27th International Symposium on
Polymer Analysis and Characterization

Book of Abstracts

June 15-18, 2014  Les Diablerets  (Switzerland)
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* ISPAC Chair

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F. Pignon, "Laboratoire Rhéologie et Procédés" (Grenoble)

F. Bergerot, "Laboratoire Rhéologie et Procédés" (Grenoble)

E. Mauret, Director of Pulp and Paper Laboratory (Pagora ingeniors school) (Grenoble)

M. Rinaudo, Professor, GBM member, secretary (Grenoble)

Th. Hamaide, Professor, President of the GFP education committee (Lyon)

Acknowledgements

The ISPAC organizers would like to thank all the sponsors and exhibitors for their support of the symposium, as well as all invited speakers and governing board members for their contributions this year and in years past.

ISPAC would like to extend a special thank to the "Laboratoire Rhéologie et Procédés, (Rheology and Process Laboratory) UMR 5520 (UJF Grenoble 1 - Grenoble INP - CNRS)" for its support of this year's symposium.

Finally, ISPAC organizers would like to thank Marguerite Rinaudo, Nadia El Kissi, Frédéric Pignon, Klara Vancso and François Bergerot for all their efforts in organizing the symposium.
Information

Oral communications have been classified and introduced in the scientific program following the selected topics of ISPAC 2014:

**Topic1:** Biobased polymers (new monomers, composites with natural fibers and biobased matrix).

**Topic2:** Polyolefins and their blends: structure, morphology, processing performance.

**Topic3:** Adsorption and adhesives: from molecules to bioadhesives; interfacial structure, biofilm.

**Topic4:** Ionic liquids in polymer science.

**Topic5:** Self assembling polymeric system, supra-molecular structure, auto-repairing materials.
**Scientific Program**

*Monday – June 16, 2014 Congress House-Main room*

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:00am</td>
<td>Registration in Congress House Hall</td>
</tr>
<tr>
<td>8:20am</td>
<td>Opening Remarks: G. Berry, J.F. Gérard</td>
</tr>
<tr>
<td><strong>Invited lectures</strong></td>
<td></td>
</tr>
<tr>
<td>8:30am</td>
<td>L1 - Nanoparticle solutions as adhesives for gels and for organ repair.</td>
</tr>
<tr>
<td></td>
<td>Ludwik Leibler, École Supérieure de Physique et de Chimie Industrielles, Paris, France</td>
</tr>
<tr>
<td>9:00am</td>
<td>L2 - Adhesion on rough or low energy surfaces: the role of viscoelasticity</td>
</tr>
<tr>
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<td>Anke Lindner, École Supérieure de Physique et de Chimie Industrielles, Paris, France</td>
</tr>
<tr>
<td>9:30am</td>
<td>L3 - Functionalized Native Nanocellulose</td>
</tr>
<tr>
<td></td>
<td>Olli Ikkala, University, Department of Applied Physics, Aalto, Espoo, Finland</td>
</tr>
<tr>
<td>10:00am</td>
<td>Discussion</td>
</tr>
<tr>
<td>10:45am</td>
<td>Refreshment Pause</td>
</tr>
<tr>
<td><strong>Contributed Lectures topic 5</strong></td>
<td></td>
</tr>
<tr>
<td>11:15am</td>
<td>O1 - Fabrication, characterization and latent heat thermal energy storage properties of encapsulated polystyrene/palmitic acid micro/nano capsules.</td>
</tr>
<tr>
<td></td>
<td>C. Alkan, A. Sarı, D. Kahraman, A. Biçer, A. Altıntaş, A.N. Özcan, C. Kızıl, C.Bilgin</td>
</tr>
<tr>
<td>11:30am</td>
<td>O2 - Electrostatic Interaction of the Alzheimer’s Amyloid β (1-42) Peptide with Short Single Stranded Synthetic Nucleotide Sequences Affects the Fibril Structure</td>
</tr>
<tr>
<td></td>
<td>J. Abraham, D. Kedracki, C. Gourmel, P. Maroni, C. Vebert-Nardin</td>
</tr>
<tr>
<td>11:45am</td>
<td>O3 - Self-Assembly of Poly(Styrene-co-Maleic Anhydride) into Patterned Films and Nanoparticles</td>
</tr>
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<td>P. Samyn</td>
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**Scientific Program**

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
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<tbody>
<tr>
<td>12:00am</td>
<td>O4 - The collective dynamics in block copolymer micelles at equilibrium. [G. Landazuri, M. Bravo, J.F.A. Soltero, Y. Rharbi]</td>
</tr>
<tr>
<td>12:15am</td>
<td>O5 - Emerging Interphases in Poly(n-Butylacrylate)/Polystyrene Core-Shell Nanoparticles Obtained via Semicontinous Miniemulsion Polymerization [S. Bonetti, M. Farina, M. Mauri, I. Andreosso, R. Simonutti]</td>
</tr>
<tr>
<td>12:30am</td>
<td>Lunch time (Poster setup in Eurotel Hall)</td>
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<tr>
<td></td>
<td><strong>Contributed Lectures topic 1</strong></td>
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<tr>
<td></td>
<td>Second floor room - Chairman: M. Cloitre</td>
</tr>
<tr>
<td>11:15am</td>
<td>O6 - Use alkali-lignin as a compatibiliser in cellulose nanofibrils/ poly (lactic acid) composites [X. Wang, L.P. Zhang]</td>
</tr>
<tr>
<td>11:30am</td>
<td>O7 - RAFT polymerisation of a lignin derived monomer [H. Willcock, J. Belbin, N. De Rybel, M. Ahmed, A.J. Clark, R. K. O’Reilly]</td>
</tr>
<tr>
<td>11:45am</td>
<td>O8 - Characterization of Acidified Chitosan Entrapped in Epoxidized Natural Rubber [G. Raju, M.R.H. Mas Haris]</td>
</tr>
<tr>
<td>12:00am</td>
<td>O9 - Influence of molar mass and concentration on the thermogelation of methylcelluloses [P. Nasatto, F. Pignon, J.L. Silveira, M.E. Duarte Noseda, M.D. Noseda, M. Rinaudo]</td>
</tr>
<tr>
<td>12:15am</td>
<td>O10 - The Effects of Nanoclays on Thermal Degradation of Polylactide via Direct Pyrolysis Mass Spectrometry [E. Ozdemir, B. Ozkan, J. Hacaloglu]</td>
</tr>
<tr>
<td>12:30am- 2:00pm</td>
<td>Lunch time (Poster setup in Eurotel Hall)</td>
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### Scientific Program

**Monday – June 16, 2014 Congress House-Main room**

<table>
<thead>
<tr>
<th><strong>Invited lectures</strong></th>
<th>Main room - Chairman: O. Ikkala</th>
</tr>
</thead>
</table>
| **2:00pm**           | L4 - Plant oils: The perfect renewable resource for polymer science ?!  
Michael A. R. Meier, Karlsruhe Institute of Technology (KIT), Institute of Organic Chemistry, Karlsruhe, Germany |
| **2:30pm**           | L5 - Bio-based PBS, an application of the biorefinery concept,  
Anthony Brésin, ARD, Pomacle (France) |
| **3:00pm**           | L6 - Surface modification of polysaccharides: from theory to practice  
Mohamed Naceur Belgacem, Laboratoire de Génie des Procédés Papetiers (LGP2), Grenoble INP-Pgora, Saint Martin d'hères (France) |
| **3:30pm**           | Discussion |
| **4:15pm**           | Refreshment Pause |

<table>
<thead>
<tr>
<th><strong>Contributed Lectures topic 5</strong></th>
<th>Main room - Chairman: H.N. Cheng</th>
</tr>
</thead>
</table>
| **4:45pm**                       | O11 - Interfacial structure of entangled polymer brushes under shear  
| **5:00pm**                       | O12 - Controlled Self-Assembly of Hydrophobic-Cationic Polymers leading to Waterborne Antimicrobial Nanogels  
S. Chattopadhyay, E. Heine, H. Keul, M. Möller |
| **5:15pm**                       | O13 - One-pot Synthesis of Responsive Polymer Nanoparticles  
H. Willcock, E. Chapman, I. Collins, R. K. O’Reilly |
| **5:30pm**                       | O14 - Hydrophobic dopant-enhanced and polymer-suppressed supramicellar assemblies,  
Z. Zhu, W. F. Reed |
| **6:00pm**                       | Poster Exhibits and Together Reception in Eurotel Hall |
| **7:30pm**                       | Dinner time |
### Scientific Program

<table>
<thead>
<tr>
<th><strong>Contributed Lectures topic 1</strong></th>
<th><strong>Second floor room- Chairman: W. De Groot</strong></th>
</tr>
</thead>
</table>
| **4:45pm**                       | O15 - Chlorite-based pretreatments of cellulosic samples prior to SEC analysis  
A.L. Dupont, O. Bénaud, G. Mortha |
| **5:00pm**                       | O16 - Oxygen Transport in Poly(ethylene furanoate) Characterized via Permeation and Pressure-Decay Sorption Methods  
S. K. Burgess, R. M. Kriegel, W. J. Koros |
| **5:15pm**                       | O17 - Copolymers of Polylactide via Direct Pyrolysis Mass Spectrometry  
T.O. Lekesiz, B. Ozkan, J. Hacaloglu |
| **5:30pm**                       | O18 - Advances in Viscoelastic Behaviour Characterization Using Dynamic Mechanical Analysis  
A. Gregorova, F. Stelzer |
| **5:45pm**                       | O19 - Synthesis and characterization of a modified chitosan grafted nanoclay  
L. Solhi, M. Atai, M. Imani, A. Nodehi |
| **6:00pm**                       | Poster Exhibits and Together Reception in Eurotel Hall |
| **7:30pm**                       | Dinner time |
## Scientific Program

**Tuesday – June 17, 2014 Congress House-Main room**

<table>
<thead>
<tr>
<th>Time</th>
<th>Invited lectures</th>
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<tbody>
<tr>
<td>8:30am</td>
<td>L7- Label-free biomolecular interaction analysis and equilibrium-fluctuation-based single-molecule studies of cell-membrane mimics, Fredrik Höök, Chalmers University of Technology, Gothenburg (Sweden)</td>
</tr>
<tr>
<td>9:00am</td>
<td>L8 - Fluorescence Imaging of Single Amphiphilic Polymer-Coated Organic and Inorganic Nanoparticles, Nikodem Tomczak, Institute of Materials Research and Engineering, A*STAR Singapore. <strong>MESA+ lecture</strong></td>
</tr>
<tr>
<td>9:30am</td>
<td>L9 - Polymer biofouling in sea water, G. Julius Vancso, University of Twente, MESA+ Institute for Nanotechnology (The Netherlands) and Institute for Chemical and Engineering Science, A*STAR, Singapore</td>
</tr>
<tr>
<td>10:00am</td>
<td>Discussion and information on the next ISPAC meeting</td>
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<tr>
<td>10:45am</td>
<td>Refreshment Pause</td>
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<table>
<thead>
<tr>
<th>Time</th>
<th>Contributed Lectures topic 2</th>
</tr>
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<tbody>
<tr>
<td>11:30am</td>
<td>O21 - Separation of Polyolefin Copolymers by Crystallization and Adsorption techniques. Discussion on the separation mechanism on an atomic level flat surface adsorbent, B. Monrabal</td>
</tr>
<tr>
<td>11:45am</td>
<td>O22 - Biohybrid glycopolymers and chimeric polysaccharides capable of ionotropic gelation, A. Wolnik, A. Ghadban, E. Renaud, L. Dumas, F. Dubreuil, F. Pignon, M. Rinaudo, L. Albertin</td>
</tr>
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### Scientific Program

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
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</table>
| **12:00am**| O23 - Molecular Structure of Linear Low Density Polyethylene  
      J.C.J.F. Tacx, B.A.H. van den Esschert, S.Kok |
| **12:15am**| O24 - Characterization of artificially aged polyethylene  
      C. Schwarzinger, I. Hintersteiner, B. Schwarzinger, B. Moser, W. Buchberger |
| **12:30am**| Lunch time                                    |
| **Contributed Lectures topic 1** | Second floor room - Chairman: M. Meier |
| **11:15am**| O25 - Synthesis and Characterisation of a Poly(L-lactide-co-ε-caprolactone) Copolymer Using a Novel Tin(II) Alkoxide Initiator for Potential Use as an Absorbable Monofilament Surgical Suture  
      S. Ruengauchawiwat, J. Siripitayanon, R. Somsunan, R. Molloy, P.D. Topham, B.J. Tighe |
| **11:30am**| O26 - Development and Characterization of Polyurethane Coatings for Enhanced Anti-Corrosive Properties  
      Praveen Kumar G, KVRS Murthy, K K. Murthy |
| **11:45am**| O27 - Nanoscale characterization of organic semiconductors using x-ray spectromicroscopy  
      P. Warnicke, N. Pilet, B. Watts, R. Fink, C. Quitmann, J. Raabe |
| **12:00am**| O28 - RheoRaman monitoring of acid acrylic polymerization  
| **12:15am**| O29 - Xe NMR Studies of Pecan Shell-Based Biochar and Structure-Process Correlations  
| **12:30am-2:00pm** | Lunch time |
### Scientific Program

**Tuesday – June 17, 2014 Congress House-Main room**

<table>
<thead>
<tr>
<th><strong>Invited lectures</strong></th>
<th><strong>Main room - Chairman: J.F. Gérard</strong></th>
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</thead>
</table>
| **2:00pm**           | **L10 - Why measuring and understanding the comonomer distribution is so important for the polyethylene industry**  
Jesus Nieto, The Dow Chemical Company (Spain). **Ingenia Lecture** |
| **2:30pm**           | **L11 - Characterization of self assembled polymer systems by scattering techniques: light, x-ray and neutron scattering,**  
Petr Stepanek, Institute of Macromolecular Chemistry, Academy of Sciences,Prague, Czech Republic |
| **3:00pm**           | **L12 - Multidimensional Analysis of the Complex Composition of Impact Polypropylene Copolymers: Combination of TREF, SEC-FTIR-HPer DSC, and High Temperature 2D-LC,**  
Harald Pasch, Department of Chemistry and Polymer Science, University of Stellenbosch, 7602 Matieland, South Africa |
| **3:30pm**           | **Discussion** |
| **4:15pm**           | **Refreshment Pause** |

<table>
<thead>
<tr>
<th><strong>Contributed Lectures topic 2</strong></th>
<th><strong>Main Room - Chairwoman: J. Duchet</strong></th>
</tr>
</thead>
</table>
| **4:45pm**                       | **O30 - How to characterize a vinylmelamine-ethylene-copolymer? Results and new issues**  
M. List, C. Schwarzinger |
| **5:00pm**                       | **O31 - Kinetic study of the crystallization of LLDPE and wax in LLDPE/wax phase-change blends used for thermal energy storage**  
T.P. Gumede, A.S. Luyt, A.J. Müller |
| **5:15pm**                       | **O32 - Crystallization monitoring of PVDF α-phase and β-phase by Raman spectroscopy and DSC analysis.**  
M. Veitmann, D. Chapron, P. Bourson, S. Bizet, S. Devisme, J. Guilmant |
<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
</tr>
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</table>
| 5:30pm | O33 - Mesophase Formation in Propylene-co-1-Octene Copolymers Studied by Fast and Conventional DSC Techniques  
J. Arranz-Andrés, R. Parrilla1, M.L. Cerrada, E. Pérez |
| 5:45pm | O34 - Characterization and properties of novel blends composed of nitrile butadiene rubber and in-situ synthesized thermoplastic polyurethane-urea  
M. Tahir, K. W. Stöckelhuber, N. Mahmood, G. Heinrich |
| 6:00pm | Poster Exhibits in Eurotel Hall                                          |
| 7:30pm | Conference Banquet at Eurotel                                           |

**Contributed Lectures topic 3**  Second floor room - Chairwoman : A. Lindner

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
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</table>
| 4:45pm | O35 - Nano-Handling of Individual Dendronized Polymers by Single-Molecule Force Spectroscopy  
L. Grebikova, P. Maroni, B. Zhang1 A.D. Schlüter1, M. Borkovec |
| 5:00pm | O36 - Characterization of diffusion processes in PVC films used in medical devices by coupling AFM to spectroscopy  
H. Alsalloum, J. Saunier, A. Dazzi, A. Tfayli, N. Yagoubi |
| 5:15pm | O37 - Several TD-NMR methods for polymer characterization  
M. Farina, M. K. Dibbanti, M.Mauri, R.Simonutti |
| 5:30pm | O38 - Characteristics of each Bonded Layer of a Polymer-Based Magnetic Tape using Rule-of-Mixtures and Dynamic Mechanical Analysis  
B. L. Weick |
| 6:00pm | Poster Exhibits in Eurotel Hall                                          |
| 7:30pm | Conference Banquet at Eurotel                                           |
### Scientific Program

#### Wednesday – June 18, 2014 Congress House-Main room

<table>
<thead>
<tr>
<th>Invited lectures</th>
<th>Main room - Chairman: P. Kratochvil</th>
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</thead>
<tbody>
<tr>
<td><strong>8:30am</strong></td>
<td>L13 - Ionic Liquids: new multifunctional agents for designing nanostructured polymers</td>
</tr>
<tr>
<td></td>
<td>Jean-Francois Gérard, INSA Lyon, F-69621 Villeurbanne, France</td>
</tr>
<tr>
<td><strong>9:00am</strong></td>
<td>L14 - Ionic Liquids as Polymer Solvents: Polyelectrolytes, Polyzwitterions, Proteins, and Poly(AMINO-ACID)s,</td>
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<td>David Hoagland, Polymer Science and Engineering Department, University of Massachusetts Amherst, Amherst, Massachusetts, 01003 USA</td>
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<tr>
<td><strong>9:30am</strong></td>
<td>Discussion</td>
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<tr>
<td><strong>10:15am</strong></td>
<td>Refreshment Pause</td>
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</tbody>
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<thead>
<tr>
<th>Contributed Lectures topics 4&amp;2</th>
<th>Main room - Chairman: D. Hoagland</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>10:45am</strong></td>
<td>O39 - Doping polymer electrolyte membranes with ionic liquids: from the microstructure to advanced functional properties</td>
</tr>
<tr>
<td></td>
<td>S. Lyonnard, R. Sood, C. Iojoiu, H. Mendil-Jakani, G. Gebel</td>
</tr>
<tr>
<td><strong>11:00am</strong></td>
<td>O40 - Preparation PBI composites of Fe₃O₄ and NiFe₂O₄ nanoparticle with ionic liquid and electrical conductivity</td>
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<td></td>
<td>E. Yılmaz, H. Dinc, I. Ozaytekin</td>
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<tr>
<td><strong>11:15am</strong></td>
<td>O41 - Deep eutectic ionic liquids as epoxy resin curing catalysts</td>
</tr>
<tr>
<td></td>
<td>H. Mąka, T. Spychaj, W. Sikorski</td>
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<tr>
<td><strong>11:30am</strong></td>
<td>O42 - Compatibilization of polypropylene/polyamide 6 blends using an ionic liquids/nanotalc combination</td>
</tr>
<tr>
<td></td>
<td>M. Yousfí, S. Livi, J. Duchet-Rumeau</td>
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<td>Time</td>
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<tr>
<td>11:45am</td>
<td>O43 - Thermodynamic study of Blends of Poly(4-vinylphenol) / Poly(vinylmethylketone) using Inverse Gas Chromatography</td>
</tr>
<tr>
<td></td>
<td>Z. Ben Abdelghani, H. Bourara, A. Etxeberria</td>
</tr>
<tr>
<td>12:00am</td>
<td>O44 - Influence of isomeric monomers on the fragmentation of polymers</td>
</tr>
<tr>
<td></td>
<td>J. Beer, K. Rode, W. Radke</td>
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<tr>
<td>12:15am</td>
<td>O45 - Morphology and rheology of binary blend of polypropylene and polyamide6: influence of multiwall carbon nanotubes</td>
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<td></td>
<td>A. R. Bhattacharyya, N. Mukhopadhyay, A. S. Panwar, P. Pötschke</td>
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<tr>
<td>12:30am</td>
<td>Concluding remarks and Lunch time</td>
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<tr>
<td></td>
<td><strong>Contributed Lectures topic 5</strong></td>
</tr>
<tr>
<td></td>
<td>Second floor room - Chairman: N. Tomczak</td>
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<tr>
<td>10:45am</td>
<td>O46 - Processable Crosslinked Epoxidized Natural Rubber</td>
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<td>L. Imbernon, E. K. Oikonomou, S. Norvez</td>
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<tr>
<td>11:00am</td>
<td>O47 - Water Soluble Multiarm Polyethylene glycol-Betulinic acid Prodrugs-Design, Synthesis, and In Vitro Effectiveness</td>
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<tr>
<td></td>
<td>L. Dai, J. He, J. D. Lei</td>
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<tr>
<td>11:15am</td>
<td>O48 - Microstructural analysis of electrospun thermoplastic polyurethane nanofibers during heating</td>
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<tr>
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<td>D. Alhazov and E. Zussman</td>
</tr>
<tr>
<td>11:30am</td>
<td>O49 - Solvent effect on fabrication of PVP/PBI and PS/PBI nanofibers</td>
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<tr>
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<td>H. Dinc, B. Buyukbeker, M.S. Yavuz, I. Ozaytekin</td>
</tr>
<tr>
<td>11:45am</td>
<td>O50 - Characterization of Polyalkylacrylate and Polyalkylmethacrylate Polymers Produced by Using ATRP Method</td>
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<td></td>
<td>D.Kahraman Döğüşcü, C. Alkan</td>
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<tr>
<td>12:00am</td>
<td>O51 - Molecular structure development of HDPE in multistage reactor process.</td>
</tr>
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<td>M.K. Yadav, K. Seshagiri, S. Shanmugam, E.H. Qua, H.Y. Molod</td>
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<tr>
<td>12:30am</td>
<td>In the main room, Concluding Remarks / Lunch time</td>
</tr>
</tbody>
</table>
Invited Lecture Abstracts
Nanoparticle solutions as adhesives for gels and for organ repair

Ludwik Leibler

Matière Molle et Chimie (UMR 7167 CNRS/ESPCI),
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Adhesives are made of polymers. We introduce a novel concept of gluing by nanoparticles and show that spreading a droplet of a nanoparticle solution on one gel’s surface and then bringing the other gel into contact with it can achieve strong and rapid adhesion between two hydrogels and demonstrate the method for synthetic and biological hydrogels [1]. This method, that we call nanobridging, relies on the nanoparticles’ ability to adsorb onto polymer gels and to act as connectors between polymer chains, and on the ability of polymer chains to reorganize and dissipate energy under stress when adsorbed to nanoparticles. Nanobridging, can be used *in vivo* to achieve rapid and strong closure and healing of deep wounds in tissues as different as skin and liver [2]. The simplicity, rapidity, and robustness of nanobridging bode well for translation to clinical applications, surgery and regenerative medicine.


Efficiently bonding a viscoelastic material to rough or low energy surfaces is an important problem in everyday life and many industrial applications. The viscoelasticity of the soft adhesive plays a particularly important role in obtaining the desired adhesive properties. Here we address this question by studying the adhesion of viscoelastic model materials on surfaces with well controlled properties.

In a first step we characterize the respective influence of elastic and viscous properties on the debonding mechanisms using homogeneous adhesive layers of a model system, allowing to go from a pure liquid, to a viscoelastic material and finally to a soft elastic solid within one material family [1]. A new 3D visualization technique allows us to characterize the exact boundary condition between the adhesive and the solid substrate during debonding [2]. We then use this knowledge to design multilayer adhesives. They are designed in such a way as to achieve improved adhesive properties on high or low energy surfaces.

We then study these materials on surfaces with well-defined periodic roughness. Depending on the material properties and the surface roughness an increase or a decrease of the adhesion energy can be observed. The detailed results show that the macroscopic adhesion energy depends on a fine balance between the elastic energy released by the adhesive upon decompression and the viscous dissipation near the contact line during adhesive detachment [3,4].

References
Long and entangled native nanofibrillated cellulose (NFC) and rod-like nanocrystalline cellulose (CNC) are colloidal level units having a few nanometer lateral dimensions. They have aroused considerable recent interest due to their high “metal strong” mechanical properties based on their native hydrogen bonded crystalline internal structure, being functionalizable and sustainable [1]. A useful template for functionalities is based on nanocellulose aerogels [2–6]. They are prepared from nanocellulose hydrogels by freezedrying or CO$_2$ supercritical drying. Unlike the classic aerogels that are brittle, the native nanocellulose aerogels are mechanically robust, ductile, even flexible, and highly porous. We describe magnetic and electrical functionalization, actuation, superhydrophobic and superoleophobic properties, spilled oil absorption, as well as optical switching between hydrophobic and superabsorbent states. Wet-spinning of nanocellulose fibers and their electric and magnetic functionalization is described [7]. Due to their rod-like character, CNCs allow different functionalities, notably by controlled surface polymerization [8]. They allow tough biomimetic composites and self-healing gels by incorporation of supramolecular units [9–10]. Finally generation dependent binding of dendronized glycopolymers on CNCs is described as well as all-cellulose thermoreversible gels [11,12].

References
In ages of depleting fossil reserves and an increasing emission of greenhouse gases, it is obvious that the utilization of renewable feedstocks is one necessary step towards a sustainable development of our future. Especially plant oils bear a large potential for the substitution of currently used petrochemicals, since a variety of value added chemical intermediates can be derived from these resources in a straightforward fashion taking full advantage of nature’s synthetic potential. Here, new approaches for the synthesis of monomers as well as polymers from plant oils as renewable resources will be discussed.\textsuperscript{[1]} For instance, we could show that different chain length $\alpha,\omega$-diester monomers can be obtained from fatty acid esters via olefin cross-metathesis (CM) with methyl acrylate taking advantage of natures "synthetic pool" of fatty acids with different chain lengths and positions of the double bonds.\textsuperscript{[2]} Moreover, thiol-ene click chemistry offers a complementary approach for the introduction of different functional groups to fatty acids in a straightforward and efficient manner, as demonstrated for the functionalization of the castor oil derived methyl 10-undecenoate with a variety of thiols.\textsuperscript{[3]} Moreover, a sustainable access to nitrogen containing monomers for the sustainable synthesis of renewable polyamides and polyurethanes will be discussed.\textsuperscript{[4, 5]} The thus obtained renewable platform chemicals are valuable starting materials for a large variety of polymers.\textsuperscript{[6-9]}

The focus of the presentation will be divided between the mentioned efficient (catalytic) routes to renewable step-growth monomers and the synthesis and properties of selected thereof derived polymers. In summary, we will thus demonstrate the versatility of plant-oil derived platform chemicals for the synthesis of a large variety of renewable monomers and polymers.

References
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Bio-based PBS, an application of the biorefinery concept

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Thanks to the molecular biology, the white biotechnology industry is now able to propose credible economical alternative to petrochemical molecules for the production of a wide range of product. One of those is the production of succinic acid by the use of genetically modified microorganisms. This molecule is a building block for many products such as polyurethanes, solvents or polyester : polybutylene succinate (PBS).

The succinic acid is produced by fermentation and uses raw materials coming from the biorefinery complex of Pomalce-Bazancourt in France. By combining the sugars coming from both a sugar beet plant or a wheat wet milling plant and the CO2 coming from the ethanol fermentation plant, we produce a bio-based succinic acid. This succinic acid after chemical hydrogenation can be transform in 1,4-Butanediol, the other monomer in the PBS chain.
The interest in using polysaccharides (cellulose mainly starch) in composite materials is constantly growing, mainly because of the many advantages associated with them. In fact, these natural renewable materials are widely used in different technologies and could be available in different sizes and morphologies. The preparation of polysaccharide-based composites is perturbed by their highly hydrophilic character, which is associated with a low interfacial compatibility with hydrophobic polymeric matrices, as well as with a loss of mechanical properties after moisture uptake. In order to reduce the hydrophilic character of cellulose and starch, which improves the strength of their adhesion to the matrix, it is necessary to undertake a structural modification of their surface. These two raw materials could be available in the form of cellulose fibres, films, microfibrils, nanofibrils or whiskers and starch grains or starch nano-plackets [1,2].

Several approaches of surface modification will be reported, namely (i) physical treatments such as corona, plasma, laser, vacuum ultraviolet and γ -radiation treatments; (ii) chemical grafting by direct condensation, including surface compatibilization with hydrophobic moieties and co-polymerization with the matrix. Thus, “grafting from” and “grafting onto” approaches will be discussed [1,2]. In this context, recent works investigating green solvent-based or solvent-less systems were reported [3,4].

The characterization of the modified surfaces involves a variety of techniques, including elemental analysis, contact angle measurements, FTIR spectroscopy and water uptake. More efficient characterization techniques were also used, such as X-ray photoelectron (XPS) and more recently Time of Flight Secondary Ion Mass Spectrometry (ToF SIMS), etc. This presentation reports the different approaches reported in the literature and assesses their merits and drawbacks [1,2].

References
Label-free biomolecular interaction analysis and equilibrium-fluctuation-based single-molecule studies of cell-membrane mimics

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Measurements of ligand binding events on membrane protein receptors in a near-natural environment would display an advantage in mechanistic studies of membrane receptors. Furthermore, the residence time of drug-target interactions is being increasingly recognized as a key parameter in evaluating drug efficacy, but is hampered by the technical challenge to perform such studies on membrane proteins. With single-molecule sensitivity, such information can be gained for both high and low affinity interactions, and be used in both drug-screening and medical-diagnostic applications. Recent advancement in nanotechnology has led to a diverse set of tools offering single molecule sensitivity. However, to yield sufficient statistics within reasonable time scales, multiple single biomolecular binding events should preferably be probed simultaneously in imaging mode. I will present a single-molecule detection concept that meets this requirement, and which enables simultaneous fluorescent and label-free operation. The principle is based on the use of fluorescently labeled lipid vesicles as enhancer elements in optical waveguide based fluorescence and scattering microscopy, making the concept compatible with analysis of both water-soluble and cell-membrane bound receptors. Focus will be put on how the concept is currently evaluated as a diagnostic assay for virus and biomarker detection as well as drug-screening applications, previously explored by us using conventional total internal reflection fluorescence microscopy[1, 2]. I will also discuss the use of the wave-guide microscopy system in the context of single-enzyme detection in complex biological fluids, with focus on single-molecule biomarker detection in cerebrospinal fluid from individuals suffering from the Alzheimer’s disease.[3] A new means of utilizing the two-dimensional fluidity of supported cell-membrane derived lipid bilayers for membrane-protein separation applications will also be discussed[4].

References
Fluorescence Imaging of Single Amphiphilic Polymer-Coated Organic and Inorganic Nanoparticles

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In single molecule/nanoparticle fluorescence imaging, individual members of a population can be followed in space and time providing an experimentally accessible property distribution function instead of ensemble-averaged values. A natural consequence of this approach is that for heterogeneous samples unique subpopulations or rare temporal events can be directly identified. We develop instrumentation, methods, and protocols to characterize the structure and photophysical properties of novel semiconductor nanoparticles (Quantum Dots) [1], conjugated polymer nanoparticles (CPNs) [2], and aggregation induced emission (AIE) nanoparticles [3]. The common feature in these nanoparticles is the use of amphiphilic copolymers in their preparation protocols. The amphiphilic polymer acts as a phase transfer agent of the hydrophobic light emitters from the organic to the aqueous phase and provides functional groups for further derivatization. Each of the probes posses a set of unique properties related to their size, brightness, photostability, and photophysical properties when observed at the single nanoparticle level. We provide several examples of the applications of the optical methods (wide-field and time-resolved confocal microscopies) to study the probe emission in details. Application of advanced optical instrumentation with novel luminescent hybrid organic/inorganic materials gives the opportunity to explore new scientific avenues in materials science and biology-related fields.

References
Polymer biofouling in sea water

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When synthetic materials are submerged in marine environments, dissolved matter and marine organisms attach to their surfaces by a process known as marine fouling. This phenomenon may lead to diminished material performance with detrimental consequences. However, certain marine organisms are not prone to fouling. Surface patterning and chemical surface modifications inspired by these naturally foul-resistant organisms present promising approaches for the design of novel functional surfaces that can prevent biofouling. Marine fouling is accompanied by secretion of proteins or proteinaceous polymers, which are employed by the foulants for temporary or permanent attachment. Fouling often begins with sub-mm large larvae “exploring” the surface by depositing small amounts of adhesive proteins to “probe” the adhesion (i.e. to probe the “suitability” of the substrate to get attached and colonize it). These biocompatible “adhesive proteins” harden out in their natural solvent, i.e. sea water, and often provide extremely strong interfacial bonding. Characterization and understanding of the molecules and molecular processes that play a role in biofouling has tremendous consequences in many fields, from preventing marine fouling, via environmental sciences and systems biology, to introducing novel bioadhesives in medical surgery.

In this presentation first a short insight is offered to marine fouling. Then surface characterization issues including contact angle and contact mechanics studies, Atomic Force Microscopy (AFM) and Surface Plasmon Resonance (SPR) imaging, single-chain macromolecular mechanics by AFM, surface chemical analysis and spectroscopy, and other relevant characterization techniques are addressed. In the bulk part of this lecture applications of surface analysis and engineering to achieve antifouling properties are illustrated by three case studies.

The first study is devoted to imaging and analysis of “footprints” left behind on substrate interfaces by larvae of “walking” barnacles in sea water using AFM [1]. Pulling of bundles of proteins and single chain proteins by AFM-based force spectroscopy provide insights at the nanoscale into the role of temporary adhesion proteins promoting wet adhesion during the first stages of the fouling process. A variation of the substrate material and of the interface (chemical composition, topology and modulus) can yield surfaces, which are not observed by the cyprids (“stealth” surfaces) thus providing perfect antifouling platforms. These offer alternatives to fouling prevention by biocides, which are still often used in marine coatings.
In the next case study we illustrate how AFM can be used to explore the interactions between cyprid temporary adhesive proteins when surfaces with different chemical composition and wetting characteristics are used [2]. Substrates with different wettability were prepared and protein adhesion was quantitatively studied by AFM-based colloidal probes. Results were correlated with laboratory bioassay experiments employing barnacle cyprid larvae, to further enhance the understanding of the barnacle fouling process.

Finally, we report on synergistic effects of surface patterns, inspired by the marine decapod crab Myomenippe hardwickii in combination with chemical surface modifications to suppress marine fouling [3]. We present a simple design of bio-inspired hierarchical surface topology that exhibit antifouling and fouling release potential. We propose a simple, yet efficient method for further chemical modification of such surfaces with thin polymeric films including zwitterionic polymer brushes, and cross-linked polyionic layer-by-layer modified surfaces, and demonstrate synergy by using laboratory essay and field test results.

These examples illustrate that if advancements are to be made in biofouling prevention and in developing new biomimetic adhesives, then further progress is needed in polymer characterization and analysis techniques, as well as in micro- and nanofabrication approaches.

References


Why measuring and understanding the comonomer distribution is so important for the polyethylene industry

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In its about 80 years of history, the world of polyethylene has expanded to a surprising level of complexity, considering its apparent simplicity: -(CH₂-CH₂)ₙ-. In order to fully describe the polyethylene molecular composition, a chemist needs to provide the distributions of molecular weight (MWD), inter and intra-molecular comonomer (or short-chain branches) distribution (CD) and, whenever present, long chain branches.

In this presentation we focus on the inter-molecular CD. Techniques designed to measure in detail the CD date back to the 1980’s, and have advanced considerably in precision, resolution, level of automation and output capability. They are all based essentially on the relationship between crystallizability of a PE molecule and its longest defect free ethylene sequence, with “defect” being a short (two to six carbons typically) side branch originated by the insertion of a comonomer molecule.

Many variables affect the CD of a polyethylene, and are discussed in the presentation. Special detail is given to the effect of catalysts and polymerization processes which can lead to a wide variety of CD’s, therefore being a critical source of differentiation and value for the industry. The relationship between the CD, other composition parameters like MWD and final macroscopic properties of industrial interest is explained through key morphological features like the tie-chains, or molecules that take part of at least two different crystals. Several properties like dart impact resistance, haze and stretchability of thin films are discussed. CD is also important to understand the behaviour of PE blends which are quite common in the industry.

Understanding the CD has led to substantial advances in modelling capabilities of the molecular composition. In parallel, the analysis of how different PE structures affect properties has provided polymer designers with the tools to model and target the desired composition for a set of performance requirements, for a given application. Both modelling capabilities together permit to the modern PE industry a very efficient process to satisfy the rapidly changing market needs, and the knowhow around the comonomer distribution plays a critical role.
Scattering of radiation is one of the most important noninvasive techniques of investigating the structure of matter. In this contribution the application of light, X-ray and neutron scattering to characterization polymer materials will be reviewed and documented with results on several polymer systems. Wide-angle, small-angle and ultra-small-angle scattering will be addressed as well as static and dynamic scattering. The systems described will include solutions, particle dispersions and bulk polymers.
Multidimensional Analysis of the Complex Composition of Impact Polypropylene Copolymers: Combination of TREF, SEC-FTIR-HPer DSC, and High Temperature 2D-LC

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A new multidimensional fractionation technique, Temperature Rising Elution Fractionation (TREF) combined to High Temperature Size Exclusion Chromatography - FTIR (HT-SEC-FTIR), HT-SEC-DSC and High Temperature Two-Dimensional Liquid Chromatography (HT-2D-LC) is used for the comprehensive analysis of a commercial impact polypropylene copolymer. HT-SEC-FTIR provides information regarding the chemical composition and crystallinity as a function of molar mass. Thermal analysis of selected SEC fractions yields the melting and crystallization behaviour of these fractions which is related to the chemical heterogeneity of this complex copolymer. The thermal analysis of the fractions is conducted using a novel DSC method – High Speed or High Performance Differential Scanning Calorimetry (HPer DSC) - that allows measuring of minute amounts of material down to micrograms.

The most interesting and complex ‘mid-elution temperature’ TREF fraction (80 °C) of this copolymer is a complex mixture of ethylene-propylene copolymers (EPC’s) with varying ethylene and propylene contents and sequence length distributions, as well as iPP. High temperature solvent gradient HPLC has been used to show that there is a significant amount of PE homopolymer and EPC’s containing long ethylene sequences in this TREF fraction. High temperature 2D-LC analysis reveals the complete separation of this TREF fraction according to the chemical composition of each component along with their molar mass distributions, see Fig. Following this approach all TREF fractions are analysed and discussed.

Ionic Liquids: new multifunctional agents for designing nanostructured polymers

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Every physical property of materials has a critical length scale where the fundamental physics of that property starts to change as well as any material property can be engineered through the controlled size-selective synthesis and assembly of nanoscale building blocks. In the last two decades, numerous studies demonstrated that new and improved physical behaviours could be achieved by introducing nanoscale structures into polymers. The lecture will describe the combination of various polymers with ionic liquids (ILs) to design polymer nanomaterials and will underline i/ the role of the design of the molecular architecture of ILs in order to control the polymer-IL interactions and ii/ the needs of proper physico-chemical characterization techniques to investigate the fundamental mechanisms and to analyze the resulting nanostructures in order to establish microstructure-properties relationships. Two types of IL-polymer combinations will be detailed for design of:

- inorganic nanostructures from tailoring the dispersion state of nanofillers such as layered silicates, i.e. nanocomposites, for which ionic liquids such as ammonium, phosphonium, or imidazolium-based ILs are used to design interfaces.

- ionic nanostructures from (nano)microphase separation of IL at low concentration in both non reactive and non reactive polymers.

References

Ionic Liquids as Polymer Solvents: Polyelectrolytes, Polyzwitterions, Proteins, and Poly(amino acid)s

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Many synthetic and natural polymers dissolve or swell in ionic liquids (ILs), facilitating the preparation of solutions, gels, dispersions, and other solvated systems displaying characteristic IL features, most notably, negligible volatility, large liquidus range, and high conductivity. Even more, these features provide opportunity for polymer characterization by new experimental methods. We first examined the dissolution of diverse polymers in diverse neat ILs, focusing on effects associated with electrostatic interactions and polymer crystallization. Mixtures were probed by classical methods such as intrinsic viscosity and light scattering to uncover the polymer state. In this manner, many polyelectrolytes were discovered to dissolve molecularly in hydrophilic ILs (those that readily mix with water), where they display coil structures akin to those of neutral polymers in conventional solvents. Significantly, classical polyelectrolyte effects are fully suppressed by the electrostatic screening. More recently, we examined several polyzwitterionic polymers of biomedical interest, finding nearly all to dissolve in common ILs. Numerous IL-polymer pairs displaying polymer crystallization upon supersaturation of mixture by cooling or addition of nonsolvent have been identified, with gels formed by crystallization in concentrated solutions and single crystals formed in dilute solutions.

Several, but not all tested, proteins and poly(amino acid)s were found to dissolve in one or more ILs, and considerable effort has sought to compare chain structures in ILs with those in aqueous buffers. The topic is motivated in part by reports that proteins in IL-water mixtures at room temperature retain activity for months, providing opportunities for IL storage and shipping applications. The most thoroughly characterized protein in IL, cytochrome c in ethylmethylimidazolium ethylsulfate, proved to be partly but irreversibly disordered, but other protein candidates show more promise. Interestingly, denatured proteins in ILs don’t aggregate, unlike their behavior in aqueous buffers. Understanding the phase behavior of IL-water-protein ternary mixtures is important to any technological applications of ILs for proteins; an initial “salting out” of protein is typically observed as water is added to protein-IL mixtures, with further addition causing re-solubilization. To simplify protein investigations, parallel experiments with poly(amino acid)s such as polyllysine and polyglutamic acid have begun; both FTIR and CD reveal helical secondary structures for these polymers similar to those noted in aqueous buffers.

Exploiting the nonvolatility of ILs, we are exploring electron microscopy, a high vacuum method, as a means for in situ imaging of the nanoscale structure and dynamics of solvated polymers systems. Despite some unresolved difficulties, images of solvated gels, dissolved proteins, and nascent growing polymer crystals have been obtained; such imaging is impossible in conventional solvents. Aspects of the IL imaging, including charging and beam damage problems, will be outlined.
Contributed Lecture Abstracts
Fabrication, characterization and latent heat thermal energy storage properties of encapsulated polystyrene/palmitic acid micro/nano capsules

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The encapsulated phase change materials (PCMs) is described as a very small bicomponent system consisting of a core material, and an outer shell or capsule wall material. In recent years, several works have been realized about the encapsulated PCMs using various polymer shells [1-3]. In this regard, this study deals with the preparation, chemical and morphological characterization and determination of latent heat thermal energy storage (LHTES) properties of polystyrene(PS)/palmitic acid (PA) as novel micro/nano encapsulated phase change material (PCM). The PS/PA micro/nano capsules were fabricated successfully via emulsion polymerization method. In the capsules, PA acted as phase change-core material as PS was used as shell material. The different parameters on the encapsulation properties of the capsules such as type and amount of crosslinking agent and initiator, temperature, homogenization rate and monomer/PCM ratio were optimized systematically. The PS shell formation reaction around the PA was confirmed by using FT-IR spectroscopy method. The SEM analysis results (Fig.1) showed that the capsules had smooth spherical shape with a fairly uniform structure with micro/nano sized. The particle size distribution (PSD) analysis showed that the diameter distribution of the capsules were between 0.01 and 100 µm (Fig. 1). The LHTES properties of the capsules were measured by using DSC analysis. The DSC results indicated that the PS/PA micro/nano capsules with weight ratio of 2:1, 1:1 and 1:2 had a melting temperature of 55.39, 55.68 and 55.71°C and a latent heat of 97.45, 103.68 and 126.85 J/g, respectively. The prepared micro/nano capsules were subjected to repeated heating and cooling cycles for 5000 times and the findings suggested that the PS/PA micro/nano capsules had good thermal reliability. In addition, the thermal degradation temperature of the capsules were determined by TG analysis and the results confirmed that the PS/PA micro/nano capsules had high thermal durability. All these properties make it potential an micro/nano encapsulated PCM for different thermal energy storage applications such as solar passive space heating in buildings.

Fig. 1. PSD and SEM analysis results obtained for the prepared PS/PA micro/nano capsules

References

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Electrostatic Interaction of the Alzheimer’s Amyloid β (1-42) Peptide with Short Single Stranded Synthetic Nucleotide Sequences Affects the Fibril Structure

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Inhibition of fibril genesis (Figure 1) as well as disassembly of fibrillar structures upon electrostatic interaction between the amyloid β(1–42) protein (Aβ42) and either synthetic polyions or short single stranded nucleotide sequences will be presented. Since the abnormal deposition of this protein is an archetype of Alzheimer’s disease (AD), the outcomes of these investigations, supported by atomic force microscopy imaging in the dry and liquid states as well as circular dichroism, are crucial for the development of potential future strategies to cure a disease that concerns an ever aging population.

Figure 1: Atomic force microscopy on mica of Aβ42 A) fibrils were assembled under controlled aggregation conditions; in presence of B) 5’-CTAGTCGACTAG-3’; C) 5’-AAAGAGAGAGAG-3’; D) 5’-TCTGAG-3’. In presence of the nucleic acid strands, fibril formation is inhibited.
Poly(styrene-maleic anhydride) or SMA are versatile copolymers available in different grades of molecular weight ($M_w = 5500$ to $170000$ g/mol) and molar percentage of maleic anhydride (22 to 50 mol-%). The specific molecular structure of high-molecular weight grades was further explained, as they allow for the formation of self-assembled polymer films including spherical capsules, short-fibrous structures and long-fibrous structures depending on the copolymer grade (Figure 1). Therefore, a broad range of SMA grades was analyzed by means of size exclusion chromatography, infrared spectroscopy, Raman spectroscopy and nuclear magnetic resonance spectroscopy. While the nominal composition could be determined by $^1$H NMR and Raman spectroscopy, the combination with $^{13}$C NMR and FTIR allowed a more detailed characterization of the molecular structure. The high-molecular weight SMA grades show a heterogeneous molecular structure with segments including high styrene and maleic anhydride moieties, respectively. The differences in global and local molar ratio of maleic anhydride was further confirmed by thermal analysis. Most interesting data results from MDSC for high-molecular weight SMA, where the transition in reversible heat flow and $\Delta c_p$ remains almost constant, while the transition in non-reversible heat flow and $\Delta c_p$ gradually increases with amount MA. Comparing low- and high-molecular weight SMA, a linear model for $T_g$ cannot be applied for the global amount of maleic anhydride, while it can be successfully implemented if a more detailed molecular structure with two constituents is considered.

This study illustrates intrinsic molecular features of SMA grades that are capable for self-assembly, and can provide a selection tool for nanoparticle formulation by further ammonolysis and imidization. The dispersions of resulting imidized nanoparticles were characterized by rheological measurements, in order to determine their suitability for further processing as coating substances.

Figure 1: Assembly of SMA into patterned films and nanoparticles.
Amphiphilic block copolymers self-assemble in water as micelles in diverse morphologies like spheres, rods etc.\textsuperscript{1} Unlike low molecular weight surfactants, which are dynamically active, block copolymers exhibit a slow to frozen kinetic.\textsuperscript{2} The dynamic of copolymer micelles is dominated by two mechanisms. The first is an individual process and involves insertion and expulsion of copolymer chains from the micelles.\textsuperscript{3} The second is a collective and occurs through fusion and fission of proper micelles.\textsuperscript{3} Fusion and fission are crucial for controlling the behaviour of amphiphilic aggregates particularly in drug delivery and for the synthesis of controlled nano-objects.\textsuperscript{1} The theories\textsuperscript{3} and randomization experiments\textsuperscript{2} have suggested that fusion-fission are not relevant in block copolymer micelles at equilibrium. In this communication, we show, for the first time, that fusion and fission take place at equilibrium in triblock copolymer micelles.\textsuperscript{4} We use a fluorescent technique, which exploits the randomization of hydrophobic pyrene derivative between micelles as a tool to probe the fusion and fragmentation.\textsuperscript{4} We also show that while fusion and fission are not effective for homogenizing the copolymer chains between micelles they are very efficient in changing their shape from spheres to rods.\textsuperscript{5,6}

References:
Emerging Interphases in Poly(n-Butylacrylate)/Polystyrene Core-Shell Nanoparticles Obtained via Semicontinous Miniemulsion Polymerization


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Selective loading of active molecules in nanocontainers has been gaining growing interest recently [1]. Miniemulsion polymerization (MiEP) has been found to be a strategic tool in the synthesis of multiphase nanoparticles for selective encapsulation of guests [2], [3]. Therefore the control of nanoparticle morphology is an essential part of producing high quality nanocontainers with specific requirements. It is thus mandatory to correlate the global multiphase nanoparticle morphology with the synthesis conditions and then to dominate the heterogeneities inside the nanostructure [4].

Here we report a comprehensive characterization (DLS, SEM, DSC, ATR-FTIR, CP-MAS and $^1$H-TD-NMR) of Poly(n-Butylacrylate)/PolyStyrene core-shell nanoparticles with different dimensions (236nm, 184nm, 127nm, 90nm and 45nm in diameter) obtained via semicontinous MiEP. Particularly, evidences of emerging interphases due to confinement phenomena are shown in 45 and 90 nm samples. ATR-FTIR (Fig.1) shows deformation of the peaks between 1150 cm$^{-1}$ and 1250 cm$^{-1}$ (region of the asymmetrical C-C=O stretching) for the overmentioned samples. Then, interphase $T_g$ ($T_g$ INT) has been detected in 45 and 90 nm samples and analyzed through Fox’s Equation for the reconstruction of the interphase composition. To study the relationship between peak deformation and $T_g$ INT, $^1$H-TD-NMR Magic Sandwich Echo (MSE) experiments have been performed (Fig.1).

Figure 1: ATR-FTIR and $^1$H-TD-NMR MSE of the 236 nm (a), 184 nm (b), 127 nm (c), 90 nm (d) and 45 nm (e) diameter samples.

MSE experiments show that the rigid fraction temperature dependence is strictly related on the nanoparticle size. In particular, a further soft component appeared in the samples of 45 and 90 nm diameter. In our opinion all these evidences can be ascribed to the emergence of an interphase due to confinement phenomena.

References
Use alkali-lignin as a compatibiliser in cellulose nanofibers/poly (lactic acid) composites

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This study was designed to determine if the addition of alkali-lignin to cellulose nanofibers/poly (lactic acid) composites was beneficial to their mechanical properties. Composites with cellulose nanofibers (CNFs) mass proportions of 10% were prepared using hot-pressing method. Neat poly (lactic acid) (PLA) and CNFs/PLA with alkali-lignin composite were produced under the same conditions. The composites were tested for tensile strength, elongation at break, stiffness and impact strength. Dynamic mechanical analysis (DMA) was also used to investigate the viscoelastic behavior of the composites. Fractured surfaces were analyzed using scanning electron microscopy (SEM). The results of the composite investigations showed that the addition of alkali-lignin has an influence on the CNFs/PLA composite characteristics. SEM investigations showed that the adhesion between CNFs and PLA could be improved by the addition of alkali-lignin. Tensile strength and Young’s modulus could be improved clearly. In all cases, the addition of alkali-lignin increased the structure properties of the composites to some degree when compared with composites with no additional alkali lignin.

Figure 1: The structure of the produced nanofibrils analyzed with AFM.

References
RAFT polymerisation of a lignin derived monomer


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Lignin is the second most abundant naturally occurring polymer (after cellulose). 50 million tons of which are produced as a by-product by the paper industry each year. [1] Less than 3% of this lignin has a current application, and the remainder is burnt. Ferulic acid, a breakdown product of lignin, can be converted to 3-methoxy-4-hydroxy styrene using ferulate decarboxylase [2] Bacillus Pumilus [3] or via a copper catalysed reaction.[4] The polymerisation of this monomer via free radical polymerisation has been previously reported [2], however only low monomer conversions and low molecular weights were achieved due to the chain transfer ability of the free phenol.[5] By protecting the phenol with an acetoxy group we have been able to show the first example of the controlled radical polymerisation of this monomer (Figure 1 top). Using Reversible Addition Fragmentation chain Transfer (RAFT) polymerisation good control over the polymerisation was achieved. Predictable molecular weights and low dispersities were obtained, as demonstrated by kinetic studies and size exclusion chromatography (SEC) analysis (Figure 1 bottom).

![Polymerisation of 3-methoxy-4-acetoxy styrene via RAFT.](image1)

![Kinetic data for the polymerization of 3-methoxy-4-acetoxy styrene via RAFT.](image2)

Furthermore, deprotection of the acetoxy protected phenol group yielded poly(3-methoxy-4-hydroxy styrene) as confirmed by $^1$H NMR. Further work is focused on studying the biodegradation of the deprotected polymer by soil based microorganisms.

References
Characterization of Acidified Chitosan Entrapped in Epoxidized Natural Rubber

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Over the year’s incorporation of chitosan in the matrices of elastomers has been of interest to researchers. However, solubility of chitosan in acidic aqueous media in contrast with epoxidized natural rubber which is not soluble has been a limitation. This has prompted us to investigate and hereby report our findings on the preparation, characterization, and the properties of biocomposites containing chitosan (CTS) and epoxidized natural rubber (ENR) prepared via latex methods. Biocomposites (CTS-t-ENR) comprising chitosan (CTS) trapped in a partially crosslinked epoxidized natural rubber (ENR) was prepared by homogenizing CTS in ENR50 (ENR with about 50% epoxy content) latex in the presence of curative agents and acetic acid. Micrographs of CTS-t-ENR reveal no phased-out entity and infrared spectra of CTS-t-ENR show only vibrational bands belonging to CTS and ENR, supporting that the former was not bonded but entrapped in the matrix of the latter. CTS loading up to 5 phr resulted in the increase in the tensile strength, elongation at break, moduli and hardness of the CTS-t-ENR. Thermal stability of CTS-t-ENR is improved compared to that of CTS. The increase in CTS loading led to an increase in water uptake and a decrease in toluene absorbency of CTS-t-ENR biocomposites. The biodegradability of CTS-t-ENR in soil revealed that the biodegradation of the biocomposites increases with the increase in CTS loading. Moreover, the absorption and desorption capacities of CTS-t-ENR for Cu(II) and 2-Naphthol in water were determined.

Keywords: Chitosan; Epoxidized Natural Rubber; biocomposites
Influence of molar mass and concentration on the thermogelation of methylcelluloses

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In this work, 4 samples of methylcellulose with different molar masses are characterized and studied. The range of MW covered varies from 32,000 up to 390,000 g/mol. From 13C NMR it is shown that their degrees of substitution are nearly the same allowing to strictly discuss the role of MW. Their MW is determined from their intrinsic viscosity.

In a first step, the viscosity of aqueous solutions at different concentrations and MW are discussed in terms of a master curve allowing to relate viscosity to the overlap parameter C[η].

In a second series of rheological experiments, thermal behavior is studied in the range 15°C up to 75°C on an increasing temperature cycle. The two steps mechanism for thermal gelation on heating is confirmed and the characteristic transition temperatures are determined and compared. The rheological parameters G’ and G’' at 75°C are analysed for different concentrations and MW.

An important remark is that the sol-gel transition occurs in a kinetic slow process depending on the mainly concentration and molecular weight (MW). The elastic modulus at 75 °C depends only on polymer concentration.
The Effects of Nanoclays on Thermal Degradation of Polylactide via Direct Pyrolysis Mass Spectrometry

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Among the materials that have high potential for wide range of industrial applications, polylactide, (PLA) and its copolymers have gained significant interest. On the other hand, degradation of PLA which is of crucial importance for various applications depends on several factors such as molar mass, temperature, pH, reactive end groups, presence of unreacted starting monomer and impurities. In order to improve flame retardancy and mechanical properties nanoparticles such as montmorillonite, halloysite and SiO$_2$ were incorporated into PLA matrices [1, 2]. The nanoscale distribution of these fillers brings up large improvements to the polymer matrix in terms of mechanical, fire retardant, rheological, gas barrier and optical properties.

In this study, we investigated the effects of amount and types modified montmorillonites on thermal degradation behaviour of PLA via direct pyrolysis mass spectrometry. In Figure 1, the variations of total ion yield as a function of temperature, TIC curves and the mass spectra at peak maxima recorded during the pyrolysis of PLA and PLA involving 5 % by weight Cloisite 20A and 30B are shown. It has been determined that the type and the amount of the modifier affect thermal characteristics of PLA.

![Figure 1: a)TIC curve and b) mass spectra at peak maxima recorded during the pyrolysis of I. PLA, II. PLA/Cloisite 20A and III. PLA/Cloisite 30B](image)

References
Interfacial structure of entangled polymer brushes under shear


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We present a neutron reflectometry (NR) study of polystyrene (PS) sheared in contact with functionalized solid surfaces. This method provides a non-invasive tool to elucidate the structure of the buried interface with sub-nm resolution. We combine the scattering experiments with in situ surface sensitive rheology to gather information about the microscopic origin of interfacial slip.

We have performed in situ shear-NR on PS melts and solutions in contact with chemically grafted PS chains. Entangled polymers can exhibit macroscopic slippage and its origin is supposed to arise from stretching of surface adsorbed chains and subsequent disentanglement from the free flowing chains. The combination of rheometry in a plate-plate torsional shear set-up and NR is potentially a unique technique to address this question by using labelled polymer chains chemically attached to the surface. We present first results on in situ shear-NR on PS melts in contact with high density PS brushes as well as entangled PS solutions flowing over grafted PS chains of the same length but lower density. In both cases we observe a change in structure of the grafted PS at a certain shear rate that may be linked to stretching and/or disentanglement of the interfacial chains.

Entangled polymers remain to this day a major challenge in rheology and unfortunately we are not aware of any theoretical framework capable of explaining the observed interfacial structure. Therefore, we are developing new physical models, using ideas from field theories as well as atomistic simulations. In the case of a constant applied shear, a non-equilibrium steady state develops for which we have applied the self-consistent field theory with an additional advective term. If, however, one is interested in an oscillatory shear and/or the gradual relaxation of the interfacial structure in time (possibly due to evolving entanglements), a full dynamical theory is required and we rely on atomistic simulations. In order to cope with the very high molecular mass, the dynamical equations are decomposed to normal (i.e. Rouse) modes and only a few slowest ones are considered, drastically reducing the number of degrees of freedom.

References
Controlled Self-Assembly of Hydrophobic-Cationic Polymers leading to Waterborne Antimicrobial Nanogels

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Hydrophobic and cationic interactions are two very important types of physical interactions found in biological systems which influence their conformation and properties. To mimic the controlled self-assembly of natural macromolecules to finally attain the very controlled conformation, new amphiphilic polymers have to be prepared and their self-assembly in aqueous solution has to be studied.

In our presentation we like to report results of our study on waterborne multifunctional poly(ethylene imine)s (PEIs). The multifunctional PEIs were prepared via the reaction of branched PEI with suitable hydrophobic and cationic building blocks in water using the coupler concept. These modified PEIs self-assembled in water in a controlled manner to form nanogels having distinct shape. The shapes of the nanogels are controlled by the degree of functionalization with hydrophobic and cationic building blocks (Figure 1). The antimicrobial efficacy of these multifunctional PEIs was studied against both gram positive and gram negative bacteria. These types of antimicrobial nanogels are potential candidates for biomedical applications as PEI based nanogels are known for anti-cancer drug delivery systems.

Figure 1: Cryo- FESEM image of the multifunctional PEI (nanogels): (A) 8% hydrophobic and 8% cationic functionalization (lamella) (B) 12.5% hydrophobic and 12.5% cationic modification (sperical).

References:
One-pot Synthesis of Responsive Polymer Nanoparticles

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Controlled radical polymerisation techniques have, in recent years, allowed the synthesis of increasing complex architectures including block copolymers, star polymers and higher order structures such as micelles.[1] In addition to this, research into stimuli responsive polymers has become increasingly more prolific, with an ever increasing number of studies on polymers responsive to pH, light and temperature.[2] Whilst polymers displaying LCST behaviour in water are well studied, polymers exhibiting an Upper Critical Solution Temperature (UCST) cloud point in water are not.

Here we report the synthesis of PDMAPS, a polysulfobetaine that exhibits a UCST cloud point in aqueous solution, by Reversible Addition Fragmentation chain Transfer (RAFT) polymerisation (Fig. 1, LHS).[3] RAFT polymerisation techniques have been used to synthesise a range of molecular weights from 5-500 kDa, whilst retaining control. A range of molecular weights of branched PDMAPS have also been synthesised, resulting in a drastically lower UCST cloud point than the linear counterparts. The branched polymers have been shown to form discreet particles in solution and furthermore, incorporation of a permanently hydrophilic monomer (PEGMA) into the branched polymers resulted in particles with a core-shell morphology, preventing aggregation. The branched polymer particles were analysed by light scattering, electron microscopy and DOSY NMR confirming their molecular weights and spherical morphology (Fig. 1, RHS). The ability of the particles to swell and contract on response to temperature has been studied using DLS.

As polybetaines are bio and haemocompatible and show very low levels of protein fouling, it is envisaged that these biocompatible, responsive polymer particles could be used in areas such as delivery or reporting.

References
Hydrophobic dopant-enhanced and polymer-suppressed supramicellar assemblies

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An aqueous system involving sodium dodecyl sulphate (SDS) and small quantities of dodecanol produced supramicellar assemblies (SMA) near the critical micelle concentration (CMC). The system is metastable at most concentrations but typically lasts for $>10^4\text{ s}$, making quasi-equilibrium measurements possible.

As a dodecanol-doped SDS solution is diluted towards the CMC a large light scattering peak (LSP) occurs, with its maximum slightly above CMC. The LSP then drops to zero near the solubility limit of dodecanol in water. The peak is due to SMAs, whose mass, $\sim10^7\text{ g/mole}$ is $\sim10^2$ greater than normal micelles. SMA are composed of SDS and dodecanol; i.e. micelles do not simply release their dodecanol payload near CMC, rather they undergo a morphological change involving both the dodecanol and SDS in a larger structure.

When SDS and the water soluble polymer polyvinylpyrrolidone (PVP) are in solution, it is well known that the SDS will associate with PVP, starting at the Critical Aggregation Concentration (CAC), and electrically charge the PVP, conferring on it polyelectrolyte properties, such as electrostatic swelling of the PVP coil with concomitant increase in intrinsic viscosity and electrostatically enhanced second virial coefficient $A_2$, which decreases the scattering. The light scattering behaviour of PVP/SDS is seen in figure 1A.

When the solution now contains PVP, SDS, and a small amount of dodecanol, where $r=0.033=\text{grams dodecanol/gram of SDS}$, the light scattering changes dramatically. Namely, the tight binding of SDS to PVP suppresses the formation of SMA, hence eliminating the LSP as $C_{\text{PVP}}$ increases. A secondary LSP at $C_{\text{SDS}}<\text{CAC}$ ($\sim7\times10^{-4}\text{ g/cm}^3$) forms due to a low concentration of SMA below the CAC. Interestingly, an ‘isoscattering point’ is found near $0.0027\text{ g/cm}^3$ where the scattering converges for all solutions. Because the LSP suppression phenomenon caused by PVP reverses the order of scattering vs $C_{\text{PVP}}$ for CAC<$C_{\text{SDS}}$<C_{isoscat}, and because above C_{isoscat} there are no more SMA, the light scattering curves must regain their order vs $C_{\text{PVP}}$, yielding a crossover near the isoscattering point.

Figures 1A,B: Light scattering (Rayleigh ratio, cm$^{-1}$) for SDS/PVP, showing how increased loading with SDS decreases light scattering due to electrostatically enhanced $A_2$. B) PVP/SDS/dodecanol; Dramatic suppression of the light scattering peak as concentration of PVP increases.
Chlorite-based pretreatments of cellulosic samples prior to SEC analysis

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The molar mass distribution (MMD) of pure cellulose is usually measured by size-exclusion chromatography (SEC) after dissolution in appropriate solvents, the more current one being LiCl-DMAC. Cellulose derivatization to form cellulose tricarbanilate (CTC) is another way to reach complete cellulose dissolution in a non-polar solvent like THF. However, none of these methods appear to be directly suited to the case of impure cellulosic samples like raw vegetal and wood, mechanical pulps, or papers containing the latter constituents. Even after several extractions with water and solvents, such samples still contain large amounts of hemicelluloses and lignin, at least partly covalently bound to cellulose. The more classical delignification treatment for chemical pulps (from kraft, soda, bisulfite or organosolv cooking of wood or plants) is chlorite oxidation. Normal conditions in the so-called “holocellulose” test are 70°C, pH 4.8, 2% fiber concentration and 2 h treatment. However, the holocellulose treatment is largely insufficient to remove lignin from natural or processed samples such as the ones cited above. Literature on the assessment of procedures for lignin and/or hemicelluloses removal from vegetal is very scarce, and only one paper [1] reports the effect of chlorite on the MMD of cellulose evaluated by SEC. In the present paper, a cold holocellulose (CH) procedure described in [2] was studied as an alternative to the classical holocellulose treatment at 70°C. The investigated substrate was a bleached paper pulp (Eucalyptus kraft pulp) chosen for its rather high hemicelluloses content and absence of lignin. This substrate (treated or not) was completely soluble in THF after carbanilation. The CH treatment was repeated several times. In another series of tests hot alkaline extractions were inserted between the CH treatments. Repetition or insertion of alkaline treatments aimed at simulating the case of lignified substrates, in order to achieve full delignification. In a separate study, Whatman No.1 paper (pure cotton cellulose) to which commercial kraft lignin was added was tested after prolonged hot chlorite delignification stages (again with the purpose of better delignification for lignified samples). Pulp viscosity in CUED (viscosity-average degree of polymerization, DP) and MMD by SEC coupled to multidetectors (DRI-UV-LALS/RALS-Visco in LGP2, MALS-DRI in CRCC) were measured. Hydrodynamic radii or gyration radii were also measured thanks to the viscometer and MALS coupling. It was found that holocellulose treatment led to a significant decrease of the cellulose DP, yet the presence of lignin counteracted that effect. A slightly higher pH of 5.4 was favourable and a better result was obtained using picolinic acid instead of acetic acid as a buffer. Conversely, the CH procedure, even repeated twice, produced insignificant degradation. However a third repetition of CH initiated degradation. A more significant degradation was observed when an alkaline extraction stage was inserted after the first CH treatment. CH treatments, single or repeated, had no effect on the hemicelluloses.

References
Oxygen Transport in Poly(ethylene furanoate) Characterized via Permeation and Pressure-Decay Sorption Methods

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The beverage container industry has been dominated by poly(ethylene terephthalate) (PET) for the past forty years, despite PET exhibiting limited oxygen barrier performance and petroleum sourcing. Initial research [1] into poly(ethylene furanoate) (PEF), a recently developed furanic and biologically-sourced analog to PET, has shown that PEF is superior to PET in regards to thermal, mechanical, and barrier properties. Particularly, oxygen diffusion in PEF is largely reduced (~11X) compared to PET due to a reduction in segmental mobility originating from the hindered furan ring-flipping mechanism [1]. The repeat structures for PEF and PET are provided in Table 1.

The current work [2] further expands the fundamental property understanding of PEF by providing a detailed oxygen transport investigation using pressure-decay sorption and permeation techniques at various temperatures. Detailed sorption measurements using a high accuracy custom-built system will be reported, along with so-called dual-mode sorption parameters for oxygen, which has very low sorption uptake in PEF. The validity of the resultant sorption parameters is demonstrated through complementary and independent permeation measurements. Furthermore, the energetic parameters associated with the oxygen transport process (i.e. enthalpy of sorption, activation energies of permeation and diffusion) are presented for PEF [2]. This study is the first detailed investigation of oxygen transport in PEF, and in combination with our prior work [1], illustrates the property improvements for PEF vs. PET.

<table>
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<tr>
<th>Poly(ethylene furanoate) (PEF)</th>
<th>Poly(ethylene terephthalate) (PET)</th>
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<td>![PEF Structure]</td>
<td>![PET Structure]</td>
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Table 1: Structural information for PEF and PET.

References
Copolymers of Polylactide via Direct Pyrolysis Mass Spectrometry

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Extensive research has been carried out for improving physical, mechanical and thermal characteristics of polylactide, (PLA). Three main approaches followed for this purpose involve copolymerization, addition of plasticisers and incorporation of additives such as micro and nano-fillers, flame retardants and thermal stabilizers [1, 2]. To enhance its hydrophilicity its copolymers with poly(ethylene glycol) (PEG) and to introduce ductility and toughness its copolymers with polybutadiene (PB) are prepared. On the other hand, to improve flexibility and impact strength copolymers of PLA with polycaprolactone (PCL) are produced. Highly ordered nanostructured materials can be fabricated by copolymerization of PLA with poly(styrene) (PS).

In this study we investigated thermal degradation behaviours of various copolymers of polylactide via direct pyrolysis mass spectrometry. As an example, in Figure 1, evolution profiles of some of the diagnostic thermal degradation products of each block recorded during the pyrolysis of PLA-b-PEG are shown. The technique allows separation of each component and identification of thermal degradation products as a function of temperature.

![Figure 1: Evolution profiles of some diagnostic thermal degradation products of PLA-b-PEG](image_url)

References
Dynamic mechanical analysis (DMA) is a sensitive technique for a determination of viscoelastic properties of materials. The development of DMA started in 1909 with the first oscillatory measurements of elasticity of materials [1]. Prevalent DMA enables to study viscoelastic properties of samples encompassing several parameters such as load, frequency, temperature and time in a single measurement [2].

Dynamic mechanical analysis combined with relative humidity (DMA–RH) is a technique supplementing above mentioned parameters with relative humidity (% RH). Many polymers and their composites (biopolymers, biodegradable polyesters and copolyesters, hydrogels, natural fibers, composites filled with natural fillers) are sensitive to moisture. Moisture combined with heat is known as a hygrothermal degradation, which causes chemical, physical and physico-mechanical changes in materials. Transient and dynamic oscillatory experiments conducted under a broad temperature range (from -120 to 300°C) and an atmosphere with an adjusted humidity (from 0 to 90 %RH) offer the possibility to estimate viscoelastic behaviour of samples under hygrothermal aging combined with mechanical stress.

This paper will present data which shows that information about the response of viscoelastic properties on multiple environmental factors can be obtained simple from a single DMA–RH experiment. Hygrothermal degradation of various samples such as single natural fibers, kraft paper [3], hydrogels and composites based on poly(lactic acid) and wood flour will be presented and discussed. Furthermore, the extension of this technique to the evaluation of an interfacial compatibility between polymer matrix and filler will be demonstrated.

References
Synthesis and characterization of a modified chitosan grafted nanoclay

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Developing a novel glycidyl methacrylate modified chitosan grafted nanoclay was the main objective of this study. The modified chitosan grafted nanoclay can be used as filler in many biomaterials such as dental adhesives due to its capability of being photocured and biocompatibility and wound healing properties of chitosan. Because of the high aspect ratio, nanoclay is efficiently used to improve mechanical properties of polymeric systems [1,2]. Incorporation of clay nanoparticles into the dilute systems such as dental adhesives, however, results in the fast sedimentation of the particles due to their higher densities. Surface modification of nanoclay platelets with a polymer, has been shown, to solve the problem due to the decrease in the density of the particles and providing interactions between the newly attached functional groups on the surface of particles with the solvent. Grafting is an efficient method to introduce functional groups onto the surface of nano-particles [3,4].

Chitosan was chemically modified by glycidyl methacrylate (GM) and the neat and modified chitosan were fully characterized. This synthetic path involves the bonding of GM onto the low molecular weight chitosan (LMWC) chain via glycidyl group of the monomer and the amine group of LMWC. The product was then dissolved in Dimethyl Sulfoxide (DMSO) which is not able to dissolve LMWC, but is a good solvent for modified-LMWC (m-LMWC). The mixture was filtered and the clear solution of m-LMWC in DMSO was separated and freeze-dried. The effect of different parameters such as the temperature, time of reaction and the reactants concentration were investigated. The FT-IR spectra confirmed the formation of m-LMWC. NMR spectra revealed that the reaction was performed mostly by the reaction of amine groups of LMWC and the glycidyl groups of GM. The product was then dissolved in DMSO and photo cured in the presence of 1,3-dibutanone as a photoinitiator. In the meanwhile the solvent was evaporated. The degree of conversion, gel content, DSC and TGA of the cured polymer were also investigated. The m-LMWC was also grafted onto the surface of nanoclay and characterized. The grafting of m-LMWC onto the nanoclay surface was confirmed by FT-IR and XRD.

References

During the industrial transformation, most polymers are involved in specific processes resulting in the macromolecular chain orientation. Such orientation is appearing from the local phase to the mesophase and sometimes even up to the macroscopic phase. Small Angle X-Ray Scattering (SAXS) is a technique well suited for investigating nano-materials and nano-structures of polymers. Information is collected on sample structure parameters such as particle shape or size, size distribution, orientation, surface to volume ratio… in the range from 1 nm to beyond 100 nm. Moreover, orientational functions can be derived from 2 dimensional x-ray patterns. Length-scales down to 0.1 nm can also be investigated in combination with Wide Angle X-ray Scattering (WAXS). In the case of samples with internal structures larger than 200 nm, USAXS (Ultra Small Angle X-Ray scattering) experimental conditions are required. USAXS allows to access heterogeneities about some hundreds of nanometers while providing the opportunity to investigate the large-scale structure evolution during the deformation of polymeric materials [1]. The progress in the performances of x-ray components and subsequent assembly offers such characterization methods in the laboratory. Hence, investigation of an injected semicrystalline polymer has been performed, emphasizing the nanostructure orientation and processing relationships. Further, recent results obtained on in-situ stretched Polybutene-1 (PB-1) [Figure 1] illustrate the capability to perform lab measurement equivalent to Synchrotron USAXS [2] highlighting microscopic structural evolution and macroscopic strain-whitening phenomenon correlation.

**Figure 1:** 2D-USAXS patterns of PB-1 crystallized at 60°C stretched at 30°C as a function of engineering strain - 50s exposure time. Stretching direction horizontal. Data courtesy of Pr. Men and Y. Wang.

References

Separation of Polyolefin Copolymers by Crystallization and Adsorption techniques.

Discussion on the separation mechanism on an atomic level flat surface adsorbent.

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Crystallization techniques such as TREF [1], CRYSTAF [2] and CEF [3] are being widely used to characterize semicrystalline polymer resins. In the case of polyolefins, the linear correlation between the comonomer content (number of short chain branches) and crystallization or dissolution temperatures has allowed measuring chemical composition distribution in polyethylene copolymers, a very important microstructure feature in semicrystalline polyethylene grades.

More recently, new chromatographic techniques have appeared to provide a similar separation of polyolefins in a well-ordered fashion when using solvent gradient chromatography on a graphitized carbon column at high temperature [4]. Good separation of polyethylene copolymers [5,6] in a short analysis time was obtained, including amorphous resins that are not possible to be analysed by crystallization techniques. The new methodology is known as solvent gradient interaction chromatography (SGIC).

The use of the same graphitized carbon columns in a thermal gradient approach was shown to provide similar results to those of SGIC in a very practical approach, known as thermal gradient interaction chromatography TGIC [7].

New adsorbents that could be used in SGIC and TGIC analysis of polyolefins have been found [8,9] providing similar retention order as graphitized carbons and a separation mechanisms has been proposed [10].

A comparison of crystallization and adsorption techniques is discussed with special emphasis on the separation of polypropylene and polyethylene. Evaluation of a new adsorbent is presented together with further discussion on the separation mechanisms on atomic level flat surface adsorbents.

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Biohybrid glycopolymers and chimeric polysaccharides capable of ionotropic gelation

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Alginate is a collective term for a family of binary heteropolysaccharides produced by brown algae and by some soil bacteria. Alginate is a linear unbranched copolymer of (1→4)-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues distributed in long homopolymeric blocks (e.g. MMM or GGG) and in shorter, mostly alternating, copolymer blocks (e.g. MGM). In aqueous solution, alginate forms transparent hydrogels upon addition of some divalent cations (e.g. Ca²⁺, Ba²⁺, Sr²⁺ and Zn²⁺) via the intermolecular complexation of said ions and the formation of junction zones (ionotropic gelation). Within the alginate chain, only (1→4)-α-L-guluronan (i.e. GGG) and alternating sequences (i.e. MGM) are involved in the formation of intermolecular junction zones. In our work, (1→4)-α-L-guluronan oligomers extracted from alginate were used as building blocks in the synthesis of biohybrid glycopolymers and chimeric polysaccharides with original gelation properties. The starting oligosaccharides were transformed into vinyl macromonomers and copolymerized with 2-hydroxyethylmethacrylamide (HEMAm) either by conventional radical [1] or by RAFT polymerization [2] to yield well defined biohybrid glycopolymers: When dialyzed against CaCl₂, poly(HEMAm-co-GulA₂₀MAm) gave a soft self-standing transparent hydrogel (Erreur ! Source du renvoi introuvable.a). Alternatively, (1→4)-α-L-guluronan chains were grafted onto hyaluronan to obtain a chimeric polysaccharide capable of ionotropic gelation in the presence of calcium ions. (Erreur ! Source du renvoi introuvable.b). The gelation properties of these materials were characterized by rheology and light scattering.

(a) (b)

Figure 1: Ionic gels formed by (a) poly(HEMAm-g- GulA₂₀) and (b) a chimeric hyaluronan bearing (1→4)-α-L-guluronan graft chains.

References
Molecular Structure of Linear Low Density Polyethylene

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Linear Low Density Polyethylene (LLDPE) is an important commercial material for various applications. It is generally known that LLDPEs made using Ziegler Natta (Z/N) catalysts show a relatively broad molar mass distribution (MMD) and decreasing average comonomer content with increasing molar mass. On the other hand, LLDPEs made using a metallocene catalyst show a narrow MMD and a more or less constant average comonomer content as function of molar mass. This was shown often in literature and also in this investigation using the LC-transform in combination with infra red spectroscopy (IR). In this investigation, two crossfractionation methods were applied. First, a preparative method separating according to molar mass[1] with subsequent characterization of the fractions according to composition using analytical temperature rising elution fractionation (aTREF). The fractionation was checked for average composition using NMR and molar mass using SEC-IR. Secondly, preparative TREF (pTREF) with subsequent characterization of the fractions using Size Exclusion Chromatography coupled with infra red (IR) was used.
From the results it was concluded that the LLDPE materials made using a Z/N catalyst system are even more heterogeneous than generally assumed.

References
Characterization of artificially aged polyethylene

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Polyethylene is the most widely used polymer and covers wide ranges of applications. In many cases the shelf life of PE products is in the order of tens of years and depending on the environmental conditions aging processes can severely influence the performance of the material.

In order to simulate natural aging many accelerated test conditions have been reported, including chemical, physical and mechanical stress tests. We have made three different samples of polyethylene, one without stabilizers, and two with different but low amounts of stabilizers. The samples were aged under different chemical conditions, more specifically: samples were put in autoclaves with water, sulfuric acid, or sodium hypochlorite and pressurized with pure oxygen; one set of samples was exposed to UV light. To investigate the penetration depth of the aging processes the samples were sliced and analyzed at different positions using mainly FTIR microscopy and analytical pyrolysis. Analytical pyrolysis was carried out using various temperature protocols to find optimum conditions for the identification of oxidation products. To determine the amount of volatile or extractable matter released during degradation GC/MS with solvent extraction was applied. The major indicators for oxidation were found to be 2-oxo-hydrocarbons, but also dioxocompounds have been identified. The influence of the aging process on the molar mass and molar mass distribution were analysed using size exclusion chromatography.

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Synthesis and Characterisation of a Poly(L-lactide-co-ε-caprolactone) Copolymer Using a Novel Tin(II) Alkoxide Initiator for Potential Use as an Absorbable Monofilament Surgical Suture

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Copolymerisations of L-lactide (LL) and ε-caprolactone (CL) initiated by stannous octoate (Sn(Oct)₂) and a novel tin(II) alkoxide initiator, bis[tin(II)(octoate)] diethylene glycol ([Sn(Oct)]₂DEG)], were carried out in bulk at 130 °C for 48 hrs. The PLLCL copolymers, obtained from an initial comonomer feed of LL:CL = 75:25 mol %, were characterized by a combination of analytical techniques, namely: Fourier-transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (both ¹H-NMR and ¹³C-NMR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The copolymers obtained using 0.01 and 0.02 mol % [Sn(Oct)]₂DEG as the initiator had number-average molecular weights, Mₙ, of 6.48 x 10⁴ and 4.09 x 10⁴ respectively which were higher than those obtained from using Sn(Oct)₂. The ¹H-NMR spectra revealed copolymer compositions of 75:25 and 72:28 mol % when using 0.01 and 0.02 mol % [Sn(Oct)]₂DEG respectively. The DSC thermograms showed crystalline melting peaks (Tₘ) at 152 and 155 °C while TGA showed initial weight loss temperatures (Tₜ) of 250 and 240 °C. For processing, both copolymers could be melt spun into monofilament fibres of uniform diameter and smooth surface appearance. The required oriented semi-crystalline morphology for use as a suture material was then built into the as-spun fibres via a series of controlled off-line annealing and hot-drawing steps resulting in tensile strengths in the region of 200-400 MPa.

References
Development and Characterization of Polyurethane Coatings for Enhanced Anti-Corrosive Properties

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Around 90% of the polyols used for in production of polyurethanes currently are based on polyethers obtained from ethylene and propylene oxides. Vegetable oils also produce green polyols.

Polyols from palm oil and palm kernel oil were explored for functional polymeric materials such as epoxy, polyesteramide, alkyd and polyurethane.

Polyurethane coatings were extensively investigated for comparative functional properties. EIS analysis of the polyurethane coated steel samples was performed for corrosion resistance analysis. Nyquist and Bode plots were estimated for degradation. Adhesion of the coatings to the metallic substrates was investigated.

Also, few interesting observations regarding the comparative coating behavior on carbon steel and galvanized steel substrates are reported in this paper.
Organic semiconductors are increasingly promising for next generation electronic devices. Owing to the possibility of solution based fabrication, the organic semiconductors can be inexpensively deposited on large-scale, and flexible substrates. The benefits of solution based deposition, however, comes with the challenge of controlling the nanostructure. Since the electronic transport properties of organic semiconductors are strongly linked to both the chemical composition and local microstructure it is desired to use techniques that provide information on both of these attributes and therefore there is a great need for complementary characterization tools. Here, we present two advanced instruments to fully characterize organic semiconducting materials on the nano-scale: NanoXAS and PolLux.

The NanoXAS instrument combines two powerful techniques, scanning probe microscopy (SPM) and scanning transmission x-ray microscopy (STXM) [1]. On one hand, the SPM can measure physical properties such as sample topography, elasticity, adhesion, friction, with nanometer resolution. Meanwhile, STXM provides quantification of the local elemental and chemical composition, as well as molecular orientation and order. Because of the coaxial design of the instrument, several detection modes can be utilized simultaneously in order to correlate various materials properties in heterogeneous samples down to the nanoscale and nanometrology (e.g. absolute density).

PolLux is a standalone STXM with an emphasis on resolution (down to ~20 nm at the carbon K-edge) and high throughput, while also providing the flexibility to incorporate user-designed environmental cells and other custom instrumentation.

To demonstrate the functionality of these instruments we present some example measurements on polymers, polymer blends, and patterned nanostructures.

References
Acrylic acid free radical polymerization in aqueous solution was studied using a new experimental setup coupling Raman spectroscopy and flow rheology in a Couette-like geometry (Fig. 1). In situ monitoring of polymer concentration and viscosity of reaction medium versus time was carried out, for different reactant concentrations (acrylic acid and initiator) and process conditions (temperature and shear rate). Experimental variations of polymer concentration and reaction medium viscosity before the occurrence of gel effect as a function of reactant concentration and process conditions were obtained. An overall model combining kinetic scheme and rheological equation was proposed. The kinetic and rheological parameters of the model will be discussed. The ability of this coupled system to highlight gel effect will be shown. These lab-scale data provided experimental and theoretical bases for process scale up to pilot-scale plant.

**Figure 1:** RheoRaman setup


129Xe NMR Studies of Pecan Shell-Based Biochar and Structure-Process Correlations

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Pecan shell-based biochar has been used as filtration medium, sequestrant for metallic ions, soil conditioner, and other applications. One process involves the use of phosphoric acid at higher temperature in partial oxygen to produce a highly porous carbonaceous material. In this work, we found 129Xe NMR to be an excellent technique to study pore volumes in biochar and complement CO2 and N2 porosimetry data. The NMR signal associated with confined xenon is intense in most samples, and its extrapolation to zero pressure indicates [1] a pore size of about 9 Å practically irrespective of treatment details. The 129Xe chemical shift at a given pressure is not strongly correlated to total pore volume. Thus, the pores with confined xenon are increasing in quantity and not in size as a function of treatment.

![Figure 1: 129Xe NMR of pecan shell biochar prepared with high oxygen flow. On the left, 2D-EXSY with 100 ms exchange time. On the right, saturation recovery of the peaks associated to free and confined gas.](image)

2D Exchange Spectroscopy (EXSY) directly detected only minimal exchange between free and confined xenon, and only in the lower chemical shift region of the very wide peak between 100 and 150 ppm. The intensity and the asymmetric shape of the 2D peak suggest that most of the gas undergoes a complex exchange pattern between different populations of confining pores [2]. The relaxation time values of the two peaks are quite similar, and far from the value usually associated with free xenon gas (tens of seconds). Thus, most of the gas is adsorbed strongly, and a small percentage of wider pores exchange with the free gas within the set time (100 ms in Figure 1).

References
How to characterize a vinylmelamine-ethylene-copolymer?
Results and new issues

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A method for increasing the flame resistance of polymers is to add nitrogen compounds (e.g. melamine, melamine-cyanurate [1], trihydrazinotriazine [2] etc.). In most of these well-known applications the principle is first to polymerize and then to add the nitrogen component e.g. in a compounding step. The disadvantage of this method in case of melamine is that it partly migrates to the surface during the process. Melamine-cyanurate tends to sublimate during the incorporation into a polymer, which means the polymer foams and the bulk density is reduced. To avoid the aforementioned problems we have tried to incorporate a melamine based flame retardant via copolymerization, thus affording a chemically homogeneous system.

We have found that methylmelamines can readily be vinylated and thus can be used as monomers in several polymerization and copolymerization reactions. A selection of these, especially pentamethylvinylmelamine (PMMv), tetramethyldivinylmelamine (TMMvv), and trimethyltrivinylmelamine (TriMMvvv), were prepared with very high purity to be used in the copolymerization with ethylene.

![Figure 1: Used vinylmelamine derivatives](image)

The different vinylmelamine derivatives were directly copolymerized with ethylene varying parameters such as catalyst, temperature, solvent, and reaction time.

Different methods for the characterization of these new polymer products were applied. The nitrogen content of the solid products was determined with elemental analysis (CHN). However the problem is that the new copolymer is not soluble in any solvents. This makes the further characterization of the copolymers difficult. Remaining methods such as FTIR, solid state NMR, and analytical pyrolysis were applied and the results are presented.

References
Kinetic study of the crystallization of LLDPE and wax in LLDPE/wax phase-change blends used for thermal energy storage

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The purpose of this research is to study self-nucleation (SN), SSA thermal fractionation, isothermal crystallization kinetics and the morphology of each of the constituents of LLDPE/wax blends as a function of composition. Wax is a phase change material (PCM) which stores and releases energy through melting and solidification. SN was performed in order to determine the ideal self-nucleation temperature ($T_{s(\text{ideal})}$) for thermal fractionation, which is the temperature that causes maximum SN without any annealing. It was performed on pure LLDPE, since this is the blend component that melts at a higher temperature ($T_m = 124 \, ^\circ\text{C}$). For this particular LLDPE $T_{s(\text{ideal})}$ was 123 °C. Thermal fractionation was performed using successive self-nucleation and annealing (SSA) in order to observe whether there is possible co-crystallization or phase segregation between the components in the blend. SSA is very sensitive to branches or any other defect that interrupts the methylene linear sequence which crystallizes. The alpha olefin in LLDPE is a defect since it introduces a branch point, and we observed several melting peaks after thermal fractionation. Soft paraffin wax is made of a polydisperse collection of linear chains. It is not sensitive to fractionation, since the technique and especially the fractionation conditions are rather insensitive to molecular weight differences. This is an indication that soft paraffin wax is essentially linear and is not susceptible to thermal fractionation. The results obtained by SSA indicate that the wax acts as a solvent for LLDPE inducing a ‘dilution effect’ without co-crystallization. This presentation will further report on the results of the crystallization kinetics and morphology studies of this system.
Crystallization monitoring of PVDF α-phase and β-phase by Raman spectroscopy and DSC analysis.

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Polyvinylidene fluoride (PVDF) is an ideal polymer for the protection of photovoltaic cells due to its UV stability and its resistance to the outside conditions. It has a semi-crystalline structure which can take several forms depending on the manufacturing process. The two main forms are α (TGG’ configuration) and β (all-TTT configuration) phases. These two forms can coexist and govern the physical properties of the polymer.

We propose through this study to understand the mechanism of crystallization of these coexisting phases. In one hand, we studied the crystallization of PVDF films during the blown extrusion process by on-line Raman spectroscopy. In the second hand, DSC study coupled with Raman spectroscopy was done to understand each stage of phase transition. For example, Figure 1 shows the evolution of crystalline spectral bands areas at 796cm$^{-1}$ (α-phase) and 840cm$^{-1}$ (β-phase) obtained by Raman spectroscopy during DSC analysis, from 20 to 220°C. Exothermic recrystallization which appears after the ageing peak, around 50°C, is entirely due to β-phase recrystallization. At 130°C, β-phase starts to melt, and immediately recrystallized into α-phase. Finally, disappearance of every crystalline phases is complete at 170°C, which is in total agreement with the DSC results.

Figure 1: Monitoring of α- and β phases of PVDF transition stage by DSC analysis coupled with Raman spectroscopy.

Thus, this coupled approach at the macro- (DSC analysis) and at the molecular scales (Raman spectroscopy) allow a better understanding of the crystallization processes in PVDF.

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Mesophase Formation in Propylene-co-1-Octene Copolymers Studied by 
Fast and Conventional DSC Techniques

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One of the topics in Polymer Science that is attracting a great interest is the structure development (or suppression) under very high cooling rates (more than about 10²-10³ °C/s), due to several reasons: i) the solidification process of polymers in typical processing conditions usually involves those very high cooling rates; ii) under such circumstances, far away from equilibrium conditions, metastable phases are often obtained. The analysis of these metastable entities under real-time conditions requires, first, the use of experimental set-ups able to permit (and control) those very high cooling rates, and second, detection systems fast enough to record the structure evolution. At present, the technique of Fast Scanning Calorimetry (FSC) is probably the best choice [1,2] allowing heating rates even above 40000 °C/s and cooling up to 4000 °C/s. It takes advantage of the use of very fast amplifiers together with rather reduced sample sizes, below the μg.

Polypropylene and its copolymers based on alpha-olefins lead, under appropriate cooling conditions, to mesophase formation. The main prerequisite for its development is the absence of crystallization. It has been demonstrated [2] that the formation rate of that mesophase in propylene-co-1-pentene copolymers can be easily tailored in a wide range covering two orders of magnitude, in such a way that the rates involved in the copolymer with highest comonomer content can be also analyzed by conventional techniques, namely DSC and real-time X-ray diffraction employing synchrotron radiation.

The aim of this investigation is, now, to find out possible differences arising from variation of length of the comonomer incorporated. Thus, the mesophase formation has been evaluated in random copolymers of iPP with 1-octene, covering a relatively broad range of compositions (up to 8.9 mol % 1-octene), using as tools the FSC technique together with conventional DSC and X-ray diffraction experiments [3]. These results are compared with those previously found in the copolymers with 1-pentene, showing both rather interesting differences and similarities. For instance, the decrease of the mesophase formation rate in these copolymers appears to be considerably higher than that described previously in propylene-co-1-pentene copolymers for the same comonomer content expressed as mol %.

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References
Characterization and properties of novel blends composed of nitrile butadiene rubber and in-situ synthesized thermoplastic polyurethane-urea

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The blending of conventional polymeric materials is an energy and cost effective route to obtain new materials with a useful combination of performance characteristics not available in individual polymers. In contrast to the conventional melt-and solvent-blending methods, the reactive-blending of thermoplastic polyurethane-urea (PUU) with nitrile butadiene rubber (NBR) is realized in this work. To follow this investigation, PUU was synthesized in-situ from its precursors during blending with NBR in an internal mixer to obtain a new kind of NBR/PUU blends. The structural characterizations of prepared blends via the Fourier transform infrared (FTIR) spectroscopy and Proton nuclear magnetic resonance (1H NMR) spectroscopy confirmed the in-situ synthesis of PUU during blending process. Importantly, the 1H NMR spectroscopic analysis shows up to 90% conversion of the precursor (chain extender) to an in-situ synthesized PUU during the reactive blending process. Blends up to 70/30 (NBR/PUU) weight ratio were prepared, structurally characterized and compounded with curatives on a two-roll mixing mill in order to vulcanize the rubber phase. The blend vulcanizates showed a remarkable improvement in stress-strain behaviour, hardness, tear strength, abrasion loss and dynamic-mechanical behaviour. Further structural and morphological characterization of the blend vulcanizates was followed by differential scanning calorimetry, x-ray analysis and transmission electron microscopy. Such blends can find cost-effective utilization in areas requiring high strength, tear and abrasion resistance like rubber rollers, industrial wheels, belting, pump impellers etc.
Nano-Handling of Individual Dendronized Polymers by Single-Molecule Force Spectroscopy

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The systematic studies of the mechanical response of individual polymers on the single-molecule level and their interaction with solid substrates are of vital importance for many applications in medicine or material sciences. Dendronized polymers (DP) with their dendritic structure provide a perfect tool to study a scaling behaviour with respect to the number of monomers in the side chain [1].

A novel atomic force microscopy nano-handling technique is presented that is capable of precise measuring of force-extension relations of individual polymer molecules. DPs of different generations were adsorbed on a chemically modified substrate and then imaged in solution. A single polymer chain was picked up with the AFM cantilever and the force curves were recorded by stretching an individual polymer molecule many times. The fact that one deals with one single molecule was verified by AFM imaging of the polymer chain in question before and after the nano-handling experiment.

The technique was used to study the mechanical response of amino-functionalized DPs that could be accurately described with the freely jointed chain model with a linear elasticity term. Monotonic dependence of mechanical properties of these polymers was found. The effective Kuhn length increased with generation at high salt concentrations and remained constant at low salt levels. The elastic constant was found to be independent of the generation and solution composition.

Figure 1: Principle of single-molecule nano-handling force experiments [2].

References
Characterization of diffusion processes in PVC films used in medical devices by coupling AFM to spectroscopy

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PVC is used in infusion sets that allow injecting drugs, nutriments or blood to patients and as the main constituent of drug blisters. In the infusion application, the migration of small molecules between the material and the liquid is a great health concern. PVC contains indeed additives and for the infusion application is soften by a plasticizer that can migrate in pharmaceutical formulations and act as a metabolic disrupter; moreover, the drug and the excipients of the formulation can sorb in the polymer matrix and this sorption can have dramatic consequences for the patient. In order to characterize the time scale of the diffusion processes and their impact on the surface, we combine chemical mapping by Raman microscopy, to AFM and AFM-IR. The impact of the plasticizer and of the liquid in contact was studied. We focused on a commercial device used to realize blood bags and infusion sets and that contain around 40% of DEHP plasticizer.

Figure 1: PVC film studied by NanoIR technology (@Anasys Instruments) : a) IR spectra corresponding to the two points on b) image. b) height image of the PVC film (contact mode) c) corresponding chemical mapping of the 1530 cm⁻¹ band absorbance revealing the presence of zinc stearate.
Several TD-NMR methods for polymer characterization

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Time domain nuclear magnetic resonance (TD-NMR) provides tools for highly precise polymer characterization. Different pulse sequences have been optimized to investigate several properties of systems as diverse as vulcanized elastomers [1], [2], innovative polymeric nanocontainers [3] and hyper cross-linked polymers [4].

By the application of sensitive double quantum (DQ) NMR technique, the network structure of vulcanized rubbers was precisely studied in terms of dipolar coupling constant and hence cross-link density. With higher precision than conventional swelling methods, we were able to appreciate even small variations in the network structure caused by over-curing reaction beyond optimum cure time (fig.1).

The performance of Magic Sandwich Echo (MSE) experiments at different temperatures allowed us to measure the rigid fraction of innovative PBA-PS core-shell nanoparticles of different size. Such measurements provided us a deep insight on their morphology and thus the mobility of the different polymer chains was successfully investigated.

The usage of T1 measurements allowed us to investigate the fundamental properties of pure polymers such as polystyrene and hypercross-linked polystyrene. In particular, we found out that the longitudinal relaxation time is strongly affected by the presence of a high density of cross-links (fig.2). Thus, the combined performance of T1 and MSE experiments gathered us a full understanding of the way cross-linking affects the temperature response of polymer mobility and relaxation properties.

References
A rule-of-mixtures approach is used with dynamic mechanical analysis (DMA) to determine the viscoelastic characteristics of individual layers of a fourth generation advanced magnetic tape used for archival storage. Such tapes are comprised of 3 bonded layers. The 0.92 μm thick front coat consists of magnetic particles held together with a poly(urethane) binder and other constituents. This front coat is applied to a 5.00 μm thick poly(ethylene naphthalate) substrate. Since the tape is wound in a reel for storage, a protective 0.64 μm thick back coat is applied to the underside of the substrate with cellulose nitrate as a constituent.

Prior work focused on creep characteristics of magnetic tapes as well as DMA measurements to characterize and understand their long-term viscoelastic properties [1,2]. This past work also included the use of rule-of-mixtures to successfully extract-out the creep characteristics of individual tape layers that cannot be measured in separate experiments [3,4]. The current work uses a similar rule-of-mixtures approach for DMA measurements to determine the storage modulus, loss modulus, and loss tangent for individual tape layers. Figure 1 provides an example for the loss modulus of the front coat as a function of temperature and frequency.

Since loss modulus represents energy dissipation, Figure 1 shows how the poly(urethane) binder contributes to viscoelastic deformation of the front coat, which in-turn contributes to bulk movement of the magnetic particles held together by the binder, and potential inability to retrieve information archived on the tape.

References
Doping polymer electrolyte membranes with ionic liquids: from the microstructure to advanced functional properties

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Optimizing the ionic transport efficiency of advanced electrochemical devices is an actual target regarding the societal demand of fossil-free clean-energy, such that it is crucial to promote the design of optimized nanostructured electrolytes for next-generation fuel cells. The Perfluorosulfonic Acid (PFSA) ionomers are the benchmark polymer electrolyte membranes used in Proton Exchange Membrane Fuel Cells (PEMFC) thanks to their excellent chemical and electrochemical stability, and high proton conductivity in hydrated states. These membranes are constituted of a Teflon-like backbone with grafted long-side or short-side chains terminated by sulfonic acid groups. The functional properties are largely determined by the phase-separation at nanoscale originating from this hydrophobic and hydrophilic character. However, the PFSA membranes suffer from severe limitations due mainly to their cost and limited operating temperatures (below 80°C). As most of the applications would benefit from a significant increase in the temperature range of operation (typically 120°C), alternative membranes based on sulfonated polyaromatic and fluoropolymer materials or inorganic-organic hybrid membranes have been extensively studied during the last 20 years. Yet, either these approaches correspond to incremental improvements, either the benefit in increasing the operating temperature is generally obtained at the expense of proton conductivity. The use of proton conducting ionic liquids (PCILs) as dopants and non-aqueous proton conducting medium has been considered as a new promising route. Trialkylammonium triflate salts (TF-TEA) are proton conductors that can be introduced in a polymer matrix. The resulting polymer electrolyte has been proven to be of interest for fuel cells [1]. However, the proton conductivity is still limited even at elevated temperatures except in the presence of sufficient amount of water. A high level of proton conductivity requires a huge doping level at the expense of the mechanical properties at elevated temperatures, and PCILs could elute from the membrane under the operating conditions of a fuel cell. The use of highly hydrophobic PCILs such as PerfluoroButaneSulfonic-TEA and PerfluoroOctaneSulfonic-TEA could avoid this expected drawback. We present here a comprehensive structural study by Small Angle Neutron Scattering of the microstructure of hybrid proton conducting ionic liquid (PCIL) Nafion membranes, carefully designed by solution-casting [2]. The hybrid PCIL-Nafion membranes appear to be promising materials for advanced anhydrous high temperature fuel cell technologies.


Preparation PBI composites of Fe$_3$O$_4$ and NiFe$_2$O$_4$ nanoparticle with ionic liquid and electrical conductivity

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NiFe$_2$O$_4$ and Fe$_3$O$_4$ nano composites were prepared by the hydrothermal method using cetyl trimethylammonium bromide (CTAB) as surfactant. And these nanoparticles were coated with Polybenzimidazole (PBI) in situ polymerization with water/ ionic liquid (1-butyl-3-methyl-imidazolium bromide [BMIM]Br) via [1]. Polybenzimidazole without catalyst at a low temperature in the presence of the ionic liquid and nanoparticles was obtained from polycondensation reactions of hydroxamoyl chloride with 3,3'-Diaminobenzidine monomers [2,3]. The nanoparticles have been characterized by the XRD analyses and FT-IR measurements and proved the presence of polybenzimidazole layer on the surface of NiFe$_2$O$_4$ and Fe$_3$O$_4$ nanoparticles. The influence of 1-butyl-3-methyl-imidazolium bromide [BMIM]Br as ionic liquid (IL) on the structure, electrical conductivity of polybenzimidazole-NiFe$_2$O$_4$-IL nanocomposite were studied. Nanocomposite structures were illuminated with SEM, FT-IR and XRD analysis.

Keywords: polybenzimidazole, nanocomposite, ionic liquid

![Figure 1: FT-IR spectrums of CTAB, NiFe$_2$O$_4$, NiFe$_2$O$_4$/CTAB, NiFe$_2$O$_4$/CTAB/IL/PBI](attachment:figure1.png)

References
Deep eutectic ionic liquids as epoxy resin curing catalysts

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Molecular ionic liquids (ILs) composed of anions and cations have found broad and still widening applications. Also in a field of polymeric materials as epoxy resin catalytic curing agents [1]. Other group of ILs, i.e. deep eutectic solvents (DES) [2] based on a mixture of ammonium salts, e.g. choline chloride (ChCl), and hydrogen donor compounds (commonly with CONH₂, COOH or OH groups) was developed. The first trials of using DES as epoxy resin curing agents have recently been reported [3,4]. This contribution presents the first systematic study of DESs usage for epoxy resin crosslinking as well as the properties of the cured epoxy materials.

Three DESs based on ChCl (2-hydroxyethyltrimethylammonium chloride) and urea (U), or guanidine thiocyanate (GTC) or 1-(o-tolyl)biguanide (TBG) with molar ratios of the both components 1:2 have been investigated as epoxy resin curing catalysts. Thermomechanical as well as thermal stability properties of cured epoxy materials were evaluated. Beside ChCl/U DESs mentioned above have not yet been described in literature. The melting points of prepared DESs (determined by DSC) were: 16, 18 and 78°C for ChCl/U, ChCl/GTC and ChCl/TBG, respectively. Epoxy compositions based on liquid epoxy resin bisphenol A type (Epidian 6, Z.Ch. Organika-Sarzyna, Poland) and the mentioned DESs were prepared in four weight ratios (3, 4.5, 6 and 9 parts per 100 parts of epoxy resin, phr) of the components.

Pot lives and curing kinetics have been investigated using rheometry (ARES, Rheometric Scientific) and DSC (Q-100, TA Instruments). Thermomechanical properties of the cured epoxy materials (glass transition temperature, tan delta, and storage modulus) have been determined using DMA (Q-800, TA) and thermal stability by TGA (Q-5000, TA).

On a basis of performed investigations the following conclusions can be withdrawn: (i) epoxy compositions with DES exhibited pot lives from 10 to above 85 days at ambient temperature, (ii) TBG – based systems were the most reactive whereas those with U exhibited the lowest reactivity at room temperature, (iii) the beginning of epoxy curing reaction at dynamic temperature increase (5°C/min) is dependent on DES type, its increasing content and changed in a sequence: 150→135°C (ChCl/GTC), 210→170°C (ChCl/TBG) and 245→185°C (ChCl/U), for 3→9 phr DES, respectively. Tg values for epoxy materials cured with 9 phr of DESs decreased in the following order: TBG: 143°C > U: 136°C > GTC: 127°C. Thermal stability of epoxy materials (expressed as 5% mass losses) decreased in the order: TBG: 338°C > GTC: 317°C > U: 306°C.

In conclusion DES can be used as cheap and environmentally safe latent catalysts for epoxy resin curing at elevated temperatures.

References
Compatibilization of polypropylene/polyamide 6 blends using an ionic liquids/nanotalc combination

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For several years, many works have demonstrated the potential of nanoparticles, especially organically modified clays (organoclays), as compatibilizing agent for several types of immiscible polymer blends such as PP/PA [1], PET/PE [2] and PC/PMMA [3]. Unfortunately, the majority of the commercially available organoclay used for the compatibilization of polymer blends are not thermally stable and their organo-modifiers degrade easily when used as interfacial agents for polymers exhibiting a high temperature of transformation [4]. For overcome these limitations, ionic liquids have been widely used for this purpose. Due to their thermal stability, non-combustibility, low volatility and other specific properties, they are widely used as modifier agents of layered silicates leading to a better dispersion of clay in the polymer matrix generally coupled with an increase of the final properties, especially thermal and mechanical properties of polymeric materials [5]. Therefore, our approach is to present the ability of using ionic liquids (ILs) to act as new processing aids of PP/PA6 blends filled with 4wt% of nanotalc prepared by extrusion. Ionic liquids based on phosphonium cations but differing by the polarity of their counteranions were introduced at various concentrations (1, 5 and 10wt\%) in the polymer blend. The synergistic effect induced by simultaneous presence of ionic liquids and nanotalc on the morphology, crystallization behaviour, thermal and mechanical properties of blends has been studied. It shows that the addition of only 1 wt\% of ionic liquids induces a significant decrease of the size of the dispersed polymer phase (PA6 droplets) from 27 µm for the virgin binary PP/PA6 blends to less than 1 µm for PP/PA6/nanotalc/ILs quaternary blends. It is also revealed that the final properties of the blends depend strongly on the polarity and concentration of ionic liquids. When the anion is more hydrophilic, the compatibilization effect is more efficient as revealed by TEM microanalysis. The thermal stability of PP/PA6 blends is also enhanced in the simultaneous presence of ionic liquids and nanotalc in the blend, and depends on the amount of ILs introduced. The stiffness of the blends was significantly improved in the presence of nanotalc/ionic liquid pair without reducing the elongation at break.

References
The study of physicochemical properties of polymer materials has been the subject of much academic and industrial research. Many experimental techniques have been used to determine the physicochemical properties of polymers and polymer blends. Among them, inverse gas chromatography (IGC) has been successfully demonstrated as promising technique and effective tool to investigate the thermodynamic and surface properties of materials such as polymers, pharmaceutical products and organic pollutants [1,2].

Our aim in this contribution is to study the miscibility and carried out a thermodynamic properties of poly (vinylphenol) (PVPh), poly(vinylmethylketone) (PVMK) and their blends using inverse gas chromatography, (IGC). Moreover, our interest is particularly focused on looking for correlation between the observed phase behavior and the obtained thermodynamic parameters such as polymer-polymer interaction parameter ($\chi_{23}$).

Firstly, we have analysed, the phase behavior and miscibility of PVPh/PVMK system, using the following expression:

$$V_{g,blend}^{blend} = w_2 V_{g,2}^{0} + w_3 V_{g,3}^{0}$$

where $w_i$ refers to the weight fraction of each polymer in blend of PVPh/PVMK. The specific retention volumes of the two corresponding polymers and their blends were measured in the temperature range 120-140 °C when the thermodynamic equilibrium was achieved. As displayed in figure (1), the plot of experimental specific retention volumes of the blend as function of PVPh weight fraction, obtained with all probes used, gives a concave, which the negative deviation from the additivity rule can be observed. Thus, the negative values of $\chi_{23}$ obtained for all compositions range is indicative that the different blends are completely miscible and in good agreement with those we have concluded recently by DSC and FTIR.

The maximum of these interactions was observed with blend PVPh/PVMK in ratio (1/3).

![Figure 1: LnVg –composition of PVPh/PVMK using seven probes at 130 °C.](image)

References

Influence of isomeric monomers on the fragmentation of polymers

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At this time one of the most efficient methods for the mass determination of intact polymers is the MALDI-TOF-MS. But only the masses of individual chains, their repeating units and the respective endgroups are available, and no information about the structure of the constituting monomers and end groups can be gained. To get these informations, collision induced dissociation (CID) can be used. In this case, the MALDI-TOF-MS is equipped with a collision gas cell, in which selected compounds are fragmented depending on their structural elements.

The present contribution investigates the influence of the difference in the configuration of the constituting monomers (e.g. poly(isoprene-1,4) vs. poly(isoprene-3,4)). Furthermore the influence of isomeric monomers (e.g poly(n-butylmethacrylate) vs. poly(t-butylmethacrylate)) is studied. Differences between the resulting fragmentation patterns can be found.

Figure 1: MALDI-CID spectra of Polyisoprene 1,4 and Polyisoprene-3,4. The highlighted mass range shows the most prominent difference between the two spectra.
Morphology and rheology of binary blend of polypropylene and polyamide6: influence of multiwall carbon nanotubes

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50/50 (wt/wt) blend of polypropylene (PP) and polyamide6 (PA6) were melt-mixed at 260 °C with multiwall carbon nanotubes (MWNTs) in a twin-screw micro-compounder in an intention to develop conducting composites. During melt-mixing, two different processing protocols, viz., simultaneous mixing and sequential mixing strategy were adopted to investigate the extent of MWNTs dispersion in the constituent phases. During sequential mixing, PP was melt-mixed with MWNTs initially for 10 min followed by the addition of PA6 for 5 min. The same composition was also prepared by melt-mixing PA6 with MWNTs initially for 10 min followed by the addition of PP for 5min. It has observed that the processing protocol is significantly influencing the localization of MWNTs in the respective phases, which manifest in the variation in morphology and rheological behaviour. It is also noticed that ‘filler-filler’ interaction dominates in the PP phase, which leads to significantly higher complex viscosity at low frequency. However, ‘polymer-filler’ interaction is dominant over ‘filler-filler interaction’ in the PA6 phase. This behaviour leads to a difference in the relaxation mode. Along with changed rheological behaviour, the ligament size of the co-continuous phase was decreased in presence MWNTs. Transmission electron microscopic analysis was carried out to investigate the localization and redistribution of MWNTs during melt-mixing. The DC electrical conductivity has been influenced by the varying processing protocol and PP based sequence has shown a significantly higher DC electrical conductivity as compared to any other blending sequence. Further, the role of novel organic modifier (Li-salt of 6-amino hexanoic acid, Li-AHA) in combination with a reactive compatibilizer (PP-g-maleic anhydride) was also exploited to investigate the rheology, morphology and the electrical conductivity of the composites. An attempt has been made to correlate structure-property relationship studies in these blends.
Processable Crosslinked Epoxidized Natural Rubber

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The rubber industry faces a major problem due to the irreversibility of the crosslinked networks, which prevents the reshaping or recycling of rubbery objects. Here, we used the disulfide metathesis reaction to create a dynamic reversible covalent network in Epoxidized Natural Rubber (ENR). ENR is a unique elastomer retaining most of the properties of natural rubber from which it derives, in particular high tensile properties and resistance to crack propagation up to 50 mol% epoxidation. Our group recently showed that ENR can be efficiently crosslinked by dicarboxylic acids [1-2]. The disulfide function was thus introduced in the rubber through the crosslinking of ENR by dithiodibutyric acid (shown on Figure 1.)

![Figure 1: Dithiodibutyric acid](image)

Disulfide metathesis was already used to produce self-healing materials [3-5]. The use of these materials is yet limited because they rearrange at room temperature, meaning that they will “flow” under stress at very long times. Here, the processable properties are triggered by a physical stimulus which permits to have a real rubber below the metathesis temperature. Indeed, this new chemically crosslinked rubber is shown to behave like a classic rubber at room temperature but to become processable above 150°C. Above the metathesis temperature, it undergoes a significant stress relaxation, it is mendable, and it “flows”, enabling it to be reshaped. We rebuilt a new sample from a grinded crosslinked ENR by pressing the rubber powder at 150°C for less than one hour. This material recovers about 50% of its initial properties (stress and strain at break) as shown on Figure 2.

![Figure 2: The rubber is repaired by heat treatment after grinding of a cured sample](image)

References
Conjugation of water-insoluble natural anti-cancer drugs to macromolecular polymers can lead to improved pharmaceutical properties and improved drug efficiency due to accumulation of the polymer–drug conjugate in tumor tissue through the enhanced permeability and retention (EPR).[1,2]. Pharmaceutical shortcomings of betulinic acid (BA) including relatively short half-life and low bioavailability, as a result of its poor solubility in solution and blood and an initial burst release effect and high peak plasma concentration from its rapid metabolism. Linear PEG is the most widely used for its simple synthetic steps and good water solubility. But the limitation of this system is its low drug loading capability[3]. To overcome this hurdle, we now report a water-soluble multiarm-polyethylene glycol–betulinic acid (PEG–BA) that produces high drug loading, significantly improved water solubility(Figure 1 C). The PEG-BA conjugates have shown excellent in vitro anticancer activity (Figure 1 F), with potency similar to that of native BA. These results strongly supported the notion that PEG-BA conjugate is a promising candidate as a prodrug of BA for cancer therapy.

Figure 1: (A) Experimental design of 8arm-PEG-BA. (B) Synthesis of multiarm-PEG-BA. (C) BA and 8arm-PEG80K-BA in different solutions. (D) Absorbance spectrum of BA and multiarm-PEG-BA conjugates in UV-Vis buffer. (E) Cell viability of A549 cells treated with 500 μg /ml of DH and PEG-BA (equivalent to native BA) was measured by CCK-8 assay. (F) Cell viability of A549 cells treated with different concentration of DH and PEG-BA was measured by CCK-8 assay.

References
Microstructural analysis of electrospun thermoplastic polyurethane nanofibers during heating

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Microstructural evolution as a function of temperature of electrospun thermoplastic polyurethane (TPU) nanofibers has been studied. At room temperature (glass transition temperature ~ -50°C), the as-spun nanofibers do not relax spontaneously although being far from equilibrium state.[1] FTIR analysis of the fibers showed that hard and soft segments are mixed and hydrogen bonded which reveals a pronounced effect on soft segment mobility. Upon heating the as-spun nanofibers, macroscopic contraction (negative strain up to 50%) was observed. Concurrently SAXS measurements of the nanofibers microstructure showed increase in the longer period length (formed by alternating sequences of hard and soft segments), while Guinier’s approximation showed decrease of radial size of scattering elements upon heating, namely the size of the ordered non-crystalline hard segments clusters is reduced. These observations, together with mechanical measurements, suggest that upon heating the destruction of non-crystalline hard segment clusters accompanied with increasing the effective length of the tie chains. Thus, above a certain temperature (60°C) structure relaxation takes place when a portion of the hard segment clusters, forming an effective physical network is destroyed resulting in massive contraction of the electrospun fibers.

Figure 1: Strain vs. time of electrospun fiber mats recorded at different isothermal conditions. For example, fiber mat sample that heated up to 40°C from room temperature at 1°C/min is labelled as ‘40°C’. Note that the onset of contraction for all samples is about 60°C.

References
Solvent effect on fabrication of PVP/PBI and PS/PBI nanofibers

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The Polybenzimidazoles (PBI) were prepared from polycondensation of hydroxamoyl chloride with 3,3'-diamino benzidine in the medium DMF at 150°C not being used catalyze [1, 2]. In 1961, Vogel and Marvel found that the molecular weights of PBIs with an inherent viscosity of 0.8 dL / g were about 54,000, this means that the molecular weights of the polymers were much higher then [3]. Synthesized sequence of polybenzimidazole PVP / PBI (4:1 ratio) in DMF, PVP / PBI (4:1 ratio) in DMF-DMAc and PSI / PB (4:1 ratio) in THF the dispersion solutions were prepared. Analyzing SEM, electrospun fiber structures on the surface properties of the coating due to the solvent effect, and differences in the fiber diameter were observed. SEM analysis has shown that the most uniform fiber structure of 150 nm thickness (DMF - DMAc) PVP / PBI solution, and the fibers obtained from 350 nm thick (DMF - THF) PS / PBI solution. SEM and FT-IR analysis of the fibers were analyzed.

**Keywords:** Polybenzimidazole, nanofibers, electrical conductivity

![SEM image of PVP / PBI in DMF, PVP / PBI in DMF-DMAc, PS / PBI in DMF-THF](image)

**Figure 1:** SEM image of a) PVP / PBI in DMF b) PVP / PBI in DMF-DMAc c) PS / PBI in DMF-THF

**References**

Phase change materials (PCMs) are popular among energy storage materials due to their high energy storage density and small temperature variations during storage and evolution [1]. The use of PCMs for energy storage has received great attention in recent years due to increasing energy consumption and environment pollution problems. Many researchers and companies have studied PCMs for applications in solar energy storage [2], smart housing [3], thermo-regulated fibres, fabrics, coatings and foams [4].

In this study, poly(stearyl acrylate/methacrylate) homopolymers were produced with atom transfer radical polymerization (ATRP) method from stearyl acrylate/methacrylate monomers in different polymerization times. The produced homopolymers were characterized structurally and thermally. Fourier transform-infrared (FT-IR) and proton nuclear magnetic resonance (1H-NMR) spectroscopy techniques were used for structural characterization, phase transition temperatures, enthalpies, and thermal stability of synthesized polymers were determined using differential scanning calorimetry (DSC) and thermogravimetric analyses instrument (TGA). Molecular weight measurements were done using gel permeation chromatography (GPC).

The average melting and freezing temperatures of the poly(stearyl acrylate) and poly(stearyl methacrylate) were 48.11-43.51 °C and 30.79-23.46 °C respectively as the average of latent heats of melting and crystallization were 100.15-(81.45) and 55.81-(44.75) J/g respectively. Besides produced poly(steayl acrylate) and poly(steayl methacrylate) are resistant to degradation up to 280-118 °C respectively. Number average molecular weights synthesized polymers ranges from 1.1x10⁶ to 9.5x10⁶ g/mol. Based on the results, it can be considered that the poly(stearyl acrylate/methacrylate) polymers have good energy storage potential.

References

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Polyethylene is one of the most important commodity polymers produced worldwide. High Density Polyethylene (HDPE) is produced using one reactor system to multi-stage reactor system to modify the properties of the polymer based on its intended application [1]. The high pressure pipe application require a good combination of high molecular weight fraction as well as low molecular weight fraction with a combination of a number of comonomer chain branching to enhance the mechanical and environmental characteristics of the pipe [2].

In this study, we have analysed samples produced in different stages of a three-stage slurry reactor system in a commercial scales polyethylene plant. Analysing the samples using Gel Permeation Chromatography (GPC) technique showed the increase in the molecular weight and chain length in different stages of the polymerisation reaction. We then expanded the study to investigate the characteristic of different PE produced. The GPC reported different molecular weight distribution for different samples and was correlated with various properties of the sample such as rheological and environmental properties.

The study shows development of molecular weight of the polymer in various reactors. It also highlights the effect of the molecular weight and its distribution on thermal and viscosity behaviour of the material.

References
Poster Presentation Abstracts
Many reports on cassava starch composite film exist in literature. As cocoyam and cassava have comparable physico-chemical and mechanical properties, therefore cocoyam starch is a good candidate to be used for preparing biocomposite films with similar characteristics as cassava starch based films. So, we designed, prepared and characterized similar biofilms with cocoyam starch on the basis of what is made with cassava starch.

Starch extracted from white cocoyam (Colocasia esculenta) grown in Cameroon (Bafia district) was submitted to different tests. The main physico-chemical properties were determined: granule morphology (with a SEM), pasting characteristics (with a Brabender viscoamylograph), swelling power and solubility, while rheological properties were determined using a controlled stress rheometer (AR 2000, TA Instruments Ltd).

The main disadvantages of biodegradable starch in general, compared to conventional polymers, are their hydrophilic character and their poor mechanical properties which lead to low stability. In order to decrease the hydrophilicity and to stabilize the mechanical properties of the films, we incorporated bi-dimensional (2D) and tri-dimensional (3D) mineral fillers, beidellite-Na and zeolite respectively into starch matrix. The 2D and 3D fillers were synthesized using hydrothermal route from known protocols. Part of zeolite colloidal suspension was lyophilized and the other one kept and used as the reinforcing phase.

Two types of starch based films were studied: Plasticized starch based films and Reinforced plasticized starch based films. Films were plasticized at different glycerol, the plasticizer used in this study, contents (30, 35, 40 and 45 % on dry starch basis). Film moisture content, film solubility in water and water vapor permeability (WVP) of films increased with glycerol content. The films were less resistant to water when containing more plasticizer. Films’ mechanical properties were strongly influenced by glycerol content. In fact, the incorporation of glycerol into the macromolecular starch chains leads to an increase of free volume and chain mobility, and decrease of films’ mechanical resistance and an increase of films’ extensibility, as well.

Cocoyam starch based films containing 30 % of glycerol, were reinforced by: Na-beidellite particles, lyophilized and non lyophilized zeolite Beta nanoparticles at 1, 2 and 4 wt% content, respectively. Compared to neat film the WVP of films reinforced by Na-beidellite and lyophilized zeolite Beta nanocrystals decreased of 30 % and 21 % respectively. Nanocomposite films reinforced with lyophilized zeolite Beta have shown a drastic increase, up to 70 %, of their mechanical properties, especially in the Young’s modulus.

An illustration and an interpretation of these results will be proposed in this contribution.
Poly(lactic acid) (PLA) displays attractive properties such as being biodegradable, biobased and biocompatible. Nevertheless PLA suffers some drawbacks: it has a low melt strength, it has a poor toughness and it has a lack of reactive side-groups. To counteract some of its disadvantages it may be beneficial to introduce branching.

Knauss et al. used glycidol as an inimer to accomplish branched PLA.[1] They showed that tin octoate (Sn(Oct)$_2$) could be used to catalyze the ring opening polymerization of both lactide and glycidol at a sufficiently high temperature (> 100 °C). It may be anticipated that 3-methyl-3-(hydroxymethyl)oxetane (MHO) could be used in a similar way. MHO is less toxic than glycidol, due to its weaker alkylating reactivity, and hence its use could be more compatible with biomedical applications of the resulting products.

MHO can be homopolymerized via an anionic or a cationic pathway. Common initiators for this ring opening polymerization (ROP) are NaH, BF$_3$.Et$_2$O and CF$_3$SO$_3$H.[2] In this work the ring opening copolymerization of MHO and lactide was performed using these initiators to synthesize branched PLA.

A linear PLA macromonomer was first synthesized using MHO as initiator (rather than as inimer) and Sn(Oct)$_2$ as catalyst. A subsequent ring opening of the oxetane-unit yielded a branched PLA polymer. Branched PLA was also synthesized in one step using a ring opening copolymerization of lactide and MHO (Fig.1).

![Possible pathways to branched PLA using MHO.](image_url)

**Fig.1:** Possible pathways to branched PLA using MHO.

**References**

High Throughput Experimentation in Rotational Rheology for Polymer Melts Applications

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Thorough knowledge of physical and chemical material properties is crucial for new product developments. Using conventional material research, limited research data on material characterization delivers limited answers to interesting research questions. In the field of Rheometry, High Throughput (HT) solutions exist for samples ranging from low viscosity liquids to paste like materials. However, the huge group of melts is still excluded from automation due to high temperature requirements as well as difficult sample application and cleaning. In this research, we demonstrate a novel HT solution for rheological polymer melt applications.

The HT solution has the comparability to conventional rheometers while meeting throughput demands for Design of Experiments. The development of an automation solution around a conventional rheometer offers flexibility and assures high reproducibility. The measurements are executed in a robotic cell featuring a fully automated rotational rheometer. Cold solid polymer discs are stored in a tray inside the robot cell. After measuring geometries have been preheated to ~200°C, the robot inserts the polymer discs into the rheometer with a high-temperature vacuum gripper. A specifically designed rotational blade automatically trims the melted polymer disc. In HT approaches for liquids and paste-like samples, the upper and lower geometries are removed and cleaned separately after the measurement. Polymer melts would pull strings throughout the entire cell, hence they have to be removed from the rheometer together at the same time. This problem is solved with a combined gripper tool, which can be used to load the rheometer separately but unload the whole stack of lower geometry, sample and upper geometry all at once.

Automated rheology has proven to be a very useful tool which helps companies to compete in modern material research. Rheological information is gained 24 hours a day, 7 days a week and is immediately available for research. The presented developments for polymer melt applications will support future material explorations in the polymer industry.
Degradation of polylactide (PLA) has been discussed in details in the literature [1, 2]. It depends on several factors such as molecular weight, temperature, pH, reactive end groups, unreacted monomer and impurities present. Various degradation mechanisms including random chain scissions, depolymerization, oxidative degradation, intramolecular and intermolecular trans-esterifications, cis-elimination, hydrolysis and radical reactions have been postulated in the literature.

Direct pyrolysis mass spectrometry analysis of PLA indicated that the amount of sample pyrolyzed affects the product distribution; as the amount of sample increases the yield of cyclic oligomers also increases due to the higher probability of the intermolecular trans-esterification reactions. The effect is more significant for DL isomer compared to L isomer. The single ion evolution profiles of diagnostic products generated by cis-elimination and trans-esterification reactions generated during the pyrolysis of 1 and 5 µg of PLLA are shown in Figure 1.

Figure 1: Single ion evolution profiles of characteristic products of PLLA recorded during the pyrolysis of a) 1µg and b) 5µg of PLLA

References
Antimicrobial Properties Of Poly (ε-Caprolactone) / Poly (Lactic Acid)/Silver Exchanged Montmorillonite Nanobioblends

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For many years silver and silver salts have been used as antimicrobial agents. Silver and other metals have been shown to provide antimicrobial behavior even in minute quantities, a property referred to as “oligo-dynamic”. This study reports on the formulation of nanobioblends based on poly (ε-caprolactone) PCL, poly (lactic acid) PLA and silver-exchanged Algerian montmorillonite prepared via solution intercalation method. Morphology, thermal and water barrier properties of the resultant materials were examined using various analytical methods. The antibacterial performance of PCL/PLA/Ag-MMT nanobioblends films against S.aureus, E.coli, Salmonella and P. aeruginosa was assessed by counting the number of bacteria in samples. These nanobiomaterials exhibit a significant effect to inhibit the growth of bacteria on surface by silver nanoparticles. Indeed, a maximum of 100 % of growth inhibition can be reached when 5 wt % of Ag-MMT are added to the PCL/PLA blends (Fig.1).

Figure 1: Growth of salmonella bacteria in the presence of PCL/PLA (50/50) bioblend and its PCL/PLA/Ag-MMT (22.5/22.5/5) nanobioblend.
Influence of isomeric end groups on the fragmentation of poly(lactide)

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MALDI-TOF-MS combined with collision induced dissociation (CID) offers the possibility to access information not only about the mass and general nature of polymers and their respective end groups but also about the structure of these end groups since they have an observable effect on the obtained fragmentation spectra. This contribution studies this effect of isomeric initiating alcohols on the fragmentation pattern of polylactides (PLA). Distinct differences between the investigated PLA can be observed.
Characterization of Structural Changes in Photoresist on silicon wafer by Pyrolysis-GC/MS Combined with Micro GPC Fractionation

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In the organic compositional analysis, separation technique is especially important to identify each component. In the case of the separation of a trace amount of mixture (e.g. photoresist on wafer), however, it becomes the problems that there is a trace amount of fraction and contamination for fractionation by chromatographic method such as column chromatography and HPLC remain main problems.

For means of solving the problem, we have evaluated organic qualitative analysis of trace components using the MALDI-MS, IR, and Pyrolysis-GC/MS combined with the micro GPC fractionation\cite{1,2}. A diagram of the system is shown in Figure 1.

![Diagram of micro-GPC fractionation system](image)

**Figure 1**: Diagram of micro-GPC fractionation system

In this study, to characterize structural changes of components in photoresist on silicon wafers after immersion lithography, Pyrolysis-GC/MS analysis combined with GPC fractionation was carried out. Components of photoresist we used are shown in Table 1. Exposure in immersion lithography was carried out with 3 illumination conditions (Annular, Dipole and Quadrupole).

<table>
<thead>
<tr>
<th>Photoresist</th>
<th>Photopolymer</th>
<th>PAG</th>
<th>Quencher</th>
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<tbody>
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<td>Resist A</td>
<td>Methacryl type A</td>
<td>TPS type A</td>
<td>General amine type A</td>
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Table 1: Photoresist evaluated in this work

Consequently, we could observe a difference in composition ratio of the photopolymer between core and surface in the photoresist. Moreover, a difference in components of the photoresists among each condition was discussed on the basis of the obtained results.

References
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A New Approach to Sample Preparation Free Micro ATR Chemical of Polymers and Laminates

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Micro ATR chemical imaging of polymers and in particular polymer laminates typically requires significant application of pressure to ensure good contact between the ATR crystal and the sample. To ensure that such thin samples can withstand the pressure without buckling, elaborate sample preparation procedures are often required to support cross-sectioned materials: embedding of sample in resin, cutting the resin and polishing the contact surface. Such procedures are tedious, require overnight resin curing and carry the added risk of cross-contamination.

Presented here is a novel method of ultralow pressure micro ATR FTIR chemical imaging that removes the need for any structural support. This allows samples to be measured "as-is" using direct contact with the ATR crystal. This unique capability is made possible through the use of Agilent’s "Live ATR imaging" technique which provides enhanced chemical contrast, and enables the exact moment of contact between the sample and ATR crystal to be determined and provides a visual measure of the quality of contact. Adhesive layers as thin as a few microns can be clearly observed in 50-micron thick polymer laminates without sample preparation.

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Figure 1: B- optical image showing the contact area of ATR; C- three chemical images created with different wavenumbers to highlight the main layers and tie layers with corresponding representative spectra as indicated by the arrows. Note: All spectra are shown in absorbance units, with axes omitted for clarity.
Non-isocyanate urethane coatings were prepared from two different renewable resources through aminolysis reaction. A five membered cyclic carbonate was synthesized from linseed oil [1] and it was reacted with an amine functional reactant from cashew nut shell liquid (phenalkamine). Porous free coatings on aluminium substrates were prepared by mixing carbonated linseed oil and phenalkamine at three different mixing ratios (1:0.5, 1:0.75, and 1:1.25) and curing each mixture at 60, 80, and 100 °C respectively. The structural changes during aminolysis reaction were studied using infrared spectrometry (FTIR) and the thermal stability of the cured films was characterized using thermogravimetry (TG). The solvent resistance, cross-hatch, impact strength, swelling, and specular gloss values of the coatings were also evaluated.

After 24 h of reaction time in the FTIR spectrum decay of the cyclic carbonate was observed at 1800 cm\(^{-1}\) and the stretching vibrations of the free and H-bonded carbonyl groups in the urethane structure was observed at 1730 cm\(^{-1}\) and 1700 cm\(^{-1}\) [2]. The combined bending vibrations of the N-H and C-N bonds of the urethane groups were noticed at 1530 cm\(^{-1}\) and 1245 cm\(^{-1}\) along with stretching vibration of N-H at 3336 cm\(^{-1}\). In TG analysis, the increase in cure temperature shifted the onset decomposition temperature toward higher values and improved the thermal stability. In contrast, it was decreased with an increase in amine concentration. The coating properties like solvent resistance and crosshatch resistance could be improved with an increase in cure temperature. The specular gloss did not show a significant difference with respect to an increase in cure temperature, where the swelling resistance could be improved. The impact strength of the coating slightly increased with an increase in amine concentration. The CLSO/phenalkamine ratio of 1:0.75 cured at 100 °C showed overall best performance in the coating properties with acceptable colour change compared to all other CLSO/phenalkamine mixtures.

References
Ballistic and numerical simulation of impacting goods on conveyor belt rubber

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Lifetime prediction of conveyor belts is of major importance in any industry where large amounts of goods must be transported over distances ranging from a few meters to several kilometres. One of the main incidents that are responsible for wear of conveyor belts is the impact of goods when loading the belt.

Lab scale experiments were conducted with a smooth bore pressure gun, which fired 9 mm steel balls at an angle of 45° onto the samples. A high speed camera system was used to measure penetration depth, angle of reflection and to estimate contact time. In addition, the energy dissipation and wear energy was determined by processing the image data. Each sample was impacted ten times to observe effects of hysteresis and damage caused by previous impacts.

To understand the impact on a scientific scale and predict the affected area as well as the distribution of strain, numerical simulations were conducted by smooth particle applied mechanics (SPAM) method and subsequently compared to the practical experiments.

The numerical simulation agreed well with the results from the practical experiments and confirmed the high energy dissipation of up to 80% depending on the examined rubber sample. The energy dissipates into the rubber samples, leading to deformation and heating.

Figure 1: Parameter-study of the penetration depth development during the impact
Characterization of ionic polysaccharides by Rheology and GPC/SEC

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Rheology and Size Exclusion Chromatography (SEC/GPC) are characterization methods of polysaccharide solutions. SEC targets characterization on a molecular scale whereas rheology offers insights into properties on a more macroscopic scale. Linking the results of independent characterization technologies results in a much more complete picture of the samples under investigation.

The use of ionic polysaccharides like Hyaluronan, Chitosan and Carrageenan in applications as medical, cosmetics and foods generates a demand for accurate material characterization. Shorter consumer product cycles put pressure on the development teams. This results in requests for shorter development times and more specific information about the materials used. Changes in material properties, originating from batch to batch variability of natural source materials or from treatment of the materials can determine the suitability of a material for a particular application. For certain applications the final product properties have to comply with regulations, and can mean that characterisation is required all the way from goods-in to R&D and final product quality control.

Knowledge about material properties, characterization methods and application requirements lead to a knowledge base to build on. Examples will be presented of the characterization of polysaccharides, explaining benefits of applying both rheological and SEC characterization on the same samples. For instance in the example below, the cross-over in G’ (elastic modulus) and G” (viscous modulus) signifies the start of the terminal region, where polymer chains have had sufficient time (1/ω) to free themselves from entanglements, allowing individual polymer chains to slip past one another. The inverse of the cross-over frequency is termed the relaxation time and is a measure of how long this disentanglement process takes. At times shorter than τ, G’ exceeds G” indicating an elastically entangled network. At times greater than τ, G” exceeds G’ indicating loss of elasticity consistent with disentanglement and translation of polymer chains.

Figure 1: G’ and G” plotted as a function of angular frequency at four concentrations with G’/G” cross-over’s ringed. Inset is relaxation time (1/crossover frequency) plotted against log [η].
Donor-acceptor alternating copolymers have received a large attention as active materials for photovoltaic devices due to their low bandgaps. This donor-acceptor systems have great technological value due to their ease of fabrication and their relatively low production costs [1]. In this contribution, we present our work on characterization of three novel conjugated polymer consists of vinylene-benzothiadiazole based alternating copolymers with carbazole, 3,6-difluoro carbazole and fluorine, which were synthesized via Suzuki coupling polymerisation in the presence of catalytic amounts of palladium (II) acetate Pd(OAc)$_2$ and tri-ortho-tolylphosphine. P(o-tol)$_3$ [2].

![Figure 1: The Three conjugated copolymer structures](image)

The molecular weights measured by gel permeation chromatography and they were characterized by NMR, IR, Elemental analysis and mass spectrometry. The physical properties and their band gaps which give idea about their conductivity are measured by UV-visible absorption and cyclic voltammetry analysis, and the results were discussed and compared with some of analogous copolymer which were used in organic solar cell applications. In addition, they were characterized thermally by Thermo-gravimetric and Differential Scanning Calorimetry analysis to study their thermal and mechanical properties.

References
Miscibility and Specific Interactions in Blends of Poly(4-vinylphenol / Poly(vinylmethylketone).

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Introduction
The research of new polymer materials with improved properties has received considerable attention in both the academic and industrial points of view. In this way, the polymer blending is an attractive approach to obtain new polymeric materials with large scale properties. It has been proven to be an effective alternative to obtain new materials with tunable properties such as better processability, lowered cost, etc. Furthermore, many techniques can be used to investigate the phase behavior and miscibility of polymer blends. For this purpose and owing to their simplicity and speed, thermal analysis, spectroscopy and microscopic methods are regularly used. These techniques offer information about the miscibility in the different range scales. [1,2]

In the present contribution, the phase behavior and miscibility of blends of poly (vinylphenol) (PVPh with poly (vinylmethylketone) (PVMK) is explored. The miscibility of these binary blends is studied by means of DSC, FTIR and SEM. We examined in detail by DSC the phase behavior and miscibility of these blends according to their glass transition temperatures (Tg’s). Moreover, the possible specific interactions such as hydrogen bonding is studied qualitatively and quantitatively by Fourier transform infrared spectroscopy (FTIR).

As an example, Figure 1 shows Tg-composition variation versus PVPh weight fraction of PVPh/PVMK systems. As can be seen in this figure, only one Tg’s for each composition is observed indicating their miscibility.

![Figure 1: Tg-composition variation versus PVPh weight fraction of blends of PVPh/PVMK.](image)

References
Design and characterization of PP-gMAH/glass fibres composite materials

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Thermoplastic materials reinforced with glass fibers (GF) as well as those with disperse nanofillers found multiple applications. Technological efforts were largely channelled to optimize existing systems. In the case of the reinforced thermoplastic materials, the most important problems are related to the preservation of the original rapport, the shape of the filling material, the ensuring of the optimal orientation and improving the adhesion between matrix and filling material.

In this paper, the process of obtaining polypropylene (PP) based composite materials, using maleic anhydride grafted polypropylene (PP-gMAH) as coupling agent and functionalized glass fibres is presented. PP-gMAH was used as a coupling agent to improve the interfacial adhesion between fibres and matrix. Reinforcing agent is inserted into the composite structure in order to increase and manage the mechanical properties of the composite materials.

The synthesis of the polypropylene (PP) based composite materials, using PP-gMAH as coupling agent reinforced with functionalized GF involves two main stages, as follow: (1) glass fibres were functionalized by hydrolysis/condensation with (3-aminopropyl) trimethoxysilane as functionalisation agent and (2) these materials were compounded at 180°C in a Brabender mixer with the polymer.

The obtained composites were morphologically and structurally characterized by X-ray diffraction (XRD), infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) but also from the point of view of mechanical properties.

Based on the SEM images it can be concluded that the morphology of composite materials is given by the PP degree of grafting. The compatibility of the two phases increase gradually, the compatibility between PP and silanized GF being intermediary between the phase compatibility of the composite obtained with pure PP and GF and the composite materials obtained by using PP and PP-gMAH and silanized GF. When using 3% PP-gMAH and silanized GF the compatibility between the phases is optimal practically all glass fibres are coated with polymer phase. From the point of view of mechanical properties, the hardness increases with increasing the percentage of glass fibres, for all composites the recorded values being in the range (71-830ShD). It is observed that increasing the proportion of 3% coupling agent significantly reduces the hardness of the mixture even at the same concentrations of glass fibres, which demonstrates that the polypropylene grafted with maleic anhydride has a double role: both as a lubricant, reducing the viscosity of the mixture and the coupling agent. This also improves the workability of the composite due to lower melt viscosity.

References
Effect of Tetraphenyl Phosphonium Modified Montmorillonite on The Non-Isothermal Crystallisation and Thermal Degradation of Poly (Ethylene Terephthalate)

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Poly (ethylene terephthalate) (PET) nanocomposites with different loadings of a novel organoclay based on montmorillonite and tetraphenyl phosphonium bromide as a modifier were successfully prepared via melt-compounding. From XRD patterns and TEM images, it was suggested the formation of mainly intercalated nanocomposites. OMMT nucleating effect was studied by using differential scanning calorimetric (DSC) analysis. DSC results showed that OMMT behaved as a nucleating agent and enhanced PET crystallization rate. Non-isothermal crystallization behavior and kinetics of PET/OMMT were investigated and compared with those of neat PET. Crystallization activation energy of PET and PET/OMMT nanocomposites was calculated, based on Ozawa and Kissinger approaches. The calculated effective of crystallization activation energy for the nanocomposites was higher than for the PET, which indicates a less perfect crystalline structure for nanocomposites during non-isothermal crystallization. PET/OMMT nanocomposites showed an improvement of thermal stability as evidenced by thermogravimetric analysis and kinetics of their thermal degradation. The activation energies (Ea) of thermal decomposition of PET and its nanocomposites were determined by Flynn–Wall–Ozawa and Tang methods. The activation energies Ea of thermal degradation for nanocomposites were higher than that of virgin PET (Fig.1), indicating that OMMT had a stabilizing effect upon the matrix’s decomposition.

Figure 1: Dependence of Activation Energy (Ea) on the degree of conversion (α) of the mass loss, as calculated with Tang method for the different samples
Observation of the new trigonal form in propylene-1-pentene copolymers by FTIR spectroscopy

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Isotactic polypropylene, iPP, exhibits a remarkable polymorphism, depending on crystallization conditions, microstructural characteristics, and other factors like the use of specific nucleants. Four different crystalline structures are well established: the monoclinic α form; the trigonal β modification; the orthorhombic γ polymorph; and a phase of intermediate or mesomorphic order [1,2].

In addition to those four crystalline modifications, a new trigonal form (δ) has been recently reported in the case of metallocene copolymers of propylene with high contents of 1-hexene or 1-pentene as comonomers [3,4] as well as in metalloocene terpolymers of propene with both 1-hexene and 1-pentene as comonomeric units at analogous compositions [5,6].

The aim of this research is to obtain a deeper understanding on the coexistence and competition between the different crystalline structures developed by propylene based materials, in particular, propylene-1-pentene copolymers, using Fourier transform infrared spectroscopy as a principal tool. Dependence on temperature of several regularity bands that involve distinct length of monomer units is evaluated to learn if the helical sequences developed in the individual crystalline structures exhibit different behavior with temperature, mainly those ascribed to the new trigonal polymorph. Accordingly, several copolymers have been explored within a broad 1-pentene composition range. X-ray experiments have been also performed to attain the required information on the different polymorphs existing at those distinct compositions analyzed.

Acknowledgements
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References
Compatibilization of polyolefin recyclates with heterophase copolymers

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Within the European Union (EU) a lot of efforts are put into the re-use of diverse waste materials, also including plastics. In Article 11(a) of the Waste Framework Directive (2008/98/EC) (http://ec.europa.eu/environment/waste/framework/) by 2020 the recycling of waste, including also plastics household waste is aimed to increase to 50%. When it comes to polyolefin (PO) recycling one of the major challenges is the reliable separation of polypropylene (PP) and polyethylene (PE) streams out of post-consumer waste (PCW). Commercially available PO PCW sources are mixtures of PP and PE in a broad concentration range. On top of contamination and smell issues the inferior compatibility between PP and PE results in limited impact strength and heat deflection resistance.

Within this work it was tried to compatibilize a commercially available PO recyclate using polypropylene impact copolymers (IPCs) available in the Borealis portfolio. These IPCs consist of PP matrix and dispersed ethylene-propylene rubber (EPR) domains. As shown in figure 1 in the used PO recyclate PE is the continuous phase (white phase). By addition of 5 wt% IPC a phase inversion takes place and the PP phase becomes the continuous one. A further increase in IPC content leads to a finer morphology indicating a better compatibility between PP and PE.

This observation could also be proven with mechanical (impact strength) and thermal tests (dynamic mechanical thermal analysis). It was also found out that depending on the composition of the recyclate (PE to PP ratio) a specific amount/composition of the EPR was needed to significantly improve the impact performance of the final compound.
Introduction
Polymeric materials contain additives such as UV absorbers (UVAs), antioxidants, and hindered amine light stabilizers to prevent degradation of polymeric materials. Direct analysis of such additives is not easy, because their concentrations are small (less than 1%). In resonance Raman spectroscopy, when the excitation wavelength is within the electronic absorption bands of the molecule, strong Raman scattering occurs from the molecule; this method can therefore be used to analyze trace components. The technique developed in the present work enables us to obtain Raman spectra for polymer additives in polymeric materials, using a UV laser, because typical polymer additives exhibit strong absorption in the UV region (210 to 350 nm).

Experimental
Raman spectra were recorded on JASCO NRS-3200, NRS-3300, and JLC photoluminescence systems, with six excitation wavelengths (244, 325, 442, 532, 633, and 785 nm). The UVAs used were isooctyl 2-[4-[4,6-bis[(1,1'-biphenyl)-4-yl]-1,3,5-triazin-2-yl]-3-hydroxyphenoxy]propanoate (HPT, BASF), and 2-(2-hydroxy-5-methylphenyl)benzotriazole (BT, Tokyo Chemical Industry). The sensitivity of detection of 0.1% UVAs in chloroform was compared for the different wavelengths. In addition, poly(methylmethacrylate) (PMMA) with 0.1% HPT was analyzed to determine whether UVAs in polymeric materials could be directly analyzed.

Results and Discussion
Using 325 nm excitation, HPT (hydroxyphenyltriazine type) could be detected with 800-fold, and BT (benzotriazole type) with 150-fold, greater efficiency than in the case of 532 nm excitation (Fig. 1). Direct analysis of the PMMA revealed that 0.1% HPT was directly detectable. We intend to report the results for other UVAs, antioxidants, and hindered amine light stabilizers at the conference.

Figure 1: Raman spectra of HPT (0.1%) in chloroform with different excitation wavelengths.
Thermal Stability and Non-Isothermal Decomposition Kinetic of A Poly (N-Butyl Metacrylate-Co-Acrylic Acid)/Maghnia Bentonite Nanocomposites

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Poly n-butyl methacrylate (PBMA) is frequently used in coatings and biomedical materials such as bone cement systems and control of drug delivery. Because of its low glass transition temperature $T_g$, the monomer n-butyl methacrylate (n-BMA) is rarely polymerized alone, it is usually copolymerized with other monomers in small quantities whose respective polymers have high $T_g$. In order to improve the properties (mechanical, thermal, fire resistance ...) of pure poly n-butyl methacrylate or copolymerized, inorganic nanofillers such as clay are often introduced to obtain nanocomposites.

Thermal stability and degradation kinetic of pure copolymers poly(n-butyl methacrylate-co-acrylic acid) BMAA and nanocomposites based on poly (n-butyl methacrylate -co- acrylic acid)/Maghnia Bentonite BMAA-x/OBT(1%) and BMAA-y/OBT (2%) (where x and y are respectively 15 and 16 % mol of acrylic acid and 13 and 14 % mol of acrylic acid and OBT at 1 and 2 %, the Bentonite was organically modified by the surfactant hexadecylammonium) were carried out by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under an inert atmosphere. The results show an improvement of the thermal stability of nanocomposites.

The kinetic methods of KAS (Kissinger–Akahira–Sunose), FWO (Flynn–Wall–Ozawa) and Tang were applied to study the mechanisms of material degradation. Finally, the activation energies of the pure copolymers and those of their corresponding nanocomposites were determined and confirmed the barrier effect of the clay organobentonite (OBT).
Chromatography of polyolefins at high temperature

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The size exclusion chromatography (or GPC: gel permeation chromatography) is used specifically to study polyolefins at high temperatures. The chromatography system includes all the columns and detectors in a furnace operating between 30 and 160 degrees Celsius. The detectors consist typically of a UV detector for measurement of concentration and a refractometer for dn/dc determination, a viscometer for measuring intrinsic viscosity, and static light scattering detectors (including LALS, RALS or a brand new MALS system with 20 detectors) and dynamic light scattering detectors to measure respectively absolute molecular weight and hydrodynamic radius of polymers. Sample preparation is important and has been automated in order to ensure reproducibility. The sample is injected by a solenoid valve which prevents cross-contamination with a flush multi-channel system. The sample is then filtered in-line and continuously at the input of the column. Several analysis of samples will be presented including polyethylene (PE and HDPE) dissolved in TCB to confirm the stability of the samples to 140 degrees. Other samples of PE loaded with carbon will demonstrate the capabilities of the automatic injection system. Measurements of long-chain branching polyethylene will be presented through the Zimm Stockmayer equations to define the branching ratio, branching number, and the branching frequency. Polypropylene (PP) is more unstable and degrades after 2h30 in the TCB. The stability of the PP will be considered depending on the temperature of the medium and testing in decalin at 135 degrees show an increase in stability of up to 19 h.

Zimm & Stockmayer use intrinsic viscosity $[\eta]$ for $g'$ determination (branching ratio) for a corresponding $M_w$ with 1475a being linear PE and NBS 1476 branched PE.

References
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Preparation of Nanocomposite of Polypropylene by Foaming

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Via batch process in an autoclave, we conducted an environmentally benign foaming processing on polypropylene (PP) copolymer/clay nanocomposites to investigate the foamability of the PP copolymer and dispersion and exfoliation of the nanoclay particles. Supercritical carbon dioxide (sc CO$_2$) and subcritical carbon dioxide (sub CO$_2$) were used as a foaming agent. The PP copolymer was found to be foamed more easily than polypropylene (Figure 1). Small amount of other olefin moieties in the backbone of the polymer facilitated better foamability than the neat polypropylene. More and smaller cells were observed when the clay was blended as a heterogeneous nuclei and sc CO$_2$ was used. A low foaming temperature and a high saturation pressure were more favorable for obtaining uniform foam. Dual role of the nano-clay particles as a foaming nucleus and a crystallization nucleus was confirmed by the cell growth observation and the nonisothermal crystallization kinetics analysis. Small angle X-ray diffraction showed that highly dispersed states (exfoliation) of the clay particles were obtained by the foaming process. Since the clay particles provided more nucleating sites for the foaming of the polymer, a well dispersed (or fully exfoliated) nanocomposite exhibited the higher cell density and the smaller cell size at the same clay particle concentration. Expansion of the adsorbed CO$_2$ facilitated the exfoliation of the clay platelets; thus, sc CO$_2$ at lower temperature was more efficient for uniform foaming-cell production. Fully dispersed clay platelets were, however, re-aggregated when subjected to a further melting processing. The reprocessed nanocomposites still had some exfoliated platelets as well as some aggregated intercalates.

Figure 1 (Left) SEM images of foams (the first row- foamed at 135°C with subcritical CO$_2$; the second row- foamed at 130°C with supercritical CO$_2$; the third row- foamed at 125°C with supercritical CO$_2$) (right) SAXS patterns for the clay, unfoamed and foamed nanocomposites

References
Compounding polymers is widely used for the preparation of new materials. The disadvantage of this research is that the polymers are usually not compatible and the preparation of compounds with suitable (mainly processing and physico-mechanical) properties is not performant. The modification of non polar polypropylene with the aim of improving some its properties is often possible with a certain amount of another additive [1]. Polypropylene/polyamide (PP/PA) composites are interesting because both components are relatively cheap, with advantageous properties, and are processable by melting [2]. The compatibilisation of binary polymer compounds can be made by the addition of graft copolymer, segments of which have physical or chemical affinity with two immiscible homopolymers [3]. In this case, polypropylene grafted with maleic anhydride (PP-g-MA) it was used. Polymer nanocomposites containing layered silicates have been considered as a new generation of composites materials due to their expected unique properties attributed to the high aspect ratio of the inorganic pellets [4-6]. Combined effects of layered silicate treatment and compatibilizer polymers (PP-g-MA) on the structure and properties of PP/PA/PP-g-MA/layer silicates nanocomposites were studies. The obtained nanocomposites are resistant to high temperatures (250°C). The optimum formulation (deduced from the resulting physico-mechanical properties) was used to prepare a series of nanocomposites under different technological conditions. The nanocomposites were characterized by means of physico-mechanical tests: Shore “D” hardness, stress at 300% (Modulus), tensile strength, elongation, density and flexibility and thermal stability in the initial condition and after accelerated ageing. Also, a correlation between their physico-mechanical properties and IR spectra (obtained by applying the ATR technique) was proposed.

References

Polymeric nanocomposites (PNCs) represent a radical alternative to the conventional filled polymers or polymer blends [1]. Direct incorporation of inorganic nanoscaled building blocks into polymers represents a typical way for preparing polymeric nanocomposites. The most important aspect in preparation of nanocomposites through dispersive blending is surface modification of the nanofillers. Based on the literature data [2], a homogeneous dispersion of nanoparticles in polymers matrices is very difficult to realize because of the high tendency of agglomeration of the nanomaterials. In addition, the hydrophilic nanoparticles and the hydrophobic polymers are limited compatibility, which leads to poor interfacial interaction [3]. It is possible to increase hydrophobicity of the fillers, enhance interfacial adhesion via chain entanglement or chemical surface modification [4]. Silicon carbide (SiC) nanoparticles are used due to their superior properties such as: hardness, corrosion resistance, and strength [5].

This paper presents the process of obtaining nanocomposites based on polypropylene and SiC nanoparticles, in a twin screw extruder granulator, and their corresponding characterization. In order to obtain a homogeneous dispersion of SiC nanoparticles into the PP matrix, it is required to decrease concentration tension occurring at the interface, due to differences in thermal expansion coefficients of the polymer and mineral filler, by treating the reinforcing agent surface with small-molecular polymerizable compounds, such as divinylbenzene.

However, to ensure good interfacial adhesion and stress transfer across the interface, chemical or physical interactions between the matrix and the treated silicon carbide nanoparticle need also to be formed due to their inert nature. The better interfacial adhesion is assured by the use of maleic anhydride grafted PP and treated silicon carbide nanoparticles. The obtained nanocomposite materials were tested in terms of composition (FTIR, XRD), morphology (SEM, TEM) and physico-mechanical properties.

References

NBR (Acrylonitrile-butadiene rubber) is widely used in the automobile, train and aircraft industry. Because NBR provides excellent resistance to petroleum oils and gasoline as well as mineral and vegetable oil. It also offers strong resistance to heat aging. These NBR products are vulcanized NBR. For the vulcanization reaction, NBR requires less sulfur and a great amount of accelerator, and the same concentration of ZnO. The most widely used accelerator is tetra methyl thiuram disulfide (TMTD), also in combination with thiazole or sulfonamide. However TMTD is carcigenic because of the production of nitrosamines during the vulcanization reaction. Tetra benzyl thiuram disulfide (TBzTD) has been developed to replace thiuram such as TMTD in case where the presence of harmful nitrosamines is of concern. The benzyl nitrosamine is not carcigenic according to published literature. In the vulcanization reaction, unneeded by-products also be generated. Sometime, these by-products may affect to reduce the sealing performance because there is a possibility that by-products bloom out to the surface. Qualitative and quantitative analysis of by-products are important for us to increase the product's function. Therefore, as traditional analysis methods, we analyzed TLC and FT-IR [1]. However, sometime, we could not analyze in detail because by-products had not been contained so much in the vulcanized NBR.

The vulcanized accelerator of this study was TBzTD. In the vulcanization reaction, thiuram-based vulcanization accelerators react with ZnO to produce zinc salts of thiuram-based vulcanization accelerators as one of by-products [2], Figure 1(A). This reaction is well known. In this study, we detected tetrabenzylthiuram disulfide zinc salt (ZTC) by using LC/MS/MS. And we recognized this reaction by analysis. Moreover, we estimated that ZTC react with sulfur (S₈) to produce TBzTD at the vulcanization reaction, Figure 1(B). We considered the probability of this reaction scheme by Molecular Orbital calculation.

Reference
Phenylenediamines are closely related to aniline and they can similarly be oxidized to the corresponding oligomers and polymers. These are easily prepared by chemical oxidation and can be used especially in biomedical applications, where the potential toxicity of aniline and its oligomers is feared. The ladder structure is widely accepted in the literature because it can be created, in principle, from any phenylenediamine isomer [1] (Fig. 1).

In this contribution we have studied the oxidation of phenylenediamines in aqueous media of various acidity, i.e. under similar reaction conditions that are used for the preparation of polyaniline. Ortho-, meta- and para-substituted anilines were oxidized with ammonium peroxydisulfate in 1 M methanesulfonic acid (Fig. 2), water, and in 1M ammonium hydroxide. The molecular structure of the products of oxidation was characterized by infrared and Raman spectroscopies with three different excitation lasers.

References
In plastic industry the products can be colored by a pigmentation process, where the color masterbatch and the polymer carrier are mixed together through a compounding extrusion. The degree of pigment dispersion in the masterbatches is a crucial point, especially in particular processing, such as fiber spinning. In this latter case in fact, the pigment aggregation may cause serious technical limitations, such as embrittlement or breakage during spinning, and low coloration quality, determining an increase of the scraps and the production times [1]. The evaluation of the pigment dispersion within the matrix has a key role for the color masterbatch quality assessment.

In this work, the dispersion of three type of commercial pigments in polyamide 6 is presented and compared by using different analytical methods. The pigments dispersion in a polymer matrix and their agglomeration tendency in fact could depend on various properties (i.e. size, shape, surface properties, crystalline structure, chemical composition of the primary crystals,…). Direct investigation techniques, such as microscopical analysis and X-ray fluorescence (EDX) could be not representative for the material, because they are related to a specific section of product. On the other hand, indirect methods such as Filter-Test, Relative Color Strength (RCS), rheological measurements and crystallization kinetic analysis were considered, because these testing methods are strictly connected to the production process and to the optical properties of the product [2].

The comparison of the obtained results indicates that an improvement of the pigment dispersion in the color masterbatch determines a reduction of the Filter Pressure Value (FPV), a reduction of C parameter, calculated from Cross equation used to fit the rheological curves, an increase of RCS and a modification of the crystallization activation energy, due to nucleation effect. Moreover an important relation was found between FPV, measured by Filter Test, and the C parameter, as shown in Figure 1.

Figure 1: The Correlation between FPV and C parameters

References
Friction properties of various polymers were studied and compared by using a self-assembled friction tool adapted on a standard tensile tester at 23°C and at 200°C. Normal forces \( (F_N) \) were applied by using a spring \( (k=1.37 \text{ N/mm}) \) in the range of 7-38N, whereas friction/tangential forces \( (F_T) \) were measured by using a dynamometer Instron mod 4502 at rate of 333 micron/sec. (contact surface of 10x30mm).

Results of dynamic friction coefficient of selected samples of polytetrafluoroethylene (PTFE), acetal (POM), polyetherketone with carbon fibers (PEK-CF) polyaryletherketone with wear additives (PAEK), polymethylmethacrylate (PMMA) and polycarbonate (PC) are presented in Table 1, according to equation \( \mu = \frac{F_T}{F_N} \).

<table>
<thead>
<tr>
<th>Polymer vs. mild steel</th>
<th>Friction coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE</td>
<td>0,11 ± 0,01</td>
</tr>
<tr>
<td>POM</td>
<td>0,20 ± 0,01</td>
</tr>
<tr>
<td>PAEK-wa</td>
<td>0,17 ± 0,01</td>
</tr>
<tr>
<td>PEK-CF</td>
<td>0,27 ± 0,01</td>
</tr>
<tr>
<td>PC</td>
<td>0,38 ± 0,13</td>
</tr>
<tr>
<td>PMMA</td>
<td>0,61 ± 0,03</td>
</tr>
</tbody>
</table>

The same approach was also applied for evaluating the mutual friction properties between PEK and PAEK both at room temperature and at 200°C. As expected a higher value of the friction coefficient was found at high temperature in dependence on the \( T_g \) of polymer. Figure 1 shows experimental data of PC and PAEK at room temperature.
Tomographic characterization of the microstructure in polymer matrix composites with the field-aided filler orientation

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The starting point of this study was an assumption that orientation of the ferromagnetic filler particles by using an external magnetic field applied to a composite in a liquid state will promote the formation of chain-like structures of particles in a volume, what will differ it significantly from originally isotropic material [1-2].

This work aimed to manufacture the epoxy matrix composites with a controlled alignment of two different fillers, namely: magnetite and strontium ferrite, by means of the magnetic field. Nanotomography was used to characterize morphology of the composites and to confirm the anisotropy as well as to correlate it with a change of the physical properties. It was found that magnetic field applied to the liquid composite structure during the curing process resulted in manufacturing of a more ordered arrangement of the filler particles in the form of a chain-like linear structures along the direction of applied magnetic field. The strongest magnetic field-aided orientation is visible for the samples with the filler volume content of 30% vol., which are shown in Figure 1.

![Figure 1](image_url)

Figure 1: Tomographic images of the composites with a controlled microstructure: a) strontium ferrite filled epoxy composite, b) magnetite filled epoxy composite (left: filler; right: matrix)

The enhancement of physical properties was obtained due to strong anisotropy of the filler within a polymer matrix. The resulting efficiency of a filler alignment and its influence on properties was assessed based on the thermal conductivity measurements. The measurements of the heat flow were performed in parallel and normal directions to the filler alignment direction, respectively. Due to magnetic field-aided filler orientation the percolation threshold can be consequently achieved at much lower filler concentrations than for the isotropic samples.

References
Physical-mechanical, technological, functional, and particularly aesthetic properties of semi-processed nappalan fur and leather depend to a great extent on the quality of pigment pastes used in the process of generating the grain layer. These cumulated properties give value of use and appearance to the various products manufactured: footwear, clothing, handbags, etc. Environmental issues require restrictions on the use of heavy metals salts (Cr, Cd, Pb, Co, Hg, Ni), of ethoxylated alkylphenols as stabilization agents, of formaldehyde as crosslinker of protein binders or on other toxic crosslinking agents in pigment pastes and resulted in new alternatives for the industry of auxiliary finishing materials [1-4]. Pigment pastes were prepared using a polyacrylic binder, iron oxide pigments (red and yellow), lauric alcohol ethoxylated with 7 moles of ethylene oxide, 100% biodegradable, as stabilizing agent and plasticizer. Stationary rheological measurements show that the pigment pastes have pseudoplastic behavior and are slightly tixotropic, which improves the storage stability and have a positive effect on leveling properties after application due to the time-dependent structure recovery. Dinamic measurements indicate that they are preponderantly elastic, which assures their functionality. The prepared pigment pastes are compatible with the other auxiliaries used in the composition of the base coats for natural leathers and nappalan furs. Optical microscopy shows that they spread uniformly on leather and fur surfaces.

References
Characteristics of natural leather surface finished with some eco-friendly mixtures of polymeric aqueous dispersions

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Many types of finishing agents are used in the leather industry [1-3]. In the present study, certain mixtures of polyacrylic copolymer aqueous dispersions or polyacrylic copolymers and polyurethane dispersions were used as environmentally friendly base coats and a polyacrylic copolymer dispersion containing an epoxy resin (AC34), as top coat. Leather samples finished with the proposed additives were characterized by FT-IR, SEM and physical-mechanical tests. The spectra of the top coated leather have the following characteristics, compared to those of the untreated ones: the band at 1642 cm\(^{-1}\), characteristic for C=O and –OC-N of leather, is absent in the spectra of the finished samples; the last ones present a peak at 1730 cm\(^{-1}\), corresponding to C=O stretching in saturated ester of the top coat; the two peaks at about 1240 and 1166 cm\(^{-1}\) assigned to the couplings of C-O and C-C stretches and to the stretching vibration of C-O-C of acrylates respectively appear in the spectra of the finished leather, while the peak at 1546 cm\(^{-1}\) (attributed to C–O–C of acid groups) disappeared, indicating a low carboxylic content in the finished samples; the peak at about 1000 cm\(^{-1}\) (attributed to the C-OH stretching vibration of vinyl group), present in the spectrum of the film obtained from AC34, is absent in the spectra of the finished leather samples; the broad band in the region 3200-3500 cm\(^{-1}\), assigned to hydroxyl and amide groups vibrations, is deeply diminished in the spectra of the top coated leather samples compared with the untreated ones; OH stretching peak at about 3680 cm\(^{-1}\) is absent from spectra of the top coated samples. The above differences between the IR spectra of the treated and untreated leather samples represent a conclusive proof for the chemical bonding of the top coat on base coat components [4,5]. The top coat not only covers the surface of leather but it is bound on the base coat, assuring thus a resistant coverage. SEM images show that the surfaces of the finished samples are smooth and uniform, that is the leather fibers and pores are entirely coated. Physical-mechanical characteristics are higher compared to standards in force. This demonstrates that the eco-friendly polyacrylic copolymer dispersion containing epoxy resin substitutes successfully the top coat nitrocellulose aqueous emulsions, the usual finishing agent, in which the nitrocellulose is found as solution.

References
Fluorescence Probe Technology (FPT) is a new method, which offers the possibility of on-line applications for monitoring of polymerization processes by means of specially designed fluorescent molecular probes that change their fluorescence characteristics upon changes occurring in their environment. During the past few years monitoring of polymerization processes using fluorescent probes has been the most popular and powerful tools that can be used in order to understand the physical and chemical processes that occur at the molecular level. This is possible because their fluorescence is sensitive to the polarity and/or microviscosity of the molecular environment in which the probe molecules are located [1]. Present FPT offers the opportunity for on-line applications. An additional advantage of the FTP method in comparison to other methods is that the FPT is applicable for monitoring of non-transparent samples in production lines (on-line), where the sample moves relative to the monitoring system and where other monitoring methods fail. Therefore, the FPT method has been used mostly for monitoring of fast photopolymerization processes [2], though it is adaptable for monitoring of other reactions as well, everywhere where changes of the reaction medium properties occur during the course of the reaction [3].

Theoretically, every process that causes change of the system polarity or microviscosity should be able to be monitored by using fluorescent probes. Most of known fluorescent probes suitable for monitoring free radical polymerization, usually do not perform well in cationic polymerization systems. Only a few fluorescent probes suitable for cationic polymerization have been reported so far [1,2]. Depending on the type of the process and the monitoring parameters, appropriate structure and characteristics of the probe are required. Therefore, there are no completely versatile probes. Most of known probes, used for monitoring of free radical polymerization, contain some sort of basic amino groups in their structure. Therefore, it is necessary to develop new probes free from basic centers to enable monitoring cationic polymerization without interference of the probe with the polymerization kinetics. In this communication new fluorescent probes containing naphthalene ring were characterized and their principal applications are presented.

Acknowledgement
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References
Analysis and characteristic of copolymers of polypropylene glycol maleate with acrylic and methacrylic acids


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Recent years were characterized by intensively increased researchers’ interest to waterswellable polymers with stimulating sensitivity and to polymer-networks with unique characteristics. They are able to absorb a large amount of water and to react reversibly by changing of their volumes, characteristics and morphology on physical-chemical composition changes of solvent or on external influences [1]. It makes possible to the researchers to carry out (fine) control over the properties of polymer systems that provides for effective use of polymer based materials as super moisture-absorbents, medical preparation carriers, thickeners, specific ion exchangers, and etc [2]. In this context, for producing of copolymers with various practically important properties - it will be interesting to study polypropylene glycol maleate (p-PGM) with acrylic (AA) and methacrylic (MAA) acids and to reveal factors determining their basic characteristics.

The composition of the obtained copolymers was determined potentiometrically [3]. The amount of unreacted double bonds of maleic groups of synthesized copolymers was determined by titrimetric method [4]. Surface morphology of the obtained hydrogels was investigated by scanning electron microscopy on IVS Supra 55VP - 3249. IR spectra of copolymers were registrated by IR Fourier spectrometer FSM 1201.

Represented data reveal that at the increasing of p-PGM in the initial stock the medium viscosity increases, this process leads to the decreasing of branching and cross-linking reactions and it can be proved by meanings of free maleic groups. It should be noted that the swelling degree of the copolymers with MAA is slightly higher than with AA. Microstructural analysis using a scanning electron microscope revealed that the test samples have a porous structure, but this index is higher in copolymers of p-PGM:MAA, which may be related to the presence of methyl substituent. Intensive absorption bands in the range of 1670 cm\(^{-1}\), which correspond to the fluctuations of the unreacted double bonds are presented in the IR spectra of copolymers of p-PGM:AA and p-PGM:MAA. There are intense absorption bands at the 1157 cm\(^{-1}\), corresponding to the fluctuations of the ether linkage, and they also conform to vibrations of methyl groups of methacrylic acid at 2926 cm\(^{-1}\), the carboxyl groups providing the swelling, which are seen in the area 1723 cm\(^{-1}\).

Thus, the experimental data have shown the perspectiveness of the use of polypropylene glycol maleate for three dimensional cross-linked polymers which are susceptible to changes of external conditions.

References
The development of new classes of polymer composite materials with emphasis on their rich molecular architecture and molecular interactions requires methods for a sensitive and non-destructive characterization. In particular knowledge of molecular organization as well as interaction at the polymer interfaces is essential for improving material properties. Methods that are relevant to characterize molecular structure are Raman and infrared spectroscopy. A new approach is the combination of non-linear methods of vibrational spectroscopy like metal nanoparticle enhanced infrared absorption or coherent anti-Stokes Raman scattering (CARS) with two-photon excited fluorescence (TPF) and second harmonic generation (SHG) which enables a high resolution imaging on the molecular level.

Here we present the potential of multimodal non-linear microscopy for imaging of polymer composites without destroying of the material. Molecular processes between bisphenol-A based polycarbonate and polyvinylamine were investigated. Vibrational spectra reveal chemical reactions and a formation of covalent bonds when the temperature is increased. The spectroscopic images indicate reaction products at the interface which can be classified as urethane, urea and more complex structures like dicarboxylic acids. In addition, changes in the ν(C=O) mode of the carbonate groups give rise to chain scissions or association by hydrogen bond formation of polycarbonate. A second type of polymers with incorporated glass fibers were image by multimodal microscopy. The SHG image clearly shows the embedded fibers whereas TPF highlights more artifacts within the composite material. The CARS image provides information about the homogeneity of the polymer matrix material. This fundamental study confirmed the suitability of non-linear optical spectroscopic imaging to assess molecular processes between polymers in a non-destructive manner and open the possibility for the in situ characterization of polymer composite materials.
Molecular Imaging of Hydrogel-Polyvinyl amine and Polycarbonate Composite formation

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Hydrogels are a special class of polymers which show a superior biocompatibility to living cells, due to the absorption of large amounts of water into their structures. Such materials are highly attractive for biomedical applications, e.g. as therapeutic and implantation devices. However, hydrogels alone exhibit usually a low mechanical stability and therefore they cannot be used as long term stable substrate material. Recently, composite materials of hydrogels coupled to synthetic polymers have received great attention for being a new type for biomaterial. Especially, functional polymers, such as Polycarbonate (PC) and Polyvinyl amine (PVAm), become increasingly important for use in bioengineering technology. In particular desirable are interfacial covalent bonds between PC and PVAm in order to form a permanent connection between the polymers. However, the chemical interactions between PC and PVAm are not well understood, yet. This concerns the physical adsorption process and the chemical bonding as well as the accompanying molecular changes.

Surface enhanced infrared imaging spectroscopy was applied to study the PC / PVAm interfacial layer. The reaction between PC and PVAm was caused by a magnetic high field pulse at a low frequency [1]. Noble metal nanoparticles are placed within the polymer interface layer. The particles transform the magnetic field energy into localized thermal energy and are afterwards used for surface enhanced spectroscopy to characterize the interface. The IR spectra of the interface layer indicate urethanes and urea as main intermediates and interfacial chemical components. Furthermore, different types of O…H hydrogen bonds could be detected and indicate a partial degradation of PC skeleton. The identification of degradation intermediates and reactions is important because such processes reduce the mechanical stability of composite material.

This fundamental study confirms the suitability of surface enhanced infrared imaging spectroscopy to study thin interfacial polymer layers in a non-destructive manner.

References
Analysis of kinetics parameters for epoxy resin curing with 1-butyl-3-methylimidazolium thiocyanate

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Ionic liquids can be used as catalytic curing agents of epoxy resin [1]. Recently, 1-butyl-3-methyl imidazolium thiocyanate ([BMIM]SCN) was described as one of the most active ionic liquid curing catalyst allowing to obtain epoxy materials, including those modified with carbon nanofillers, with high thermomechanical features [2]. Activation energy of epoxy resin curing with various weight ratios of [BMIM]SCN has been determined using Ozawa and Friedman [3-5] methods for the selected curing conversion rates. Moreover, kinetic parameters of curing reaction k and n for the following models were calculated: n-th reaction order [6] as well as Kamal [7] and Sestak-Berggren [8]. The conversion rates and kinetics parameters were determined on a basis of curing data from dynamic DSC and rheometric measurements performed with four heating rates: 1, 2, 5 and 10K/min. The curing experiments have been performed using DSC (Q-100, TA Instruments) in temperature range 273-653K and ARES rheometer (Rheometric Scientific) in temperature range 313-573K (parallel plate-plate configuration, 40 mm diameter, gap 1 mm). The rate of epoxy resin conversion was calculated by integrating the area under the peak on DSC thermogram by comparing the viscosity value at given temperature to maximal viscosity value, determined on a basis of DMA rheometric curve (equation 1) [9].

\[ \alpha(t, T) = \frac{\eta(t,T)-\eta_{\text{min}}}{\eta_{\text{max}}-\eta_{\text{min}}} (1) \]

where \( \eta(t,T) \) is viscosity at given temperature or time, \( \eta_{\text{min}} \) is minimal viscosity (at beginning of curing process), \( \eta_{\text{max}} \) jest maximal viscosity reached during curing reaction (for full conversion rate \( \alpha=1 \)).

Sesták-Berggren and Kamal models properly described curing reaction of epoxy resin with the ionic liquid applied. Increasing ratio of [BMIM]SCN in epoxy composition caused slight increase of autocatalytic process as well as activation energy.

On a basis of DSC as well as rheometric results it was found that for determination of curing reaction kinetics parameters both Sestak-Berggren and Kamal models can be used. Moreover, kinetics parameters calculated on a basis of rheometric curves better described main curing process.

References
Epoxide/MCNT and Epoxide /BN₃ composite materials and their characterization


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Epoxide polymers are polyepoxide composites having high thermal and mechanical strength properties[1]. In our study with insitu techniques cetyl trimethylammonium bromide (CTAB) in the polymer composite ionic liquid medium (epoxide/CTAB/BN₃, epoxide/CTAB/CNTs) are performed. NPEK 114 for epoxy monomers were used in the preparation of composite for CNT / epoxy and BN₃/epoxy composites 0.6% (epoxy / CTAB / CNTs, epoxide/CTAB/BN₃) were prepared mixture ratio. The composite mixture stirred 20 min in an ultrasonic dispersion 30% epoxide hardener (PC17 to EPAM ) and epoxide accelerator and 1% ( DMP 30 ) was added. Composite materials are transferred into the prepared mold, to cure respectively at 40, 80 and 100 ° C in a vacuum oven was allowed to stand one day. Physicomechanical properties of the composite structure is removed from the mold and FT-IR were analyzed by SEM and XRD analysis. The intensity of the band at 913 cm⁻¹ decreases with increasing degree of curing , which means that the band at 913 cm⁻¹ can sensitively reflect the change of the epoxy groups and better obeys the Beer-Lambert Law [2,3]. The degree of curing of composite materials polyepoxide 91% - 92% in the range was calculated. SEM images of the composite structure are given below.

Keywords: Epoxide, nanocomposite, CTAB

![SEM image of CNT/CTAB/epoxide polymers composides pH:11](image1a)

![SEM image of BN₃/CTAB/epoxide polymers composides pH:11](image1b)

Figure 1: a) SEM image of CNT/CTAB/epoxide polymers composides pH:11, b) SEM image of BN₃/CTAB/epoxide polymers composides pH:11

References
As a next generation material, hydrogels for their desirable mechanical and chemical properties have found widespread applications from 3D-printing to tissue engineering. A more recent development—Magnetic hydrogels, which incorporate super-paramagnetic nanoparticles (SMNPs) into the gel system, have attracted much attention recently [1] due to their responsiveness to external magnetic fields.

Previous work [2] has suggested that the Bloembergen-Purcell-Pound (BPP) \(^1\)H relaxation model, with three distinguishable types of water, could be used to describe the water dynamics inside many hydrogels. However, for magnetic hydrogels the SMNP provide additional relaxation pathway which complicate the picture. In this study, magnetic hydrogels prepared with different polymer types and fabrication methods were investigated through Fast Field Cycling NMR (FFC-NMR) Relaxometry, HR-MAS DOSY, and SEM with a view to clarifying the contributions to the re-orientational and translational water dynamics to the NMR response. The application of NMR analysis to the study the nanoscale structure of the hydrogels, and also of their magnetic responsiveness will be discussed.

Figure 1: left: magnetic hydrogel; right: NMRD curves of magnetic hydrogels with different MNP doping concentration.

References
Heterophase Polymerization of Pyrrole and Ethoxylated Nonylphenol by Cerium (IV)

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Redox systems of Ce$^{4+}$ salts and organic reducing agents are well known initiators for vinyl polymerization in aqueous media. Homopolymers, block copolymers and graft copolymers were obtained via Ce$^{4+}$ salts and reducing compounds such as alcohols, polyoils, acids, amines, thiols, thiourea[1] and ketonic resins[2]. Polystyrene, polyacrylonitrile and polyacrylic acid containing chain ends of ethoxylated nonylphenol(ENP) were prepared using ceric-ENP redox initiator system[3].

In this work, copolymers of pyrrole and ENP were synthesized via redox polymerization at room temperature. Polymerization of pyrrole was performed by cerium(IV) ammonium nitrate(CAN) in combination with ENP in acidic aqueous media. ENP served both as a reducing agent of the redox system and an emulsifier for pyrrole with poor solubility in water. ENPs with changing number of ethoxy units (ENP10 and ENP30) were used in order to investigate the influence of ethoxylated component on the properties of the copolymers.

\[
\begin{align*}
\text{C}_9\text{H}_{18}+\frac{O}{(\text{CH}_2\text{CH}_2\text{O})_n}\text{H} & \xrightarrow{\text{Ce}^{4+}} \text{C}_9\text{H}_{18}+\frac{O}{(\text{CH}_2\text{CH}_2\text{O})_n}\text{H} \\
\text{Pyrrole (P)} & \quad \text{ENP}\text{H} \\
\text{(Intermediate complex)} & \\
\text{C}_9\text{H}_{18}+\frac{O}{(\text{CH}_2\text{CH}_2\text{O})_n}\text{H} + \text{H}^+ + \text{Ce}^{3+} & \rightarrow \text{C}_9\text{H}_{18}+\frac{O}{(\text{CH}_2\text{CH}_2\text{O})_n}\text{H}+\text{H}_2\text{O} + \text{Ce}^{4+}
\end{align*}
\]

Figure 1: The formation of pyrrole and ethoxylated nonylphenol copolymers.

The resulting copolymers were characterized with spectroscopic methods. The effect of the concentration of Ce$^{4+}$ salt and pyrrole on yield, solubility and conductivity was investigated, as well as ENP type. Results showed that yield of the copolymers strongly depend on Ce$^{4+}$ concentrations while electrical conductivities of copolymers were measured to be $10^{-3}$ S/cm.

References
Synthesis and Characterization of Poly (alkyloxyethylacrylate-co-methacrylate) As Solid Solid Phase Change Materials for Thermal Energy Storage

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In this study, 2-hydroxyethyl acrylate has been copolymerized with methacrylate after esterified with acyl chlorides of three different fatty acids to obtain polymeric solid-solid phase change materials. Polymers have been synthesized as a result of the reaction between produced monomers and methacrylate at 3 different weight ratios. Produced copolymers were characterized by structural and thermal aspects. For the synthesis of the novel PCMs, myristic acid, palmitic acid, and stearic acid were chosen and they were transformed to acyl chlorides by thionyl chloride in the presence of dimethylformamide catalyst \cite{1}. Fatty acid acyl chlorides were bound to 2-hydroxyethylacrylate monomer from hydroxyl group.

FT-IR and NMR spectroscopy techniques were used to characterize the produced PCMs structurally as molecular weight measurements were done using Gel Permeation Chromatography (GPC) technique. Molecular weight of the produced polymers decreased by the fatty alkyloxyethylacrylate monomer content and with increasing paraffinic side length. Melting and crystallization temperatures and enthalpies and degradation temperatures of the synthesized PCMs were investigated using Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) instruments respectively and it was found that produced polymers have potential to be used as thermal energy storage materials and stable up to considerably high temperatures. On the other hand structural and thermal consistency of the polymers was confirmed by FT-IR and DSC measurements after accelerated thermal cyclings.

Thermal conductivity of the polymers was found to be similar to the thermal conductivities of fatty acids \cite{2}. Besides polarize optical microscopy was used for morphology investigation of polymers below and above phase transition temperatures.

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Acknowledgments: We would like to thank the Scientific & Technical Research Council of Turkey (TUBITAK) for their financial support for this study (The Project Code: 108T865-TBAG).
Synthesis and Characterization of ABA-type tri-block copolymer through Atom Transfer Radical Polymerization containing benzothiazole derivative

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Atom transfer radical polymerization (ATRP) is a simple route to synthesize well-defined copolymers having predetermined molecular weight, narrow molecular weight distribution, [1-2]. It has been effectively applied to the preparation of polymers with precisely controlled functionalities, topologies, and compositions [3]. Variety of polymers with different structures and architectures have been prepared through ATRP like polymer brushes, block copolymers, graft copolymers, star shaped copolymers etc. In present investigation, novel ABA-type poly (4-(2-(benzothiazol-2-yl) vinyl) phenyl acrylate – polyurethane – poly (4-(2-(benzothiazol-2-yl) vinyl) phenyl acrylate i.e. (PBVPA – PU – PBVPA) tri-block copolymers, with pendant triphenylamine group, were successfully synthesized via the copper catalysed atom transfer radical polymerization. 2-methyl-2- bromopropionate terminated polyurethane (Br-PU-Br) was first synthesized from diol containing triphenylamine pendant and used it further as a ATRP macroinitiator to synthesize tri-block copolymers using CuBr as a catalyst and N,N,N’,N”,N”-pentamethyldiethylenetriamine (PMDETA) as a ligand. 4-(2-(benzothiazol-2-yl) vinyl) phenyl acrylate was synthesized as reported in literature [4] to be used as monomer. Monomer, Macroinitiator and triblock copolymer was characterized by FTIR, Proton NMR, $^{13}$C – NMR, UV—Visible Spectroscopy, and Gel permeation chromatography (GPC).

References
Cure Kinetic Study of Catalyzed and Non-Catalyzed Thiol-Isocyanate Reaction

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The high reactivity between thiols and isocyanates under base catalysis has been well-known in small molecule organic and polymer chemistry for over half a century.[1] This reaction generates thiocarbamates in high-to-quantitative efficiency. But it was not until the recent definition of the ‘click’ reaction concept,[2] when the thiol-isocyanate reaction has gained more relevance in materials science. An interesting field of application of thiols and isocyanates results in the field of self-healing materials. In the case of using epoxy-amine resin as the matrix, the tertiary amine formed after the reaction can act as catalyst for the thiol-isocyanate reaction.[3]

Here, we use calorimetric techniques for the kinetic study of the shelf-healing agents in absence or presence of the matrix as catalyst. The unexpected two-step mechanism in the thiol-isocyanate reaction at low temperature led us to the use of spectroscopic techniques to determine the intermediate products formed during the reaction.

References
Latent heat thermal energy storage (LHTES) was identified as an attractive alternative way to get better thermal performance from solar passive heating and cooling devices. Contrasted with sensible energy storage, the LHTES method based on the use of phase changing material (PCM) is more preferred due to its providing important advantageous such as high-energy storage per unit volume at an almost constant servicing temperature and more contribution to an efficient and environmental friendly energy usage [1]. In general, PCMs have been generally encapsulated by polymeric shell that plays an important role in improving the structural stability, light permeability, controlled release, and thermal stability of encapsulated PCMs [2,3].

In this work is aimed to prepare, characterize and determine of thermal energy storage properties of micro/nano encapsulated palmitic-lauric acid eutectic mixtures (PA-LA) with polymethyl methacrylate(PMMA) shell. The eutectic combination and the optimum melting temperature of the binary system of the PA-LA binary system were determined prior to the encapsulation. By using emulsion polymerization method, the PMMA/(PA-LA) micro/nano capsules was synthesized successfully as novel encapsulated phase change materials (PCM) for different monomer/(PA-LA) ratios. The polymerization reaction to be occurred around the PA-LA as core material was proved using Fourier transform infrared (FTIR) spectroscopy. The polarized optical microscopy (POM), scanning electron microscopy (SEM) analysis results and the particle size distribution (PSD) showed that the synthesized encapsulated PCM was consisted of uniform spherical shape-capsules with micro/nano sizes. The differential scanning calorimetry (DSC) measurements revealed that the prepared micro/nano capsules containing the highest PA-LA content had a melting temperature of about 30°C and latent heat storage value of about 107J/g. Thermogravimetry analysis (TGA) demonstrated that the PMMA/(PA-LA) micro/nano capsules were durable up to 240°C and had good thermal and chemical stability even after subjecting them to 5000 melting/freezing cycles. Furthermore, the prepared micro/nano capsules had reasonable thermal conductivity values. Furthermore, from the determined thermal energy storage properties of the synthesized four kinds of PMMA/PA-LA micro/nano capsules make them a promising encapsulated PCM especially for solar passive heating and cooling applications in building and thermal regulation of food storage, textile, medical and electronic materials.

References

Acknowledgments: We would like to thank the Scientific & Technical Research Council of Turkey (TUBITAK) for their financial support for this study (The Project Code: 112T864-KBAG).
Polypyrrole Nanotubes and their Composites with Silver

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Polypyrrole nanotubes have been prepared by the oxidation of pyrrole with iron(III) chloride in the presence of methyl orange \cite{1,2} (Fig. 1). The models describing the nanotubular growth have been proposed. The conductivity of polypyrrole nanotubes was 60 S/cm.

The nanotubes have subsequently been used for the reduction of silver ions \cite{1}. The resulting polypyrrole/silver composites are conveniently characterized by FTIR and Raman spectra. The composites had conductivity 21 S/cm only.

Similar composites have been prepared also by the alternative way, by the oxidation of pyrrole with silver nitrate, again in the presence of methyl orange. Such composites also contained one-dimensional polypyrrole nanostructures and they had conductivity of 3400 S/cm. They were, however, macroscopically heterogeneous and contained silver particles visible by the naked eye.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{nanotubes.jpg}
\caption{Polypyrrole nanotubes}
\end{figure}

\textbf{References}


Nanocomposite Production from Fiber Structure Sepiolite and Polysulfone

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Nanofibers are the materials in the fiber form that have diameter equal to or less than 100 nm. Nowadays, its potential applications include filtration devices, textile industry, tissue engineering scaffolds, sensors, membrane and coating materials development, electronic applications, etc. Natural clay is one of the alternative biodegradable fiber materials for the use of this purpose. In natural fiber clays, sepiolite has an special importance due to the fact that Turkey has the second biggest sepiolite reserve on the earth. Sepiolite is a hydrate magnesium silicate fiber that is also one of the well known layered clays of the montmorillonites where has several unique channels and pores within.

Polysulphone (PSU) is a membrane polymer which is mostly used in waste water treatment for its good mechanical properties, structural and chemical stability. But unfortunately PSU is hydrophobic and because of this its surface aim to pollute easily [1]. In order to resolve this problem, PSU surface is rendered hydrophilic by addition of the sepiolite nanofibers. Sepiolite channels give great capacity of absorption and good surface properties. Therefore sepiolite is used in many industrial products due to its moisture durability, bio-degradability, naturality, strength and low price [2].

![PSU](image)

Figure 1: Polysulphone

In this study sepiolite fibers are used for the polysulphone membrane preparation. Sepiolite added polysulphone membranes were characterized by AFM, XRD, FTIR, DSC, permeability, antifouling and filtration performances. All mechanism starting from compatibility of polymer/clay, fouling mechanism, chemical fouling and mechanism, membrane porosity, membrane surface properties will be discussed by AFM measurement facilities.

References

Synthesis and Characterization of Polysulphone from Different Bisphenols

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Polysulphones (PSU) show useful properties such as high strength and stiffness even at elevated temperatures, high continuous use and heat deflection temperatures, excellent resistance to hydrolysis by acids and bases, and good dimensional stability even in complex geometric shapes [1]. These materials have been synthesized via a variety of different routes. The most important commercial routes being nucleophilic aromatic substitution [2] and, to a lesser extent, electrophilic aromatic substitution. There are two ways to functionalize PSUs. The first type of modification in which the polymer is modified after polymerization. The second type involves direct copolymerization of functionalized monomers [3].

In this study, polysulphone is synthesized from two kinds of bisphenol such as Bisphenol A and Bisphenol AP. Physical and chemical properties are compared between two kinds of polysulphones.

Scheme 1. Formation of Polysulphone

References
Rheological properties and self-healing kinetics of supramolecular polymer network

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A series of supramolecular polyisobutylene melt samples showing self-healing properties was investigated by small angle x-ray scattering and rheological experiments in order to get a microscopic understanding of structure formation and mechanical properties. All samples were bi-functionalized with barbituric acid groups which can form hydrogen bonding with each other. The molecular weights of the samples were varied from 4 kg/mol to 28 kg/mol.

Analysis of the SAXS data and linear rheology showed that the samples form a reversible network of interconnected micelles in which barbituric acids clusters act as physical cross-links and the PIB chains bridge the clusters. Startup shear experiments with large shear strain and high shear rate led to shear yielding accompanied by a fast stress relaxation, indicating failure of the supramolecular network. Small amplitude oscillatory shear measurements after shear yielding were performed to measure the recovery of network and experimental data at different temperatures were compared. Based on the results, we propose a two-step model for the self-healing process: (i) the modulus largely recovers on a time scale given by the terminal relaxation time, followed by (ii) a further increase due to a perfectioning.

Figure 1: schematic picture of the supramolecular network.
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Congress House Hall

Conferences
Main Room *(first floor)*

Exhibition room

Conferences
Second Floor Room
*Salon Vert*

Coffee Break

Entrance

Participant Registration