8th Workshop on Green Chemistry and Nanotechnologies in Polymer Chemistry

6–8 September 2017
Prague
Czech Republic

BOOK OF ABSTRACTS AND PROGRAMME
8th Workshop on Green Chemistry and Nanotechnologies in Polymer Chemistry

6–8 September 2017 Prague Czech Republic

Book of Abstracts and Programme
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8th Workshop on Green Chemistry and Nanotechnologies in Polymer Chemistry

Organized by the Institute of Macromolecular Chemistry, Czech Academy of Sciences

Hynek Beneš
Conference Chairman

Petr Štěpánek
Deputy Director of the Institute

Daniela Illnerová, Marie Rodová, Marcela Havelková, Jana Kredatusová, Aleksandra Paruzel
Local Organizing Team

Josef Jůza, Jiří Kaprálek
Technical Support

Address:
Institute of Macromolecular Chemistry
Czech Academy of Sciences
Heyrovského nám. 2
162 06 Prague 6
Czech Republic

Phone: (+420) 296 809 331
Fax: (+420) 296 809 410
E-mail: sympo@imc.cas.cz
Website: http://www.imc.cas.cz
Conference Chairman

Hynek Beneš

Institute of Macromolecular Chemistry,
Czech Academy of Sciences

Scientific Committee

Filomena Barreiro (Portugal)
José Vega Baudrit (Costa Rica)
Hynek Beneš (Czech Republic)
Ugis Cabulis (Latvia)
Janusz Datta (Poland)
Miroslava Dušková (Czech Republic)
Arantxa Eceiza (Spain)
Jana Kredatusová (Czech Republic)
Andrea Lazzeri (Italy)
Aleksander Prociak (Poland)
Tomáš Vlček (Czech Republic)
8th Workshop on Green Chemistry 
and Nanotechnologies in Polymer Chemistry

Dear Colleagues,

It is my honor and pleasure to welcome you at the 8th Workshop on Green Chemistry and Nanotechnologies in Polymer Chemistry in Prague on behalf of the organizers from the Institute of Macromolecular Chemistry, Czech Academy of Sciences.

The Workshop on Green Chemistry and Nanotechnologies in Polymer Chemistry (GCNPC) is a yearly scientific conference dedicated to recent trends in polymer science. GCNPC includes two popular areas of current research: it is the green approach utilizing renewable resources and mild reaction conditions on the one hand, on the other hand innovative nanotechnologies enabling to design novel polymer materials with advanced properties. The 8th edition of GCNPC will demonstrate that combination of these two approaches, on the first view incompatible ones, will enable the development of greener concepts for advanced polymer materials.

The scientific sessions are thematically focused, covering all frontiers topics in (i) Green Polymer Chemistry: green materials composed of renewable resources, biodegradable materials, low environmental impact routes such as microwave assisted polymerizations, green solvents comprising ionic liquids, polymer waste valorization, etc., and in (ii) Polymer Nanotechnologies: nanomaterials with bio-based and functional nanofillers, nanostructured networks, polymer nanoparticles for sustainable technologies, etc.

I hope that this event will offer you fruitful scientific two days in a friendly environment for encouraging open discussions, exchanging ideas and initiating novel collaborations. Have an enjoyable time in Prague!

Hynek Beneš  
Conference Chairman
CONFERENCE PROGRAMME

Wednesday, 6 September 2017

16:00 – 19:00 Registration with welcome buffet

Thursday, 7 September 2017

9:00 – 9:10 Opening Ceremony

LECTURE SESSION: Advanced nanostructured polymers

Chaired by: Arantxa Eceiza (Spain)

9:10 – 9:50 Invited lecture IL-01
Jean-François Gérard (France)
Generation of nanostructures within polymer networks from self-assembling and (nano)phase separation processes

9:50 – 10:10 Oral communication OR-01
Noor Hana Hanif Abu Bakar (Malaysia)
Enhanced adsorption of methylene blue by modification of natural rubber with halloysite nanotubes or chitosan

10:10 – 10:30 Oral communication OR-02
Marietjie Lutz (South Africa)
EVOH nanocomposites with improved antimicrobial properties

10:30 – 11:15 Coffee break

10:50 – 11:15 Coffee break
**LECTURE SESSION: Composites and functional nanoparticles**

*Chaired by: Jean-François Gérard (France)*

11:15 – 11:45 Keynote lecture KL-01  
**Andrea Lazzeri (Italy)**  
Biocomposites based on polyesters and natural fibres

11:45 – 12:05 Oral communication OR-04  
**Na Re Ko (Republic of Korea)**  
Novel graphene quantum dot-based theranostic agents for breast cancer treatment

12:05 – 12:25 Oral communication OR-05  
**Marcin Masłowski (Poland)**  
Reinforced smart magnetic polymer composites

12:25 – 12:45 Oral communication OR-06  
**Anna Margot Beltzung (Switzerland)**  
Microporous polyacrylonitrile nanoparticles for CO₂-capture

12:45 – 14:15 **Lunch**

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**LECTURE SESSION: Bio-based materials and composites**

*Chaired by: Marietjie Lutz (South Africa)*

14:15 – 14:45 Keynote lecture KL-02  
**Arantxa Eceiza (Spain)**  
Biobased polyurethanes and nanocomposites

14:45 – 15:05 Oral communication OR-07  
**Sébastien Livi (France)**  
Ionic liquids: New promising additives for biopolymers

15:05 – 15:25 Oral communication OR-08  
**Marcin Włoch (Poland)**  
Chemical structure and properties epoxy resins cured using amine derivative of dimerized fatty acids

15:25 – 15:45 Oral communication OR-09  
**Justyna Miedzianowska (Poland)**  
Natural rubber composites containing cereal straw
15:45 – 16:05  Oral communication OR-10
Carlos Eduardo Orrego (Colombia)
Biobased-foamed epoxy resin composite as support for lipase immobilization

16:05 – 16:30  Coffee break

LECTURE SESSION: Visegrad Session- ABIOG Group
Chaired by: Maria Lujan Auad (USA)

16:30 – 17:00  Keynote lecture KL-03
Szczepan Bednarz (Poland)
Itaconic acid: Branched nanogels and imperfect polymeric networks

17:00 – 17:20  Oral communication OR-11
Nóra Hegyesi (Hungary)
Controlled bulk degradation of poly-ε-caprolactone by the entrapment of lipase enzyme into halloysite nanotubes

17:20 – 17:40  Oral communication OR-12
Eliška Číková (Slovakia)
Electroactive scaffolds based on the modified electrospun poly(ε-caprolactone) fibres

17:40 – 18:00  Oral communication OR-13
Jana Kredatusová (Czech Republic)
Microwave synthesis of PCL/LDH nanocomposites

18:00 – 19:00  Poster Session

20:00 – 22:30  Conference dinner
**Friday, 8 September 2017**

**LECTURE SESSION: From renewable resources to polymers**  
*Chaired by: Maria Filomena Barreiro (Portugal)*

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<td>Invited lecture IL-02</td>
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<td></td>
<td><strong>Alessandro Gandini</strong> (<em>France</em>)</td>
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<td></td>
<td>The Diels-Alder reaction applied to polymers from renewable resources:</td>
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<td>Thermal reversibility and recyclability</td>
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<td><strong>Aleksander Prociak</strong> (<em>Poland</em>)</td>
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<td>Rigid polyurethane foams modified with lignin based bio-polyols</td>
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<td>10:10 – 10:30</td>
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<td><strong>Mikelis Kirpluks</strong> (<em>Latvia</em>)</td>
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<td>Investigation of tall oil fatty acid epoxidation kinetics</td>
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<td>10:30 – 10:50</td>
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<td><strong>Maria Kurańska</strong> (<em>Poland</em>)</td>
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<td>Synthesis and characterization of bio-polyols from post-used vegetable</td>
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<td>10:50 – 11:10</td>
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<td><strong>Paulina Parcheta</strong> (<em>Poland</em>)</td>
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<td>Fully bio-based polyester polyols for polyurethanes</td>
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<td>11:10 – 11:35</td>
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**LECTURE SESSION: Polyurethanes and environment**  
*Chaired by: Aleksander Prociak (Poland)*

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<td><strong>Ugis Cabulis</strong> (<em>Latvia</em>)</td>
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<tr>
<td></td>
<td>Mechanical and thermal properties of polyurethane foams obtained from</td>
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<td>renewable and recyclable components</td>
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12:05 – 12:25 Oral communication OR-17
Isabel P. Fernandes (Portugal)
Development of a modified pre-polymer method to produce NMP-free polyurethane-urea aqueous dispersions

12:25 – 12:45 Oral communication OR-18
Patrycja Maria Jutrzenka Trzebiatowska (Poland)
Characterization of cast polyurethanes with high content of recycled polyol

12:45 – 13:05 Oral communication OR-19
Sylwia Członka (Poland)
Natural oils as a chain extenders in the synthesis of rigid polyurethane foams

13:05 – 14:30 Lunch

LECTURE SESSION: Structured hydrogels and hybrid polymers
Chaired by: Alessandro Gandini (France)

14:30 – 15:00 Keynote lecture KL-06
Miroslava Dušková (Czech Republic)
Microstructured pHEMA-hydrogels as sustainable materials for biological studies

15:00 – 15:20 Oral communication OR-20
Maria Lujan Auad (USA)
Interpenetrating hydrogel networks for use in tissue engineering and agricultural applications

15:20 – 15:40 Oral communication OR-21
Kamol Dey (Italy)
Preparation and assessment of high performance gelatin-based hydrogels for tissue engineering

15:40 – 16:00 Oral communication OR-22
Alexandra Gârea (Romania)
Organic-inorganic hybrid polymer: A new organophylization agent for layered silicates

16:00 – 16:10 Closing ceremony

16:10 – 16:40 Farewell coffee
LIST OF POSTERS

POSTER SESSION A – GREEN CHEMISTRY OF POLYMERS

P-01  A. Abolins, V. Yakushin, D. Vilsone
Properties of polyurethane coatings based on linseed oil phosphate polyols

P-02  P. Jutrzenka Trzebiatowska, A. Gelo, E. Głowińska, M. Włoch,
P. Kosiorek, P. Parcheta, K. Błażek, J. Datta
Rigid polyurethane foams based on semi-product from polyurethane decomposition process

P-03  N. Petkova, G. Gencheva, D. Vassilev, M. Koleva, P. Denev,
A. Krastanov
Microwave-assisted isolation and acetylation of inulin from Helianthus tuberosus L. tubers

P-04  P. Parcheta, J. Datta, P. Jutrzenka Trzebiatowska, P. Kasprzyk,
K. Błażek, E. Głowińska, M. Włoch
The catalyst impact on the fully bio-based poly(propylene succinate) structure

P-05  D. Vassilev, N. Petkova, M. Koleva, P. Denev
Application of ultrasound assisted sythesized sucrose palmitate as bio-plasticiser of poly vinylchloride

P-06  E. Vanags, M. Kirpluks, U. Cabulis
Epoxidation of free fatty acids distilled from tall oil by in situ formed peracetic acid

P-07  A. Fridrihsone, U. Cabulis, F. Romagnoli
Cellulose production by-products as a raw material for polyurethane industry – a life cycle assessment approach

P-08  R. Bouza, S. Malmir, B. Montero, M. Rico, L. Barral
Biodegradable films of PHBV/cellulose nanocrystals: Thermal and rheological properties

P-09  M. Méndez-López, C. Saldías, A. Ramos, V. Moreno, D. Radić,
A. Leiva
Preparation and characterization of polysaccharide/ conducting polymer films
P-10 V. Moreno-Serna, M. Méndez-López, A. Leiva, D. Radić
Preparation and characterization of chitosan:poly(3-hexylthiophene) and quantum dots hybrid films

P-11 C. M. Trindade, L. C. G.de S. Santos, E. Ayres
Effect of sorbitol on swelling behavior of chitosan films prepared with lactic acid

P-12 L. C. G.de S. Santos, E. Ayres, M. L. B. Almeida, R. L. Oréfice
Synthesis and evaluation of bio-based waterborne

Natural rubber vulcanizates obtained using chemical recycling products of polyurethanes as a plasticizers

P-14 S. Michałowski, M. Palka, A. Prociak
Rigid polyurethane foams obtained using reactive catalysts

Biodegradation of polyester polyols-based polyurethane foams for agricultural landscape applications

P-16 K. Beyaz, A. Benaboura, C. Vaca-Garcia, S. Thiebaud-Roux
Graft-copolymerization of acrylic monomers onto cellulose extracted from palm leaves

POSTER SESSION B – NANOTECHNOLOGIES IN POLYMER SCIENCE

P-17 L. Sartore, K. Dey
Organic-inorganic hybrid composites for removal of heavy metal ions from water

P-18 E. Głowińska, J. Datta, M. Włoch, K. Załęska, P. Jutrzenka
Trzebiatowska
Structure, morphology and thermal properties of polyurethane composites containing spirulina

P-19 E. Głowińska, J. Datta, M. Włoch, P. Parcheta, N. Kaźmierczak
New aproches of spirulina as a filler in natural rubber based composites
P-20  P. Threepopnatkul, W. Thongsong, C. Kulsetthanchalee
Effect of nano fillers on properties of PBAT/PET thin film

P-21  M. Włoch, J. Datta, E. Głowińska, K. Błażek, P. Kosiorek
Green natural rubber-based composites filled with buckwheat husks powder

Thermoplastic starch composites with high contents of titanium dioxide particles and homogeneous morphology

P-23  E. Pietrzykowska, A. Chodara, B. Romelczyk, T. Chudoba, W. Łojkowski
New production methods of orthopedic composites from polymers and ceramic

POSTER SESSION C – VISEGRAD ADVANCED MATERIAL GROUP (ABIOG)

P-24  W. Kasprzyk, W. Mak, S. Bednarz, D. Bogdał
Citric acid based fluorescent polymers

P-25  A. Eckstein - Andicsová, A. Šišková, E. Kozma
Potential application of silk fibroin as biomaterials

P-26  B. Gyarmati, E. Krisch, B. Szilágyi, A. Szilágyi
Thiolated poly(amino acid)s displaying in situ oxidation induced gelation

P-27  A. Paruzel, H. Beneš, J. Kredatusová, Z. Kruliš, K. Tošovská, P. Innemanová
Biodegradable polyurethane foams from polyester-ether polyols and renewable resources

P-28  H. Beneš, A. Paruzel, Z. Walterová, O. Trhlíková
Role of natural oil structure for polycarbonate conversion into polyurethane polyols
INVITED LECTURES
GENERATION OF NANOSTRUCTURES WITHIN POLYMER NETWORKS FROM SELF-ASSEMBLING AND (NANO)PHASE SEPARATION PROCESSES

J.-F. Gérard\textsuperscript{a}, J. Duchet\textsuperscript{a}, S. Livi\textsuperscript{a}, S. Pruvost\textsuperscript{a}, F. Lortie\textsuperscript{a}, A. Gallon\textsuperscript{a}, T. K. L. Nguyen\textsuperscript{a}, L. Dai\textsuperscript{b}

\textsuperscript{a}IMP UMR CNRS 5223 – Université de Lyon/INSA-Lyon, 20, Avenue A. Einstein, F-69621 Villeurbanne, France
\textsuperscript{b}College of Materials, Xiamen University, Kuxue Building #433, Siming Nan Road #422, Xiamen, 361005, China
(jean-francois.gerard@insa-lyon.fr / http://www.imp-cnrs.fr)

The introduction of organic nanostructures as well as inorganic or organic-inorganic nano-objects into polymer networks from conventional dispersion route and/or (nano)phase separation or self-assembling processes is known to be an efficient way to design multi-functional polymer materials. Different routes offered for nanostructuration of polymer networks such as polyepoxy will be detailed in this lecture. For all of them, a reaction induced (nano)phase separation phenomena allows to generate desired nanostructures:

- synthesis and introduction of supramolecular units from a functionalized comonomer, i.e. ureidopyrimidinone functionalized amine, which could self-assemble to form multifunctional physical crosslinks combined with chemical crosslinks
- use of phosphonium-based ionic liquids to synthesize epoxy networks. From a proper selection of the anion-cation combination, ionic nanophases could be \textit{in-situ} generated
- introduction in the reactive systems of organic or organic-inorganic block copolymers leading after polymerization to nanoparticles or co-continuous nanophases

For each route, the nanostructuration mechanisms and consecutive morphologies as well as the resulting physical properties will be reported in the lecture.
THE DIELS-ALDER REACTION APPLIED TO POLYMERS FROM RENEWABLE RESOURCES: THERMAL REVERSIBILITY AND RECYCLABILITY

A. Gandini

Laboratoire de Génie des Procédés Papetiers (LGP2), UMR CNRS 5518, Grenoble INP-Pagora – 461, Rue de la Papeterie, 38402 Saint-Martin-d’Hères, France
São Carlos Institute of Chemistry, University of São Paulo, Avenida Trabalhador São-Carlense 400, 13566-590, São Carlos, SP, Brazil (agandini@iqsc.usp.br)

The Diels-Alder (DA) reaction applied to monomers incorporating furan and maleimide moieties is discussed in terms of the synthesis of different macromolecular structures including linear, branched and crosslinked architectures of homo- and co-polymers. Emphasis is placed, on the one hand, on the interest associated with this strategy regarding the thermal reversibility of these DA materials, which allows their mendability and recyclability to be readily attained, and, on the other hand, on the specific application of these features to monomers or polymers from renewable resources, such as plant oils, starch, cellulose, chitosan, gelatin and natural rubber, quite apart from the ubiquitous presence of the furan heterocycle in all the systems described.
KEYNOTE LECTURES
The utilization of “bio-polymers” for the production of “bio-plastic” is worldwide an assessed priority with the aim of reducing dependence from petro sources, and handle the concern for disposal of waste generated from not degradable plastics. The present contribution reviews some recent research developed in our unit on bio based composites particularly by using compostable polymers such as polylactic acid (PLA), and polymers degradable even in soil and marine water such as polyhydroxyalkanoates (PHAs) with natural fibres\(^1\)\(^-\)\(^3\) developed in the framework of the Regional project PHA “Produzione eco-sostenibile di polidrossialcanoati (PHAs) e loro utilizzo in materiali compositi per applicazioni in campo marino/costiero e agricolo/vivaistico”, Project POR FESR 2014-2020 and of the European Union’s Horizon2020, Project AGRIMAX Agri & Food waste valorization co-ops based on flexible multi feedstock biorefining processing technologies for new high added value applications” GA: n° 720719.

Most of the polymers we use nowadays are of petrochemical origin. The development and advancement around these materials make that they continue replacing materials such as metals or glass for instance, due to factors such as lightness, low cost and design versatility. However, the scarcity and increased cost of fossil sources, and growing environmental consciousness, have aroused interest in the use of renewable raw materials for the synthesis of chemicals. Polyurethanes (PU) constitute an important part of the polymer market, ranking in the fifth place in European plastics demand.\textsuperscript{1} That is why the interest of raw materials of renewable origin has also extended to the synthesis of these polymers. Polyol is the major component of the PU formulation, so the total or partial substitution of polyols of petrochemical origin by polyols of renewable origin contributes to increase the renewable carbon content in the final material.\textsuperscript{2} The interest in the replacement of petroleum derived isocyanates by biobased is also growing,\textsuperscript{3} contributing to reduce even more the dependence on non-renewable sources. Therefore, biobased polyurethanes (foams, crosslinked and thermoplastics) containing polyols, low molecular mass diols and/or diisocyanates, derived from vegetable oils, sugars and amino acids, among others, as well as bionanocomposites with renewable nanoentities have been synthesized and characterized.

Financial support from the Basque Government in the frame of Grupos Consolidados (IT-776-13), the Spanish Ministry of Economy and Competitiveness (MAT2016-76294-R) and technical support provided by SGIker (UPV/EHU) are gratefully acknowledged.

Itaconic acid is an unsaturated dicarboxylic acid produced industrially by fermentation in biotechnological processes. The acid can be an interesting and renewable starting material for synthesis of polymers due to their dual polymerization mechanism i.e. by formation of ester bonds and also by free-radical mechanism.1-3 Here we report properties of cross-linked products obtained by reaction of the acid with N,N'-bismethyleneacrylamide both in aqueous solution and in a low transition temperature mixture of itaconic acid with choline chloride. Tentative structures of prepared nano- and macrogels were proposed.

Acknowledgement: This research was supported in part by Polish-Czech bilateral projects (ID/PL 9023/R14/R15, ID/CZ 7AMB14PL021) and by International Visegrad Fund under Small Grant Programme (ID 21620101).

Nowadays, a large number of polyurethane (PU) systems modifications relies on the use of different bio-polyols, as described in literature. Among them, one of the most important is the incorporation of bio-polyols based on plant wastes such as lignin. In this work, two bio-polyols have been synthesized from a technical lignin and applied to obtain rigid PU foams (10-30wt. in polyol premix). The lignin, obtained by an organosolv process (aqueous ethanol) proceeds from hardwoods and was converted into liquid bio-polyols by an oxypropylation process. The addition of the lignin-based bio-polyols to the PU system increased its reactivity, as confirmed by a faster decrease of the dielectric polarization and an increase of the maximum temperature in the foam core during the foaming process. The foam modified with these bio-polyols had a slightly lower apparent density and compressive strength. The obtained foams have an apparent density and a closed cell content of about 40 to 45 kg/m³ and 86-89%, respectively. The compressive strength of the foams decrease as the bio-polyol content increased. On the other hand the thermal conductivities of the obtained materials were similar ca. 23 mW/m·K. Concerning thermal stability, lignin-based foams start to degrade at lower temperatures and show a slower degradation pattern (high residue in TG).


Acknowledgement: POCI-01-0145-FEDER-006984 (LA LSRE-LCM), funded by ERDF, through POCI-COMPETE2020 and FCT; Project NORTE-01-0145-FEDER-000006, funded by NORTE2020 under PT2020, through ERDF.
Here we report new formulations of aromatic polyester polyols, which were synthesized from building blocks of rapeseed oil (RO) and depolymerized PET oligomer, and their use in the manufacturing of rigid PU foams for thermal insulation applications. The synthesis of PU bio-based polyols was carried out in three steps: (1) the transesterification of RO with triethanolamine (TEA); (2) the industrial PET waste depolymerization by the transesterification reaction with diethylene glycol (DEG) in the presence of various concentrations of functional additives glycerol (GL) and adipic acid (ADA); and (3) synthesis of the final PU polyol by the transesterification of the above-mentioned intermediary components. On average, the polyols blends that were processed into the PU rigid insulation foams consisted of 55% renewable and recycled components. The structure and mechanical properties of the processed PU rigid foams were investigated.

By varying the ADA and GL content of the foams, we were able to modify the chain structure, branching, and functionality of the polyols. These modifications significantly improved the mechanical properties of the obtained material. The increase in the additive concentration in the polyol allowed us to gradually enhance the mechanical characteristics of the foams. Using compression tests on PU rigid foams, we found that for some GL/ADA contents the rigidity increased almost 3-fold; whereas the strength increased almost 2-fold. The water absorption of the foams was below 3 wt.%.

Using DMA and TMA methods PU rigid foams were characterized in wide temperature interval.
Modern society seeks alternatives to testing on animals done for example to comply with the REACH, FDA or other standards. To avoid in vivo testing, in vitro studies using cells, tissues or organs are performed. Synthetic hydrogels based on poly(2-hydroxyethyl methacrylate), pHEMA, are example of a perfect carrier for in vitro also for their non-toxicity. In our recently started joint project “Computational design of microstructured hydrogels” we focus at modeling of hydrogel structure and properties to tailor the materials for specific biological models. One of the aims is to control stiffness on the microscopic level – i.e. to retrieve information what individual cells feel when seeded on the hydrogel. The input information includes theory of (visco)elasticity of the swollen system, and sorption of fluids (water+additives). The models are based on statistical thermodynamics of molecular systems. We have adopted the approach of scanning and digital reconstruction of the 3-D materials structure. The central node of our computational design program is the Finite Element Method (FEM) solver which offers the characterization of macroscopic as well as selected microscopic properties of the material subjected to loads of various geometries. Examples will be shown in this presentation, namely: analysis of a swollen macroporous gel by confocal microscopy and 3-D reconstruction, deformation response of the gel in comparison with non-porous material, mechanical behavior of a swollen particulate composite; tensile and shear moduli and stress and swelling degree distribution on the scale of several filler particles.

Acknowledgement: Czech Science Foundation – Project No 17-08531S and the Institutional support RVO: 61389013.
ORAL COMMUNICATIONS
ENHANCED ADSORPTION OF METHYLENE BLUE BY MODIFICATION OF NATURAL RUBBER WITH HALLOYSITE NANOTUBES OR CHITOSAN


School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Pulau Pinang, Malaysia
(hana_hanif@usm.my)

Natural rubber (NR) can be modified by incorporating halloysite nanotubes (HNT) or grafting with chitosan to improve its adsorption properties towards methylene blue. For the natural rubber – halloysite nanotube (NR-HNT) films, a series of samples were prepared by incorporating various weight percentages (wt%) of halloysite nanotubes (HNT) into natural rubber latex (NRL). The mixture was cast into films and the distribution of HNT was investigated using scanning electron microscope (SEM) while thermogravimetric analysis was employed to gain insight on the stability of the nanocomposites. At lower wt%, the HNT was well-dispersed. When the wt% was increased, aggregation of HNT occurred. This influenced the stability of the composites. Higher T$_{\text{onset}}$ and T$_{\text{max}}$ were observed for the NR-HNT as compared to pristine NR. These values varied depending on HNT distribution. MB adsorption studies were carried out to investigate the ability of the NR-HNT samples to adsorb dye. Results showed that all the NR-HNT films exhibited more than 80 % MB removal in comparison to 40 % by NR within 3 hrs. The 10 wt% NR-HNT showed the highest q$_t$ value. The films were capable in removing MB completely up to five times. This is similar to free HNT, however the time for complete adsorption differed significantly. In contrast to the NR-HNT films, when NR was grafted to chitosan (wt ratio Chitosan/NR (%) = 1, 4 and 5), it was found that the removal of MB increased drastically within 30 minutes depending on the wt ratio (%) of chitosan/NR. In this case, 76 % removal was achieved for the chitosan/NR wt ratio (%) = 5. Further investigations are being carried out to understand this phenomenon.
EVOH NANOCOMPOSITES WITH IMPROVED ANTIMICROBIAL PROPERTIES

M. Lutz, N. A. Dyayiya

Department of Chemistry and Polymer Science, Stellenbosch University,
De Beer Street, Stellenbosch, 7600, Stellenbosch
(mlutz@sun.ac.za)

The fabrication of polymeric nanocomposite materials with antimicrobial activity received much attention in the past few years. These materials have a wide variety of applications, which include food packaging, medical device technology and water purification applications.\textsuperscript{1-3} Combinations of different antimicrobial agents and good distribution thereof in a specific matrix may lead to better antimicrobial properties.

This study therefore investigates the incorporation of individual as well as combinations of three different antimicrobial agents in different loadings (ranging between 1 wt\% to 10 wt\%) into a poly (ethylene-co-vinyl alcohol) (EVOH) matrix. The antimicrobial agents incorporated were chitin nanowhiskers (ChNWs), chitosan reduced silver nanoparticles (AgNPs) and the antimicrobial peptide, Gramicidin S. ChNWs and AgNPs were incorporated into EVOH by way of solvent casting and electrospinning, individually as well as combined, in order to produce nanocomposite films and nanocomposite fibre mats respectively. The distribution of the antimicrobial agents within the EVOH matrix was investigated using correlative light electron microscopy (CLEM). The nanocomposites were then dip coated in a Gramicidin S solution and the successful attachment of the peptide to the surface of the films and fibre mats was shown by field emission scanning electron microscopy (FESEM).

The peptide showed a tendency to attach more to nanocomposite films and fibres containing higher loadings of ChNWs and AgNPs. The antimicrobial activity evaluated by measuring the bacterial growth inhibition of the nanocomposite films and fibres revealed a higher growth inhibition for the nanocomposites compared to neat EVOH films and fibres. The nanocomposite films showed higher antimicrobial activity when compared to the fibres and all the silver containing nanocomposites had the highest antimicrobial activity, with the 10 wt\% combination of AgNPs and ChNWs revealing a growth inhibition of more than 100%.

\textsuperscript{1} Valeria Chiono, V., Mozetic, P., Boffito, M. \textit{et al.} Interface Focus. 4: 1–11, 2013.
The scope of this study was to obtain elastomer composites filled with conductive carbon black (Printex Xe-2b) exhibiting superior mechanical and electrical properties. It is likely that high specific surface area of Printex Xe-2b allows to obtain polymer composite with enhanced mechanical properties. However, the main problem with this type of materials is their tendency to agglomeration in elastomer matrix. As a result the accumulation of stress as well as deterioration of composite properties may occur. From the literature it follows that ionic liquids may improve the dispersion of the filler particles in polymer matrix. The obtained results have clearly showed that acrylonitrile-butadiene/Printex Xe-2b composites indicated ability to reversible changes of electrical conductivity under the influence of organic solvent vapour. The samples were placed in desiccator in the presence of polar solvent vapour (chloroform). After swelling period the electrical conductivity of the composites was tested. Afterwards samples were dried for 24 hours and their electrical conductivity was measured again. Furthermore, it is worth underlying that application of selected ionic liquids resulted in improved dispersion of the filler particles and formation of “conductive paths”. Additionally, elastomer composites exhibited improved mechanical properties. Polymer composites exhibiting reversibility of their properties under the influence of external factors are called „smart materials” and can be applied in many areas of industry.

A novel graphene quantum dot (GQD)-based nanocarriers with Herceptin (HER) and β-cyclodextrin (β-CD) was developed as a promising candidate of theragnosis agent for active targeting of breast cancer cells. In this strategy, HER allows for the active targeting to HER2-overexpressed breast cancer and the effective accumulation in the cancer cells. β-CD can load hydrophobic anticancer drugs Doxorubicin (DOX) via “host-guest” chemistry, ensuring the dispersity of DOX. The accumulated nanocarriers also enable to diagnose cancer using an optical property of the GQD with blue-color emission. In response to acidic environment of cancer cells, the GQD-complex was degraded and DOX was released in a controlled manner to inhibit proliferation of cancer cells. This multi-functional drug delivery system leads to a synergistically enhanced anticancer activity in cellular environment. The intracellular trafficking results, combined with cell viability and confocal laser scanning microscopy, suggest that the GQD-complex offers versatility in HER2-overexpressed breast cancer targeting drug delivery applications.
REINFORCED SMART MAGNETIC POLYMER COMPOSITES

M. Masłowski, K. Strzelec
Lodz University of Technology, Institute of Polymer and Dye Technology, 90-924 Lodz, Stefanowskiego 12/16, Poland
(marcin.maslowski@p.lodz.pl, www.pb.p.lodz.pl)

Current challenges include designing and production of multifunctional materials that are “smart” at the material level. Reference to material intelligence images three basic functions: sensation of changes, processing the information obtained and response to such changes. Magnetorheological elastomer composites (MREs) are smart materials, consist of magnetically permeable particles in non-magnetic polymer matrix. MRE change their rheological properties under the influence of an external magnetic field. Their rheological properties can be modified continuously, rapidly and reversibly by changing an external magnetic field. This behavior is described by the magnetorheological effect.

The aim of the study was to receive smart magnetic polymer composites with the best mechanical characteristics. MRE based on different magnetoactive fillers in ethylene-octene rubber are reported and studied. To improve mechanical properties of polymer mixtures, also carbon black was added during the composites preparation process. Micro and nan-sized magnetites (Fe$_3$O$_4$) as well as gamma iron oxide (γ-Fe$_2$O$_3$) and carbonyl iron powder (CIP) add together with carbon black were found to be an active fillers systems improving both static and dynamic mechanical properties of elastomers. They also changed magnetic properties of composites.

Dynamic-mechanical analysis (DMA) indicates the presence of strongly developed secondary structure in vulcanizates. Reinforcing character of applied different fillers systems results in an increased stress at 100% elongation, tensile strength and crosslinking density of the vulcanizates. Mechanical properties analysis of vulcanizates subjected to the processes of aging both thermo-oxidizing and ultraviolet indicate that fillers do not cause deterioration of the mechanical properties of vulcanizates. Studies investigated by vibration sample magnetometer (VSM) proved that all composites exhibit good magnetic properties.
Reducing the release of greenhouse gases in the atmosphere is one of the big challenges of this century. Focusing on CO₂ capture, systems are emerging but most of them remain too expensive to be seriously considered for an industrial implementation. For this purpose, we propose a novel and simple material based on highly microporous polyacrylonitrile (PAN) nanoparticles. Microporosity within the nanoparticles is introduced with a three-step heat treatment (oxidation, stabilization and pyrolysis). The first two steps are responsible for two stabilizing chemical reactions: cyclization of the neighboring cyanide groups and the dehydrogenation of the polymer backbone. Lastly, pyrolysis at 900 °C is creating the micropores (0.35-1.5 nm). In this work, the influence of the oxidation temperature on the final microporosity and extent of CO₂-capture was determined. In addition, we explored the presence of basic N-atoms in the structure and its effect on the CO₂-binding.

In the field of biopolymers, academic and industrial research has focused on the development of sustainable composites or nanocomposites based on aromatic or/and aliphatic polyesters filled with nanoparticles (montmorillonite, layered double hydroxide, mica) or with renewable resources such as cellulose, soy stalk, starch and lignin for various applications such as food packaging or compostable films.1,2 Thus, different ways are investigated to lead to nanostructured polymers with unprecedented properties. Very recently, one innovative pathway is the introduction of ionic liquids (ILs) within polymer matrix.3-5 In fact, these organic salts have unique physical-chemical properties such as their inflammability, their low vapour pressure, their excellent thermal and chemical stability and their endless number of cation/anion combinations which make them suitable ideal additives for advanced biopolymers. For these reasons, the combination of the excellent intrinsic properties of phosphonium ionic liquids to biodegradable aliphatic and/or aromatic polyesters such as polylactide (PLA), poly(butylene-adipate-co-tetraphthalate) (PBAT) have been studied.

The influence of the chemical nature of phosphonium ionic liquids (chloride, bistriflimide, phosphinate, carboxylate) has been investigated as new compatibilizing agents of polymer blends blends composed of PBAT / PLA and PBAT / PLA / lignin.

1. S. Livi, V. Bugatti, Bluma G. Soares, J. Duchet-Rumeau, Green chemistry. 2014, 16 (8), 3758.
CHEMICAL STRUCTURE AND PROPERTIES EPOXY RESINS CURED USING AMINE DERIVATIVE OF DIMERIZED FATTY ACIDS

M. Włoch, J. Datta, E. Głowińska

Gdańsk University of Technology, Faculty of Chemistry, Department of Polymers Technology, G. Narutowicza Str. 11/12, 80-233 Gdańsk, Poland (marcin.wloch@pg.gda.pl, www.pg.gda.pl)

Modern polymer science and technology focus on the development of green polymers using renewable resources. In accordance to the literature, the special place is occupied by the vegetable oils and their derivatives (e.g. fatty acids dimers) which can be transformed into valuable “green monomers” e.g. epoxidized vegetable oils.\(^1\) Amine-functional compounds can be obtained by chemical modification of bio-based molecules, as e.g. cardanol, vanillin, pentaerythritol, isosorbide, isosodide, dimers of fatty acids or vegetable oils, and mentioned compounds can be used for the synthesis of epoxy polymers, polyamides or non-isocyanate polyurethanes.\(^1-6\) The main aim of this work was to investigate the influence of biobased diamine (amine derivative of fatty acid dimers) on the performance of epoxy materials. The bio-based curing agent was used separately or in the mixture with petrochemical commonly used curing agent i.e. triethylenetetramine. Chemical structure, mechanical mechanical properties (e.g. tensile properties, hardness), thermal properties and thermal stability of obtained materials were determined and discussed.

Nowadays, public concern about the environment and the availability of limited fossil fuel resources has forced governments, companies, and scientists to find alternatives to crude oil and to develop sustainable materials from renewable resources. Such materials are named ‘‘green composites’’. Green composites are a specific class of biocomposites, where a bio-based polymer matrix is reinforced by natural fibers, and they represent an emerging area in polymer science.\textsuperscript{1} The analysis of literature clearly indicates, that there are no evident research works carried out to improve and verify the properties of elastomer composites with addition of straw. Study designed to characterise thermoplastic polymers containing agricultural crop residues are focused mainly on fibers and do not cover the end of cereal waste management problem.

New technological solution is natural rubber (NR)-based biocomposites containing cereal straw as abundant reinforcing bio-fillers derived from agricultural waste. The studies provide a series of new results from major types of renewable resources, as reinforcing fillers, which are plentiful in nature.

Biofillers were found to be an active fillers improving wide range of rubber composites functional properties like: static mechanical, damping, barrier properties and hardness. The use of straw as a filler also increased crosslinking density. Dynamic-mechanical analysis (DMA) indicates the presence of strongly developed secondary structure of examined fillers in vulcanizates. Moreover, all of the vulcanizates proved to be resistant to thermo-oxidative degradation.

\textsuperscript{1} Zini E., Mariastella S., Polymer composites 32.12:1905-1915, 2011.
BIOBASED-FOAMED EPOXY RESIN COMPOSITE AS SUPPORT FOR LIPASE IMMOBILIZATION


aInstituto de Biotecnología y Agroindustria, Departamento de Física y Química, Universidad Nacional de Colombia Sede Manizales. Km7 Vía al aeropuerto, AA 127 Manizales, Colombia

bFacultad de Ingeniería y Arquitectura, Departamento de Ingeniería Industrial. Universidad Nacional de Colombia Sede Manizales. Km7 Vía al aeropuerto, AA 127 Manizales, Colombia

cFacultad de Ingeniería y Arquitectura, Departamento de Ingeniería Química. Universidad Nacional de Colombia Sede Manizales. Km7 Vía al aeropuerto, AA 127 Manizales, Colombia

(ceorregoa@unal.edu.co)

A biodegradable porous composite based on epoxidized oil resin, polymethylhydrosiloxane (foaming agent),1 and filled with cellulose fibers (CF) was fabricated. The material was stable in pH solutions from 2 to 8. The fibers, extracted from passion fruit stalks by reducing particle size and successive treatments with NaOH and NaClO₂, were activated with glutaraldehyde and ethylene diamine.2 The foamed and filled composite was used as support for covalent immobilization of Candida rugosa lipase.3 The hydrolytic activity and operational stability of the biocatalyst were evaluated by using olive oil as substrate.4 The observed catalytic behavior was equal or higher than those reported in previous works on lipase catalysis.3

CONTROLLED BULK DEGRADATION OF POLY-ε-CAPROLACTONE BY THE ENTRAPMENT OF LIPASE ENZYME INTO HALLOYSITE NANOTUBES

E. Hodosi\textsuperscript{a,b}, N. Hegyesi\textsuperscript{a,b}, D. Weiser\textsuperscript{c}, B. Pukánszky\textsuperscript{a,b}

\textsuperscript{a}Polymer Physics Research Group, Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1519 Budapest, P.O. Box 286, Hungary

\textsuperscript{b}Laboratory of Plastics and Rubber Technology, Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, H-1521 Budapest, P.O. Box 91, Hungary

\textsuperscript{c}Department of Organic Chemistry and Technology, Budapest University of Technology and Economics

Polyesters are prone to enzymatic degradation because of the presence of ester groups in the polymer backbone. Poly-ε-caprolactone (PCL) is a particularly promising polyester for biomedical uses because of its biocompatibility, but its degradation rate is rather slow and thus, must be adjusted according to the lifetime expected in the intended application. Time-consuming surface erosion has already been studied, but enzymatic bulk degradation of PCL has not been reported yet.

We aimed at the preparation of PCL matrices with increased and controlled degradation rate. To this end, lipase enzyme was immobilized in the whole volume of the polymer. As enzymes are very sensitive to elevated temperature or to the use of non-aqueous medium, and the molding of the PCL matrix is done at high temperatures and/or in organic solution, thus halloysite nanotubes were employed as enzyme carriers to protect their activity. These clay nanotubes adsorb the enzyme molecules both on their inner and outer surfaces,\textsuperscript{1} thus the enzyme can be expected to distribute evenly inside the polymer matrix after entrapment in the tubes.

The adsorption of lipase enzyme on the surface of halloysite nanotubes was studied in our present work. The effect of adsorption on enzymatic activity was determined.

Electrospinning is a method to create a material that has shown promising results in tissue engineering. Therefore, the aim of this study was to create electrically conductive polymer scaffolds and to examine the combined effect of nanofibers material and electrical stimulation. Conductive meshes were produced by in situ chemical oxidative polymerization of polypyrrole (PPy) on randomly electrospun poly(ε-caprolactone) (PCL) nanofibers. Pyrrole polymerization conditions were studied and various analytical methods such as XPS and FTIR were used for the characterization of prepared conducting textiles. The PCL/PPy nanofibers were also characterized in terms of morphology, electrical conductivity, and stability. Selected samples were tested for biological activity and toxicity on mouse fibroblastic cells.

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In this work, rapid microwave-assisted LDH/PCL nanocomposite preparation using solvent-free ring-opening polymerization of ε-caprolactone in the presence of organically modified LDH has been studied.\textsuperscript{1} Phosphonium ILs containing phosphinate, carboxylate and phosphate anions were used for the ion-exchange reaction with Mg-Al LDH and the modified LDHs were fully characterized using FTIR, XPS, XRD and TGA techniques. We found that the successful modification of LDH with phosphonium-based ILs leading to formation of intercalated IL-anion was able to catalyse ring-opening polymerization of CL and simultaneously to promote exfoliation of LDH. The whole process was accelerated using microwave irradiation, since 85 – 95 wt. % yield of polymer (depending on the LDH content) was reached within only 3 min of microwave irradiation. Within the same time, nanocomposites with fully exfoliated nanofiller morphologies were obtained.

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INVESTIGATION OF TALL OIL FATTY ACID EPOXIDATION KINETICS

M. Kirpluks, E. Vanags, U. Cabulis, J. Andersons

Polymer Laboratory, Latvian State Institute of Wood Chemistry,
Dzerbenes st. 27, Riga, Latvia, LV-1006
(mkirpluks@gmail.com, www.kki.lv)

Different plant oils have been proposed as a replacement feedstock for bio-based polyurethane (PU) production. Unfortunately, most vegetable oils, like rapeseed oil, soybean oil and sunflower oil are considered as first generation renewable materials, because their production has to compete with food production. Tall oil is a by-product of the wood pulping process and it can be considered as cheap raw material for polyol production. This study will show how it is possible to introduce oxirane rings fatty acids of tall oil.

Epoxidation of fatty acids as one of the steps for polyol production is done with peracetic acid which is obtained in situ from hydrogen peroxide and acetic acid. A high conversion rate to oxirane – 80.3% has been reported for fatty acid methyl esters. Although final conversion of double bonds and epoxy group yield is high in case of tall oil in the first step of the process methyl esters must be obtained. In this study, free fatty acids were epoxidized to propose more cost effective process.

Different catalyst influence, H₂SO₄ and ion exchange resin Amberlite IR120 and acetic acid content influence on epoxidation kinetic were studied. Epoxidation process was followed as change of conversion to oxirane as well as by change of iodine value, which was determined from a change of 3008 cm⁻¹ absorption band in FTIR. Obtained epoxidized tall oil contained up to 2.31 mmol/g of epoxy groups which is 41.9 % of oxirane oxygen yield. Such epoxidized tall oil can be used for further polyol production as well as other products, like surfactants and lubricants.

Components for synthesis polymeric materials based on petroleum have generated many problems for environment. In literature, there are research works on alternatives to obtain components from renewable raw materials,\textsuperscript{1-5} but only a few of them are focused on the synthesis of polyols from post-used cooking oils.\textsuperscript{6} The presentation will show a synthesis of bio-polyols from waste cooking oils using the two-step method: (i) reaction of oil epoxidation and (ii) oxirane ring opening. The effect of catalyst type and concentration on the opening rings reaction as well as physical and chemical properties of the obtained bio-polyols were investigated. The results of experiments show that the bio-polyols from waste cooking oil were successfully synthesized taking into account their characteristic for potential applications in polyurethane foams. Moreover, the type of catalyst and the concentration have a major impact on physical and chemical properties of the bio-polyols produced.

FULLY BIO-BASED POLYESTER POLYOLS FOR POLYURETHANES

P. Parcheta, J. Datta

Department of the Polymer Technology, Chemistry Faculty, Gdansk University of Technology, Narutowicza St. 11/12, 80-233 Gdansk
(paulina.parcheta@pg.gda.pl, janusz.datta@pg.gda.pl)

Nowadays, one of the most important trend in chemistry constitute the possibility to biorenewable resources utilization in the polymer industry.\textsuperscript{1,2} It is also seen in the field of polyols for the polyurethane obtaining (PUR). Currently, readily accessible are the bio-components which allow to produce the polyester polyols even in 100 % from bio-resources.\textsuperscript{3} The polyurethanes obtained with the use of polyester polyols are less resistant to hydrolysis compared to the polyether polyols, which give the greatest possibilities for obtaining the biorenewable PUR materials. They have more crystalline structure and better thermal and fire resistance than the polyether-based PUR and superior solvent resistance.\textsuperscript{4}

**Experimental**

In this study the polyols prepared with the use of biorenewable resources were investigated. The bio-based succinic acid (bio-SA) and the bio-based 1,3-propanediol (bio-PDO) were used. The polyols with 100 % bio-carbon content were synthesized under various temperatures in two-step polycondensation reaction. The molecular structure of the three prepared polyester polyols were analyzed. The Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) and rheological measurements results will be presented. The results indicate that novel polyester polyols revealed good macromolecular structure with selective properties corresponding to polyols dedicated to polyurethane materials.

DEVELOPMENT OF A MODIFIED PRE-POLYMER METHOD TO PRODUCE NMP-FREE POLYURETHANE-UREA AQUEOUS DISPERSIONS

I. P. Fernandes\textsuperscript{a}, M. R. Costa\textsuperscript{b}, M. J. Ferreira\textsuperscript{c}, M. F. Barreiro\textsuperscript{a}

\textsuperscript{a}Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Polytechnic Institute of Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

\textsuperscript{b}Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Faculty of Engineering University of Porto, R. Dr. Roberto Frias, 4200-465, Porto, Portugal

\textsuperscript{c}CTCP, Portuguese Footwear Technological Centre, Rua de Fundões - Devesa Velha, 3700-121 S. João da Madeira, Portugal

(barreiro@ipb.pt, www.ipb.pt)

A modified pre-polymer process was developed for the synthesis of NMP (N-methyl-2-pyrrolidone)-free polyurethane-urea aqueous dispersions. The pre-polymer process is based on the use of dimethylol propionic acid (DMPA, hydrophilizing diol), which requires dissolution in NMP to be introduced in the reactive mixture. NMP is difficult to remove from the dispersion remaining in the final product. In this work we present a modified pre-polymer process composed by four main stages: (1) pre-polymer synthesis in two stages: (i) reaction of the isocyanate with the polyol at 80°C, and (ii) introduction of DMPA pre-neutralized in acetone and proceeding of the reaction at 50°C, (2) Pre-polymer dispersion in water, (3) Chain extension with a diamine; and (4) Co-solvent removal. Several dispersions were synthesized using different DMPA contents (3.0, 4.0, 5.0\%, keeping the pre-neutralization degree at 100.0\%), and different DMPA pre-neutralization degree (100.0 and 90.0\%, using 5.0 \% of DMPA). The effect of these variables in the particle size and dispersion stability was evaluated. Based on the obtained results, the modified pre-polymer process is a feasible alternative to obtain NMP-free PUD, thus fulfilling the restrictions imposed by the European Union.

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Polyurethanes (PUs) are one of the most important synthetic polymers, offering a wide range of products with applications in diverse sectors. PUs can be obtained in the form of foams, elastomers, adhesives, coatings etc. Nowadays due to economic and environmental concerns, the development of low-cost polyols from renewable and recycling resources has gained an increasing attention in polyurethane industry.\(^1\) Very often produced in that way substrates properties close to commercial substrates. It is known from the literature, that products of chemical recycling can be used to obtain new polyurethane material e.g. elastomers or foams.\(^2,3\)

**Experimental**

Cast polyurethanes were synthesized in two step method using mixture of petrochemical polyol with glycerolysate and isocyanate. In the second step the prepolymer was reacted with chain extender, glycol. Glycerolysate (recycled polyol) was produced from polyurethane foam decomposition using crude glycerin as a degradation agent. Rest of glycerolysate was incorporated into polyurethane structure and co-created a soft segment. Obtained polyurethanes were characterized by TGA, DMA, FTIR and mechanical test.

NATURAL OILS AS A CHAIN EXTENDERS IN THE SYNTHESIS OF RIGID POLYURETHANE FOAMS

S. Członka, A. Strąkowska, K. Strzelec

Institute of Polymer & Dye Technology, Lodz University of Technology, Stefanowskiego 12/16, 90-924 Lodz, Poland
(czlonkasylwia@gmail.com)

Rigid polyurethane foams are highly crosslinked, three-dimensional polymers with most-often a closed-cell structure. The popularity of that group of materials is connected with the fact that their physical and mechanical properties can be selectively modified through alterations of the PU foam chemical formulations. Thanks to the fact that RPUFs exhibit very good thermal insulation and mechanical characteristics, high resistance to weather conditions, low moisture permeability, and relatively low apparent density, they are commonly used in a variety of industries.

One of the biggest problems associated with a large-scale production of PUR foams is their dependence on petroleum-derived precursors. In this regard, a growing tendency to modify rigid PUR foams with additives obtained from renewable, bio-based sources has been observed. Currently, plant oils are mainly used as a renewable feedstock in the preparation of polyols, which can be used as raw materials in the preparation of bio-based polyurethane foam. Considering the fact that linseed oil contains long, aliphatic chains in the molecule, they can be successfully applied as chain extenders in the synthesis of rigid PUR foams.

The aim of this work was to determine the influence of the rapeseed and castor oil on the foam morphology and physical properties. The major goal was to optimize the foam formulation, including the adequate content of aforementioned oils in the reaction mixture. The formulations were modified with an addition of plant oils in concentrations of 5, 10 and 15 php (per hundred polyols) in relation to the total polyols mass. The final PU foams were characterized by analytical techniques (FTIR), morphological (optical microscopy) and mechanical analysis (bending test and compression test). Additionally, the apparent density, dimensional stability, contact angle, water absorption and flammability were determined for the synthesized materials.
Hydrogels are crosslinked polymers that can reversibly absorb and release large amounts of water. They fall into the category of superabsorbent polymers (SAPs) and are used in industry for coal dewatering, and food additives among other things. Current hydrogel research is largely focused on developing this technology for medical applications such as 3D printing artificial human tissue and controlled drug release.

Thus, the main purpose of this project is to engineer interpenetrating hydrogel networks that are biocompatible, mechanically strong, electrically conductive as well as porous and superabsorbent. These materials find applications in the medical field, biocompatible electronics or electrically conductive implants, which could replicate nerve activity.

The mechanical strength of hydrogels is often a limiting factor in their design. To create a mechanically strong biocompatible hydrogel, a cellulose/alginate network was interpenetrated with an acrylate network. This effectively increased the crosslink density of the resulting interpenetrated network (IPN) without decreasing the elasticity. The IPNs also showed significant mechanical strength improvements while still maintaining a high swelling ratio. In addition, more uniform porosity was shown to be obtained through sequential network synthesis.
Hydrogels, hydrophilic 3D polymeric networks, have become an incredibly prolific area of research in the field of tissue engineering and regenerative medicine, because of their high water content, excellent biocompatibility, mechanical similarity to natural tissues, and ease of processability.\(^1\) Inspired by enormous potential of hydrogels, we have designed, developed and optimized polyethylene glycol (PEG) cross-linked gelatin-based hydrogels that are structurally stable and mechanically robust and show excellent cellular compatibility. Choosing the correct composition of gelatin and PEG becomes more crucial as the latter can have a determining effect on the quality of the resulting hydrogels and subsequently cell culture outcomes. Post-curing process is essential to achieve suitable structural stability and controlled degradation resistance of the hydrogels. Hydroxyethyl cellulose and chitosan are incorporated to tune the mechanical properties of the hydrogel as well as to better mimic the compositional cues of native extracellular matrix. The obtained hydrogels are characterized in terms of structural composition, morphology, mechanical properties, swelling and degradation behavior. Biological evaluation of L6 rat myoblasts and Human Foreskin Fibroblasts (HFF) cells illustrates good cell adhesion and growth. Taken together, the obtained results demonstrate that the proposed synthetic strategy is a valuable toolbox for fine-tuning the structural and physico-mechanical properties of the gelatin-based hydrogels, augmenting their potential range of application in the biomedical field.

In this work, new intercalated-exfoliated nanocomposites based on epoxy matrix and modified layered silicates were prepared. The silicates with different structures and morphologies were modified with an organic-inorganic hybrid polymer to improve the dispersion of clays within the epoxy matrix. FTIR Spectroscopy, Thermogravimetrical analysis and X-Ray Photoelectron Spectroscopy highlighted the presence of modifier agent on the silicates surface. The XRD analysis showed that the layers of silicates were also intercalated by the modifier agent. TEM and SEM images showed that the dispersion of layered silicates in the epoxy resin was improved by the functionalization of silicates with the hybrid polymer (Figure 1).

Figure 1. SEM image of nanocomposite based on epoxy and modified clay

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PROPERTIES OF POLYURETHANE COATINGS BASED ON LINSEED OIL PHOSPHATE POLYOLS

A. Abolins, V. Yakushin, D. Vilsone

Polymer Department, Latvian State Institute of Wood Chemistry,
27 Dzerbenes str., Riga, LV-1006, Latvia
(abolins_a@inbox.lv, www.kki.lv)

Phosphorus-containing polyols synthesized by different methods are used to decrease the flammability of bio-based polyurethanes (PU).\(^1\) In the present work, linseed oil phosphate polyol synthesis conditions and the properties of PU based on the synthesized polyols were studied. Linseed oil was epoxidized using hydrogen peroxide (\(\text{H}_2\text{O}_2\)), acetic acid (\(\text{CH}_3\text{COOH}\)) and ion exchange resin Amberlite IR-120 as the catalyst. Epoxidized oil was separately dissolved in isopropyl alcohol (IPA) or diethylene glycol butyl ether (DGBE) and phosphorylated with different amounts of phosphoric (\(\text{H}_3\text{PO}_4\)) acid (1%, 2%, 3% and 5%). Epoxidation and phosphorylation were monitored by determining the epoxy conversion value at regular intervals. PU in the form of both free films and coatings, applied on wood samples, were prepared. Linseed oil diethylene glycol ester polyol PU coatings were used as the reference. For FTIR spectra characterization of polyols and PU, a Nicolet iS50 Analytical FTIR Spectrometer was used. The tensile properties of PU were determined according to ASTM-D 882-10. The thermal stability of PU in nitrogen atmosphere was tested using TGA/SDTA 851e METTLER TOLEDO. The flammability parameters of wood samples with PU coatings at a heat flux of 35 kW/m\(^2\) were determined using a FTT Cone Calorimeter.

Conditions for linseed oil epoxidation, at which epoxidized linseed oil reached the maximum epoxy conversion value, were defined, and the linseed oil phosphate polyol synthesis in the presence of IPA and DGBE was described. In the FTIR spectra of all polyols and PU, the absorption band of the \(\text{P} = \text{O}\) group was detected. PU coatings based on two kinds of the synthesized polyols had a higher char yield and lower flammability parameters than the reference PU.

Recycling of polyurethanes became popular due to the greater consumption of these materials and is mostly driven by ecological sustainability concerns. The primary purpose of polyurethane feedstock recycling is to recover the starting polyol. One of the decomposition methods can be glycerolysis, in which crude glycerin from biodiesel production is used as a decomposing agent. Very often obtained during decomposition semi-products indicate properties close to commercial substrates, therefore many researchers obtained new polyurethane materials such as elastomers or rigid or flexible foams.

**Experimental**

Rigid polyurethane foams (RPU) were prepared using “one-shot” technique at isocyanate index 1.2. The foam was synthesized from the polyol mixture of glycerolysate and commercial polyol (Rokopol RF 551, PCC Rokita, Poland), isocyanate (pMDI, BorsodChem, Hungary) and water used as blowing agent. The polyol mixture in an amount of 0, 5, 10, 20, 40 and 100 glycerolysate parts per hundred parts polyol. Glycerolysate was obtained during flexible foam decomposition with crude glycerin of purity of 84% (Rafineria Trzebinia S.A, Poland).

The obtained foam was characterized by FTIR, DMA, apparent bulk density, compressive strength and water absorption.

Jerusalem artichoke (Helianthus tuberosus L.) tubers are industrial crop considered as promising source for inulin production. Green method was performed for accelerated extraction of inulin from Helianthus tuberosus L. tubers by application of microwave irradiation. Further pretreatment of extract with acetone and ethanol yielded inulin (10 %), with purity 89 % and degree of polymerization 22. Jerusalem artichoke inulin (JAI) was characterized by FT-IR and NMR spectroscopy. Eco-friendly synthesis of acetylated inulin was performed by the reaction of JAI with acetic anhydride, without solvent, but only with NaOOCCCH₃ as a catalyst under microwave irradiation for 60 sec (Figure 1). The degree of substitution (DS=2.70) and the structure of inulin esters were confirmed by ¹H and ¹³C NMR. The suggested microwave-assisted acetylation shortens significantly the esterification reaction.

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THE CATALYST IMPACT ON THE FULLY BIO-BASED POLY(PROPYLENE SUCCINATE) STRUCTURE

P. Parcheta, J. Datta, P. Jutrzenka Trzebiatowska, P. Kasprzyk, K. Błażek, E. Głowińska, M. Włoch

Department of the Polymer Technology, Chemistry Faculty, Gdansk University of Technology, Narutowicza St. 11/12, 80-233 Gdansk (paulina.parcheta@pg.gda.pl, janusz.datta@pg.gda.pl)

The principles of green chemistry and the growing ecological trend in the industries caused that a number of researchers studied the products obtaining in 100% from biorenewable materials and collated them with petrochemical based polymers. In many cases, the results shown that there was no significant differences between the product with the bio-based carbon content and its lack in the product.1,2

The main group of polyols, which give major possibilities to the biorenewable PUR materials obtaining, constitute the polyester polyols. Nowadays, easily accessible are the bio-components which allow to produce the polyester polyols even in 100% from bio-resources.3,4

Experimental
The polyurethane polyols were prepared with the use of bio-based succinic acid (bio-SA) and the bio-based 1,3-propanediol (bio-PDO). During bio-based polyester polyols synthesis via two-step polycondensation reaction, the various catalyst content was used. The molecular structure of the four prepared polyester polyols were analyzed. The poster will presented the results of the Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) and rheological measurements results. Moreover, the primary properties, which verifying the polyols usage in the industrial processes, will be collected and compared.

APPLICATION OF ULTRASOUND ASSISTED SYNTESIZED SUCROSE PALMITATE AS A BIO-PLASTICISER OF POLYVINYL CHLORIDE

D. Vassileva\textsuperscript{a}, N. Petkova\textsuperscript{b}, M. Koleva\textsuperscript{a}, P. Denev\textsuperscript{b}

\textsuperscript{a}Department “Physics, Chemistry and Ecology”, Technical University of Gabrovo, 4 Hadji Dimitar str., 5300 Gabrovo, Bulgaria

\textsuperscript{b}Department of Organic Chemistry and Inorganic Chemistry, University of Food Technologies, 26 Maritza blv., 4002 Plovdiv, Bulgaria

(dvasilev@tugab.bg)

Plasticizers used in the treatment of polyvinyl chloride (PVC), which in most cases are esters of carboxylic acids with linear or branched aliphatic alcohols (phthalates, octanoates, etc.), possess excellent functional properties. However, they prove to be somewhat toxic. Therefore, they should be replaced with safer and more effective substances like plasticizers. Sucrose esters could play that role since they are non-toxic biodegradable surface-active substances. Nevertheless, their industrial synthesis based on non-selective and low-productivity esterification processes seems to be problematic. They could be intensified by using ultrasounds which can accelerate the processes without affecting product composition and structure. In this sense the paper considers the findings of an experimental study on the application of sucrose palmitate, synthesized by means of ultrasound in our previous work, in its capacity as a PVC plasticizer. The plasticizing effect of the sucrose ester has been evaluated by the glass transition temperature $T_g$ defined by DSC and the deformation behavior upon extension of PVC-films containing sucrose palmitate 10, 20, 40 and 60%. Data show a decrease in $T_g$, the elasticity module and the load at break when the sucrose palmitate content increases in the polymer, as well as an increase in the work to break and the elongation at fracture. Those results prove the plasticizing effect of sucrose palmitate.
Plant oils have been one of the most important renewable feedstocks of the chemical industry in the past and in the present.\(^1\) One of such valuable renewable sources is a mixture of tall oil fatty acids (TOFA) which is important renewable by-product of the craft pulping process. TOFA consists mostly of oleic and linoleic acids.\(^2\) Relatively high unsaturation level makes TOFA to be an appropriate raw material for epoxidation reactions.

The main purpose of this study was to determine the highest oxirane content that can be introduced in TOFA without using any carboxyl group protection. The result of this study could let to avoid of free fatty acid carboxyl group protection process, thus eliminating additional reagents, waste products and work required for the protection process.

TOFA was epoxidized by \textit{in situ} formed peracetic acid using H\(_2\)O\(_2\), acetic acid and two different acid catalysts: H\(_2\)SO\(_4\) and Amberlite IR-120. Oxirane content was determined according to ASTM D1652-04 standard. Iodine value of TOFA and reaction products was determined according to Hanus method. Reaction process and products of epoxidation were analyzed by FTIR and GC-MS.

Conditions for TOFA epoxidation were defined at which the maximum epoxy conversion and selectivity were reached.

\textbf{Acknowledgement:} The work has been financed by European Regional Development Fund Contract No 1.1.1.1/16/A/031.

2. Panda, H. Handbook of Tall Oil Rosin Production, Processing and Utilization; Asia Pacific Business Press Inc.: Delhi, 2013, p. 5 – 82.
Modern industrial technologies make it possible to produce versatile polymers with highly tunable properties and to be used in wide range of applications. In Imatech project innovative and multifunctional composite materials for sustainable buildings were developed. Plywood rib stiffened sandwich type panels were filled with lightweight polyurethane foams which contributed positively to properties, such as, soundproofing and thermal insulation.

Bio-based feedstocks for polyurethane industry have been studied intensively in last decades. Tall oil is a suitable raw material for biobased polyol synthesis further to be used in polyurethane production. However, sustainability of the production of polymers from biomass feedstock, has been greatly debated. Life Cycle Assessment (LCA) is a valuable tool that can be successfully used to quantify environmental burden of bio-based chemicals. LCA compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle. LCA approach will be used to evaluate the environmental performance of polyurethane foams obtained from tall oil polyols.

Acknowledgement: The work has been financed from Latvian State Research Programme under grant agreement “Innovative and multifunctional composite materials for sustainable buildings (IMATECH).”
P-08

BIODEGRADABLE FILMS OF PHBV/CELLULOSE NANOCRYSTALS: THERMAL AND RHEOLOGICAL PROPERTIES

R. Bouza, S. Malmir, B. Montero, M. Rico, L. Barral

Universidade da Coruña, Grupo de Polímeros, Departamento de Física, Escuela Universitaria Politécnica, Serantes, Avda. 19 de Febrero s/n 15471, Ferrol, Spain

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a well-known biobased and biodegradable polymer which can be used to replace petroleum-based materials in food packaging industry. Cellulose nanocrystals (CNC) are nano scale fillers used in biodegradable matrices due to good properties. Bionanocomposites of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) with cellulose nanocrystals (CNC) were prepared by melt mixing method. Differential scanning calorimetry (DSC) results showed that introducing CNC particles led to higher rate and degree of crystallinity in filled samples. X-ray diffractometric (XRD) analysis also showed the presence of more crystalline zones in the nanocomposites compared to PHBV. Scanning electron microscopy (SEM) was done in order to study the impact of filler loading on the morphology of the samples and related images exhibited that the CNC particles were dispersed uniformly with low filler loadings (2 wt.% and 4 wt.%) while slight agglomerations were appeared in high filler content (6 wt.%). Rheological studies showed that storage modulus of PHBV increased at low frequency zone upon incorporation of CNC particles, which was related to strong adhesion between filler and matrix.

PREPARATION AND CHARACTERIZATION OF POLYSACCHARIDE/ CONDUCTING POLYMER FILMS
M. Méndez-López, C. Saldías, A. Ramos, V. Moreno, D. Radić, A. Leiva

Laboratorio de Macromoléculas, Departamento de Química-Física, Faculta de Química, Pontificia Universidad Católica de Chile, Vicuña Mackenna 4860, Región Metropolitana, Chile (mtmendez@uc.cl)

Programa de química, Facultad de ciencias básicas, Universidad del Atlántico, kilómetro 7 vía puerto Colombia, Barranquilla, Colombia

In recent years, Scientists have been studying conducting polymers and polysaccharide blend, because there are many applications where these can be used, as biomedical engineering.1 Also, it is possible to take advantage of polysaccharides properties, such as, ions metal absorption, to obtain new materials where chitosan / conductive polymer / metallic nanoparticles (or quantum dots) are combined.2 In this work, chitosan / poly (thiophene) derivative and arginate / poly (thiophene) derivative films were obtained, at different conductive polymer concentrations. Films were characterized by spectrum attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR), Polarized optical microscopy, Thermal degradation (TGA), Differential scanning calorimetry (DSC), Atomic force microscopy (AFM), Contact angle system and UV-Vis spectroscopy. Results showed blends were compatible in both cases, showing better mechanical properties of the chitosan / conductive polymer films. The next step is to obtain composite materials with metallic nanoparticles or quantum dots.

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PREPARATION AND CHARACTERIZATION OF CHITOSAN:POLY(3-HEXYLTHIOPHENE) AND QUANTUM DOTS HYBRID FILMS

V. Moreno-Serna, M. Méndez-López, A. Leiva, D. Radić

Laboratorio de Macromoléculas, Departamento de Química-Física, Facultad de Química, Pontificia Universidad Católica de Chile, Vicuña Mackenna 4860, Región Metropolitana, Chile
(vmoreno2@uc.cl)

In this work, conductive hybrid films were first prepared by blending P3HT (poly(3-hexylthiophene)) and chitosan. P3HT was chemically synthesized. Chitosan: P3HT hybrid films were prepared by solvent casting of chitosan in acetic acid 1% and P3HT 0.05 and 0.1% w/v solution in THF to form films containing 0.5, 1.5, 3 and 4.5% w/v of conductive polymer. The fabricated bio-hybrids films were characterized by fourier transform infrared spectroscopy (FT-IR), UV–visible spectroscopy, Polarized optical microscopy, Thermal degradation (TGA), Differential scanning calorimetry (DSC) and Atomic force microscopy (AFM). Results indicated a strong interaction between the conductive polymer and chitosan. AFM micrograph showed films of blends heterogeneous and slightly rougher than chitosan and P3HT films. Cadmium sulfide (CdS) semiconducting quantum dots (QDs) were prepared using in situ synthesizing method in crosslinked chitosan:P3HT films. The experimental results confirmed that crosslinked chitosan:P3HT films provided a confined matrix for CdSe QDs growth in uniform size through chelation between cadmium ions and amino groups in chitosan chains. The Energy band gap of fabricated biohybrid films was determined by optical methods.

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EFFECT OF SORBITOL ON SWELLING BEHAVIOR OF CHITOSAN FILMS PREPARED WITH LACTIC ACID

C. M. Trindade, L. C. G. de S. Santos, E. Ayres

Postgraduate in Design Program, State University of Minas Gerais, 7545, Antônio Carlos Avenue, Belo Horizonte, MG 31270-010, Brazil
(eayres.pu@hotmail.com, www.uemg.br)

In this work chitosan films (QS) were prepared from filmogenic solution with 1g of chitosan / 100 mL of lactic acid solution (1%) (LA) by casting method. Sorbitol (SOR) as plasticizer in different contents of 0.25, 0.50 and 0.75% w/v solution was added. The QS + LA film without plasticizer (SOR) swelled up to 3000% and was solubilized after 24 h of immersion in water. Possibly hydrolysis of chitosan has occurred with consequent reduction in molar mass and subsequent dissolution of the film in water.1

Fig. 1 shows the swelling behavior in water of the films QS + LA + SOR.

Figure 1. Swelling in water (%) of QS + LA + %SOR films: (a) 0.25%, (b) 0.50% and (c) 0.75%.

In respect to Fig. 1 it is possible to observe that after 72 h the film with 0.5% of SOR presents the lowest swelling percentage. This result is in agreement with the hypothesis of occurrence of two opposite factors: the interaction between SOR and QS, which increased crosslinking and therefore reduced swelling called antiplasticizing effect,2 and the hydrophilic SOR acting as true plasticizer, increasing the interaction between QS film and water.

SYNTHESIS AND EVALUATION OF BIO-BASED WATERBORNE POLYURETHANES

L. C. G. de S. Santos\textsuperscript{a}, E. Ayres\textsuperscript{a}, M. L. B. Almeida\textsuperscript{b}, R. L. Oréfice\textsuperscript{b}
\textsuperscript{a}Postgraduate in Design Program, State University of Minas Gerais, 7545, Antônio Carlos Avenue, Belo Horizonte, MG 31270-010, Brazil
\textsuperscript{b}Department of Metallurgical and Materials Engineering, Federal University of Minas Gerais Belo Horizonte, MG, Brazil
(lilianecruzbh@gmail.com, www.uemg.br)

A series of aqueous dispersion of polyurethane (PUD) has been successfully synthesized from bio-based polyols derived from castor oil (Biopol-411\textsuperscript{TM}, Poly-Urethane-Brazil) and soybean oil (Bioline\textsuperscript{TM} 065, Etruria-Brazil). The conventional pre-polymer method used has been widely described in the literature.\textsuperscript{1} The effect of the molar ratio between the two polyols on PUD characteristics was preliminarily evaluated. The prepolymer with high contents of Biopol-411 was viscous and difficult to be dispersed in water without the aid of acetone.\textsuperscript{2} Probably is due to the functionally higher than two of this polyol (2.7). The formulations with lower content of Biopol-411 provided aqueous dispersions with good storage stability and transparent films, as shown in Fig. 1.

\textbf{Figure 1.} PUD with 10% of Biopol 411 (molar ratio on total polyols)

The growing amount of plastic waste produced every year resulted in development of mechanical and chemical recycling methods of polymers. In the case of polyurethanes (PUs), which are produced in form of flexible foams, rigid foams, coatings and elastomers, the total worldwide production in 2013 was equal nearly 16 mln ton, so the development of the cost-effective and environmentally friendly recycling technology is needed.

Polyurethane waste can be recycled by mechanical methods (i.e. grinding and applying as a filler) and chemical methods (mainly by e.g. glycolysis). There is also possibility to the recovery of energy from polyurethanes waste (by e.g. incineration). The glycolysis is the chemical process which can be performed on the industrial scale, and involves the chemical decomposition of urethane groups by active hydro-gen atoms presented in the structure of glycols. In this work, the glycolysate was used as a plasticizer for the processing of natural rubber. The main aim was to examine the influence of glycolysate type and content on the mechanical and thermo-mechanical properties of prepared natural rubber vulcanizates. All results were compared with properties of reference samples (prepared using commonly used in rubber technology plasticizer i.e. naphthenic oil).

The research results on the application of reactive catalytic systems in the production of rigid polyurethane foams will be presented. Such foams are used as excellent material for thermal insulation both in low and high temperatures.\textsuperscript{1,2}

The polyurethane foams were obtained in a two step mixing process. In the first step, the polyol premix (component A) contained also catalysts, water as a chemical blowing agent and surfactant was prepared by mechanical stirring. In the second step polymeric 4,4'-diphenylmethane diisocyanate (pMDI) as component B was added to component A.

The effect of selected amine catalysts with primary and secondary hydroxyl groups on foaming process (changes of dielectric polarization, temperature, pressure and rise velocity) of various polyurethane systems and selected physical-mechanical properties (apparent density, thermal conductivity, compressive strength and closed cells content) of obtained foams was analyzed.

The application of reactive catalysts with primary hydroxyl groups caused a gradually decreasing reactivity of polyurethane system, while amine derivatives with secondary groups prolonged gel time and reduced pressures during the foaming process of polyurethane systems.

The results have shown that the use of reactive catalysts in the production of rigid polyurethane foams can reduce emissions of volatile organic compounds into the environment, without significant changes of the foams properties.

BIODEGRADATION OF POLYESTER POLYOLS-BASED POLYURETHANE FOAMS FOR AGRICULTURAL LANDSCAPE APPLICATIONS

K. Tošovská, P. Innemanová, H. Benes, A. Paruzel, J. Kredatusová, Z. Kruliš

aFaculty of Science, Charles University, Albertov 6, 120 00 Prague 2, Czech Republic
bInstitute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2, 162 06 Prague 6, Czech Republic
(katerina.tosovska@natur.cuni.cz)

The effort to reduce the amount of plastic debris has led to the development of biodegradable plastics for various applications. Biodegradable polyurethane (PUR) foams were developed as a matrix for repellent fences protecting crops in agricultural landscapes. The biodegradability of PUR foams was tested respirometrically according to the ASTM D 5988 under laboratory conditions for 9 months. Beyond the standard method, carbon dioxide (CO₂) released from the biodegradation process was stabilized by reaction with barium chloride. According to a preliminary test, this step was crucial for accurate results. Cellulose used as the positive control was mineralized by 100 %. The incorporation of starch (28 wt. %) into PUR foam formulation increased the rate of biodegradation and the PUR foam was mineralized by 42 ± 4 %. The biodegradability in soil was compared with abiotic hydrolysis tests. Hydrolytic cleavage of ester bonds reduces the molecular weight of material and can enhance an attack by microorganisms.¹

Degradation tests were evaluated by CO₂ release, weight loss, FTIR and thermogravimetric analysis.

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The graft-copolymerization of monomers onto cellulose is one way to link two entities with different physicochemical properties within the same macromolecule. Grafting can be used to improve certain physicochemical properties of cellulose. Thermoplasticity or solubility is expected to be attained due to the diminution of hydrogen bonding during grafting, but at the same time, these properties depend in large amounts from the nature and size of the side-chains and their statistical distribution along the backbone chain.

This work deals with the synthesis of graft-copolymers from cellulose extracted from palm leaves cultivated in Algeria and (2,2-dimethyl-1,3-dioxolan-4-yl) methyl acrylate was studied to determine the optimal conditions for grafting. The maximum grafting weight gain was 27% obtained after 72 min of reaction at 65°C with 6.4 mmol KPS/eq OH and 1.51 mol DMDMA/eq OH.

The structures of the various copolymers obtained from cellulose by grafting were characterized by structural (FTIR spectroscopy, X-ray diffraction), thermal (TGA) and microscopy (SEM) analyses.

Heavy metal pollution is one of the most widespread environmental concerns threatening human health and ecosystems due to their recalcitrance and persistence nature in environment and high water solubility facilitating environmental mobilization or even bioaccumulation. As a consequence, the determination and removal of trace concentrations of metal ions in man-made and natural water resources is of current trend of interest to have a check on the ecosystems. Organic-inorganic hybrid materials with excellent heavy metal ions chelating properties were prepared by covalent bonding of vinyl-terminated polyamidoamine (PAA) onto aminated silica particles. Two series of polyamidoamine grafted silica, differing in the PAA chemical structure, were synthesized and their heavy metal ions chelating properties were investigated. The adsorption behaviour of the materials was evaluated in different ionic strength solutions as well as in the drinking water. Experimental results showed that hybrid materials containing more carboxy groups possessed very strong adsorption ability for metal ions. Moreover, the materials exhibited excellent regenerating property using diluted hydrochloric acid solution as eluent. The adsorption/desorption property trended to steady more than 20 cycles. The facile, low-cost, and environmental friendly synthesis method as well as highly efficient adsorption ability and excellent recyclability made it become promising adsorbents for the removal of toxic heavy metals at low or trace concentrations from water.

Algae can be classified as active fillers what is caused by their chemical structure and functional groups content. Interest of algae application in polymers already is known e.g. source to the polyester synthesis.\textsuperscript{1,2} This study was focused on chemical structure, morphology and thermal properties of polyurethane composites containing 10 wt. % of spirulina (micro algae) as active fillers. In order to prepare the bio-polyurethane matrix of composites two step method of synthesis was used. Pre-polymers were synthesized using 4,4’-diphenylmethane diisocyanate (MDI) and a polyester polyol (Polios 55/20). Two different pre-polymer were synthesized (excess of NCO equal 8 and 10%). As a chain extender 1,3bioPDO was used. The composites were obtained by addition filler to the prepolymer. Synthesized samples in the molar ratio [NCO]prepolymer/[OH]chain extender equal 1,1 and 1,05 were subjected to analysis. The chemical structure of prepared materials was determined by FTIR spectroscopy, while SEM technique was used to the morphology determination. The thermal properties of materials were characterized using thermogravimetric analysis (TGA). Generally, spirulina addition to the polyurethane matrix strongly affected on the thermal stability compared to reference sample. Microscope analysis showed good dispersion of the spirulina particles in the polyurethane matrix.

NEW APPROACHES OF SPIRULINA AS A FILLER IN NATURAL RUBBER BASED COMPOSITES

E. Głowińska, J. Datta, M. Włoch, P. Parcheta, N. Kaźmierczak

Gdańsk University of Technology, Narutowicza street 11/12, 80-233 Gdańsk, Poland
(ewa.glowinska@pg.gda.pl)

Widely known is the application of algae in food and pharmaceutical industry. Literature indicates that algae can be used in industrial application as well. Algae are a future potential source of renewable energy and a platform for oleochemicals because they can generate many times more oil per acre than other plants used for biofuels, such as corn or soybean\textsuperscript{1} or can be used to bio-plastic preparation\textsuperscript{2}.

This work is focused on investigation of the influence of spirulina, bio based component used as a filler, on the characterization of prepared natural rubber based composites. The rubber mixtures containing 5, 10, 20 and 30 phr (parts per 100 parts of natural rubber) of spirulina (micro algae) were prepared. The vulcanization process was carried out by using hydraulic press. Obtained samples were subjected to the number of tests e.g. tensile test, compression test, mechanical analysis at the dynamic condition. Hardness, rebound resilience, density, and abrasion resistance were examined as well. Based on the results, it was noted that increasing content of spirulina filler in rubber compounds caused increase of hardness, density, hysteresis, modulus of 100, 200, 300\%, and compression stress. Positive results indicate possibility and therefore the need to expanding using of spirulina additive in different practice materials. Moreover, it was found that spirulina can be used as plasticizer as well in some types of rubbers.

The influence of nanofillers i.e., TiO$_2$ and ZnO on antibacterial, thermal and barrier properties of polyethylene terephthalate (PET) and polybutylene adipate-co-terephthalate (PBAT) blends were investigated. The blends of PET:PBAT ratio of 90:10 were compounded with TiO$_2$ and ZnO (1.0 and 2.0 wt%) in a twin-screw extruder. The films were made by film extruder and then were characterized by differential scanning calorimeter and gas permeability tester for thermal and barrier properties. Antibacterial activities of thin film were studied by dynamic shake flask test method. PET/PBAT blends thin film with ZnO could exhibit more efficient on inhibiting of E. coli and S. aureus than the one with TiO$_2$. In addition, compounding with either TiO$_2$ or ZnO into PET/PBAT would increase glass transition temperature ($T_g$) from 56.1 to 58.7- 71.1 °C and capable of reducing the percentage of crystallinity of PET/PBAT blends. In term of barrier properties, PET/PBAT blend thin film with ZnO would be able to reduce the oxygen permeability and carbon dioxide permeability than the thin film with TiO$_2$.

**Keywords**: Thin Film; Polyethylene terephthalate; Polybutylene adipate-co-terephthalate

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GREEN NATURAL RUBBER-BASED COMPOSITES FILLED WITH BUCKWHEAT HUSKS POWDER

M. Włoch, J. Datta, E. Głowińska, K. Błażek, P. Kosiorek

Gdańsk University of Technology, Faculty of Chemistry, Department of Polymers Technology, G. Narutowicza Str. 11/12, 80-233 Gdańsk, Poland (marcin.wloch@pg.gda.pl, www.pg.gda.pl)

The growing interest in polymers and composites derived from renewable resources is observed. Several bio-based substances (including, e.g. vegetable oils), were proposed as the potential feedstock for the polymer industry. Some of polymers and composites derived from industrial crops (e.g. natural rubber and natural fibre/natural rubber composites) have already industrial applications. The literature covers a wide range of natural fillers, which can be used for the preparation natural rubber composites, e.g. short jute, sisal, palm oil, banana fibres, grass fibres, bamboo fibres, oil palm wood flour, rattan powder or peanut shell powder. In this work, green composites were obtained by incorporation of powdered buckwheat husks in natural rubber matrix using a laboratory two-roll mill. The influence of bio-based filler on the morphology, selected mechanical properties (e.g. tensile properties, hardness and behavior under cyclic compression), dynamic mechanical properties, thermal stability and swelling properties was examined.

The starch containing polymers are important biodegradable materials based upon renewable resources. The plasticization process of starch is rigorous as it involves transforming the granular starch into an amorphous and homogenous thermoplastic matrix for most of its applications in account of the melting temperature of native starch being higher than that of its degradation. The plasticization of starch has been intensively investigated and results have shown that the preparation of thermoplastic starch (TPS) depended on many factors. Recently, wide interest has been paid to the TPS-based composites with different kinds of fillers, e.g. montmorillonite,\(^1\) titanium dioxide (\(\text{TiO}_2\)),\(^2\) natural fibers, kaolin. \(\text{TiO}_2\)-based particles represent attractive fillers in composites due to their biocompatibility with the tissue, blood and bone cells. To the best of the authors’ knowledge little of information exists concerning the effects of \(\text{TiO}_2\) on properties of thermoplastic starch.

In this work, composites of TPS with different (5, 10, 15 and 20 wt.\% content of titanium dioxide particles (average size \(0.2\,\mu\text{m}\)) with very homogeneous matrix and well-dispersed \(\text{TiO}_2\) filler were prepared by a two-step method, including solution casting followed by melt mixing.\(^2\) This study focuses on the morphology, rheology and mechanical properties of these thermoplastic starch composites containing \(\text{TiO}_2\) filler in high concentrations.


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NEW PRODUCTION METHODS OF ORTHOPEDIC COMPOSITES FROM POLYMERS AND CERAMIC

E. Pietrzykowska, A. Chodara, B. Romelczyk, T. Chudoba, W. Łojkowski

\textsuperscript{a}Institute of High Pressure Physics, Polish Academy of Sciences, Sokolowska 29/37, 01-142 Warsaw, Poland
\textsuperscript{b}Faculty of Materials Science and Engineering, Warsaw University of Technology, Warsaw, Poland
\textsuperscript{c}Faculty of Management Białystok, University of Technology, Białystok, Poland

(e.pietrzykowska@labnano.p, www.labnano.pl/)

The Institute of High Pressure Physics of the Polish Academy of Sciences (IHPP) has developed technologies of the calcium deficient nano-synthesis (called GoHAP), obtained by microwave reactor and the high pressure consolidation technology for ceramic- polymer composites. Our work shows mechanical properties of consolidated HAP-polymer composite. The high pressure consolidation technology permits to obtain dense ceramic with mechanical properties close to the natural bone. The process was carried out in extreme pressure up to 1GPa and temperature under 200°C. Thanks to this, the GoHAP nanopowder structure and biological properties are preserved in composite. The mechanical properties of this nanoceramic were investigated and the compressive strength reach assign value above 130 MPa (natural bone is in range from 100 to 200 MPa).

Tissue engineering is an interdisciplinary field of science that engage specialists in materials engineering, chemists, biologists, pharmacologists and representatives of medical sciences in development of synthesis and characterization of biomaterials able to replace or improve functionality and regeneration of natural tissues. Researchers worldwide conduct intensive investigations on synthesis of novel materials capable of conforming expectations of developing regenerative engineering. Therefore many efforts have been devoted to design materials for tissue engineering covering wide range of mechanical properties of human soft tissues. Recently, poly(diol citrates) (PDC) evolve into one of the most promising biomaterial for the fabrication of soft tissue scaffolds. It was assessed that these materials are biocompatible and biodegradable and constitute a proper scaffold for proliferation of living cells.

The main objective of this research was the fabrication of novel antioxidative and fluorescent materials for soft tissue engineering through surface modification of polyester materials prepared from poly(diol citrates) (PDC) with panthenol and/or glutathione and/or specific amino acids. It was found that above amines are able to react with citric acid moieties present in the surface layers of POC materials to form esters, amides and derivatives of ring fused 2-pyridones.1-3 As a consequence above modification assured introduction of luminescent and antioxidant properties to the material. Aforementioned properties may become crucial considering reduction of postimplantation oxidative stress, treatment of restenosis as well as in bioimaging and tracking of implant degradation products.

POTENTIAL APPLICATION OF SILK FIBROIN AS BIOMATERIALS

A. Eckstein-Andicsová, A. Šišková, E. Kozma

\(^a\)Polymer Institute SAS, Dúbravská cesta 9, 84541 Bratislava, Slovakia
\(^b\)Istituto per lo Studio delle Macromolecole, CNR, Via Alfonso Corti 12, 20133 Milano, Italy

(anita.andicsova@savba.sk, www.polymer.sav.sk)

The use of natural materials for biochemical applications has increased notably in the last years, due to their biocompatibility combined with exceptional physical, mechanical and chemical properties. Among these materials, silk fibroin from B. Mori is a natural polymer having outstanding mechanical robustness, high optical transparency and compatibility with living systems. For these reasons, it is widely explored as functional material in surgery, have potential application in fields such as tissue engineering, drug release systems, implantable electronics, microfluidic devices, optics and photonic systems.

In this work we present the preparation and characterization of silk fibroin based composites in various forms such as films, electrospun mats, nano- and microparticles. The effect of various forms of the silk properties is also described.

\textit{Acknowledgement:} This work was supported by the Slovak Grant Agencies VEGA project No. 2/0161/17 and by bilateral project SAS-CNR (Danko/Galeotti).
Liquid pharmaceutical formulations provide easy administration of the active compound to the eye surface, but the efficiency of therapy is usually low due to the protective mechanisms of the eye. A series of bioadhesive polymers has already been developed to increase the residence time of the formulation at the site of action. Only a few of such polymers can be used as transparent gellable solutions because of the various requirements e.g. low viscosity, sufficient stability, fast gelation of the pre-cursor solution and high strength of the forming gel. We synthesized thiolated poly(aspartic acid) (PASP) by using cysteamine side groups to achieve in situ gelation upon oxidation. The benefit of using PASP and its derivatives is their expected biodegradability and biocompatibility due to the poly(amino acid) structure as proven for various derivatives. In addition, the synthetic pathway implies mild reaction conditions and the absence of any side products. The aqueous solution of the PASP polymers displayed oxidation induced gelation due to intermolecular disulphide formation and the time of gelation could be adjusted between 1 to 10 minutes. This work is continuing with the synthesis of thiolated PASP displaying rapid gelation in the presence of air. To this end, thiolated derivatives was synthesized by using thiolactone chemistry from polymers with primary amine pendant groups. The modification of polymers was done in aqueous solution to make the synthesis greener. We expect fast atmospheric gelation and improved adhesion from the novel polymers due to the presence of longer, flexible spacer chains and their cationic nature.

In recent years, considerable attention has been paid to biodegradable materials especially these based on renewable resources. The biodegradation of polyurethane (PUR) foams is limited by many factors including chemical structure, cross-linking density, crystallinity, etc. Microbiologically induced deterioration of the urethane bonds in PUR foam is greatly influenced by the different polyols types, i.e. polyether or polyester polyols.¹ PUR foams made from polyester polyols are susceptible to microbial attacks, whereas polyether PUR foams are relatively resistant to microbial degradation.²

The aim of our work is to prepare biodegradable PUR foams exhibiting the controlled rate of degradation during their outdoor applications. The degradation rate will be driven by a suitable precursor selection and a balanced ether / ester ratio. The first part of our work is focused on the preparation of biodegradable PUR precursors (designed polyols) and their detailed characterization. The second part involves the preparation of PUR foams based on selected precursors. The third part evaluates degradation behavior of the prepared PUR foams using abiotic hydrolysis and biodegradability testing in soils according to ASTM D 5988 before and after accelerated weathering.

Acknowledgment: The authors are grateful to Technology Agency of the Czech Republic (grant No. TA04020853) for financial support.

2. Eddie F. Gómez, Xiaolan Luo, Cong Li, Frederick C. Michel Jr., Yebo Li, Biodegradability of crude glycerol-based polyurethane foams during composting, anaerobic digestion and soil incubation, Polymer Degradation and Stability 102 (2014) 195e203
ROLE OF NATURAL OIL STRUCTURE FOR POLYCARBONATE CONVERSION INTO POLYURETHANE POLYOLS

H. Beneš*, A. Paruzel, Z. Walterová, O. Trhlíková

Institute of Macromolecular Chemistry, Czech Academy of Sciences,
Heyrovského nám. 2, 162 06 Prague 6, Czech Republic
(benesh@imc.cas.cz, www.imc.cas.cz)

Broad worldwide production of polycarbonates leads to the generation of high amount of polycarbonate waste. Methods of physical recycling are not always suitable for this kind of waste, since it is prone to degrade during the reprocessing. Alternatively, we have developed the method of chemical recycling utilizing natural oils as reagents for polycarbonate depolymerization.

In the first step, natural oils (castor oil, rapeseed oil or coconut oil) were transesterified with trimethylol propane or glycerol to gain a natural oil-based reagent with sufficient high amount of OH groups enabling to react with carbonate units of polycarbonate chain.

In the second stage, the polycarbonate is conversed by means of this reagent into recycled polyols suitable for preparation of polyurethanes. This reaction might be advantageously accelerated using microwave (dielectric) heating.
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