypothesis by the reduction on the distance between the fiber and polymer. We conclude that modified in fiber with mercapto groups increased the mechanical properties in TPV producing a new TPV with better mechanical properties. To obtained a TPV with natural fiber is not necessary to put higher amount of fiber and peroxide, but modified the fiber surface with mercapto groups.

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PREPARATION AND PROPERTIES OF POLYPROPYLENE/NATURAL FIBER COMPOSITES:EFFECTS OF FIBER TYPE, CONCENTRATION AND SURFACE TREATMENT

Tihminlioglu Funda*, Atikler Ulaş

Department of Chemical Engineering, İzmir Institute of ,Technology, Gulbahce Urla İzmir 35430, Turkey
E-mail:fundatihminlioglu@iyte.edu.tr

Keywords*: natural fiber, surface treatment, polypropylene .*

In this study, three natural fibers, namely cellulose (C) (not necessarily a fiber), sawdust (is no fiber) (SD) and wheat straw (WS) were employed as reinforcement to polypropylene polymer (PP) matrix. The most important problem encountered with natural fiber/PP composites is the inherent incompatibility between hydrophilic natural fibers and hydrophobic PP matrix, thus coupling agents were employed to alter incompatibility between fiber and matrix. Coupling agents enhance interfacial interactions by chemical and physical bonding between fiber and matrix. Surface treatment of natural fibers were carried out with two kinds of silanes; (3-aminopropyl)-triethoxysilane (AS) and methacriloxy propyl trimethoxy silane (MS), and maleic anhydride grafted polypropylene (MAPP). Silane coupling agents were agitated in aqueous ethanol solution in the presence of fibers at weight percents of 0.5, 1 and 2.5 with respect to fiber weight. MAPP was compounded during melt mixing of fiber and PP at weight percents of 2.5, 5 and 10 with respect to PP weight.

PP/fiber composites were prepared in a rheomixer equipped with two rotor blades and adjustable temperature, mixing rate and mixing time. Composites were prepared at 185 ^{o}C, 50 rpm mixing rate and 10 minutes mixing time. Torque values of each composite formulation were recorded with respect to time to determine changes in rheological properties of composites. It was found that increase in fiber loading increases stabilization torque of composites.

Mechanical properties of PP/fiber composites were significantly enhanced by employment of coupling agents and MAPP was found to be the most effective coupling agent. Mechanical properties of SD composites were found to exhibit the best performance compared to C and WS. Extent of interfacial interactions were evaluated with Pukanszky and Nielsen models [1-2] and superior performance of MAPP in enhancing interfacial interactions was confirmed by these two models. Optimum conditions for coupling agents were found to be 1 wt % for silane coupling agents and 5 wt % for MAPP.

It was found that water sorption and void fraction of the composites decreased with employment of coupling agents. Among the coupling agents, MAPP exhibited the best performance in decreasing water sorption and void fraction of composites confirming results of mechanical tests. Scanning electron micrographs (SEM) used to illustrate the effect of coupling agents on adhesion between fiber and matrix and fracture modes of the composites. In addition, FTIR analysis revealed the decrease in hydrophilicity of fibers with silane treatment and new bond formations with employment of MAPP.

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NOVEL BIOBASED NANO-STRUCTURED CORROSION PROTECTIVE COATING MATERIAL

Deewan Akram, Eram Sharmin, Sharif Ahmad*

Materials Research Lab., Dept. of Chemistry, Jamia Millia Islamia, New Delhi-110025, India
E-mail: deewanakram@rediffmail.com

Keywords: *Castor oil; TEOS; Coatings.*

There is a growing urgency to develop and commercialize new biobased products and other innovative technologies that can reduce widespread dependence on fossil fuel and at the same time would enhance national security[1]. Bio-based polymers which can compete or even surpass with the existing petroleum-based materials on a cost-performance basis with the added advantage of eco-friendliness. Bio-based feedstocks such as starch, cellulose, proteins, chitin, gums, and seed oils are being actively utilized for the production of bio-based polymers, in academic research and chemical industry worldwide[1-2]. Among them, seed oils hold significance as bio based precursors to polymers synthesized through environmentally benign route, owing to their ease of availability, cost effectiveness, non toxicity, and biodegradability as well as varied chemical attributes[1-3].

Polymer nano-structured coatings have attracted great interest because of dramatically improved properties (e.g. physical, barrier, flammability, smoothness, thermal, and others)[3-4]. They consist of nanosized mineral particles dispersed in polymer matrix; among them polymer-clay nanocomposites (clay nanolayers dispersed in polymer matrix) is one of the most promising materials and exhibit enhanced thermal, mechanical and improved barrier properties even when very low (less than 5wt%) amount of nanoreinforcements are used[4-5]. The main reason for these improved properties is the strong interfacial interactions between the matrix and layered silicate as opposed to conventional composites. Montmorrilonite (MMT), by far the most commonly used clay for the preparation of polymer-clay nanocomposites, is a crystalline 2:1 layered clay mineral with a central alumina octahedral sheet sandwich between two silica tetrahedral sheets[5-6].

Considering these facts, we have attempted to develop organic-inorganic hybrid polyurethane/clay nanocomposite (COSiPU/MMT) and their application as anticorrosive coating material. Synthesis carried out in two steps- (i) synthesis of organic-inorganic hybrids (COSi) from natural polyol (CO-Castor oil) as organic and tetraethoxyorthosilane (TEOS) as inorganic precursors, respectively through sol-gel process, and (ii) COSi further treated with toluene 2,4 di-isocyanate to form their polyurethane (COSiPU), furthermore, MMT (Cloisite 30B) used as filler, was dispersed in COSiPU matrix in different wt% (1, 3 and 5) through sonication technique to obtain polymer-clay nanocomposites (COSiPU/MMT). COSiPU/MMT was applied on mild steel strips to evaluate their coating performance. The structure, morphology, and thermal stability, of the resulting COSiPU/MMT have been investigated by FTIR, X-ray diffraction, transmission electron microscopy (TEM), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The physico-mechanical and corrosion/chemical resistance (by weight loss and electrochemical method in various corrosive media such as 3.5%HCl, 3.5%NaOH, Xylene, Salt mist test) performance were conducted to evaluate the coating properties of synthesized COSiPU/MMT. These studies revealed the impeccable behavior of the synthesized polymeric materials, which serve as novel and promising candidates for use as nanostructured corrosion protective coating materials and can be safely employed up to 240°C.

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SURFACE-ACTIVE AND ASSOCIATIVE PROPERTIES OF IONIC POLYMERIC SURFACTANTS BASED ON CARBOXYMETHYLCELLULOSE

Vladimíra Tomanová *, Iva Sroková*, Anna Ebringerová, Vlasta Sasinková****

**Faculty of Industrial Technologies – Trenčín University of Alexander Dubček, I. Krasku 492/30, 020 01 Púchov, Slovakia*
***Institute of Chemistry – Slovak Academy of Sciences, Dúbravská cesta 9, 845 38 Bratislava, Slovakia*
E-mail: tomanova@fpt.tnuni.sk

Keywords: *carboxymethylcellulose, transesterification, rapeseed oil, microwave irradiation, polymeric biosurfactants,*

The increasing interest for biocompatible and biodegradable materials makes natural polymers like polysaccharides attractive raw materials for the preparation of polymeric surfactants [1], which have potential application in food and non-food sectors. Modification of the highly hydrophilic water-soluble polysaccharides by grafting a low amount of hydrophobic groups like alkyl chains leads to water-soluble amphiphilic derivatives, which usually exhibit associative properties in water, viscosity-increasing effects and surface-active properties enabling to control foaming or emulsion stability [2, 3].

Among the commercial polysaccharides, the water-soluble, anionic cellulose ether carboxymethylcellulose (CMC) was used as a source of biopolymers for further chemical modification. In our previous paper carboxymethylcellulose was partially hydrophobized in order to prepare polymeric surfactants by the transesterification reaction using the complex of fatty acid methyl esters prepared from rapeseed oil [4]. Since fatty acid esters are found in nature as triacyl glycerides, attempts have been made to use them as non-expensive acylation reagents for modification of polysaccharides [5].

The present work is focused on polymeric surfactants prepared from CMC by transesterification of rapeseed oil triacyl glycerides (RO). The hydrophobization was performed in reaction media H_2O/DMF with potassium laurate as catalyst at various reaction conditions using microwave irradiation as heating source. Variations of the CMC/RO mass ratio, reaction time and temperature, and power of the microwave heating were served to prepare water-soluble CMC derivatives. The obtained CMC esters were characterized by FT-IR and NMR spectroscopic techniques, which indicated a very low content of ester substituents. The surface-active (surface tension, critical micelle concentration), emulsification and associative properties (capillary viscosimetry measurements, spectroscopy - Coomassie Brilliant Blue (CBB) technique) were evaluated. All tests used to characterize the surface - active properties of CMC esters were described in detail in the previous paper [3].

Prepared CMC esters regardless the moderate surface tension lowering effect exhibited remarkable emulsifying properties comparable to the commercial synthetic emulsifier Tween 20. All derivatives form emulsions of the oil in water (O/W) type, but differences were observed in the stability of the emulsions by comparing the onset of creaming, expressed as 'delay time'.

Solution properties indicated that the CMC derivatives establish hydrophobic associations in bulk solution while adsorbing on the air/water interface.

The results suggested that suitable polymeric biosurfactants can be prepared from CMC under microwave heating at reaction times in the range of several minutes representing a great advantage in comparison to transesterification reactions lasting up to 6 h at conventional heating. Of importance is also the proved applicability of RO as acylation agent contributes to a further valorisation of the rapeseed biomass.

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REGULATION OF THE CARBON-CHAIN POLYMER SURFACE PROPERTIES

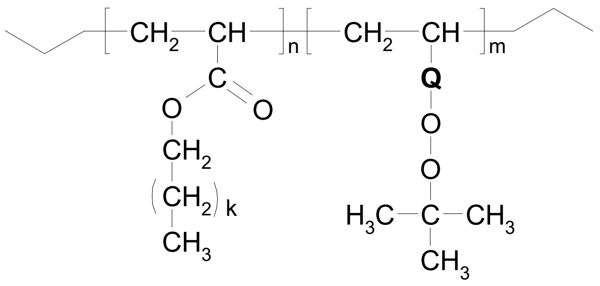
Sergiy Varvarenko, Volodymyr Samaryk, Nataliya Nosova, Nataliia Puzko, Ihor Tarnavchyk, Andriy Voronov, Ananiy Kohut, Stanislav Voronov

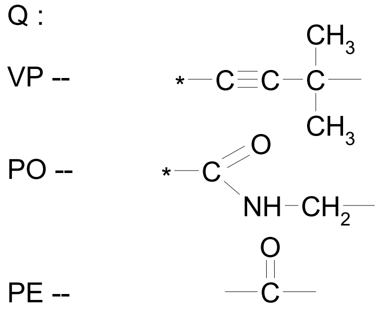
National University "Lvivska Polytechnika", S. Bandera 12, Lviv 79646, Ukraine
E-mail: nnosova@polynet.lviv.ua

Keywords: *polyperoxide, modification, surface activating*

There is a great interest to the research of polymer materials surface properties modification due to some restrictions established by these properties on polymer the materials applications. Low free surface energy of these materials, hydrophobicity, low adhesive properties, favorable conditions for microorganisms significantly limit the applications of these materials. To attach specific properties we propose a number of polymer surface activating techniques with further modification. The majority of these methods are based on the functional polymer chains grafting to polymer surface, which controls hydrophilic - hydrophobic surface balance and therefore provide improvement of the adhesive properties, the formation of bactericidal or hemocompatible layers on the polymer surface.

The majority of technique includes the stage of surface activation, which determines success of the modification, before grafting of functional polymer to the surface. The present report is dedicated to the principal laws of polymer surface modification due to grafting to the layer of cross-linked polyperoxide with following structure:





As reported previously [1, 2], this method of activation, includes covalently grafted 20-60 nm high layer immobilization on the polymer surface, which contains $(1 \div 3)\cdot 10^{-5}$ mole/m^2 of peroxide groups of different nature (VP, PO, PE). This report is dedicated to the mechanism of polyperoxide layer formation on the polymer surfaces of different nature. It is shown that thermodynamic compatibility of modifier molecules and polymer surface must be taken into consideration during polyperoxide layer formation. It is also shown, that there should be interaction between polyperoxide molecules and surface macromolecules to achieve successful polyperoxide layer formation. At the same time, excessive interaction can cause “partial” thermodynamic compatibility [3] of polyperoxide molecules and surface macromolecules, resulted in their diffusion in bulk polymer and disturbance of polyperoxide layer formation. Prognostic model has been investigated, which allows to correlate polyperoxide structure with its ability to form a grafted polyperoxide layer on polymer surfaces of different nature.

In present report the initiating ability of polyperoxide layers grafted on different surfaces is shown in the process of radical polymerization on functional surfaces.

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STUDY OF METAL COORDINATION INTERACTION, STRUCTURE AND PROPERTIES OF METALLIC SALTS FILLED NITRILE-CONTAINING POLYMER COMPOSITES

Haiyan Mou *, **Qingfeng Shi***, **Fei Shen****, **Weihong Guo***, **Yuanyi Cao***, **Chifei Wu***

**Polymer Alloy Laboratory, School of Materials Science and Engineering, East China University of Science and Technology, Address: Meilong Road, 130, 391, Shanghai200237, P.R. China*
*** Polymer Processing Institute, Suite New Jersey Institute of Technology, Address: Central Ave., 218, GITC Bldg, 3901 , Newark 07102, USA*
E-mail: mouhaiyan@mail.ecust.edu.cn

Keywords: *coordination crosslinking; metallic salts; nitrile*

Inorganic particles filled polymer composites have drawn great interest for a few decades due to their great versatility and high performance, as well as the low cost. The interaction between the inorganic particles and the polymeric matrix is always at the core of polymeric composite research field. Generally, the particles and the matrix can form sound interactions via covalent bonds[1], ion bonds[2] or hydrogen bonds[3]. The most research interests in polymer/inorganic composite focus on the formation of particle-matrix covalent bonding. Metal coordination bonding is a special covalent interaction because the metal cation simply acts as the electron pair acceptor, itself donating no electrons to the bond, while the ligand provides all the electrons. Because of the complicated and special nature of coordination compounds, coordination bonding has been extensively used in the assembly of supramolecular structure, polymer formation or crosslinking[4-7]. Large numbers of distinct coordination interactions between transition metal ions and ligands are stable, reversible and selective, even at high temperature. Coordination polymers have been applied in many fields, such as liquid crystalline polymers[8], electrolytes[9] and catalysis[10]. The process of coordination bonding is usually completed in dilute solution and has poor practicality.

Our research efforts have involved non-solvent-phase metal coordination bonding in bulk polymers[11-15]. It not only supplemented the research content of the main interaction in the polymer/inorganic particle composite, but also introduced the metal coordination reaction from the traditional liquid/gas-phase system to the non-liquid processing of bulk polymeric system. By incorporating fine inorganic metal salt particles into nitrile-containing polymers such as NBR, NBR/PVC and SAN, we fabricated novel particle-filled polymer composites that could be reinforced by metal coordination reactions. A variety of transitional metal ions, such as Zn^{2+}, Cu^{2+}, La^{2+}, Mn^{2+}, Co^{2+} and Fe^{3+}, could become the candidates to form coordination complex with nitrile group. A three-dimensional network could be formed in NBR/$CuSO_4$, NBR/PVC/$CuSO_4$, NBR/$ZnCl_2$ or NBR/$ZnSt_2$ system as the coordination reaction between nitrile groups and transitional metal ions took place. The coordination reactions were characterized by dynamic mechanical analysis (DMA), Fourier transformation infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and electronic paramagnet resonance (EPR). The efficiency of such solid phase coordination reactions could be enhanced by water of crystallization, small molecule plasticizers and some plastics. The resulting polymers have excellent tensile properties, oil resistance and cohesive strength.

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THE INFLUENCE OF SOME POLYCARBOXYLATE ETHERS ON THE HYDRATION OF CALCIUMSULFATE HEMIHYDRATES

Christian Pritzel, Thomas Wenzel, Reinhard Trettin

Institut für Bau- und Werkstoffchemie, Universität Siegen, Paul-Bonatz-Str. 9-11, 57076, Siegen, Germany

E-mail: Pritzel@chemie.uni-siegen.de

Keywords: *Polycarboxylatether, gypsum, morphology*

The technical properties of gypsum are depending very much on the morphology of the crystals which are formed while hydration[1]. This morphology depends also on the influence of additives. Typical additives to influence the setting time of gypsum are organic acids like citric acid or metal salts or polyphosphates. For inorganic binders superplasticizers based on polycarboxylatethers are used. All these additives have some wanted influences and some side effects. One of these side effects is a change in the morphology of the gypsum. The polycarboxylatethers which are in use have different backbone length and different side chain lengths. The influence of different superplasticizers and different amounts of them on the morphology of gypsum are investigated by optical microscopy. The results are compared to other additives.

To observe the hydration of gypsum by optical microscopy a special measure cell was invented. The cell is built from a rubber ring which is glued on a glass slide by grease which is not soluble in water. The cell was filled with the hemihydrate, water and additive and closed by a cover glass, which was also glued with grease[2].

Then the observation starts with an Olympus BX61 optical microscope. It is used in reflection mode in bright field. The pictures are taken with 300 times magnification every 60 for about 8 hours.

The explained measure cell has the disadvantage that a very high water to gypsum ratio must be used. To check the influence of that water gypsum ratio all of the samples were prepared with the technical used ratios and the resulting morphologies were examined by the scanning electron microscopy. The kinetic of the reaction was tested by heat flow calorimetry.

It could be determined that different technical used superplasticizers have a large influence on the hydration of gypsum. The type of influence depends on the used superplasticizer. Superplasticizer 1 (PCE1) leads to smaller, shorter gypsum crystals than the reference material without additive. The crystals have a smaller aspect ration with superplasticizer. The crystals are comparable to those which were grown with citric acids. For citric acid it is well known in literature that they were occupied on the fastest growing crystal surface of the dihydrate. This crystal surface could not grow anymore and the decelerating of the additive and the change in morphology could be explained [2,3]. PCE1 is working with the same mechanism. It does not change the solution rate of the hemihydrate but it is also decelerating the hydration.

Another PCE (PCE2) is decelerating the hydration very much. There is more hemihydrate getting solved in the water and the reaction stops. There could no new created dehydrate be observed. The same behaviour could be investigated with EDTA or with cationic changer resin. So all this additives EDTA, the ion changer and PCE2 are collecting Ca^{2+}-Ions out of the solution and therefore no gypsum could be created and no more hemihydrate can get solved.

The advantage of optical microscopy is, that *in situ* observation is possible and so it is possible to get qualitative information about the cinetics to and no covering of the sample with gold. The advantage of the SEM is the use of a technical water gypsum ratio and a higher resolution.

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INVESTIGATION OF THE SOLUBILITY OF ETTRINGITE AND CALCIUM SULFATE DIHYDRATE IN THE PRESENCE OF SUPERPLASTICIZERS

Wenzel, Thomas, Trettin, Reinhard*

Institut für Bau- und Werkstoffchemie, Universität Siegen, Paul-Bonatz-Str. 9-11, 57076, Siegen, Germany, E-mail: Wenzel@chemie.uni-siegen.de

Keywords: *Superplasticizer, solubility, ettringite*

Superplasticizers (SP) are often used in the concrete industries as dispersing agents. These organic admixtures are natural or artificial water-soluble polymers. The use in concrete technology allows the reduction of water by 50%. The reduction of the amount of water leads to a dense and compact structure and thus to higher mechanical properties. Other advantages derived by the use of superplasticizers include production of concrete having high workability for easy placement. These concretes are known as High Performance Concrets (HPC) or Ultra High Performance Concrete (UHPC).

Cement/Superplasticizer interactions can be discerned into physical and chemical effects

- Physical Effects occur instantly (t=0), absorption because of electrostatic forces, electrostatic repulsion and steric repulsion
- Chemical Effects are consequences of the cement hydratation (alternation of early hydratation reactions and hydration products) [1,2,3]

The most widely used superplasticizers are: polycarboxylate based superplasticizers (PCE), sulphonated melamine formaldehyde condensate (SMF), sulphonated naphthalene formaldehye condensate (SNF), modified lignosulphonates (MLS) and Lignosulphnates. This paper is focused on two types of polycarboxylate based superplasticizers.

PCEs are a type of graft copolymers with a long main chain ("backbone"). Side chains connected to this backbone possess a number of ether bonds. In this paper, the PCEs are made by copolymerisation of methacrylic acid and polyethylene glycol mono-alkyl ether methacrylate.

Immediately after cement comes into contact with water, a rapid dissolution of ionic species into the liquid phase to form Ca^{2+}, SO_4^{2-} and Al^{3+} Ions begins. Because of the structure of the superplasticizers, they are able to form complexes with these ions.

To investigate the influence of PCE to the solubility of ettringite[5] and calcium sulfate dihydrate, firstly ettringite and calcium sulfate dihydrate were formed by precipitation from supersaturated solution. These mineral phases were added in exess to a solution containing different amounts of PCE. Samples from these solutions were taken after different times and filtered by pressure filtration. In these filtrates, the amount of Ca^{2+}, SO_4^{2-} and Al^{3+} Ions were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) and ion-exchange chromatography. As reference, a solution of EDTA instead of PCE was used.

With increase of the concentration of superplasticizers the amount of ions in the solution increases. This increase was also found for the EDTA and so it is obvious that this effect is a result of the complexation of the ions. The ion concentration for ettringite increases from 100 to up to 700%; for calcium sulfate dihydrate it increases to 150%. The increase of the ion concentration is a result of the formation of complexes in the solution.

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CONDUCTIVITY AND DIELECTRIC STUDIES ON NEW MG2+ ION CONDUCTING BLENDS OF PVA/PVP BASED POLYMER ELECTROLYTES

Anji Reddy Polu , Ranveer Kumar

Solid State Ionics Research Laboratory, Department of Physics, Dr. Hari Singh Gour University (A Central University), Sagar, Madhya Pradesh 470003, India.
E-mail: reddyphysics06@gmail.com

Keywords: *Polymer electrolytes, ionic conductivity, Magnesium nitrate*

Solid polymer electrolytes (SPEs) based on Mg^{2+} - ion conducting salts have attracted considerable attention in the recent years as promising candidates to fabricate all solid state electrochemical power sources. The present day scenario in the field of battery technology is that most of the commercially available solid state rechargeable batteries are based on Li / Li^+ - ion SPEs. Li metal as well as Li^+ - salts suffer from several operational limitations viz. difficulty in handling in open ambience due to highly reactive materials, high cost etc. Instead, solid state rechargeable batteries based on Mg / Mg^{2+} - ion salt SPEs look very attractive as they are expected to give battery performance capabilities close to that of Li / Li^+ - ion SPE batteries. This is due to the fact that Mg^{2+} - ions have comparable ionic size and equivalent weight as Li^+ - ions.

The blend-based polymer electrolyte consisting of poly vinyl alcohol (PVA) and poly vinyl pyrrolidone (PVP) as host polymers and magnesium nitrate ($Mg(NO_3)_2$) as the complexing salt was studied. The polymer electrolyte samples were prepared using solution cast technique with distilled water as solvent. An attempt was made to investigate the effect of magnesium nitrate concentration in the PVA/PVP polymer electrolyte system. Complex impedance analysis was used to calculate the bulk resistance of the polymer electrolytes. The typical complex impedance spectrum of the optimum sample at different temperatures consists of a compressed semicircle in the high frequency region followed by a tail (spike) in the lower frequency region. The conductivity results indicate that by adding magnesium nitrate to a certain concentration (30 wt. %) the ionic conductivity increases and upon further addition the conductivity decreases. The ionic conductivity for pure PVA/PVP film was 2.96×10^{-8} S/cm. The maximum ionic conductivity 3.78×10^{-5} S cm^{-1} is obtained for PVA/PVP–$Mg(NO_3)_2$ (50/50–30 wt %) system at room temperature (303 K). The conductivity has been improved 1277 times when the magnesium nitrate salt was introduced into the PVA/PVP system. The frequency dependent ac conductivity of optimum sample at different temperatures show a frequency independent plateau in the low frequency region and exhibits dispersion at higher frequencies. The temperature dependent ionic conductivity for optimum sample exhibits a linear increase in conductivity as temperature increased including at conductivity jump at 50^0C. The variation of imaginary and real parts of dielectric constant with frequency shows increase in dielectric constant with temperature at lower frequencies and constant at higher frequencies. The temperature dependent imaginary and real parts of dielectric constants at different frequencies shows decrease in dielectric constant with increase in frequency and constant at higher frequencies. The variation of a dielectric constant with temperature is different for nonpolar and polar polymers.

In general, for nonpolar polymers the dielectric constant is independent of temperature. But in the case of strong polar polymers the dielectric permittivity increases as the temperature increases. The variation of imaginary and real parts of electric modulus with frequency shows decrease in electric modulus with temperature at higher frequencies and constant at lower frequencies.

RAMAN SPECTROSCOPY OF POLYANILINE FILMS PREPARED *IN SITU* DURING PRECIPITATION AND DISPERSION POLYMERIZATION OF ANILINE

Zuzana Rozlívková, Miroslava Trchová, Ivana Šeděnková, Milena Špírková, Jaroslav Stejskal

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, CZ-162 06 Prague 6, Czech Republic
E-mail: rozlivkova@imc.cas.cz

Keywords: *polyaniline, thin films, Raman spectroscopy*

Many applications of a conducting polymer, polyaniline (PANI), such as sensors, antistatic and anticorrosive coatings, require thin films. The technique of *in-situ* surface polymerization, giving rise to thin PANI films, has often been used in the coating of various materials with a conducting polymer overlayer.

Thin PANI films prepared by *in-situ* standard precipitation and dispersion polymerizations[1] on gold and silicon supports in the forms of emeraldine salt and base were at first characterized by atomic-force microscopy, and UV–visible and FTIR spectroscopies. Raman microscope has been used for molecular structure analysis with two different laser excitations at 633 and 514 nm (Figure 1).[2,3]

It has been shown, that the films prepared by dispersion polymerization, *i.e.* in the presence of poly(*N*-vinylpyrrolidone) stabilizer, are thinner, they are more resistant towards the deprotonation by 0.1 M ammonium hydroxide, and they are easily degradable by atmospheric oxygen.

In both cases, the films prepared on silicon supports are more stable with respect to ageing in air than those prepared on gold supports. The latter films are, on the other hand, more stable with respect to laser heating.

Emeraldine salt films have well-developed brush-like morphology. The emeraldine base films are more compact then those of salts, but indications of brush-like ordering still can be observed.

By using Raman microscopy, a variety of objects within the films, such as granules or various coloured film areas, were studied. It has been observed that granules or thinner film are as well less resistant to deprotonation and to heat treatment.

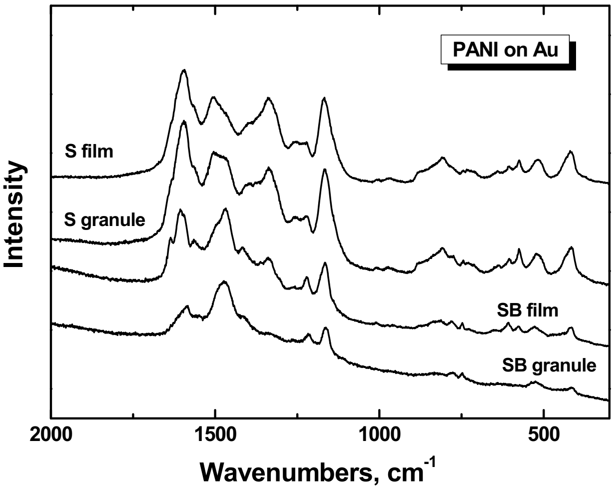

Figure 1. Raman spectra of standard polyaniline films in emeraldine salt (S) and base (SB) forms deposited on gold substrate, and the spectra of polyaniline granules adhering to such films.

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IN-SITU PHOTOACOUSTIC INFRARED SPECTROSCOPIC CHARACTERIZATION OF ANILINE POLYMERIZATION IN SOLID STATE

Ivana Šeděnková*, Elena N. Konyushenko*, Miroslava Trchová*, Jaroslav Stejskal*, Jan Prokeš**

** Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2,*
162 06 Prague 6, Czech Republic;
*** Charles University Prague, Faculty of Mathematics and Physics, 182 00 Prague 8, Czech Republic*
E-mail: sedenkova@imc.cas.cz

Keywords: *polyaniline, photoacoustic FTIR spectroscopy, solid-state reaction*

Polyaniline (PANI) is an interesting conducting polymer due to its possible applications. PANI or its ring-substituted derivatives are prepared by the oxidation of the corresponding monomers. The reaction usually proceeds in liquid aqueous media. Nevertheless, the solvents can be omitted in the reaction and the conducting material is prepared directly by the solid-state oxidation.

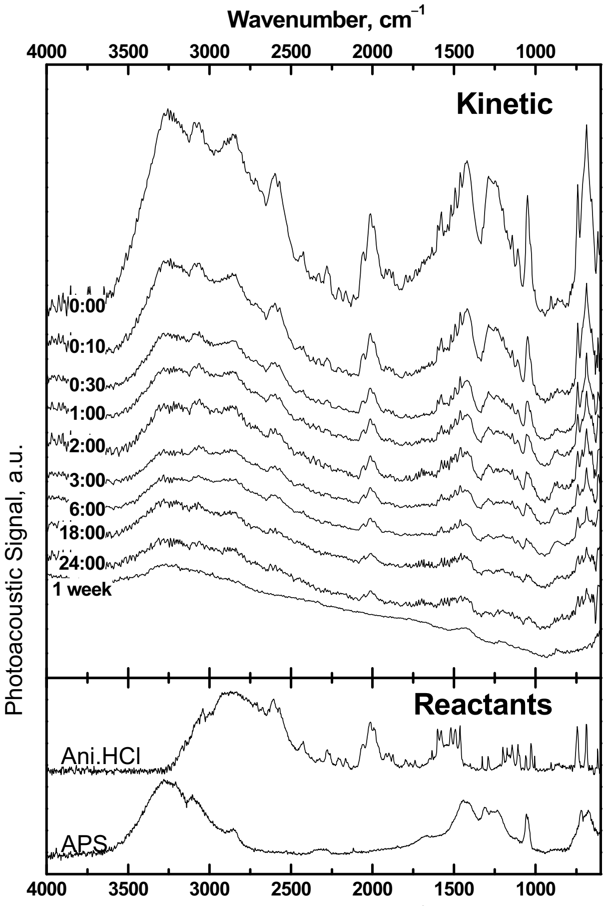

Figure 1: Photoacoustic FTIR spectra of the reaction mixture composed of aniline hydrochloride and ammonium peroxydisulfate at various oxidation stages.

Solid-state oxidation, *i.e.* the reaction between the aniline salt and a solid oxidant, has been reported[1] but the reaction mechanisms are still not sufficiently described. In solid-state polymerizations, the reactants, aniline salts and peroxydisulfate, enter the mechanochemical reaction as solids and are pulverized with a pestle and mortar or they are ball-milled. In the present study, aniline hydrochloride (Ani.HCl) was oxidized with ammonium peroxydisulfate (APS). In addition to the understanding of solid-state aniline oxidation, the preparation of a conducting material in solid state was the goal.

FTIR spectroscopy has previously been used to characterize the products of solid-state reactions.[2] The photoacoustic FTIR spectroscopy was chosen to monitor the reaction kinetics. This unique method allows following the solid-state reaction without interfering with the sample evolution any further. Ani.HCl (2 mmol) was mixed with APS (2.5 mmol) and hand-ground for 3 min. The powder was left for 24 hours to complete the oxidation reaction.

The depletion of both Ani.HCl and APS is reflected in the photoacoustic spectra measured *in situ* during the oxidation (Fig. 1). As arising oxidation products are strong absorbers in infrared region, the spectrum of the final product is significantly less intensive. Despite of the lower quality of the spectrum, the presence of PANI, as well as that of by-products (ammonium sulfate and ammonium hydrogen sulfate), can be confirmed by its detailed investigation. The spectrum of the final reaction product was also measured in KBr pellets.

In addition, the course of the reaction was monitored by conductivity measurement. The morphology of the final product was determined by transmission and scanning electron microscopy.

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GRAFTING POLYANILINE TO SILICA – A NOVEL LOW SOLVENT METHOD

Walt Wheelwright, Sudip Ray, Allan Easteal

Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand
E-mail: vkol006@aucklanduni.ac.nz

Keywords: *Silica, Polyaniline, Silylation*

Conducting polymers (CP) are speciality polymers and possess multifunctional properties.
An effective way to further development of their applications is preparation of hybrid materials, where a CP is combined with a commercial inorganic polymer-substrate. Silica is one of the most popular substrates due to its many existing and potential applications. It is very important to create a covalent substrate-CP bond that could increase stability and therefore spheres of applications of these novel materials. Polyaniline (PANI) is a frequently used CP that forms mixtures with different fillers[1]. However, PANI does not easily form a direct chemical bond with silica. To connect them, coupling agents such as silanes are widely applied[2]. Usually silanes react with silica in suspension with a large amount of solvent. We have developed a "low solvent" method for silylation in a very small amount of methanol, which has the advantages of both "green chemistry" approach and a one-pot procedure.
Silica gel 922 (44-74 µm diameter; surface area 450 $m^2 g^{-1}$; pore diameter 6 nm; pore volume 0.75 ml g^{-1}) was the substrate in the experiments. The coupling agent, 3-(phenylaminopropyl)trimethoxysilane (PAPTMOS), was dissolved in a very small amount of absolute methanol and mixed with silica. The mass ratio silane:methanol:silica was 1:4:4. The reaction mixture (RM) was heated at 110°C in vacuum for about 40 h to complete the chemical reaction and cure the product. The resulting products were washed with methanol by centrifugation and decanting, and vacuum dried at 60°C for 24 h. Elemental analysis results gave the C:N ratio near to that for the 3-phenylaminopropyl radical, and showed about 15 % of PAPTMOS bonded to silica. Formation of the desired products was confirmed by the presence of the diagnostic bands for the benzene ring at 1503 and 1601 cm^{-1} in FTIR spectra obtained using ATR with diamond crystal.
Grafting of PANI was carried out by suspending the reaction product in a solution of aniline in 1 M aqueous HCl, and adding aqueous ammonium peroxydisulfate (APS) dropwise with magnetic stirring. The black precipitate was dedoped by treatment with aqueous ammonia. All physically absorbed PANI-homopolymer was removed by washing with tetrahydrofuran (THF) and N-methyl-2-pyrrolidone (NMP). Formation of desired products was supported by elemental analysis, the C:N ratio approaching the value 6 for PANI chain. FTIR (KBr pellets) showed the strong signals at about 1509 and 1598 cm^{-1} that are characteristic of the benzyl radicals of PANI.
Finally, I the product was re-doped with 1 M aqueous methanesulfonic acid, then washed and vacuum dried at 50°C. Formation of the product (containing the green emeraldine salt form of PANI) was proved by elemental analysis and FTIR (KBr pellets). The conductivity of the PANI grafted silica was found by the 4-point probe method to be 1.2×10^{-3} S cm^{-1}. The procedure described above can be applied to other aluminosilicates or metal oxides.

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THEORETICAL STUDY ON THE MORPHOLOGY OF SUBSTITUTED PYRROLE AND PHENYLENE OLIGOMERS

Erol Yıldırım, Mine Yurtsever, Nurcan Tüzün

Istanbul Technical University, Department of Chemistry, Computational Chemistry Labaratory, 34469 Maslak, Istanbul, Turkey
E-mail: yildirimero@itu.edu.tr

Keywords: *polymer morphology, graft copolymers, conjugated polymers, dissipative particle dynamics*

Polypyrrole (PPy) and polyparaphenylene (PPP) are important conjugated polymers frequently used in commercial applications due to their long-term stability and conductivity. Unfortunately, PPy is an amorphous, insoluble and powdery product and PPP is a rigid polymer with low processability.

Graft copolymers are very important methods for preparing nanocomposites of PPy and PPP due to their unique morphologies in the nanometer range. Depending on different parameters such as composition, chain lengths and interaction parameter between blocks and polydispersity, the copolymer self assembles into different structures like spherical, cylindrical or lamellar microdomains.

Mecerreyes[1] synthesized a series of PPy-g-PCL copolymers via chemical oxidative copolymerization of pyrrole and pyrrole-end PCL macromonomers which shows the effect of grafting on the conductivity and microphase morphology. In addition, Demirel[2] showed the effect of poly(2-methyl-oxazoline) (POx), poly(ε-caprolactone) (PCL), poly(styrene) (Ps) side chains with various chain lenghts as side chains, on the structural and morphological properties of the rigid backbone of phenylene oligomers. The microphase separation between the chemically incompatible side chains together with the favorable interactions of the side chains with interfaces in the case of thin films allow the control of morphology of phenylene oligomers synthesized by these way. The phase behaviour is controlled by changes to the molecular architechture and the molecular interactions between side chains. Similar to other block copolymer types phase behaviour of these hairy-rod copolymers results from microphase separation, in this case driven by the incompatibility between the rigid backbone and flexible side chains.

In this study, results for several graft copolymers of PPy and PPP is presented in which the phase morphology due to hydrophilic and hydrophobic interactions determined by AFM pictures is explained theoretically by mapping the well determined interaction parameters between monomers of the backbones and side chains,. Dissipative Particle Dynamics[3] (DPD) is used which is an off-lattice mesoscopic simulation technique involves a set of particles moving in continuous space and discrete time to determine morphological and dynamical properties. It is shown that the DPD simulations successfully produce the similar patterns in nanometer scale observed in AFM images in micrometer scale.

The extent of the microphase separation and the driving forces are studied at different size scales by quantum mechanical calculations of the electronic structure, a modified Flory-Huggins Technique incorporated with molecular simulations and as well as dissipative particle dynamics simulations to determine nanoscale morphology.

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PHOTOCHROMIC MATERIALS BY SURFACE MODIFICATION OF POLYSTYRENE

Apichat Aphaiwong, Mark G Moloney

** Chemistry Research Laboratory – University of Oxford, Address: Mansfield Road, Oxford, OX1 3TA, England*
E-mail: apichat.aphaiwong@sjc.ox.ac.uk, mark.moloney@chem.ox.ac.uk

Keywords: *photochromic, polystyrene*

Apart from common chemical reactions such as silanisation, oxidation, chlorination, and acylation that require harsh conditions and are limited to some specific polymer types, the use of diaryl diazo compounds for the direct surface modification of polymers is a novel post-polymerisation method, which is suitable for adjustment of the surface characteristics of materials for particular applications, without changing their bulk properties[1]. The method involves solution coating followed by evaporating the solvent slowly to adsorb the pre-intermediate diazo substances, which then activated thermally or photochemically to decompose the diazo compounds leading to rapid decolourisation and reaction of the generated carbene with the surface of polymers. The mechanism of the process is bond-insertion to X-H single bond or addition reaction at C=C double bond of the carbene intermediate, in a process which is chemically irreversible.

The work aims firstly to improve the efficiency of chemical synthesis. The structure of diazo compounds was altered to achieve a molecule with a good balance of reactivity and stability that can be used as a central core for conjugation with other fragments with desired functional groups. Secondly, the project aims to establish an efficient method for the introduction of photochromism onto materials. The spiropyran system was chosen because it exhibits a rapid response[2] and high sensitivity of the two thermally (meta)-stable states[3], namely spiropyran neutral closed isomer and merocyanine open isomer. A spiropyran molecule was independently synthesised and coupled with a diazo compound prior to surface modification of polystyrene beads which gave a coloured material. To show the degree of physical adsorption, the spiropyran unit, which had a highly intense colour and could contribute to the colouration of the modified polymers, was also applied to polymers by the standard method described above. Although a slight physical adsorption was observed, which indicated that a trace amount of the spiropyran compound was coated on the surface, the mechanism of functionalisation by carbene insertion was demonstrated by the change in colour of the coated polymer beads upon heating, as a result of structural changes of diazo moiety.

Combustion analysis of the functionalised materials, including the polymers from physical adsorption, proved the existence of nitrogen. This was consistent with the presence of nitro group and/or spiropyran moiety on the surface of modified polystyrene beads. XPS data confirmed the presence of nitrogen-type species from N1s signals, implying successful surface incorporation of the diazo unit into the polymer surface. And ATR-IR spectroscopy revealed the existence of important functional groups that were traced back to the corresponding diazo substances. An examination of the photochromic properties found that the photoinduced process was demonstrated with one complete cycle by irradiation with UV light but could not be repeated on a second cycle.

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NOVEL MULTIFUNCTIONAL PHARMACEUTICAL EXCIPIENTS PREPARED BY COMPATIBILIZED REACTIVE POLYMER BLENDING

Philip Builders, *Agbo Bonaventure, *Adelakun Tiwalade, **Larry Okpako, Anthony Attama**

**Department of Pharmaceutical Technology and Raw Material Development, National Institute for Pharmaceutical Research and Development Abuja, Nigeria.*
***School of Pharmacy, University of Bradford, Bradford, United Kingdom.*
****Department of Pharmaceutics, Faculty of Pharmaceutical Sciences, University of Nigeria Nsukka 410001, Nigeria.*
E-mail: aaattama@yahoo.com

Keywords: *MCC-maize starch-composites, functional properties, direct compression.*

The choice of excipients remains a critical factor in pharmaceutical formulations. Microcrystalline cellulose-maize starch composites (MCC-Mst) were prepared by mixing colloidal dispersions of microcrystalline cellulose (MCC) with 10 %w/w of chemically gelatinized maize starch at controlled temperature conditions for use as multifunctional excipients with direct compression and enhanced disintegration abilities. The novel excipient was evaluated for its direct compression and enhanced disintegrant properties and the result compared with the properties of the individual components. Some of its physicochemical and thermal properties were also determined together with effects of freeze-thaw cycles of processing on the functional and physicochemical properties. The scanning electron micrograph showed that the particles of the MCC-Mst were irregular in shape and multiparticulate with a marked degree of asperity. The indirect assessment of the powder flow properties as determined by Carr's compressibility index and angle of repose showed that the MCC-Mst possesses better flow compared with MCC and maize starch. MCC-Mst is moderately hygroscopic and show a Type III moisture sorption isotherm. There was a gradual increase in moisture sorption between 31% to 84 % RH by the three polymers followed by a sharp increase between 84% and 100% RH. The FTIR spectra and DSC thermograms of the composite were different from those of MCC and maize starch. The FTIR spectra of MCC and starch were characterized by five strong peaks, which were identified at 2926.89, 2357.85, 1457.85, 1376.45 and 1031.65 cm^{-1}, and 2935.71, 2342.98, 1469.39,1376.66 and 1022.82 cm^{-1} respectively while the MCC-Mst composites showed only three strong peaks which were identified at 1457.39, 1016.76 and 722.64 cm^{-1}. The hardness of aspirin tablets was enhanced by incorporating MCC-Mst and MCC, but was reduced by maize starch. While the tablets prepared with MCC-Mst and maize starch disintegrated within 7 min, aspirin compacts devoid of any excipient and those prepared with MCC did not disintegrate even after 2 h. The tablets prepared with MCC-Mst composite generated at the fourth freeze-thaw cycle had the least disintegration time (2.1 ± 0.4 min). The disintegration time of the aspirin tablets prepared with this sample of MCC-Mst composite had a disintegration time of 6.25 ± 0.8 min while that prepared with maize starch had a disintegration time of 8.00 ± 1.2 min. Acetaminophen compacts prepared with MCC and MCC-Mst showed similar compact hardness characteristics and loading properties. The loading capacity of the different samples of the composite decreased with increase in the freeze thaw cycle. The loading capacity of the different materials as assessed by their compact hardness efficiency can be represented as follows (MCC>To>T1>starch>T2>T3>T4). The MCC-Mst composites are characterized by physicochemical and functional properties similar to both MCC and maize starch.

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OPTICAL AND FLUORESCENCE STUDIES ON CHALCONE DERIVATIVE DOPED PMMA

V. Ravindrachary[*], S. D. Praveena[*], Rajashekhar Bhajantri[*], Ismayil[*], J. Seetharamappa[**], Vincent Crasta[***]

[*] *Department of Studies in Physics, Mangalore University, Mangalagangotri-574 199, India*
[**] *Department of Chemistry, Karnatak University, Dharwad- 580 003, India*
[***] *Department of Physics, St. Joseph Engineering College, Vamanjoor, Mangalore 575 028, India*
E-mail: vravi2000@yahoo.com

Keywords: *Poly(methyl methacrylate), Chalcone derivative, UV-Vis, Fluorescence.*

In recent years, organic chromophore-doped functionalized polymers have attracted scientific and technological researchers due to their low cost, easy processability and light weight as well as some special structural and optical properties useful in optical memories, switches, polarization, color change, polymorphism, modulators and sensing applications. Poly(methyl methacrylate) (PMMA) is a colorless, high transparent and low birefringence polymer, which has proven to be a potential candidate for many applications. Among the organic NLO chromophores, chalcone derivatives embedded in a polymer show good optical properties like polarization, color change, polymorphism, molecular refraction, halochromism behavior etc. Hence the optical properties of these chalcone chromophore doped polymers should be studied extensively to understand the microstructural modifications[1].

PMMA films doped with different amounts of MPDMAPP [1-(4-methylphenyl)-3-(4-N,N,dimethylaminophenyl)-2-propen-1-one] were prepared by solution casting using dichloromethane as a common solvent. The FTIR study was carried out using Thermo Nicolet Avatar 330 FTIR spectrophotometer in the range 400-4000cm^{-1}.The UV-visible study was performed using SHIMADZU (UV-1601) UV-Visible Spectrometer in the wavelength range 195-700nm. The Fluorescence spectrometric measurements were conducted using Hitachi F-7000 Fluorescence Spectrophotometer with 500W Xenon lamp as an excitation source by exciting the sample with 270 nm and 450 nm wavelengths. The Fluorescence images of the films were taken using OLYMPUS BX-51 optical microscope with different optical filters of wavelength ranges: 330-385nm, 470-490nm and 510-550nm.

From the FTIR spectra it is understood that there is a small shift and variation in intensity indicates that there exists a strong inter/intramolecular interaction of chalcone with polymer, which modifies its microstructure. The UV-Visible spectrum reveals that there are three absorption bands at 220, 260 and 365nm for the doped PMMA attributed to $n\rightarrow\pi^*$, $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions respectively. It is observed that these bands shifted to 225, 265 and 402nm respectively, for higher dopant concentration. The optical energy band gap E_g is determined by translating the absorption spectra into Tauc's plots. Here three optical band gaps were observed and are decreases with increasing dopant level. The fluorescence spectroscopic studies have been carried out for 270nm and 450nm excitation wavelengths. The fluorescence peak intensity increases and emission wavelength shifts to higher wavelength upon doping. The fluorescent behavior of MPDMAPP molecules within the PMMA matrix shows "aggregation-induced enhanced fluorescence emission". This is mainly due to the dominant nonradiative intermolecular fluorescence resonance energy transfer (FRET). The MPDMAPP contains donor-acceptor system in which a donor starts to emit when the excited molecule (donor molecule) sees a nearby molecule (acceptor molecule) within a few nanometers. The emission peak (497nm) for higher doping suggests that there is a strong hydrogen bonding interactions between PMMA and chalcone which create charge transfer groups. The Fluorescence microscopic imaging for these samples shows interesting optical properties. The yellow colored film emits Blue color under 330nm excitation; Green color under 470nm and Red color on 510 nm excitation. This behavior of our chalcone doped PMMA samples shows photochromatic nature[2]. Hence the incorporation of such multifunctional photochromic chalcone derivative in polymers represents the future of digital optical storage.

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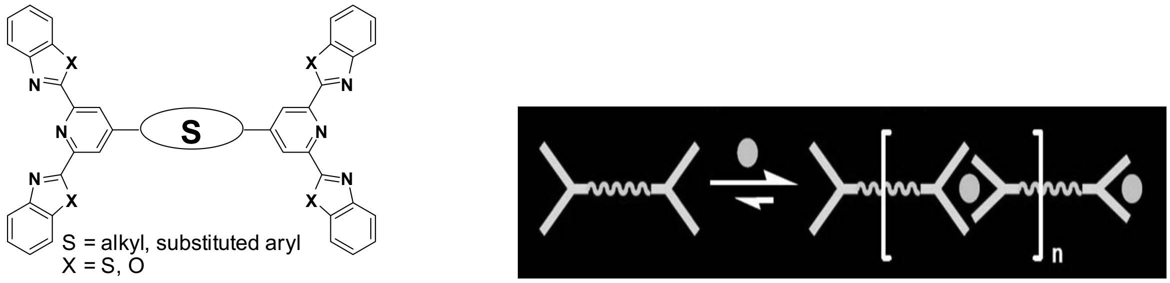
OPTICAL AND MAGNETIC PROPERTIES OF NEW METALLO-SUPRAMOLECULAR POLYMERS

Prasanta J. Goutam, **Parameswar K. Iyer**

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati-781039, Assam, INDIA
E-mail: pki@iitg.ernet.in

Keywords*: Metallo-supramolecular polymer***,** *Optical property, Magnetic Property.*

Synthesis of new ditopic monomers (Figure.1a) containing two 2,6-bis(benzimidazolyl)pyridine (BIP) based binding units is presented. Both π – conjugated aryl and non conjugated alkyl moieties are inserted as spacer between the two binding units allowing tuning of optical, thermal, magnetic and mechanical properties. UV visible spectroscopy of the mixed solutions of monomer and transition metal ions (from metal-perchlorate) at different Metal: Monomer ratio establishes that metal–ligand interactions between metal ions (Zn^{2+} ,Ni^{2+} etc.) and ditopic low-molecular weight monomers lead to the formation of metallo-supramolecular polymers with interesting optical properties. In particular the electronic spectra of the systems comprising monomer and metal ion nicely reflect the presence of various species upon metal-induced polymerization and allow for a unique elucidation of the different stages of the self-assembly process.These data also illustrate the potential of tailoring the electronic properties on corodination with different metals. Monomers exhibit electronic properties that are significantly different from those of similar BTP ligands. The UV-visible absorption spectrum of monomers shows a band associated with the BTP moiety (around 325 nm) and additionally displays transitions around 360 and 390 nm that appear to originate from the chromophore constituted by the BTP ligands and the spacer bridge. Monomers are much more emissive than similar BTP ligands, which are not further conjugated. The emission associated with the isolated BTP moieties is virtually absent, instead, an emission band around 450 nm is observed, which on account of an excitation scan allowed us to link this band with the electronic transition (presumably π– π *) that is also responsible for the lowest-energy absorption of monomer. On gradual addition of the salts of metal, the formation of the metallo-supramolecular polymer was observed in the UV-vis data. At a 1:1 metal to monomer ratio a metallo-supramolecular polymer has formed where each of the metal is complexed to two different monomer units (Figure 1b) resulting alternative ligand-metal-ligand association. Depolymerization starts above ligand to metal ratio of 1:1 and finally at 1:2 ratio monomer units with two metals are expected to be formed. Photoluminescence (PL) spectroscopy of monomer upon titration with metal solutions is also indicative of the metal-ligand binding. Temperature dependent magnetic properties of the polymers, studied using VSM and SQUID magnetometer reveals that variation of the spacer length changes the magnetic interaction between two metals ions. These interesting results will impact the development of organic-inorganic hybrid magnetic materials and devices. As conclusion, new ditopic monomers featuring BIP ligands were synthesized and polymerized via metal ligand coordination. The optical and temperature dependent magnetic properties of the polymers were studied.



(a) **(b)**

Figure: 1 Chemical structure of ditopic monomer (**a**) and formation of metallo-supramolecular polymer (**b**)

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USE OF NATURAL RUBBER LATEX WASTE AS ADDITIVE FOR NEWS THERMOPLASTIC ELASTOMER VULCANIZED (TPV).

Renan G. Maciel*; Matheus M. Cossa, Alex S. Sirqueira*, Bluma G. Soares****

** Centro Universitário Estadual da Zona Oeste – UEZO; Rua Manuel Caldeira de Alvarenga 1203, 23070300, Campo Grande, Rio de Janeiro, RJ, Brasil.*
***Instituto de Macromoléculas – IMA/UFRJ, Centro de Tecnologia, CP 68525, RJ.*
E-mail: asirqueira@click21.com.br

Keywords: *Mechanical properties, Thermoplastic Elastomers, Natural rubber, waste rubber.*

The amounts of waste in the world are increasing every year, and proportionally the polymer waste, too. It is due the news advance in polymer science like nano-technology, news catalysis, control in the polymerization plant, processing improvement; these actions will produce ways for news applications and can reduce the cost of material. In few years the world populations will have problems with the changes in the weather and temperature caused by the pollution. Because the polymers have a long time to decomposition, it will contribute for the damage in the environment. To change this situation, many researches focused theirs efforts in reduce the amount of polymer waste, by re-use in others in news purposes, produce ecological polymer or used raw removable source. Natural rubber (*Hevea brasiliensis)* are the most popular rubber in the world due their unique elastic characteristics and lost cost. Polyethylene is the commodities thermoplastic produced in large scale in Brazil. In this paper we used the residues of natural rubber latex and polyethylene to obtained Thermoplastic Elastomers Vulcanized (TPV) with good elastic and processing facilities with polymer waste. To improve the mechanical properties of the TPV sisal fiber were used as reforcing agent replacing the classical agent like carbon black and silica. To vulcanize the elastomer phase the dynamic vulcanization technique were used.

Experimental

The natural rubber latex, Polyethylene and sisal fiber were ground in a knife mill, dry in a oven at 60°C for 10 h. The TPV were done in Brabender plastograph, in 50:50 %wt of latex and PE, at 170°C and 80 RPM. Dicumyl peroxide was used as cure agent and bismaleimid as co-agent cure. In this step of the investigation a Design Factorial Experiment with 2 factors (sisal fiber and peroxide) was used to optimize the TPV. The physical-mechanical properties were measurement as tensile, modulus, hardness, swelling in hot oil, aging and crosslink density.

Results

The TPV produced with sisal fiber had higher torque mixer, modulus, lower oil uptake and any significant changes in the properties after aging (air oven at 70°C/ 48 hours). The hardness was of the same value in TPVs, variations were in the standard deviation. TPV without sisal fiber had higher tensile strength and crosslink density, this effect was attributed to reactions of peroxide with the polymers. the SEM analysis of TPV with higher amount of peroxide and fiber had a structure that can suggest the crosslink between fiber and polymer phase, which will be the responsible for the improvement in the modulus values. The use of fiber as reinforcing agent can be used for development of new TPV with residue of rubber and a thermoplastic phase.

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HIGHLY ION-SELECTIVE MEMBRANES PREPARED UPON LAYER-BY-LAYER ASSEMBLY OF POLYELECTROLYTE BLENDS

Kristina Hoffmann, **Bernd Tieke**

Universität zu Köln, Department Chemie, Physikalische Chemie, Luxemburger Str. 116, Köln, Germany
E-mail: tieke@uni-koeln.de

Keywords: *layer-by-layer assembly; polyelectrolyte blends; ion separation.*

Electrostatic layer-by-layer assembly of oppositely charged polyelectrolytes on porous substrates is a useful method for preparation of composite membranes with high selectivity in ion transport[1,2]. For example, membranes consisting of polystyrene sulfonate (PSS) and polyallylamine hydrochloride (PAH) show separation factors α($NaCl/MgCl_2$) up to 112.5 and α($NaCl/Na_2SO_4$) up to 45.0[3].

In order to further improve the ion separation characteristics, multilayer membranes consisting of PAH and blends of PSS and polyacrylic acid (PAA) were prepared. The influence of PAA on stability, morphology and thickness of PAH/PSS-PAA blend multilayer films is described in the literature[4]. Since PAA is a weak polyelectrolyte, the hydrophilicity and interfacial behaviour of the membranes can easily be changed by varying the PAA content in the blend.

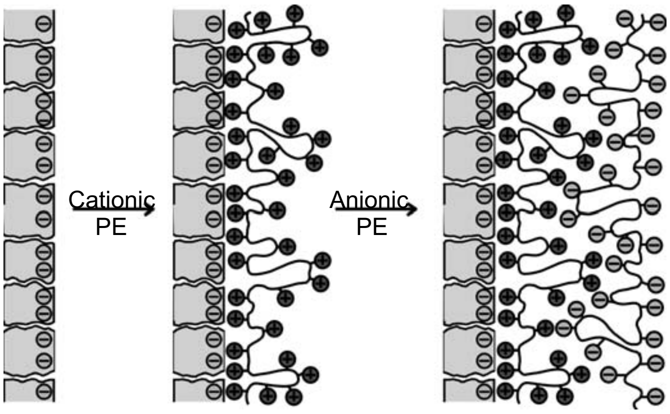

Fig. 1: Scheme of membrane preparation upon alternating layer-by-layer assembly of two oppositely charged polyelectrolytes on a porous PAN/PET supporting membrane.

Here we report on the separation capability of polyelectrolyte blend membranes containing PSS and PAA in various compositions. The influence of the pH of the polyelectrolyte solution and the PAA content in the blend on multilayer built-up, morphology and film thickness will be discussed.
In ion permeation under dialysis conditions, the blend membranes show a highly improved anion selectivity compared with the pure PAH/PSS membrane up to 200 % depending on the blend composition.
Under reverse osmosis conditions, the blend membranes show a higher stability than the pure PAH/PSS membrane, and with a PAH/PSS-PAA (1:1) blend membrane, a salt rejection up to 85 % for sodium chloride and 97 % for sodium sulfate can be reached.

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WEAR RESISTIVE COATINGS FOR HIGH DENSITY DATA STORAGE

T. Kaule*, S. Pihan*, S.G.J. Emmerling, Y. Zhang*, R. Förch*, J. Gutmann*, H.-J. Butt*, R. Berger*A. Knoll, B. Gotsmann**, U. Dürig****

**Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany*
***Zurich Research Laboratory, IBM Research, 8803 Rüschlikon, Switzerland*
E-mail: kaule@mpip-mainz.mpg.de

Keywords: *ultra-high density data storage, thin polymer films, plasma-polymerization*

Thermo-mechanical properties of thin polymer films are of special interest when using such films as recording media for scanning probe based high-density data storage system[1]. A number of factors determine if a polymer film is suitable as a recording media. Some key factors are: wear resistivity during copious readout cycles, long time stability of the written information, low roughness and high homogeneity within the film. One approach to satisfy these requirements is to use sandwich structures composed of a silicon-wafer as substrate, a deformable film for thermo-mechancial mechanical writing and a thin, hard layer providing wear resistivity. Here we report on our investigations to fabricate wear resistive polymeric films deposited by a plasma process from low molecular weight precursor gases. This technology offers some unique possibilities to adjust the surface properties of the deposited film which is difficult to achieve by other polymer preparation methods such as spin coating.

The plasma reactor used for depositing the films is a 30 cm long and 10 cm diameter glass cylinder that is equipped with a coil antenna to deliver a 13.56 MHz radio frequency (RF) and is operated at low pressures of approx. 0.050 mbar. Additionally a homemade pulse generator is attached to the generator to allow variation of ton and toff times (duty cycle). A homemade glass tripod is used as a sample holder, providing that the substrate face is perpendicular to the flow direction of the gas in the reactor. In the plasma radicals are generated from the precursor monomers. These radicals react with each other on the substrate surface and form a thin, homogenous film. By increasing the plasma power more radicals can be formed which can result in a more crosslinked polymer film. Furthermore, we found that changes of RF-pulse length and duty cycle times influenced the mechanical properties of the deposited films as well. In order to control the hydrophilicity of surfaces the polymer deposition can be performed in the presence of gases in the plasma reactor, e.g. oxygen. We developed methods for the deposition of films from two different monomers. At first we used hexamethyldisiloxane (HMDSO) as a monomer and determined conditions under which good protection covers were formed. Further research was then done with norbornene to investigate the tribochemistry by contact mode scanning force microscopy (SFM). We found that quite different deposition parameters have to be used for the two monomers in order to get wear resistive films. Deposition time, RF-power and duty cycles have to be adjusted not only depending on the monomer but also depending on the substrate. The same conditions may lead to a thin, hard film on a PS-film, but will result in no film on a silicon wafer. As a test for the mechanical stability of the deposited protection films we used a SFM-based nano-wear experiment [2]. For HMDSO we demonstrated that 2-6 nm HMDSO covering a PS film gave a mechanically stable surface, the same we showed for a 20 nm norbornene cover. The surface roughness was then determined by imaging 1 µm² areas using SFM, the RMS values were always well below 0.5 nm. For film thicknesses <10 nm we used grazing incidence x-ray-diffraction to determine precise thickness data. Both static and dynamic contact angles have been measured which provided information about the surface hydrophilicity. Finally, the writing properties were investigated by using heatable SFM tips for making small indentation at different loads and temperatures. These experiments showed that data storage densities >1 Tbit/in² can be readily achieved on a plasma polymer covered PS storage media.

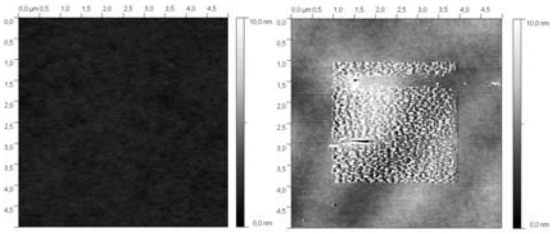

Fig.1: PS unprotected (left) and protected (right) by norbornene film after nanowear test

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SOLUTION ELECTROSPINNING OF POLYOLEFINS

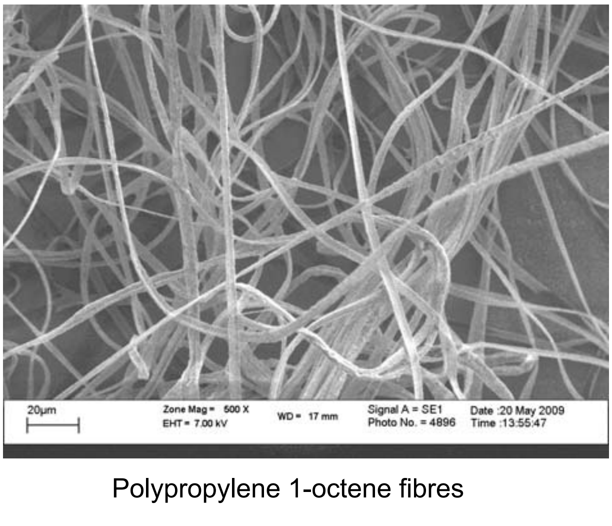
Liesl Keulder*, Albert van Reenen*

**Department of Chemistry and Polymer Science, University of Stellenbosch, Private Bag X1, Matieland, 7602, SouthAfrica*
E-mail: lk@sun.ac.za

Keywords: *Solution Electrospinning, polyolefins*

The field of melt electro-spinning of polyolefins has received some attention in recent years. However, solution electro-spinning of polyolefins has been largely ignored, due to the problems experienced with polymer solubility in a suitable solvent system with high conductivity for electro-spinning. Initial work involved the use of propylene-higher alpha olefin copolymers as materials for solution electrospinning. These highly crystalline copolymers appear to be more easily soluble than the corresponding polypropylene homopolymer. The determination of an appropriate solvent system for the electro-spinning process of these polyolefins was the initial goal. It was found that a combination of polar and non-polar solvents were the only way to prepare stable solutions of these polymers at intermediate temperatures. For example, a combination of cyclohexane, dimethyl formamide and aceteone was used to prepare solutions at 110 °C and electrospinning at 50 °C was successful in producing poly(propylene-co-1-octene) nanofibres. Further improvements in fibre morphology was obtained when selected salts were added to the spinning solution, for example LiCl. An example of the types of fibres produced are shown in the SEM micrograph below. The method of incorporating the salt to the solvent mixture proved to be critical as well. Results in this regard will be presented.

Further work consisted of obtaining fibres from different olefin homo- and copolymers and using them to create composites and investigating the mechanical properties of these composites. The use of these fibres in composites will broaden the spectrum of applications in which these materials can be used. As an example, we produced a series of nanofibres and microfibres by electrospinning poly(ethylene-co-vinyl alcohol). This polymer was much easier to dissolve in an appropriate solvent for electrospinning and the fibre diameters were also in the nano-metre range (250-300nm), which is much smaller than the polypropylene fibres which were more in the micro-metre range (4μm). These fibres, which typically melt at around 160 °C, were used as fibrous reinforcement in the preparation of polyolefin/nanofibre composites. The fibres were fully characterized, by SEM, DSC and WAXS analyses. The properties of the nanocomposite materials were determined, inter alia, by dynamic mechanical analysis, and compared to the matrix polymer without the presence of the nanofibres. We observed significant changes after incorporation of the nanofibres. These results will be presented in detail.



Polypropylene 1-octene fibres

INTERNAL STRUCTURE OF ELECTROSPUN NANOFIBERS FOR TISSUE ENGINEERING

Dorota Kolbuk, Pawel Sajkiewicz

Institute of Fundamental Technological Research, Polish Academy of Sciences, Pawinskiego 5B, 02-106 Warsaw, Poland
email: dkolbuk@ippt.gov.pl

Keywords: *nanofibers, electrospinnig, polycaprolactone, polymers, scaffolds*

Tissue engineering is a fast-moving interdisciplinary area that combines medicine, cell biology, materials science, and nanotechnology allowing for regeneration of damaged tissues and organs. Polycaprolactone (PCL) is a biodegradable, nontoxic polyester with a low melting point of around 60°C. PCL is degraded by hydrolysis of its ester linkages in physiological conditions (such as in the human body) and it is generally accepted in biomedicine. Electrospining process enables to form nanofiber mats. There are several papers trying to optimize this process. One of them is a description of Kowalewski[1].Those 3D structures are very useful to help control cell functions in tissue engineering. Their external properties are similar to components in the extracellular matrix (ECM) and mimic its fibrillar structure, providing essential cues for cellular organization, survival and function[2.].

The aim of our study is to investigate the influence of parameters of electrospinning on a structure of PCL nanofibers and their ability to support growth of hepatocytes. There are only few papers trying to analyze the internal structure of individual nanofibers[1,3].

PCL with Mw = 80,000 g/mole from Aldrich Chemical Co was used. Electrospinning was performed using two solvent mixtures: chloroform with N.N-dimethylformamide (DMF) and chloroform with methanol. In addition to standard analysis of geometry of nanofiber mats by microscopy, the analysis of internal structure was performed. The direct measurements of birefringence was performed using Pluta polarizing-interference microscope (Biolar PI) produced by Polish Optical Works (PZO) [Fig. 1.]. Crystallinity was determined from DSC measurements. Additionally, calculation of unknown intrinsic birefringences of crystal and amorphous phases has been done in order to estimate the molecular orientation of individual fibers from birefringence measurements. SEM observations were applied for estimation of morphology of growing hepatocytes.

Our results indicate that not only thickness of electrospun fibers but also the molecular orientation depends strongly on processing parametrs, like applied voltage, concentration and type of solvent used in elestrospinning. Molecular orientation as measured from birefringence is in general relatively weak and nonuniform along the fibers (Fig.1). DSC measurements show that the temperature of crystal melting as well as crystallinity is lower for nanofibres than for cast films. Crystallinity of constrained nanofibers determined from the area of melting peaks is around 0,4. This observation can be explained by low size and/or high concentration of defects in crystals formed during electrospinning. SEM images show preferred adhesion and great viability of hepatocytes growing on PCL scaffolds.

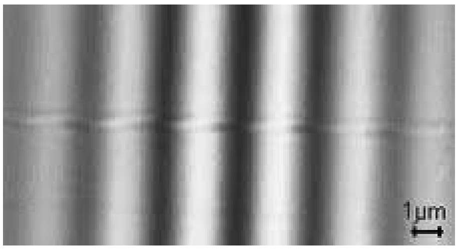


Figure 1. Fringed interference field for PCL fiber spun from 7% w/w solution of chloroform/methanol mixture at 10kV..

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POLYIMINOARYLENE WITH TERPYRIDINE SUBSTITUENT GROUPS: SOLVATOCHROMISM, IONOCHROMISM AND COORDINATIVE ASSEMBLY IN ELECTROCHROMIC FILMS.

Anna Maier, A. Raman Rabindranath, Hassan Fakhrnabavi, Bernd Tieke

Universität zu Köln, Department Chemie, Physikalische Chemie, Luxemburger Str. 116, 50939 Köln, Germany
E-mail: anna.maier@uni-koeln.de,

Keywords: *coordinative supramolecular assembly, ionochromism, electrochromism.*

In previous studies[1-3] we described the synthesis and multifunctional properties of polyiminoarylenes with different arylene units and terpyridine substituent groups (Fig. 1). The polymers are luminescent and solvatochromic in solution with quantum yields of 12 to 68 % dependent on the solvent. Complex formation of the terpyridine ligands with divalent metal ions allows prepare thin films upon coordinative supramolecular sequential assembly. After a few dipping cycles into THF solutions of metal hexafluorophosphates and the polymer, homogeneous coordination polymer films of 10-50 nm in thickness were obtained. The films are ionochromic, i.e., the colour depends on the transition metal ions complexed by the terpyridine ligands. Films containing Zn or Ni ions are yellow, while Co-based films are red. The divalent metal ions can be replaced on solid support by dipping of the coated substrate in another metal salt solution. The replacement of zinc ions against iron, cobalt and copper ions indicated by a colour change of the films from yellow to dark green, brown or dark red, respectively.

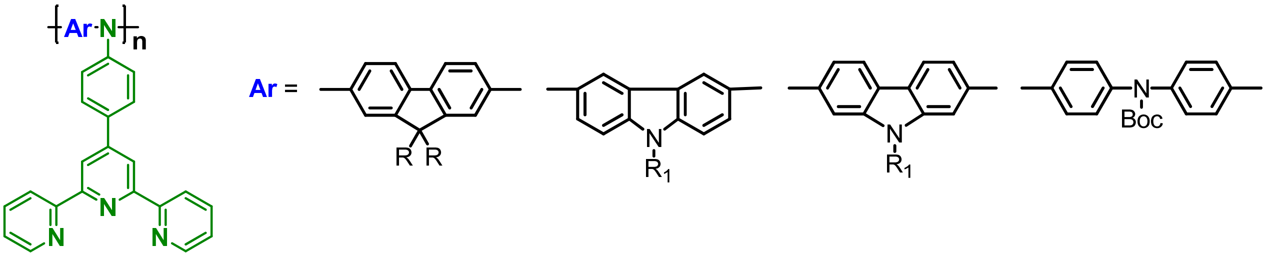

Fig. 1: Structure of polyiminoarylenes

Cyclovoltammetric studies indicate reversible oxidation and reduction accompanied with a colour change from yellow to red and blue, from yellow to green and blue, and from red to blue, dependent on the arylene units in the main chain. Electrochemical properties and colour switching can be modified by an incorporation of electroactive anions in the coordinative film structure.

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ETHYLENE (VINYL ACETATE)-*g*-POLYLACTIDE BY CATALYTIC REACTIVE EXTRUSION AS A NOVEL FLEXIBLE BIOPLASTIC

Busayarat Pattanaponganun, Rathanawan Magaraphan*

***Polymer Processing and Polymer Nanomaterials Research Unit–Petroleum and Petrochemical College, Chulalongkorn University, Phyathai Road, Soi Chula 12, Pathumwan, Bangkok 10330, Thailand*
**E-mail: Rathanawan.K@chula.ac.th*

Keywords: *bioplastics, ethylene (vinyl acetate)-g-polylactide, catalytic reactive extrusion*

A variety of packaging and medical products produced from biopolymers such as polylactide (PLA) are benefit from biodegradability within 4–5 weeks by heat, humidity and microorganisms; however, polylactide has some disadvantages such as rigidity, brittleness and low toughness. The poor properties could be overcome by copolymerization or blending with other polymers with careful consideration to retain biodegradability. In this work, graft copolymerization of polylactide onto ethylene (vinyl acetate) (EVA) by using catalytic reactive extrusion was selected in order to enhance flexibility of PLA.

Ethylene (vinyl acetate) was firstly modified by transesterification[1] prior to react with polylactide. The ratio of ethylene (vinyl acetate) : polylactide was chosen to be 40 : 60[2]. The conversion of modified ethylene (vinyl acetate) at each screw rotating speed was examined by solvent extraction and Fourier Transform Infrared Spectroscopy (FTIR). The thermal properties, and dynamic mechanical properties of the modified ethylene (vinyl acetate)s were also investigated.

Transesterification reaction of ethylene (vinyl acetate) was done in an intermeshing co-rotating twin–screw extruder, 20 mm diameter and L/D ratio is 40:1, with 1-dodecyl alcohol and dibutyl tin dilaurate (DBTL) as a catalyst. The screw rotating speeds were varied of 10, 20, 30 and 40 rpm. The conversions of modified ethylene (vinyl acetate) for each screw rotating speed were higher at screw rotating speeds of 20 and 30 rpm. The results from dynamic mechanical test revealed that the lower screw rotating speed gave the higher tan δ with the lower loss modulus, which could imply that hydroxyl substitution was achieved and hydrogen bonding was occurred. The obtained (modified) ethylene (vinyl acetate) was mixed with polylactide and catalyst. The optimum amount of catalyst giving the highest conversion was examined. Moreover, its thermal properties, mechanical properties, dynamic mechanical properties and morphology will be studied.

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EFFECT OF BLEND COMPOSITION OF NATURAL RUBBER/POLY(VINYLIDENE FLUORIDE) VIA DYNAMIC VULCANIZATION ON PROPERTIES OF RUBBER USED IN FUEL SYSTEM

Khantharat Phothiphon*, **Rathanawan Magaraphan***

** Polymer Processing and Polymer Nanomaterials Research Unit, Petroleum and Petrochemical College, Chulalongkorn University, Phayathai Road, soi Chula 12, 10330, Patumwan, Bangkok, Thailand*
E-mail: rathanawan.k@chula.ac.th

Keywords*: Dynamic Vulcanization, Natural Rubber, Poly(vinylidene fluoride), Thermoplastic Elastomer.*

Some properties such as oil resistance and thermal resistance are required for automotive rubber parts, especially those used in fuel transportation system. However, the rise in use of gasohol is so obvious with the aim to reduce global warming. This leads to the revolution of the rubber parts used in fuel system. That is the resistance to polar solvent has to be considered as well as the substitution of the synthetic rubbers. To achieve this aim, a new thermoplastic elastomer (TPE) of high performance is developed as an alternative with a cheaper cost.

For making this novel thermoplastic elastomer, natural rubber (NR) and poly(vinylidene fluoride) (PVDF) are the good candidates for reducing cost. Natural rubber provides properties of elastomeric materials for use in rubber parts. Poly(vinylidene fluoride) provides properties such oil and thermal resistances instead of fluoro rubber. Both of them were blended together via dynamic vulcanization technique at various blend compositions. The vulcanization system was also varied with a conventional system (CV system), an efficient vulcanization system (EV system) and peroxide system. For the systems involving sulfur, a sulfur:accelerator ratio of 2.0 was used in the conventional vulcanization system while the ratio of 0.5 was used in the efficient vulcanization system. For a peroxide system, 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane (Luperox® 101 or DBPH) was used as a vulcanizing agent at various content, which were 1, 3, 5 and 7 phr. The thermoplastic elastomer was carried out by blending in an internal mixer at 150 °C and speed 80 rpm following the formulae and mixing schedules. Afterwards pre-heat at 180 °C for 2 minutes and sequently compressed at 180 °C with a 20 ton press for 10 minutes by compression molding.

The morphology of thermoplastic elastomers (NR/PVDF blend) was observed by scanning electron microscope (SEM). The mechanical properties were studied before and after aging at 100 °C for 22 hours according to ASTM D573 – 04. The results of mechanical properties before and after aging had the same trend and quite had the same values. The tensile strength and elongation at break were determined according to ASTM D 412 – 06a, ISO 37 (Type 1) and the tear strength was determined according to ASTM D 624 – 00 and ISO 34. It is found that the tensile strength given from peroxide system was higher than sulfur system (CV and EV systems), but the elongation at break and the tear strength indicated the opposite. Because the C-C linkages from peroxide system is stronger than C-S and S-S linkages from sulfur system.[1] In addition, the C-S and S-S linkages are more flexible than C-C linkage so they need more force to tear them and showed the higher elongation at break. The oil resistance test was also done at room temperature for 24 hours according to ASTM D 471 – 06 and ISO 2285 (Method A). In this study the biodiesel oil and gasohol with 10% and 20% ethanol were used as the test liquid and calculated the degree of swelling in percent by weight increase. The result showed that the degree of swelling in sulfur system was higher than the peroxide system. The biodiesel oil gave the lowest degree of swelling and the degree of swelling decrease when increase the curing agent content.[2]

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COEXTRUSION OF POLYCARBONATE AND FLUOROPOLYMER FIBER FOR OPTICAL APPLICATION

Kunthalee Phuthasattha*, Rathanawan Magaraphan*, Athikom Reonsabutr, Sarawut Langwongsa*****

** Polymer Processing and Polymer Nanomaterials Research Unit– Petroluem and Petrochemical College, Chulalongkorn University, Phayathai Rd, soi Chula 12, 10330, Patumwan, Bangkok, Thailand*
*** Department of Telecommunication Engineering– Mahanakorn University of Technology, Cheum-Sampan Rd., 51, 10530, Nong Chok, Bangkok, Thailand*
**** PTT Phenol Co. Ltd.,Son Tower B, 123,10990, Vibahvadi Rangsit,Chatuchak, Bangkok, Thailand*
E-mail: rathanawan.k@chula.ac.th

Keywords: *Co-extrusion, Polycarbonate, Poly(vinylidene fluoride), Poly(methyl methacrylate)*

A waveguide fiber is a core-shell bicomponent fiber, made of transparent materials. The refractive index of the core should be higher than that of the cladding so that light was kept in the core by total internal reflection. Polycarbonate (PC) is a transparent material which has high glass transition temperature and refractive index of 1.59.[1] It was found that polyvinylidene fluoride (PVDF) and polymethylmethacrylate (PMMA) were miscible and gave suitable properties at 3:2 PVDF/PMMA blended ratio.[2] Since the refractive index of PVDF is 1.42 and PMMA is 1.49, so the refractive index of this blend could be less than PC.[1] This work aims to study morphology and mechanical properties of coextruded fibers–PVDF/PMMA blended (3:2) coated on polycarbonate–by varying piston speed ratio of core and cladding.

PVDF/PMMA blend was prepared by twin screw extrusion and dried at 80°C for 12 hours before used. For PC pellet (wonderlite® PC 110) was dried at 120°C under vaccum. In order to select the processing temperature of PC and PVDF/PMMA blend, their viscosities were studied by capillary rheometer at 250-280°C. Then, core-sheath bicomponent fibres were prepared by melt-spun co-extrusion process. The co-extruder has two barrels with independent pistons and heating units and a heating unit on die. The diameter of special designed die is 1 mm. The core-sheath piston speed ratio is varied; 1:1, 1:1.2, 1.25:1, 2:1.

From the capillary rheometer, the viscosity of PC and PVDF/PMMA blend are closed to at 250°C and 270°C, respectively. So these temperatures were used as processing temperature. The optical microscope images showed the obtained fibers have core's diameters 0.8 – 1.4 mm depended on piston speed. When piston speed is increased, the diameter of core is increased due to swelling property. This enhances light launching along the fibers easily. Since PVDF/PMMA blended is more viscous than PC so cladding is still thick while diameter of PC change. From the transmission spectra of polycarbonate, the obtained fibres at 660 nm and 760 nm show highest transmittance. So the numerical aperture, attenuation, operation temperature, and allowable bending radius will be determined from light transmission testing at these wavelengths.

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QUATERNIZED POLYSULFONE/ZrO_2 NANO COMPOSITE MEMBRANE: SYNTHESIS, CHARACTERIZATION AND ALKALINE FUEL CELL APPLICATION

R. Vinodh*, **D. Sangeetha***

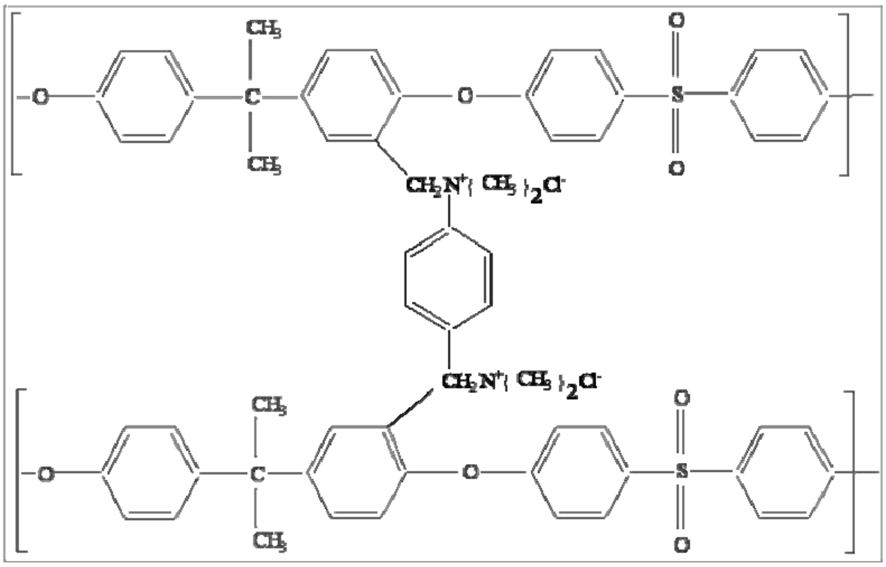
**Department of Chemistry, College of Engineering, Anna University Chennai, Chennai – 25, India*
E-mail: vinoth6482@gmail.com, sangeetha@annauniv.edu

Key words: quaternized polysulfone*, nano filler; alkaline fuel cell*

In the recent years, fuel cells are considered to be the best alternative for the internal combustion engines as it is efficient in energy conversion as well as eco-friendly due to the non-emission of hazardous gases like the oxides of sulphur, carbon etc. Among the different types of fuel cells, alkaline fuel cells (AFCs) are very promising as future energy source due to their high energy conversion efficiency and will help to solve the environmental concerns in energy production. Anion exchange membrane (AEM) is recognized as the key element for an efficient AFC.

In this present study, the AEM used was quaternized polysulfone (QPSU) obtained from polysulfone via. Chloromethylation and subsequent Quaternization. Zirconia (ZrO2) nano fillers were incorporated into the quaternized Polysulfone matrix in different proportions. QPSU/ZrO2 nano composite membrane was prepared by solution casting method. This study focused on the behavior of composites on the introduction of ZrO2 nano fillers. The composite membrane was subjected to several physicochemical characterizations including XRD, Raman spectroscopy, UV-DRS and Transmission Electron Microscopy. The thermal stability of the composite membrane was observed by TGA & DSC thermal analyses. The effect of variation in temperature on the conductivity of the composite membranes was measured by Impedance spectroscopy. Also, the membrane was subjected to few laboratory studies, such as ion exchange capacity (IEC), water and methanol absorption, methanol permeability, anion permselectivity and transport number. Finally the composite membranes were subjected to a performance evaluation in the alkaline fuel cell

Structure of quaternized polysulfone (QPSU) :



Acknowledgement: The authors would like to thank Department of Science and Technology (DST), New Delhi, India (Letter No. SR/S2/CMP-06/2008, dated 21-08-2008) for funding the project.

DEVELOPMENT OF POLYCARBONATE OPTICAL FIBER BY SOLUTION COATING PROCESS

Jiranun Saithong, Rathanawan Magaraphun*, Sarawut Lunvongsa, Athikom Roeksabutr*****

**Polymer Processing and Polymer Nanomaterials Research Unit,*
**Petroleum and Petrochemical College, Chulalongkorn University, Phayathai rd, Chula 12,10330, Patumwan, Bangkok, Thailand*
***Ptt Phenol Company Limited, Vibhavadi-Rangsit rd, 123, 10900, Chatuchak, Bangkok, Thailand*
**** Department of Telecommunication Engineering, Mahanakorn University of Technology, Cheum Sampan rd, 51, 10530, Bangkok, Thailand*
E-mail:kibua_kib@hotmail.com

Keywords*: Plastics optical fiber, Polycarbonate, Core, Cladding, Melt Spinning*

Plastic Optical Fiber (POF) is an optical fiber made of polymers. The applications of polymer optical fiber are for illumination, medical application, data communication including automobile optical data link system and sensor[1]. In this work, polycarbonate (PC) is used as the core material while various types of fluorinated materials e.g. polyvinylidene fluoride (PVDF) and highly fluorinate material are used as the cladding materials.

In fact, PVDF/PMMA blend, crosslinkable-perfluoropoly(arylene ether ketone)s (FPAEKs)[2] which has degradation temperature and glass transition temperature about 480 °C and 122 °C respectively, and the new developed cladding material are used to fabricate the POF. For the first step, 1,1,1-tris(4-hydrophenyl)ethane and 2,3,4,5,6-pentafluorostyrene with cesium fluoride and cacium hydride as catalyst are reacted to form 1,1-Bis(4-hydroxyphenyl)ethyl-1-phenyl 2,3,4,5,6-tetrafluoro-styrol ether (BHPFS). BHPFS is furthered reacted with fluoroacrylate to produce a new fluoro-cladding material. Two compositions of BHPFS are used, 25 and 30%wt. All the cladding materials are characterized by FTIR, NMR, GPC, TGA and DSC. Furthermore, after PC fiber extrusion by melt spinning, the cladding is applied on the fiber by drawing through the cladding solution at various drawdown ratios and dried in the oven. However, the thickness of optical fibers depends on drawdown ratio if the drawdown ratio increases the fibers thickness will decrease. For example, the drawdown ratio about 1:0.238 represented the core thickness of optical fiber about 0.426 mm. and after coating by cladding solution, the fiber thickness slightly increased about 0.05 mm. These results can determine by optical microscope(OM) to confirm the perfectly coated PC fiber. And further characterized, the mechanical, thermal, physical, and optical properties of the obtained polymer optical fibers will be carried out.

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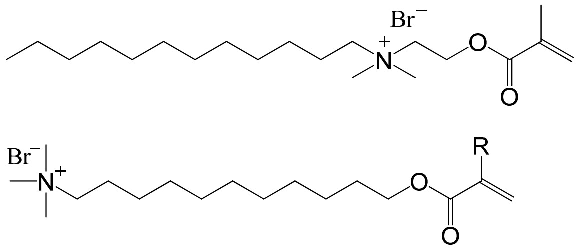
RHEOLOGICAL CHARACTERISATION OF THERMORESPONSIVE COPOLYMER HYDROGELS PREPARED VIA GAMMA-RAY INDUCED POLYMERIZATION OF MICELLAR MONOMER SOLUTIONS

Tatjana Friedrich*, Bernd Tieke *, Florian J. Stadler **, Christian Bailly **

** Universität zu Köln, Department Chemie, Physikalische Chemie, Luxemburger Str. 116, 50939 Köln, Germany*
*** Université Catholique de Louvain, Unité de Physique et de Chimie des Hauts Polymères, Croix du Sud 1, 1348 Louvain-la-Neuve, Belgium*
E-mail: tatjana.friedrich@uni-koeln.de

Keywords: *NIPAAm copolymers, mechanical stability.*

Thermoresponsive copolymer hydrogels based on N-isopropylacrylamide (NIPAAm) are prepared in a one-step, gamma-ray induced polymerization of micellar monomer solutions containing NIPAAm and a polymerizable surfactant (surfmer).[1] The copolymerized micelles act as additional cross-linking units and thereby increase the mechanical stability of the system. In our contribution the results on NIPAAm-copolymer hydrogels containing three different cationic surfmers (2-methacryloylethyl)dodecyldimethylammonium bromide (MEDDAB), 11-methacryloylundecyltrimethyammonium bromide (MUTMAB) and 11-acryloyloxy-undecyltrimethylammonium bromide (AUTMAB) (Fig. 1) will be presented.



MEDDAB

R = CH_3 MUTMAB
R = H AUTMAB

Fig. 1: Molecular structures of MEDDAB, MUTMAB and AUTMAB.

Elongational flow measurements show that the addition of surfmers leads to a decrease in stiffness for NIPAAm-copolymers containing any of the three surfmers. The decrease in stiffness can be explained by an increase of the chain length between the cross-linking units in the network. NIPAAm is partially incorporated in the shell of the micelles as proven by structure studies with SANS and determination of the phase behaviour. For hydrogels containing MEDDAB and AUTMAB (Fig. 2) the stress at break increases with increasing surfmer concentration. When MUTMAB is copolymerized the hydrogels are disrupted at lower stress compared with pure NIPAAm hydrogels. The differences in the mechanical properties of the copolymer gels can be ascribed to the different chemical structures of the surfmers especially to position and hydrophilicity of the polymerizable groups.

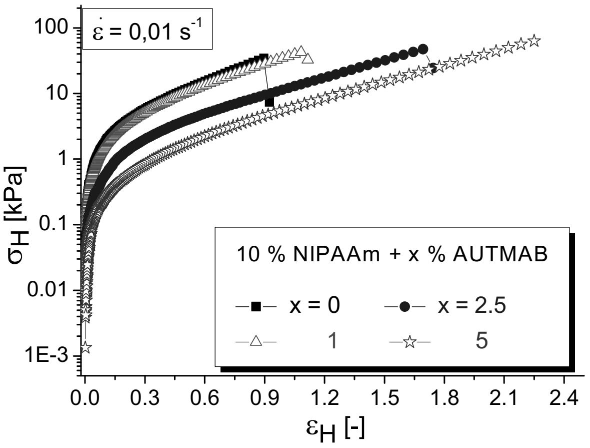


Fig. 2: True stress vs Hencky-strain for a pure NIPAAm-hydrogel and AUTMAB/NIPAAm-hydrogels containing 10 % NIPAAm.

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PH SENSITIVE HYDROGELS OF CHITOSAN AND ACRYLIC ACID FOR DRUG DELIVERY

Anu Gupta *, Ajit Kumar **

** School of Engineering & Technology, Indira Gandhi National Open University, New Delhi – 110068, India*
E-mail: anu339@gmail.com

Keywords: *Chitosan, pH Sensitive Hydrogels, Drug Delivery*

One of the most attractive applications of the drug delivery system is the deliver of bioactive agents from polymeric materials at specific site.However, there are many problems to be overcome in that the bioavailability of these drugs after oral administration is usually very low because the molecules undergo degradation in the gastrointestinal tract and a substantial portion of the amount absorbed is removed and metabolized by the liver. Hydrogels are three-dimensional polymeric networks, capable of imbibing large amounts of water or biological fluids. These polymeric hydrogels are prepared from a limited number of synthetic polymers and their derivatives such as copolymers of methacrylic acid, acrylamide and N-isopropylacrylamide. Hydrogels have excellent carriers for release of drugs and bioactive macromolecules either in their swollen state or dynamically swelling systems. Their major disadvantage *(i.e.* their relatively low mechanical strength) can be overcome either by cross linking, by information of interpenetrating networks. In particular, chitosan has been largely evaluated as a potential vehicle for drugs administered orally because of its cationic nature and high charge density in the solution. Moreover, it is acknowledged that chitosan posses good mucoadhesive properties, thus sustained release and improved bioavailability of drugs can be achieved by prolonging the residence time of drug carriers at the absorption site. Chitosan is a (1,4)-linked 2-amino-2-deoxy-β-D-glucan and can be presented by N-deacetylation of chitin. Chitosan has both reactive amino and hydroxyl groups that can be used to chemically alter its properties under mild reaction conditions. It was known that poly(acrylic acid) (PAAc) has been considered as *pH* and electrical sensitive materials due to ionic repulsion between anionic charged groups and thus forms polymer complexes with polybases such as poly(ethylene oxide), polyvinylpyrrolidone. Chitosan is a weak base with an intrinsic pKa of 6.5. PAAc contains carboxylic groups that become ionized at *pH* values above its pKa of 4.7.Therefore,a swelling ratio of chitosan is high at low *pH*, whereas swelling of PAAc is low at low *pH*.

In this study we report on the preparation of polymer composed of chitosan and AAc and characterize on the basis of swelling ratio, FTIR. Drug release characteristics of Chitosan/PAAc were studied

We prepared IPN hyrogels based on chitosan and PAAc. Equilibrium swelling of Ch and Ch/AAc films was calculated against GA and Bis at *pH* 3.0 and pH 7.4 and effect of GA on swelling of pure chitosan at *pH* 7.4 and *pH* 3 respectively. Swelling is maximum in blend ratio of Ch/AAc 1:1 having bis 2%(w/w). Swelling has decreased as the amount of Bis increases. Acrylic acid has also strong effect on swelling .%age swelling has decreased in pH 3 and increased in *pH* 7.4 as amont of acrylic acid increases. FTIR spectroscopy confirmed the structure of IPN composed of chitosan/PAAc network. Pure chitosan exhibit distinctive absorption band at 1658 cm^{-1} (amide I), 1595cm^{-1} (amide II) and 1314 cm^{-1} (amide III). Absorption bands at 1154 cm^{-1} (anti symmetric stretching of C-O-C bridge), 1082 cm^{-1} and 1032 cm^{-1} (skeletal vibrations involving C-O stretching) are characteristics of its saccharide structure. FTIR analysis confirmed amidation between amino groups of chitosan and carboxylic group of PAAc. FTIR analysis showed that due to addition of AAc , there is shifting and broadening of peaks due to interactions between various molecules.

Drug release experiments of mertronidazole from LVC/AAc and HVC/AAc films prepared with various formulations were carried out in *pH* 1.2 at constant temperature of 25°C. The pK_a for metronidazole is 2.5. The drug release profiles of metronidazole were established in *pH* 1.2.The profiles showed that drug release has taken place within 15 minutes but on increasing AAc, drug release decreased.

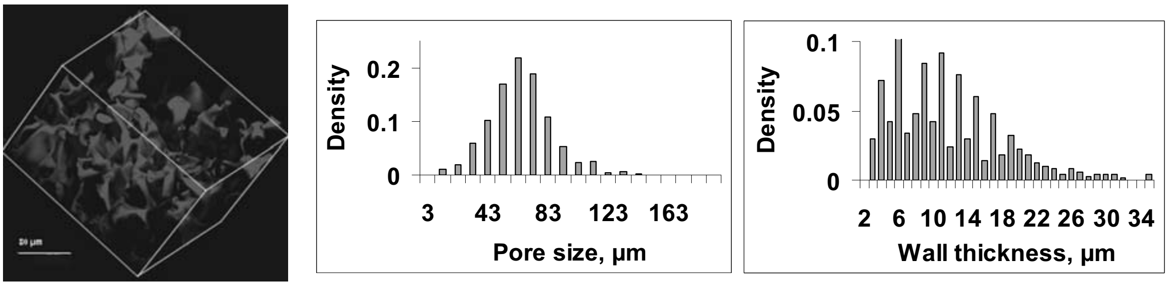
MACROPOROUS HYDROGELS POROUS STRUCTURE CHARACTERIZATION

Irina Savina *, **Maria Dainiak****, **Igor Galaev*****, **Sergey Mikhalovsky******

** School of Environment and Technology, University of Brighton, Address: Cockcroft Building, Lewes Road, BN2 4GJ, Brighton, UK*
*** Protista Biotechnology AB, Address: IDEON, SE 223 70, Sweden*
**** DSM, Address: P.O. Box 1, 2600 MA Delft, Netherlands*
***** School of Pharmacy and Biomolecular Sciences, University of Brighton, Address: Cockcroft Building, Lewes Road, BN2 4GJ, Brighton, UK*
E-mail: i.n.savina@brighton.ac.uk

Keywords: *macroporous hydrogels, pore characterization, confocal laser scanning microscopy*

Porous hydrogels has been used in many biotechnological and biomedical applications over the past 40 years. Porous structure of a hydrogel determines many of its performance characteristics, e.g. swelling capacity and molecular permeability. High levels of porosity and interconnectivity are essential for manufacturing hydrogels intended for use as material for tissue engineering, separation matrixes or for making bioreactors. However the characterization of hydrogels remains challenging task. Due to hydrogel softness and high water content the techniques that are currently used for obtaining structural information of porous material are not ideally suited to hydrogels.[1-3] Mercury porosimetry, gas flow porosimetry, micro-computed tomography and conventional scanning electron microscopy, for example, all require dry samples or samples mechanically which can withstand high pressure. Hydrogels could be dried, but drying are likely to impact on the structure of hydrogels by shrinking, collapsing or distorting pores to an extent that is difficult to determine. Environmental scanning electron microscopy, confocal laser scanning microscopy (CLSM) and multiphoton microscopy (MPM) allows characterising hydrogels in their native state or something close to it. Thus confocal laser scanning microscopy (CLSM) imaging was employed in this study to analyse the pore structure of macroporous hydrogels prepared using a cryogelation technique. The advantage of CLSM, that it allows the study of hydrogels in their native hydrated state. It is a non-destructive technique that allows "optical" sectioning of the hydrogel matrix into a series of 2-D images, from which a 3-D model can be reconstructed. MPM image analysis provided similar results. Quantitative data on the porosity of the hydrogels were obtained from the CLSM and MPM images using ImageJ software.



Figures 1). Macroporous HEMA hydrogels, 3-D structure; 2) Pore size distribution; 3) Wall thickness distribution.

Acknowledgments
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FUNCTIONALIZATION OF HYDROGELS BASED ON N-ISOPROPYLACRYLAMIDE AND CATIONIC SURFACTANT MONOMERS VIA COUTERION EXCHANGE

Anna Trinker, Tatjana Friedrich, Bernd Tieke

Universität zu Köln, Department Chemie, Physikalische Chemie, Luxemburger Str. 116, 50939 Köln, Germany
E-mail: tieke@uni-koeln.de

Keywords: NIPAAm copolymers, counterion exchange.

Recently we reported on new hydrogels containing copolymerized NIPAAm and cationic polymerizable surfactants (surfmers). Upon high energy irradiation of aqueous micellar surfmer solution containing additional NiPAAm a chemically and physically cross-linked network structure is formed consisting of blocks of poly-NIPAAm and polymerized surfmer.[1] Aim of this work is to functionalize the hydrogels via counterion exchange (Fig. 1) of cationic surfmers 11-acryloyloxyundecyltrimethylammonium bromide (AUTMAB) and 11-methacryloylundecyltrimethyammonium bromide (MUTMAB).

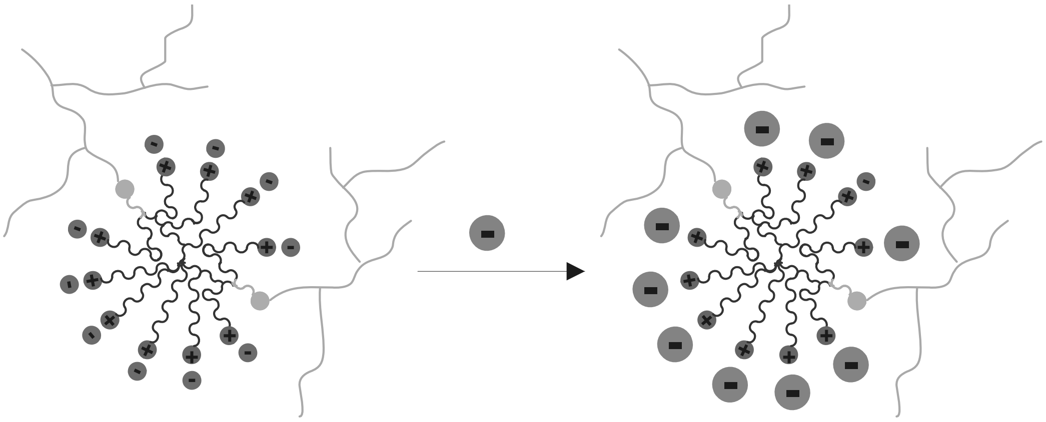

Fig. 1: *Structure model of the exchange of the counterions in order prepare hydrogels with functional properties.*

Exchange of counterions is facilitated using the thermoresponsive swelling and shrinking of the gels. After shrinking at 50 °C, gels are cooled to 20 °C and re-swollen in a solution containing either organic counterions or inorganic complex counterions, which are able to replace the bromide ions present in the gels to counterbalance the surfmer ammonium head groups. Two examples are described:
First, tetrachloropalladate is electrostatically adsorbed at the micelles and subsequently reduced with sodium borohydride to yield catalytically active palladium nanoparticles. The catalytic activity was studied by investigating the reduction of p-nitrophenol with sodium borohydride as a model reaction. A detailed kinetic study of the dependence of the catalytic activity on surfmer concentration, temperature and cross-linking density of the network is presented.
Second, the incorporation of 1-pyrenesulfonic acid was studied resulting in fluorescent hydrogels with high emission below and no emission above the phase transition temperature of the gel. It is also demonstrated that the system can be used for release applications which can be controlled by the pH of the surroundings.

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CONJUGATED DIKETOPYRROLOPYRROLE (DPP) POLYMER NETWORKS

Kai Zhang*, Bernd Tieke*, Filipe Vilela, John Forgie**, Peter J. Skabara****

**Department für Chemie, Universität zu Köln, Luxemburger Str. 116, D-50939 Köln, Germany*
***Department of Pure and Applied Chemistry, Thomas Graham Building, 295 Cathedral Street, Glasgow, G1 1XL, UK*
E-mail: zhang.kai@uni-koeln.de

Keywords: *Conjugated networks, electropolymerization, electrochromism*

Diketopyrrolopyrrole, known as DPP, and some of its derivatives represent high-performance pigments used in paints, color inks and plastics.These materials show intense red colors, strong red photoluminescence, and electroluminescence, which render them attractive as active materials in a variety of electronic devices, such as such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic solar cells.

In this work, a series of cross-linked conjugated polymers based on poly[tetrakis(thienylphenyl)diketopyrrolopyrrole (DPP)] is described, with the thienyl groups being 3-hexylthiophene, EDOT and EDTT (Figure 1). Polymerization of these compounds was achieved using electrochemical oxidation or chemical oxidation with ferric chloride. The properties of the polymers were investigated using cyclic voltammetry and UV/vis absorption spectroscopy.

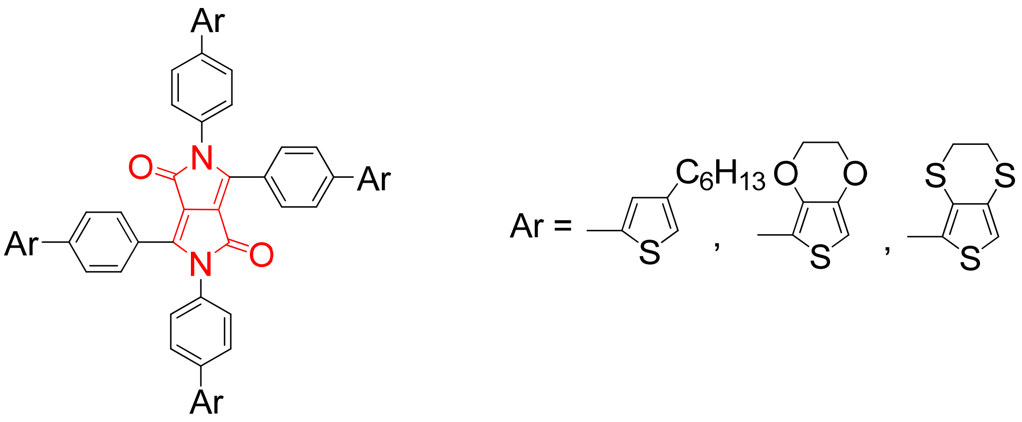

Figure 1: DPP monomers for preparation of cross-linked polymers.

The polymer networks show a broad absorption with maxima around 510 nm. They also show low oxidation onset potentials of +0.4 to +0.8 eV and band gaps of 1.7 to 1.8 eV. Within this series, the cross-linked polymers based on 3-hexylthiophene- and EDTT-substituted DPP units are electrochromic upon anodic oxidation, whilst the polymer containing EDOT-substituted DPP does not show any color change. The reason might be a sulfur-oxygen interaction between adjacent EDOT units, which leads to a well-packed structure preventing the ion exchange within the polymer network.

The conjugated polymer networks might be useful in fields of organic electronics. Furthermore, due to their cross-linked structure, they are microporous materials, which might be used for gas storage, molecular separation, or heterogeneous catalysis. Relevant studies will be presented in our poster.

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CROSSLINKING OF EPOXY-OLIGOMERIC MIXTURES IN THE PRESENCE OF CYANURIC EPOXY RESIN PEROXY DERIVATIVES

Oksana Iatsyshyn, **Taras Chervinskyy, Michael Bratychak, Galyna Strap**

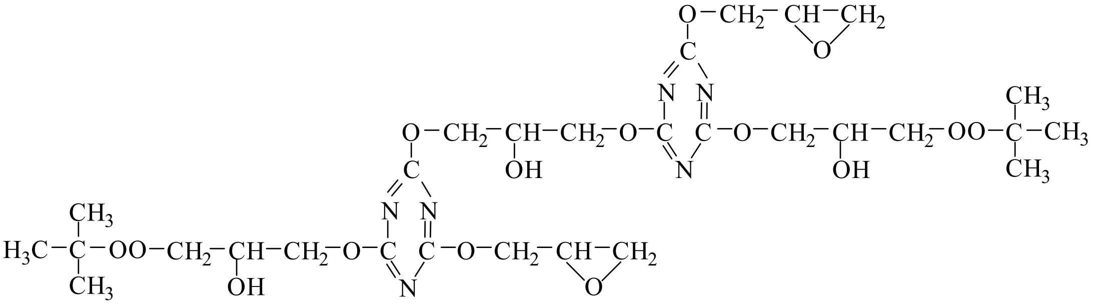
Department of Petroleum Chemistry and Technology, Lvivska Polytechnika National University, 12, S. Bandery str., 79013 Lviv, Ukraine;
E-mail: mbratych@polynet.lviv.ua

Keywords: *cyanuric epoxy resin, peroxide, crosslinking*

Polymeric composition and materials on the basis of epoxy resins are characterized by unique operational properties and great possibilities of their modification. Therefore they are widely used in different branches of industry. The wares properties may be improved by combination of epoxy resins with other high-molecular compounds. The best characteristics have products in which all components are bounded into one three-dimensional polymer. Mixtures on the basis of ED-20 epoxy resin and unsaturated polyesters are of the greatest interest. The introduction of polyester molecules into the epoxy-polymeric composition allows to reduce a price of the wares on the one hand and to improve their properties – on the other hand.

It has been shown earlier[1] that epoxy resins modified by hydroperoxides are widely used in radical and polycondensation processes. The simultaneous presence of epoxy and peroxy groups in their molecules allows to use them as active additives during forming of protective lacquer coating on the basis of industrial dianic epoxy resins.

This work deals with the possibility of crosslinking of epoxy-oligomeric mixtures based on ED-20 industrial dianic epoxy resin in the presence of synthesized by us peroxy derivative of cyanuric epoxy resin (PDCER):



PDCER is a product obtained from cyanuric epoxy resin and tert-butyl hydroperoxide in the presence of 18-Crown-6 + $ZnCl_2$ in a 1:3 ratio as catalyst. It has molecular weight 650, epoxy number 9.0 % and active oxygen content 3.8 %.

Epoxy-oligomerc mixtures consisting of ED-20 (70 mass parts), PDCER (25 mass parts), petroleum resin with epoxy groups (5 mass parts) and TGM-3 oligoesteracrylate (10 mass parts) were prepared by mix at room temperature. Compositions were poured over degreased glass plates and crosslinked first under normal conditions for 24 hours and then at 383, 403 and 423 K for 15, 30, 45 and 60 minutes. The structural changes were controlled by the determination of gel-fraction content using Soxhlet apparatus and film hardness using M-3 pendular device.

It has been established that the amount of insoluble products in the crosslinked product is 70 % at room temperature and thei hardness does not exceed 0.14 rel. units. Further heating increases film hardness and gel content. These values depend on crosslinking time and temperature.

Films obtained at 403 K after 45 minutes have hardness of 0.62 rel. units and gel- content of 78 %. Polymer films obtained in the presence of PDCER may be recommended as anticorrosive coatings for metals.

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HYDROLYTIC STABILITY AND SOLUTION PROPERTIES OF UREA-FORMALDEHYDE RESINS OF DIFFERENT FORMALDHYDE/UREA MOLE RATIOS

Byung-Dae Park, Ho-Won Jeong

Department of Wood Science and Technology, Kyungpook National University
1370, Sankyug-Dong, Buk-ku, Daegu, 702-701, Republic of Korea
E-mail : byungdae@knu.ac.kr

Keywords: *urea-formaldehyde resin, hydrolysis, solution properties*

Urea-formaldehyde (UF) resin, one of the most important wood adhesives, is a polymeric condensation product of formaldehyde with urea, and being widely used for the manufacture of wood-based composite panels, such as plywood, particleboard or medium density fibreboard. In spite of its advantages such as fast curing, good performance in the panel, water solubility, and lower cost, UF resin possesses a critical disadvantage, i.e., formaldehyde emission, which is one of the factors affecting sick building syndrome in an indoor environment. Therefore, the formaldehyde emission issue has been one of the most important aspects of UF resin since 1980s. The hydrolysis of cured UF resin was known as a major factor affecting long-term formaldehyde emissions.[1] Much attention has been paid to investigate the hydrolysis of UF resin to understand the mechanisms of formaldehyde release from cured UF resins. The susceptibility of hydrolytic degradation of cured UF resin depends on its chemical structure and the degree of cross-linking, and could be accelerated by high temperature and strong acidic conditions.[2] Although much work has been done to reduce the formaldehyde emission of UF resins by lowering formaldehyde/urea (F/U) mole ratio, the influence of F/U mole ratio to hydrolytic stability and solution properties of UF resin was not well studied. Therefore, as a part of abating the formaldehyde emission of UF resin, this study investigated the hydrolytic stability of cured UF resins and solution properties of UF resins at different F/U mole ratios, using wet chemical analysis and dynamic light scattering (DLS).

In order to achieve the objectives, laboratory-synthesized UF resins at four different F/U mole ratios (1.6, 1.4, 1.2, and 1.0) adjusted by adding different amounts of the second urea were characterized. As the F/U mole ratio decreases, the hydrolytic stability of cured UF resin slightly increases and then decreases, indicating that lower F/U mole ratio improves the hydrolytic stability of cured UF resin (Fig. 1). The DLS results showed that the hydrodynamic radius (R_h) of UF resin decreased with a decrease in the F/U mole ratio (Fig. 2), and the radius of gyration (R_g) also decreased. These results indicated that UF resin of lower F/U mole ratio were much less branched and more or less a linear structure. These results also suggested that lower F/U mole ratio improved the hydrolytic stability of UF resins, which provided a partial explanation for a low formaldehyde emission of low F/U mole ratio UF resin used for wood panel products.

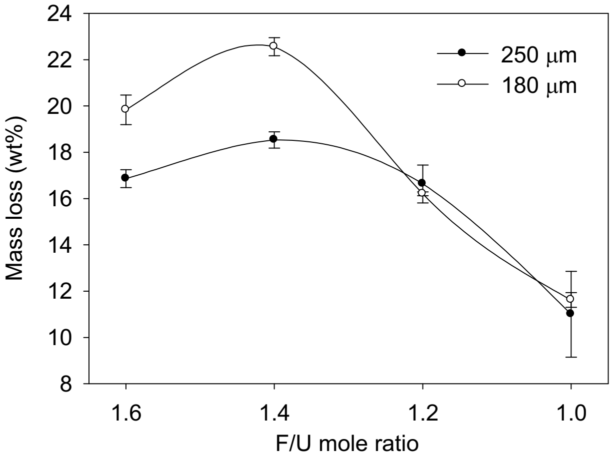

Fig. 1 Hydrolytic stability (mass loss) of cured UF resins with different F/U mole ratios

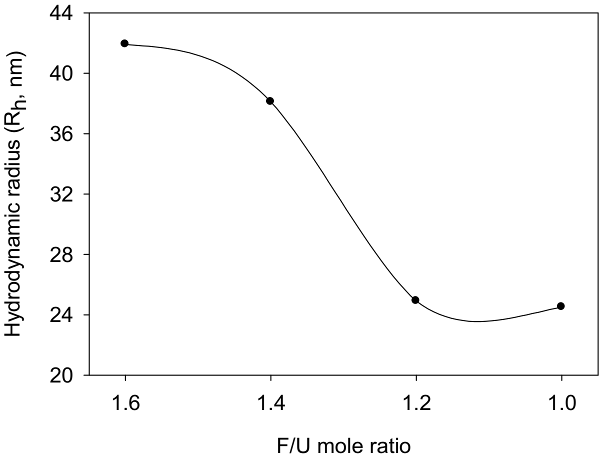

Fig. 2 Hydrodynamic radius (R_h) of UF resins with different F/U mole ratios

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pH-DEPENDENT HYDROGELS, BASED ON CHITOSAN COPOLYMERS, COVALENTLY BONDED TO TEXTILE SURFACE

N.Solomko*, A.Popadyuk*, O.Budishevska*, A.Voronov, A.Kohut**, S.Homyak*, S.Voronov***

**Department of Organic Chemistry, Lviv National Polytechnic University, Address: Bandera str. 12, 79013, Lviv, Ukraine*
***North Dakota State University, Dept. 2760, P.O. Box 6050, Fargo, ND 58108-6050, USA*
E-mail: nadia.solomko@gmail.com

Keywords: *chitosan, graft hydrogel, drag delivery*

The aim of our work was to provide therapeutical wound dressing materials with prolonged healing abilities. Such a wound dressing material was obtained through modification of cotton textile with *pH*-dependant hydrogel, covalently bonded to the textile surface. This hydrogel is based on chitosan which has antibacterial and imunomodulating abilities. The process of textile modification goes via radical graft-copolymerization of vinylpyrrolidone and modified chitosan (Fig. 1) in aqueous solution, initiated by peroxide fragments of modified chitosan, and simultaneous bonding to the textile surface. Modified chitosan was obtained through polymer analogousl reaction between chitosan and tert-butylperoxymethyl ester of butenedicarboxylic acid. During this process a 3-D polymer network of graft-copolymer chitosan-graft-polyvinylpyrrolidone is formed, which is like hydrogel matrix, bonded to textile surface.

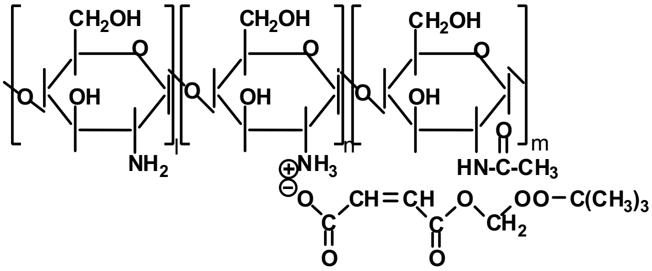

Figure 1. Chemical structure of modified chitosan

Chitosan chains in graft copolymer makes the copolymer *pH*-dependent. The resulting wound dressing material is capable to absorb drugs and has prolonged drug-release abilities at *pH* lower than *pH* of collapse and can be used to treat skin diseases which cause changes of *pH*. It was found, that chitosan-graft-polyvinylpyrrolidone hydrogel, bonded to a cotton surface could be loaded with cephazoline sodium (Fig. 2) which makes it suitable for slow drug-delivery. Absorbance and release of cephazoline sodium were investigated using UV-spectroscopy. It was found that amount and rate of absorbance and release depend on structure and composition of the hydrogel polymer network. Raising concentration of initiator – peroxide fragments in composition of modified chitosan – increases number of grafted polyvinylpyrrolidone chains in chitosan-graft-polyvinylpyrrolidone copolymer and decreases absorbtion capability of hydrogel.

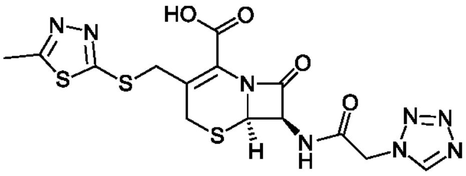

Figure 2. Chemical structure of cephazoline sodium

It was proven that absorption capacity of sample hydrogels ranges between 80 and 220 mg (of cephazoline sodium in 1 g of xerogel) during 24 hours at *pH* 4. Meantime, cephazoline sodium release amount from chitosan-graft-polyvinylpyrrolidone hydrogel is 22-28% in 50 hours and reaches 40% in 220 hours (% of pre-adsorbed cephazoline sodium).

The new modified wound dressing materials would provide antibacterial properties with prolonged drug-delivery.

PREPARATION OF SILSESQUIOXANE CONTAINING EPOXY GROUPS IN THE PRESENCE OF SILICA NANOPARTICLES AND ITS USE IN THE MODIFICATION OF EPOXY RESIN

Ana Paula Fiuza Solymossy, Bluma Guenther Soares

Instituto de Macromoléculas Professora Eloísa Mano – Universidade Federal do Rio de Janeiro - Centro de Tecnologia, Ilha do Fundão, RJ,Brazil
E-mail: apfiuza@ima.ufrj.br

Keywords: *Epoxy Resin, POSS, nanocomposites*

Epoxy resins are used in a variety of applications since their properties, such as thermal stability, mechanical response, low density and electrical resistance, can be varied considerably.[1] Polyhedral oligosilsesquioxanes (POSS) are an interesting class of clusters derived from the hydrolytic condensation of trifunctional organosilicon monomers.[2] POSS can be incorporated into linear or thermosetting polymers improving their thermal and oxidation resistance and reduced flammability. [3] A method for obtaining these hybrids is the in situ sol–gel process that involves a series of hydrolysis and condensation reactions starting from a hydrolysable, multifunctional alkoxysilane as a precursor for the inorganic domain formation.

This work deals with the preparation of silsesquioxane by a hydrolysis/condensation of 3-glycidoxypropyl-trimethoxy silane (GPTS) alone or in the presence of either hydrophilic fumed silica (R200), and polydimethylsiloxane modified fumed silica (R202). The sol-gel process was carried out at pH = 3, in order to favor the hydrolysis.

After the synthesis of the silsesquioxanes, an amount corresponding to 2 phr related to the epoxy resin was dispersed in the epoxy matrix with the help of a mini-turrax.

The systems were cured with triethylenetetramine (TETA).

The degree of condensation in the silsesquioxanes was determined by Solid State ^{29}Si Nuclear Magnetic Resonance (^{29}Si NMR). The epoxy networks modified with the different silsesquioxanes were characterized by Small-Angle X-ray scattering (SAXS) and dynamic mechanical analysis (DMA).

The silsesquioxane prepared without the presence of silica resulted in a degree of condensation around 90%. The presence of silsesquioxane in the epoxy resin resulted in a significant increase of the storage modulus, suggesting a reinforcing action of these hybrid materials. The better results were obtained with systems prepared in the presence of silica nanoparticles. The glass transition temperature of the epoxy network decreased with the addition of POSS probably because of the presence of free volume, located at the interface between the hybrid materials and the epoxy matrix. The nanoscopic structure of the hybrid silsesquioxane particle dispersed inside the epoxy matrix was characterized by SAXS and confirmed by transmission

Due to the better adhesion to the aluminum substrate of the OH groups, the hybrid material shown improved adhesive properties. In fact, as indicated by SAXS experiments, the sol-gel product, dispersed electron microscopy. The lowest particle size was obtained with POSS without the presence of nanosilica. However, the better adhesion properties in aluminium substrate was obtained when silica nanoparticle was used together with GPTS. This behavior can be explained by the presence of hydroxyl groups in the surface of silica nanoparticles, which enhance the adhesion properties.

Acknowledgments

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ORIGIN OF THE MELT MEMORY EFFECT DURING THE CRYSTALLIZATION OF HIGH-DENSITY POLYETHYLENE WITH DIFFERENT CROSSLINKING DEGREES

Joanna Krakowiak*,, Weidong Zhang *,** , José A. Martins*,**, Maria C. D. Cramez***

** Departamento de Engenharia de Polímeros, Universidade do Minho, Campus de Azurém 4800-058 Guimarães, Portugal;*
*** CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal*
E-mail: jamartins@dep.uminho.pt (corresponding author), zwd@dep.uminho.pt (presenting author)

Keywords: *melt memory, crosslinking, ordered regions*

At least, two different explanations were given for the erasing of melt memory effect, or *the slowing down of crystallization kinetics*. Because according to the classical nucleation theory, active nuclei are generated from embryos existing in the supercooled melt, it was considered that at high temperatures, even when the annealing treatment is performed for longer time, some embryos must survive, becoming latter active nuclei.[1] The slowing down of crystallization was then explained as resulting from the embryos' destruction by the annealing treatment. No physical argument was presented to explain why some privileged embryos should survive at high temperatures, even above the equilibrium melting temperature, for long time.

The other explanation considers precursor structures for crystallization, which are also embryos, but are considered in different perspectives by different authors. Some authors consider that nucleation precursors are only created by shear flow, being absent in quiescent melts with their melt memory erased.[2] It is considered that flow causes the orientation of polymer molecules, promoting alignment and interactions of chains, increasing the number of stable nuclei and crystallization kinetics. By making basic considerations about relevant relaxation times and chain dynamics, we will show that this conclusion is not valid for crystallization from pre-sheared melts. The other perspective considers precursor structures as conceptual objects containing crystallites.[3] It is assumed that during crystallization its volume grows with time. At high melt temperatures, where the memory effect was erased, the objects are void from crystallites, while at lower melt temperatures they are being progressively filled with crystallites. According to this view, the melt memory effect originates from changes in the creation rate of crystals within the precursor structures. In the conceptual explanation of this model, it was also recognized that no direct signals from these objects in their initial form, *i.e.* prior to their filling with crystallites, was detected.

We show in this work that melts of linear polymer chains and melts of slightly crosslinked polymer chains, sheared above their equilibrium melting temperature may have their crystallization kinetics saturated when they are sheared up to a steady state. Partial crosslinking was achieved by reactive extrusion of the melt (PE, M_n = 9700 g/mol, M_w = 36600 g/mol) with 0.01wt% and 0.05%wt% peroxide concentration yielding melts with flow activation energies of around 35 kJ/mol and 68 kJ/mol, respectively, higher than the 30 kJ/mol measured for the uncrosslinked polymer. Samples with higher peroxide concentration need larger strain values to reach the steady state and reptation time in these samples is also longer.

Annealing during several hours the melt sheared up to the steady state erases the memory of deformation applied during flow, which is manifested by the slowing down in the crystallization kinetics. The polymer melt in this condition is considered to be fully relaxed of its previous thermal and mechanical history.

Samples crystallized at the same temperature, but cooled from these two different melt states, relaxed and sheared up to a steady state, have similar average spheulite size. Comparison of the half-crystallization time in these two samples with the values evaluated for the average spherulite size and the increase in the equilibrium melting temperature as a result of the pressure applied during the flow exclude these two factors as responsible for the different crystallization kinetics of melts sheared up to the steady state. The observed acceleration is assigned exclusively to the lower viscosity of melts sheared up to the steady state, which is a disentangled state. Confirming further these results, it was recently found that crystallization kinetics in disentangled melts proceeds faster than that of more entangled melts.[4]

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IMPACT OF TRANSITION METAL HALIDE ON THE OPTICAL AND ELECTRICAL CHARACTERIZATION OF POLYMER ELECTROLYTE FILMS

Subramanya K, Manjunatha V, Devendrappa H*

Dept. of Physics, Mangalore University Mangalagangothri, Mangalore-574 199, India
E-mail: dehu1@rediffmail.com

Keywords: *PEO and Transition metal, UV-visible spectra, Electrical conductivity.*

Studies on optical and electrical properties of doped polymers have attracted much interest in view of their potential applications in optical and electrical devices. The polymers have emerged as a promising class of optical materials due to their impact-resistance, ease of fabrication, low density, and cost-effective technologies. In this paper, the effect of cadmium chloride ($CdCl_2$) dopant on optical and electrical characterization of polyethylene oxide (PEO) films has been studied.

The pure and $CdCl_2$-doped PEO films were prepared using solution casting technique at different weight percentage. The films were charactered using Fourier Transform Infrared (FTIR) in KBr medium. The study of optical absorption is a useful method for investigation of the induced optical transition and providing information about the optical energy gap of the materials. Optical absorption studies were done using UV-visible spectrometer in the wavelength range from 190–800nm for pure and doped PEO films. The DC conductivity measurements were carried out using two-probe technique in the temperature range from 303-333K. The FTIR results show that there is a significant change in the intensities as well as frequencies. It was also observed that change in existing peaks and the appearance of new peaks confirm the better complexation of dopant $CdCl_2$ in PEO, perhaps due to interaction between dopant and ether (CH_2) group of PEO. The UV–visible spectra show the absorption bands at 198nm and shoulders at 210-250nm with different absorption intensities for all doped films. The optical band gap was studied using Tauc's expression and it was found to decrease from 4.00-2.25 eV (direct) and from 6.05-5.29eV (indirect) for doped PEO films. The number of carbon atoms involved in direct and indirect transition was calculated, they were found to increase from 4.55- 8.08 and from 3.01-3.44 in a cluster. This indicates decreases in the band gap with increase in the number of carbon atoms in cluster. The UV–visible spectra observed shift in the absorbance edge from 5.79 to 3.96eV for doped PEO respectively. Using absorption data, we estimated optical parameters like molar extinction coefficient, dipole strength, transition dipole moment, and oscillator strength, which are of great importance, especially when polymer properties are being modified by doping. The changes in the dipole strength, transition dipole moment, oscillator strength, and activation energy have been investigated as a function of the dopant concentration. This may be explained on the basis of the fact that the incorporation of small amounts of dopant forms charge transfer complexes in the host polymer matrix. The electrical conductivity is found in the order of $2.5x10^{-}7$sm/cm for $CdCl_2$ doped PEO. It increases with increasing dopant concentration and temperature, which is attributed to the strong hopping mechanism in the polymer chain.

These results suggest the suitable candidature for solid state battery and the other potential applications in optical and electrical devices like actuators, super capacitors, fuel cells, sensors, electro chromic display devices, and optoelectronic devices etc.

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PREPARATION AND RHEOLOGICAL CHARACTERISATION OF MODEL NANOCOMPOSITES BASED ON LAPONITE AND POLY(ETHYLENE OXIDE)

Jesmy Jose, Omar Abakar Adam, Jean-Francois Tassin*

Polymères, Colloïdes, Interfaces Lab. – Université du Maine, Avenue Olivier Messiaen, 72085 Le Mans Cedex, France
E-mail: jesmyjose@hotmail.com

Keywords: *polymer nanocomposites, rheology, laponite*

The present study investigates the rheology of model polymer-clay nanocomposites prepared by various polymer intercalation techniques, i.e., from solution, melt and by mixed processes. The model system consists of geometrically well defined, protected Laponite clay particles, that are further dispersed in a polyethyleneoxyde (PEO) matrix of various molecular weights and molecular weight distribution. Laponite protection was carried out by either adsorption or grafting of PEO chains in solution, and the protected particles are finally recovered by freeze-drying[1]. For preparation via solution intercalation, the protected Laponite dispersion in water was feeded with a PEO solution in water and, the nanocomposites were finally recovered by freeze-drying. The melt intercalation procedure involves the dispersion of protected Laponite into the PEO matrix via melt blending in a laboratory scale twin-screw extruder. The mixed preparation procedure includes a combination of the aforementioned methods, the concentrated nanocomposite obtained from solution technique being diluted in the molten state by using pure PEO.

Irrespective of the nature of preparation, all PEO-Laponite systems exhibited a solid viscoelastic behavior in the terminal region owing to the formation of a three dimensional clay network structure[2] (for example Figure 1). The state of dispersion has been characterized using X-ray scattering. The influence of the preparation method on particle's dispersion and on the rheological behavior will be discussed. The effect of adding high molecular weight PEO chains into the matrix on the clay network structure and its rheological properties will be further discussed to tackle the influence of chain confinement on the properties.

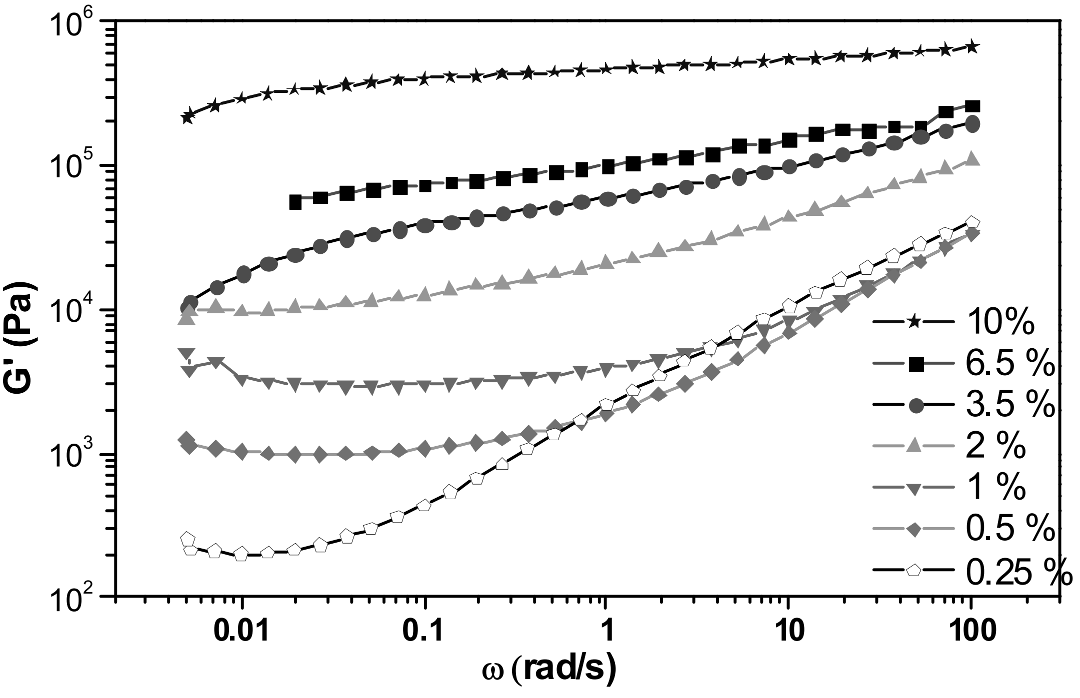

Figure 1: Storage modulus vs frequency at 110 °C, for different laponite particle loadings(weight percent) in a PEO(130k) matrix prepared by solution intercaltion method.

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