PROGRAMME AND PROCEEDINGS

Institute of Polymer Materials
Riga Technical University

Latvian State Institute of Wood Chemistry

Riga Technical University

Institute of Technical Physics
Riga Technical University
GENERAL SPONSOR

TENAX Grupa, SIA TENACHEM
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Dr. Marcis Dzenis
## CONFERENCE AGENDA

### 16. September

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<th>Time</th>
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<tr>
<td>16.00 - 18.00</td>
<td>Registration in the hotel „SIGULDA“ (Pils 6)</td>
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<tr>
<td>20.00</td>
<td>WELCOM DRINK (Vidus 1)</td>
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### 17. September

<table>
<thead>
<tr>
<th>Time</th>
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<tbody>
<tr>
<td>9.30-10.00</td>
<td>Registration in the hotel „SIGULDA“</td>
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<tr>
<td>10.00-10.30</td>
<td>OPENING</td>
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<tr>
<td></td>
<td>Prof. M.Kalnins; Prof. L.Ribickis; Prof. T.Juhna</td>
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<tr>
<td>10.30-11.00</td>
<td>PLENARY</td>
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<tr>
<td></td>
<td>M. Rutkis, A. Šarakovskis, A. Šternbergs</td>
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<tr>
<td></td>
<td>NATIONAL RESEARCH PROGRAM “MULTIFUNCTIONAL MATERIALS AND COMPOSITES, PHOTONICS AND NANOTECHNOLOGY”</td>
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<tr>
<td></td>
<td>Institute of Solid State Physics University of Latvia, Riga, Latvia</td>
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<tr>
<td>11.00-11.30</td>
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<tr>
<td></td>
<td>R. Makuška</td>
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<tr>
<td></td>
<td>RAFT POLYMERIZATION OF (METH)ACRYLATES DIRECTED TOWARDS MULTIBLOCK COPOLYMERS AND THEIR BRUSH DERIVATIVES</td>
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<td></td>
<td>Department of Polymer Chemistry, Vilnius University, Vilnius, Lithuania</td>
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<tr>
<td>11.30-11.50</td>
<td>COFFEE BREAK</td>
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### SESSION 1 Chairman: M. Kalnins

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<tbody>
<tr>
<td>11.50-12.20</td>
<td>P. J. Skabara</td>
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<td></td>
<td>THE USE OF HETEROATOM INTERACTIONS TOWARDS BAND-GAP TUNING AND PSEUDO-RIBBON PLANAR STRUCTURES IN CONJUGATED POLYMERS</td>
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<tr>
<td></td>
<td>WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, United Kingdom</td>
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<tr>
<td>12.20-12.35</td>
<td>P. Bucinskas(^1), D. Volyniuk(^1), G.V. Baryshnikov(^2), B.F. Minaev(^2), K. Ivaniuk(^2), V. Cherpak(^2), P. Stakhira(^2) and J. V. Grazulevicius(^1)</td>
</tr>
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<td></td>
<td>PERYLENE AND CARBAZOLE BASED DERIVATIVES AS GLASS FORMING MOLECULES FOR ORGANIC LIGHT-EMITTING DIODES: EXPERIMENTAL AND THEORETICAL APPROACH</td>
</tr>
<tr>
<td></td>
<td>(^1)Department of Polymer Chemistry and Technology, Kaunas University of Technology, Kaunas, Lithuania; (^2)Lviv Polytechnic National University, Lviv, Ukraine</td>
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### SESSION 2 Chairman: A. Krumme

<table>
<thead>
<tr>
<th>Time</th>
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<tr>
<td>12.35-12.50</td>
<td>J. Blums, K. Ozols, A. Linarts, M. Knite</td>
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<td></td>
<td>POLYMER/NANOstructured CARBON COMPOSITES FOR ENERGY HARVESTING</td>
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<tr>
<td></td>
<td>Institute of Technical Physics, Faculty of Material Science and Applied Chemistry, Riga Technical University, Riga, Latvia</td>
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<tr>
<td>Time</td>
<td>Speaker</td>
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</table>
| 12.50-13.05| R. Krishni Narasimhan, D. Zeleniakienė | MODELLING OF HONEYCOMB CORE SANDWICH PANELS WITH FIBRE REINFORCED PLASTIC FACESHEETS AND ANALYSING THE MECHANICAL PROPERTIES | 1 Department of Production Engineering, Kaunas University of Technology, Kaunas, Lithuania  
2 Department of Mechanical Engineering, Kaunas University of Technology, Kaunas, Lithuania |
| 13.05-13.25| K. Faulhaber, V. Sauer, S. Gövert, J. Schnieders, H.-P. Heim | INTEGRATION OF ELECTROCHROMIC DEVICES BY THE INJECTION MOULDI NG PROCESS | 1 Institute of Material Engineering, Polymer Engineering, University of Kassel, Kassel, Germany  
2 3 Pi Consulting & Management GmbH, Paderborn, North Rhine-Westphalia, Germany |
| 13.25-14.20|                             | LUNCH                                                                 |                                                                                                |
| 14.20-14.35| A. Hejna, Ł. Piszczynski, P. Kosmela, J. T. Haponiuk | INCORPORATION OF CRUDE GLYCEROL INTO POLYURETHANE TECHNOLOGY | Department of Polymer Technology, Faculty of Chemistry, Gdańsk University of Technology, Gdańsk, Poland |
| 14.50-15.05| S. V. Kostjuk, I. V. Vasilenko, F. Ganachaud, F. Peruch | A CATALYST PLATFORM FOR UNIQUE CATIONIC (CO)POLYMERIZATION IN AQUEOUS EMULSION | 1 Research Institute for Physical Chemical Problems of the Belarusian State University, Minsk, Belarus  
2 INSa-Lyon, IMP, CNRS, UMR5223, Villeurbanne, France  
3 Université de Lyon, Lyon, France  
4 Laboratoire de Chimie des Polymères Organiques, UMR 5629, CNRS/UB1/IPB University of Bordeaux, Pessac Cedex, France |
| 15.05-15.20| E.V. Chernikova, K. O. Mineeva, A.V. Plutalova, A.V. Tolkachev, N.S. Serhacheva, N.I. Prokopov, I.R. Nasimova, E.Yu. Koizunova | CORE-SHELL PARTICLES SYNTHESIS IN THE COURSE OF BUTYL ACRYLATE EMULSION POLYMERIZATION STABILIZED BY HYDROPHILIC POLYMERIC RAFT AGENT | 1 Lomonosov Moscow State University, Faculty of Chemistry, Moscow, Russia  
2 Lomonosov State University of Fine Chemical Technology, Moscow, Russia  
3 Lomonosov Moscow State University, Faculty of Physics, Moscow, Russia |
| 15.20-15.35| G. Sini | CHARGE SEPARATION AT DONOR-ACCEPTOR INTERFACES IN POLYMER-POLYMER BHJ SOLAR CELLS: EXPERIMENTAL AND THEORETICAL INSIGHTS | Laboratoire de Physicochimie des Polymères et des Interfaces (LPPI), Université de Cergy-Pontoise, Cergy-Pontoise Cedex, France |
| 15.35-15.50| A. Jurkane, S. Gaikovskov | PREPARATION AND CHARACTERIZATION OF HOT-PRESSED Li+ ION CONDUCTING PEO COMPOSITE ELECTROLYTES | 1 Institute of Polymer Materials, Riga Technical University, Riga, Latvia  
2 Institute of Polymer Materials, Riga Technical University, Riga, Latvia |
| 15.50-16.05| N. A. Kukhta, D. Volyniuk, J. V. Gražulevičius | IMPROVING THE THERMAL STABILITY OF THE AMBIPOlar MULTICHROMOPHORE FLUORENONE-BASED COMPOUNDS | 1 Department of Polymer Chemistry and Technology, Kaunas University of Technology, Kaunas, Lithuania |
A.A. Efimova$^1$, A.V. Sybachin$^1$, A.A. Yaroslavov$^1$, S.N. Chvalun$^2$, A.I. Kulebyakina$^2$

**CORE-SHELL MULTI-LIPOSOMAL CONTAINERS BASED ON BIODEGRADABLE POLYLACTIDE PARTICLES**

$^1$ Polymer Department, Faculty of Chemistry, M.V. Lomonosov Moscow State University, Moscow, Russia

$^2$ National research centre "Kurchatov Institute", Moscow, Russia

### 16.05-16.20

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<td>16.05-16.20</td>
<td>POSTER SESSION &amp; COFFEE BREAK</td>
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<td>16.20-17.20</td>
<td>GALA DINNER</td>
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### 18. September

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<th>Time</th>
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<td>9.00-10.00</td>
<td>POSTER SESSION</td>
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**SESSION 1 Chairman: V. Jankauskaite**

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<tr>
<th>Time</th>
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<tr>
<td>10.00-10.30</td>
<td>H. Tenhu</td>
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<td></td>
<td>POLY(N-VINYLCAPROLACTAM) AS A CARRIER FOR ORGANIC SUBSTANCES</td>
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<td>Department of Chemistry, University of Helsinki, Finland</td>
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<tr>
<td>10.30-10.45</td>
<td>V. Barsukov$^1$, V. Khomenko$^1$, O. Chernysh$^1$, I. Makveyeva$^1$, M. Koliada$^1$, S. Isikli$^2$, F. Gauthy$^2$</td>
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<td></td>
<td>GREEN ALTERNATIVE BINDERS FOR HIGH VOLTAGE ELECTROCHEMICAL CAPACITORS AND LITHIUM-ION BATTERIES</td>
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<td></td>
<td>$^1$Kiev National University of Technologies &amp; Design, Kiev, Ukraine</td>
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<td></td>
<td>$^2$Solvay S.A. Functional Nanomaterials, Brussels, Belgium</td>
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<td>10.45-11.00</td>
<td>K. Batrakov$^1$, P. Kuzhir$^1$, S. Maksimenko$^1$, A. Paddubskaya$^1$, N. Volynets$^1$, T. Kaplas$^2$, Yu. Svirko$^2$, M. Lobet$^3$, N. Reckinger$^3$, Ph. Lambin$^3$</td>
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<td>GRAPHENE/POLYMER SANDWICHES AT HIGH FREQUENCIES. INFLUENCE OF CVD GRAPHENE QUALITY ON THE ELECTROMAGNETIC SHIELDING PERFORMANCE</td>
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<tr>
<td></td>
<td>$^1$Research Institute for Nuclear Problems, Belarusian State University, Belarus</td>
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<tr>
<td></td>
<td>$^2$Department of Physics and Mathematics, University of Eastern Finland, Finland</td>
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<td>$^3$Physics Department, University of Namur, Belgium</td>
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<td>11.00-11.15</td>
<td>M.N. Gorbunova, D.M. Kisel’kov, V.O. Nebogatikov</td>
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<td>NEW GUANIDINE-CONTAINING NANOCOMPOSITES WITH CYTOTOXIC ACTIVITY</td>
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<td>Institute of Technical Chemistry, Ural Branch of Russian Academy of Sciences, Perm</td>
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<td>ORGANIC MICROCAVITIES: FROM METAL LAYER TO OLED INTEGRATION</td>
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<td>Institut f. Angewandte Photophysik, TU Dresden, Dresden, Germany</td>
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<td>11.30-11.45</td>
<td>P. Franciszczak, A.K. Bledzki</td>
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<td>IMPROVING NOTCHED IMPACT STRENGTH OF POLYPROPYLENE SHORT-FIBRE COMPOSITES BY SELECTIVE TAILORING OF FIBRE-MATRIX INTERFACES</td>
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<tr>
<td></td>
<td>Institute of Materials Science, West Pomeranian University of Technology Szczecin, Szczecin, Poland</td>
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<tr>
<td>11.45-12.00</td>
<td>J. Simokaitiene$^1$, L. G. Gerling$^2$, S. Mahato$^2$, C. Voz$^2$, J. Puigdollers$^2$, J. V. Grauzulevicius$^1$</td>
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<tr>
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<td>STUDIES ON THE POTENTIAL DONOR PROPERTIES OF DIPHENYLETHENYL-SUBSTITUTED BRIDGED-TRIPHENYLAMINES IN ORGANIC SOLAR CELLS</td>
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<td></td>
<td>$^1$ Department of Polymer Chemistry and Technology, Kaunas University of Technology, Kaunas, Lithuania</td>
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<td></td>
<td>$^2$ Department of Electronics Engineering, Universitat Politecnica Catalunya, Campus Nord, Barcelona, Spain</td>
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<td>12.00-13.00</td>
<td>LUNCH</td>
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<td>13.00-13.15</td>
<td>S. Bak, A. Prociak&lt;br&gt;Flexible Polyurethane foam composites modified with cellulose fillers of different fibers size&lt;br&gt;Department of Organic Technology, Kaunas University of Technology, Kaunas, Lithuania</td>
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<td>13.30-13.45</td>
<td>S. Stepina¹, G. Sakale¹, M. Knite¹&lt;br&gt;Temperature influence on chemical sensor-effect of polymer nanostructured carbon composites&lt;br&gt;¹Institute of Technical Physics, Faculty of Material Science and Applied Chemistry, Riga Technical University, Latvia</td>
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<td>13.45-14.00</td>
<td>A. Petravičius¹², D. Petruulis¹, S. Petruiltyé¹&lt;br&gt;New modifications of polymeric tape yarns&lt;br&gt;¹Department of Materials Engineering, Kaunas University of Technology, Kaunas, Lithuania&lt;br&gt;²Klmeta Co., Kaunas, Lithuania</td>
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<td>14.00-14.15</td>
<td>G. D. Soto, N. E. Marcovich, M. A. Mosiewicki&lt;br&gt;Bioderived polyurethane foams based on tung oil: synthesis and characterization&lt;br&gt;Institute of Materials Science and Technology (INTEMA), University of Mar del Plata - National Research Council (CONICET), Argentina</td>
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<td>14.15-14.30</td>
<td>A. Kukhta¹, A. Paddubskaya¹, P. Kuzhir¹, S. Maksimenko¹, A. Avchinnikova², S. Vorobyova², S. Belucchi³, P. Khanna⁴&lt;br&gt;Conducting, magnetic, and luminescent graphene based polymer composites&lt;br&gt;¹Research Institute for Nuclear Problems, Belarusian State University, Minsk, Belarus&lt;br&gt;²Research Institute for Physical and Chemical Problems, Belarusian State University, Minsk, Belarus&lt;br&gt;³Frascati National Laboratory, National Institute of Nuclear Physics, Frascati, Italy&lt;br&gt;⁴Defence Institute of Advanced Technology, Deemed University, Pune, India</td>
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<td>14.30-14.45</td>
<td>T. Matulaitis¹, J. V. Gražulevičius¹&lt;br&gt;Effect of the spacer on the thermal properties of bipolar molecular materials&lt;br&gt;¹Department of Polymer Chemistry and Technology, Kaunas University of Technology, Kaunas, Lithuania</td>
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<td>14.45-15.00</td>
<td>M. Kirpluks¹, D. Kalnbunde², U. Cabulis¹&lt;br&gt;High functionality polyols from rapeseed oil as raw material for polyurethane thermal insulation&lt;br&gt;¹Polymer Laboratory, Latvian State Institute of Wood Chemistry, Riga, Latvia&lt;br&gt;²Faculty of Chemistry, University of Latvia, Riga, Latvia</td>
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<td>15.00-15.15</td>
<td>D. Volnyuk¹, V. Cherpak², P. Stakhira², K. Ivaniuk², N. Kostiv¹, T. Deksnys¹, J. Simokaitiene¹, D. Gudeika¹, J.V. Grazulevicius¹&lt;br&gt;New carbazole derivatives for light-emitting devices: photophysical, photoelectrical and electroluminescent properties&lt;br&gt;¹Department of Polymer Chemistry and Technology, Kaunas University of Technology, Kaunas, Lithuania&lt;br&gt;²Lviv Polytechnic National University, Lviv, Ukraine</td>
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CLOSING SESSION
Fifteen years of BPS, remembrance, passing the baton

16.00
EXCURSION

POSTER SESSION
17. September

1. J. M. Buffa, M. I. Aranguren, V. L. Mucci
   TEMPO-MEDIATED OXIDATION OF CELLULOSE NANOCRYSTALS: KINETICS AND ESR STUDY
   Institute of Research in Materials Science and Technology (INTEMA), National University of Mar del Plata - National Research Council (CONICET), Av. Juan B. Justo 4302, (7600) Mar del Plata, ARGENTINA

   RESEARCH ON BIO-DERIVED POLYMERS, COMPOSITES AND NANO COMPOSITES IN INTEMA (ARGENTINA)
   Institute of Research in Materials Science and Technology (INTEMA), National University of Mar del Plata - National Research Council (CONICET), Av. Juan B. Justo 4302, (7600) Mar del Plata, ARGENTINA

3. M. Viirsalu, T. Kivirand, A. Krumme, N. Savest
   AIR VORTEX ASSISTED ELECTRO SPINNING UNIT FOR NANOYARN PRODUCTION
   Institute of Polymer Materials, Tallinn University of Technology, Tallinn, Estonia

4. V. Jankauskaitė¹, A. Vitkauskienė²
   IMPROVEMENT OF ANTIBACTERIAL ACTIVITY OF GRAPHENE OXIDE AND METAL PARTICLES NANO COMPOSITES
   ¹ Faculty of Mechanical Engineering and Design, Kaunas University of Technology, Kaunas, Lithuania
   ² Faculty of Medicine, Lithuanian University of Health Science, Kaunas, Lithuania

5. V. Jankauskaitė¹, A. Lazauskas³, P. Narmontas²
   PREPARATION AND CHARACTERIZATION OF NANO STRUCTURED SUPER HYDROPHOBIC POLYDMETHYLSILOXANE SURFACE
   ¹ Faculty of Mechanical Engineering and Design, Kaunas University of Technology, Kaunas, Lithuania
   ² Institute of materials Science, Lithuanian University of Health Science, Kaunas, Lithuania

6. A. Paberza¹², V. Mucci³, P. M. Stefani², M. I. Aranguren³
   NANOCELLULOSE REINFORCED POLYURETHANE OBTAINED FROM HYDROXYLATED SOYBEAN OIL
   ¹ Polymer Laboratory, Latvian State Institute of Wood Chemistry, Riga, Latvia
   ² Institute of Polymer Materials, Riga Technical University, Riga, Latvia
   ³ Institute of Research in Materials Science and Technology (INTEMA), National University of Mar del Plata - National Research Council (CONICET), Mar del Plata, Argentina

7. R. Merijs Meri¹, J. Zicans¹, T. Ivanova¹, R. Berzina¹, P. Kuzhir², S. Maksimenko²
   STRUCTURAL AND RELAXATION PROPERTIES OF MULTIWALLED CARBON NANOTUBES AND SINGLE LAYER GRAPHENE CONTAINING POLYMER COMPOSITES OBTAINED VIA SOLVENT ROUTE
   ¹ Institute of Polymer Materials, Faculty of Materials Sciences and Applied Chemistry, Riga Technical University, Riga, Latvia
   ² Institute for Nuclear Problems, Belarus State University, Minsk, Belarus

8. G. A. Kloster¹, D. Muraca², M. A. Mosiewicki¹, N. E. Marcovich¹
   PREPARATION AND CHARACTERIZATION OF NANO COMPOSITES FILMS BASED ON CHITOSAN AND MAGNETITE
   ¹ Institute of Materials Science and Technology (INTEMA), University of Mar del Plata - National Research Council (CONICET), Mar del Plata, Argentina
   ² Institute of Physics Gleb Wataghin, University Estadual de Campinas, Campinas-SP Brazil
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<th>No.</th>
<th>Title</th>
<th>Authors</th>
<th>Institution</th>
<th>Country</th>
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<td>9.</td>
<td>RIGID POLYURETHANE FOAMS BASED ON A RAPESEED OIL POLYOL AND THEIR MODIFICATIONS WITH GLYCEROL AND CELLULOSE</td>
<td>M.A. Mosiewicki¹, P. Rojek², S. Michałowski², M. I. Aranguren¹, A. Prociak²</td>
<td>Institute of Materials Science and Technology (INTEMA), University of Mar del Plata - National Research Council (CONICET), Mar del Plata, Argentina</td>
<td>Argentina</td>
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<tr>
<td>10.</td>
<td>LIQUID AND SOLID ANIONIC LIPOSOMES CONTAINING CHOLESTEROL LOADED WITH BIOACTIVE COMPOUNDS IN CONTACT WITH SPHERICAL POLYCATIONIC BRUSHES</td>
<td>A.A. Efimova, O.V. Zaborova, A.V. Sybatchin, A.A. Yaroslavlov</td>
<td>Polymer Department, Faculty of Chemistry, M.V. Lomonosov Moscow State University, Moscow, Russia</td>
<td>Russia</td>
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<tr>
<td>11.</td>
<td>PRODUCTION AND CHARACTERIZATION OF BIOPOLYOLS FROM BRAN AND STRAW OAT</td>
<td>Ł. Piszczyk, A. Hejna, P. Kosmela, M. Szmajda, M. Strankowski</td>
<td>Department of Polymer Technology, Faculty of Chemistry, Gdańsk University of Technology, Gdańsk, Poland</td>
<td>Poland</td>
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<td>12.</td>
<td>APPLICATION OF CARBON MATERIALS TO PRODUCE OF FIREPROOF BIOPOLYMERS AND COMPOSITES</td>
<td>V. Plavan, V. Barsukov, O. Romanij, M. Koliada</td>
<td>Department of Applied Ecology, Technologies of Polymers and Chemical Fibers, Kyiv National University of Technologies &amp; Design, Kyiv, Ukraine</td>
<td>Ukraine</td>
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<td>13.</td>
<td>STRUCTURATION OF DERMA COLLAGEN BY MODIFIED DISPERSIONS OF MONTMORILLONITE</td>
<td>M.O. Maruhlenko¹, V.A. Palamar², O.R. Mokrousova²</td>
<td>Department of Materials Engineering, Kaunas University of Technology, Kaunas, Lithuania</td>
<td>Lithuania</td>
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<td>14.</td>
<td>NUMERICAL MODELLING AND EXPERIMENTAL STUDIES OF IMPACT BEHAVIOUR OF CARBON FIBRE REINFORCED METHYL METHACRYLATE COMPOSITE</td>
<td>K. Žukienė¹, P. Griskevicius², T. Žukas¹, V. Jankauskaitė¹</td>
<td>Department of Materials Engineering, Kaunas University of Technology, Kaunas, Lithuania</td>
<td>Lithuania</td>
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<td>15.</td>
<td>INFLUENCE OF SILVER Selenide TREATMENT ON PROPERTIES OF DIFFERENT NATURE FIBERS</td>
<td>D. Milašienė¹, R. Ivanauskas²</td>
<td>Department of Materials Engineering, Kaunas University of Technology, Kaunas, Lithuania</td>
<td>Lithuania</td>
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<td>16.</td>
<td>NUTRIENTS FOR PLANTS BASED ON BIODEGRADABLE MULCH FILMS</td>
<td>J. Treinytė¹, V. Grazuleviciene¹, I. Grigalaviciene²</td>
<td>Institute of Environment and Ecology, Aleksandras Stulginskis University, Akademija, Kaunas dist., Lithuania</td>
<td>Lithuania</td>
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<td>17.</td>
<td>EXPRESS PROCEDURE FOR EVALUATION OF DURABILITY OF COMPLEX SHAPE PULTRUDED COMPOSITE PROFILES</td>
<td>A. Aniskevich, V. Kulakov</td>
<td>Institute of Polymer Mechanics, University of Latvia, Riga, Latvia</td>
<td>Latvia</td>
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<tr>
<td>18.</td>
<td>POLYSISOPRENE – REDUCED THERMALLY EXFOLIATED GRAPHENE OXIDE COMPOSITE FOR SENSOR APPLICATION</td>
<td>A. Berzina¹, V. Tupureina², M. Knite¹</td>
<td>Institute of Technical Physics, Faculty of Materials Science and Applied Chemistry, Riga Technical University, Riga, Latvia</td>
<td>Latvia</td>
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2Institute of Polymer Mechanics, University of Latvia, Riga, Latvia

CATIONIC POLYMERIZATION OF ISOBUTYLENE IN TOLUENE: TOWARDS WELL-DEFINED HIGH MOLECULAR WEIGHT POLYMERS AT ELEVATED TEMPERATURE

1Laboratory of Catalysis of Polymerization Processes, Research Institute for Physical Chemical Problems of the Belarusian State University, Minsk, Belarus

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Research Institute for Physical Chemical Problems of the Belarusian State University, Minsk, Belarus

SYNTHESIS OF POLYMERIZABLE IONIC LIQUID MONOMER AND ITS CHARACTERIZATIONS

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2University of Tartu, Institute of Chemistry, Tartu, Estonia

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3Institute of Macromolecular Compounds of RAS, Saint-Petersburg, Russia

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A new Latvian National Research Program “Multifunctional materials and composites, photonics and nanotechnology” (further Program) are launched for period 2014-2017.

The realization of the Program will develop knowledge base in photonics, nanotechnology, innovative and advanced materials as well as enhance human resources and improve the competitiveness of the state economy according to the European Commission Key Enabling Technologies in the areas where Latvia possesses high scientific potential and demand of the economy.

The program is thematically structured in 4 projects:

1. Photonics and materials for photonics;
2. Nanomaterials and nanotechnology;
3. Nanocomposite materials;
4. Nanomaterials and nanotechnologies for medical applications.

In the implementation of the projects more than 150 scientists and more than 100 students will be involved. Within the frames of the program the students will elaborate their scientific and academic qualification works. As the results of the program more than 250 SCI reports in high-ranking scientific journals, around 200 presentations at international conferences and around 100 interactive activities including popular science publications, seminars, exhibitions are expected.

The Program, as a framework for research projects, is supported by “National Center for Research of Nanostructured and Multifunctional Materials, Constructions and Related Technologies” (Center). This new research infrastructure network is built by ERDF (~ 11 mil EUR) project realized 2012 -2015. Institute of Solid State Physics University of Latvia have been chosen as coordinator for both national activities.

Within our presentation we would like discuss potential impact of Program on Latvian material science in general and on polymer material research in particular context of Baltic Polymer symposium.
RAFT POLYMERIZATION OF (METH)ACRYLATES DIRECTED TOWARDS MULTIBLOCK COPOLYMERS AND THEIR BRUSH DERIVATIVES

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One of the most versatile methods of living/controlled radical polymerization is RAFT, because of facile experimental setup and ability to mediate the polymerization of most vinyl monomers. Moreover, RAFT is suitable for direct polymerization of acidic monomers giving a possibility to obtain block and comb copolymers with pH-responsive properties. It was shown recently [1] that RAFT polymerization is well suited for the synthesis of high-order multiblock copolymers by one-pot sequential monomer addition, where each step is taken to near full monomer conversion without intermediate purification. In the present study, one-pot methodology was used for the synthesis of amphiphilic multiblock copolymers which were transformed to brush derivatives obtaining anionic multiblock brush copolymers mimicking natural biolubricants like mucin or lubricin.

Amphiphilic or hydrophilic multiblock copolymers containing the blocks of 2-hydroxyethyl methacrylate (HEMA), butyl methacrylate (BMA), dimethylamino ethyl methacrylate (DMAEMA), and poly(ethylene oxide) methyl ether methacrylate (PEOMEMA) were synthesized by one-pot RAFT polymerization using difunctional RAFT CTA, which allowed the extension of growing chains into two directions [2]. Conversion of the monomers was monitored by $^1$H NMR spectroscopy, and molecular weight of multiblock copolymers was determined by SEC with triple detection. Trying to obtain “pure” blocks, polymerization was carried out up to very high conversions (usually, over 98 mol.%), and then the next monomer was added. Dispersity of pentablock copolymers containing rather long interjacent blocks of pBMA (DP up to 100) and outer blocks of pHEMA (DP up to 100) was very low, down to D 1.1.

Pentablock copolymers pHEMA-pBMA-pHEMA-pBMA-pHEMA were modified attaching pendent butylthiocarbonothioylthio moieties to nearly every unit of pHEMA blocks [3]. RAFT polymerization of acrylic acid (AA) in the presence of a pentablock copolymer decorated by multiple butylthiocarbonothioylthio moieties resulted in anionic pentablock brush copolymers, in which DP of pAA side chains was 20 to 40. Brush polyelectrolytes containing anionic side chains were weaker acids compared to linear polyelectrolytes. Hydrodynamic diameter of the brush molecules bearing relatively short side chains of pAA was pH-sensitive increasing upon increase of pH from 4.6 to 6.5.

Acknowledgements. Financial support from the Research Council of Lithuania under the project MIP-54/2015 is gratefully acknowledged.

References


THE USE OF HETEROATOM INTERACTIONS TOWARDS BAND-GAP TUNING AND PSEUDO-RIBBON PLANAR STRUCTURES IN CONJUGATED POLYMERS

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The extent to which the optoelectronic properties of molecules are controlled by their conformation and packing is now well appreciated. In particular, the planarity (or nonplanarity) of a molecule has a dramatic influence on its behavior, and hence on its potential application. In the context of light emission, disorder can be beneficial in controlling aggregation, but for photovoltaics and transistors where low energy absorption and effective charge transport are key issues, planar molecules are preferable. Of particular relevance to this talk is the development of planarised conjugated architectures that should support much-enhanced charge transport properties as a result of their ability to self-assemble into tightly packed frameworks. This high level of self-assembly is achieved not only through π-π stacking but also non-covalent interactions between heteroatoms of adjacent monomers. The nature of these interactions is not entirely clear, but one possible source of an attractive potential is a 3c-2e interaction between lone pairs and relatively low-lying antibonding orbitals, although these are likely to be counteracted to some extent by significant lone pair-lone pair repulsions. For example, polymer 1 (μ = 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}), has a planar repeat unit in the solid state as a result of close intramolecular sulfur/fluorine and hydrogen/fluorine contacts.\(^1\) Interestingly, variations in the absorption spectrum of these molecules suggest that the band gap is very sensitive to the degree of planarity. Whilst the mobility values for 1 are modest, the importance of the work is that it establishes a principle for the rational design of second generation materials with enhanced charge-transport properties.

This lecture will discuss several further examples that underline the importance and influence of non-covalent interaction in organic semiconductors.

References

PERYLENE AND CARBAZOLE BASED DERIVATIVES AS GLASS FORMING MOLECULES FOR ORGANIC LIGHT-EMITTING DIODES: EXPERIMENTAL AND THEORETICAL APPROACH

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Organic π-conjugated heteroarenes have been studied by many research groups worldwide because of their charge-transporting or electroluminescent properties, which make them useful for the applications in organic electronics.¹,² In this work, we focused on the search of compounds which can be employed as charge transporting or emitting materials in organic light emitting diodes (OLEDs). Our work was directed to the search of organic semiconductors featuring superior hole and electron mobilities and high luminescence quantum yield.

We synthesized a series of new ambipolar glass-forming perylene derivatives, consisting of N-annelated perylene building block symmetrically disubstituted at C-3 and C-10 positions with 2-carbazolyl, 3-carbazolyl or 9-carbazolyl units (Figure 1). In addition, we investigated optical, thermal, electrochemical, photophysical properties of the synthesized compounds. All the derivatives showed ambipolar behaviour. Time-of-flight hole and electron drift mobilities in their amorphous layers exceeded 10⁻³ cm²/Vs at high electric fields. Moreover, new compounds act as highly efficient green emission luminophores with photoluminescence quantum yields reaching 51% in the solid state. The synthesized materials were used as green-emitters to obtain OLEDs with a maximum brightness exceeding 61000 cd/m² (Figure 1).

In addition, the theoretical study based on the density functional (DFT) methods of the new compounds was performed and the results were compared with those obtained by the experimental tools.

References

POLYMER/NANOSTRUCTURED CARBON COMPOSITES FOR ENERGY HARVESTING

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Research represented in this work is an attempt to improve an efficiency of electrostatic harvesters. In such type of devices mechanical energy conversion to electrical energy is achieved through deformation of insulator (dielectric) layer between plates of charged capacitor. As a result of such deformation the capacitance of the capacitor is decreased and voltage between plates increased and, thus, charge of the capacitor can be stored at higher than initial voltage. To increase the change of voltage during the deformation of dielectric layer between capacitor plates, the use of elastic dielectric with variable dielectric constant is needed. The dielectric constant of such a dielectric should decrease with increasing distance between capacitor plates, i.e., with tensile deformation of dielectric layer. As a candidate for such a dielectric material polymer/nanostructured carbon (PNC) composite was chosen.

Capacitor samples containing PNC dielectric layer were elaborated from 1) SWR-3L natural rubber with added curing ingredients (this is used as a matrix); 2) high structure Degussa™ Printex™ EX-2 carbon black with average particle size 30 nm (filler); 3) two brass electrodes (thickness 2 mm). Brass electrodes were tightly attached to PNC composites during vulcanization (T = 150 °C, t= 15 min, p = 3 MPa). Diameter of samples is 18 mm, thickness is one millimeter. The concentration of filler in PNC composite was chosen to be slightly lower than percolation threshold. Tensile and compressive deformation of samples was realised using Zwick/Roell Z2.5 universal material testing machine. Measurements of dielectric constant were carried out on Agilent E4980A LCR meter.

Tensile and compressive deformation measurements conducted on PNC samples showed, that under tensile and compressive deformation dielectric constant of PNC composite is changing non monotonically (Fig.1.). The decrease of the dielectric constant with increasing deformation of the dielectric layer can be seen. It can also be seen, that character of dielectric constant change for both - tensile and compressive deformation - is different. The change of dielectric properties observed indicates about complex processes taking place in the PNC dielectric layer.

![Dielectric constant of a composite (NR/CB6) as a function of relative deformation.](image)

Fig.1.
MODELLING OF HONEYCOMB CORE SANDWICH PANELS WITH FIBRE REINFORCED PLASTIC FACESHEETS AND ANALYSING THE MECHANICAL PROPERTIES

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The fibre reinforce polymer composite sandwich structures are commonly use in aerospace, marine and transport applications. The honeycomb core sandwich composites are widely use in weight sensitive and damping structures where high flexural stiffness is required, in many industrial applications and can support causal loading like tensile and bending. The honeycomb core sandwich composites are exponentially being used to replace the traditional material in loading applications [1-2]. In order to increase the performance and use of this material in different applications, knowledge of the mechanical behaviour is required. This motivates to develop complex numerical models and experimental methods, which characterise the design, material models and optimizing the honeycomb sandwich panels in certain specific conditions.

The object of the investigation is the sandwich composite with facesheets made of wounded glass fibre and polyvinylester resin and core made of recycled paper hexagonal honeycomb impregnated in polyvinylester resin.

The aims of this study are to find the appropriate numerical material models and compare these models with experimental data; using obtained numerical models to determine the optimal strength and stiffness properties to increase the mechanical behaviour of sandwich structure.

Testing the each component of sandwich structure was carried out separately and each test was carried out according to the testing standards for facesheets (ISO 527, ISO 604, ISO14129) and for honeycomb core (ISO 844, ISO 1922) and the mechanical properties were determined. Using experimentally obtained data the finite element models of sandwich structure comprises of glass fibre reinforced polyvinylester resin facesheet and recycled paper hexagonal honeycomb impregnated with polyvinylester core were designed. For the verification of the finite element models of sandwich structure, two different tests were conducted. The tension test was carried out for verification of facesheet material model and three point bending test for sandwich structure.

The appropriate finite element models were compared with experimental data. The finite element modelling results had a good agreement with experimentally obtained ones. This finite element methodology allowed determination of optimal strength and stiffness properties with increased the mechanical properties of the sandwich structure. The model can also be used to determine the mechanical behaviour of various industrial applications using honeycomb core sandwich structure.

References

The functionalization of polymer components can achieve by various procedures. Adding filling materials during the process chain allows an improvement in thermic or electrical conductivity. Due to a subsequent surface treatment, the wetting capacity is able to be adjusted. A further option is available through the implementation of a foil, which, aside from its decorative purposes, also possesses certain functional properties. The integration of an electrochromic (EC) device, based on a polycarbonate foil (Figure 1), is an attractive aspect for opaque components. It allows a reversible modification of the transmission. Simultaneously, due to the internal design of the EC-cell, ultraviolet and infrared radiation is strongly damped. Practical applications for functionalized components could be roofing modules for vehicles. Implementing such components allows a notable reduction in total weight through the replacement of heavier glass parts. Furthermore, the replacements have a positive effect on the driving dynamics by reducing the vehicle’s center of gravity.

In the research project “ProTeck” we used an EC-composite system which consists of multiple individual layers, each with different physical attributes. The partially pressure sensitive, yet above all temperature sensitive, layers should not be damaged in any way, to guarantee their functionality further. This represents a challenge to the process and tool technology for subsequent processing.

This paper shows the manufacturing process of the electrochromic device and furthermore the possibility to integrate these systems into the plastic processing, especially the injection moulding process.

**Figure 1:** Principal construction of an electrochromic device

**Acknowledgements** The results depicts were generated by the research project „ProTeck“, which was funded by the Federal Ministry for Education and Research.
Crude glycerol is the main by-product of biodiesel production process. It is available in huge amounts (about 1 million ton annually in Europe) and latest forecasts indicate growing interests in biofuels, so its production should be raising in the future, at least until 2020. Crude glycerol can be successfully used in polyurethane manufacturing. This review briefly evaluates reported in the literature attempts of crude glycerol applications in polyurethane technology. There are discussed various processes leading to value-added products obtained from crude glycerol, such as fermentation, oligomerization or biomass liquefaction. Moreover, examples of value-added polyurethane products based on substrates obtained from crude glycerol are presented.
HYPERBRANCHED POLYMERS BASED ON ISATIN AND ELECTRON RICH ARENES: SYNTHESIS AND APPLICATIONS

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An overview is given of our work (since the first publication in 2002) on the super acid catalyzed condensation reaction of AB$_2$ monomers of different molecular architecture, containing both isatin (or other diketones) and electron rich aryl moieties to hyperbranched polymers. The two-component A$_2$ + B$_3$ approach and the corresponding dendrimer analogues are also discussed. The resulting materials can be functionalized and are of importance as molecular containers, starting points for core-shell nanoparticles or as catalysts for biomass conversion.

References


A CATALYST PLATFORM FOR UNIQUE CATIONIC (CO)POLYMERIZATION IN AQUEOUS EMULSION

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Cationic polymerization in aqueous emulsion or suspension is nowadays acknowledged by most polymer chemists. This approach is believed to solve the main problems of conventional cationic polymerization, i.e. the necessity to work at low temperatures and under strictly anhydrous conditions.1 Different generations of catalysts have been tested over the last 15 years. Yb(OTf)3 was the first water tolerant Lewis acid successfully used to catalyze the cationic polymerization of p-methoxystyrene (pMOS) in aqueous suspension or emulsion at 30 °C. Styrene (St), cyclopentadiene and isoprene (IP) polymerizations were performed in aqueous suspension and/or emulsion for the first time using a singular Lewis acid, B(C6F5)3, which does not decompose in water.1,2 However, the molar masses of all synthesized polymers were not higher than 3,000 g mol−1, a limit value above which interfacial polymerization ceases.1

In this work, the new catalyst platform for fast, efficient cationic (co)polymerization of industrially relevant monomers into high molecular weight polymers in aqueous emulsion and moderate temperature will be reported.3 This new catalyst platorm consists of sodium dodecyl benzene sulphonate, with a polydisperse and hyperbranched stucture, combined with rare earth salts to generate highly water-dispersible Lewis acid surfactant combined catalysts (LASCs).3 It was shown that LASCs induced cationic polymerization of pMOS in aqueous emulsion at 60 °C to afford poly(pMOS) with M_n up to 40,000 g mol−1. Even higher molecular weight polymers (M_n=80,000–200,000 g mol−1) were obtained in aqueous emulsion in the case of polymerization of St and IP, respectively, at 40 °C. Finally, the successful copolymerization of St and IP was performed. Interestingly, statistical copolymers with monomodal MWD and single T_g's were obtained at St/IP molar ratios below 75:25. The copolymers synthesized at larger molar ratios, however, showed two T_g's, the lower one for IP-rich blocks, the higher one ascribed to St-rich blocks. Such characteristics are the signature of thermoplastic elastomers.3

Acknowledgements. This work was supported in part by the ANR project "SYNBIORUB" BLAN08-1_340665 and Belarusian Republican Foundation for Fundamental Research (X15PM-041).

References

CORE-SHELL PARTICLES SYNTHESIS IN THE COURSE OF BUTYL ACRYLATE EMULSION POLYMERIZATION STABILIZED BY HYDROPHILIC POLYMERIC RAFT AGENT

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Nowadays the problem of design of nano- and micro-structured materials, including ones based on polymer systems, assumes ever greater importance. The increased interest to the structured polymer materials is caused by formation of nano- and micro-scale heterogeneous structures, which results in combining the individual properties each of phase and/or displaying absolutely new properties.

Recently an approach based on formation the systems with predetermined morphology (“core–shell” particles) directly in the cause of polymerization due to self-assembly of synthesizing amphiphilic block-copolymers has been proposed [1, 2]. In contrast to the previous approaches to “core–shell” particles synthesis, which could not provide the formation of define structures, in the latter one due to application of controlled radical polymerization techniques this problem has been overcome. It became possible owing to using a hydrophilic polymer containing hydrophobic moiety capable to both stabilize emulsion of low soluble in water monomer and provide realization of “living” mechanism of polymerization. RAFT (reversible addition–fragmentation chain transfer) technique seems to be here a versatile one due to low sensitivity to monomer functionality and convenient conditions of practical implementation.

Aim of the present research was to develop technique of self-assembling block-copolymer synthesis basing on (co)polymers of acrylic acid carrying mid-chain or end-chain trithiocarbonate group and poly(butyl acrylate) in conditions of emulsion polymerization.

A range of (co)polymers of acrylic acid with \( M_n = (7 - 15) \times 10^3 \) Da and \( M_w/M_n < 1.4 \) has been synthesized via a bulk or solution RAFT polymerization using symmetrical bifunctional (R–S–C(=S)–S–R) or non-symmetrical monofunctional (R–S–C(=S)–S–R’) trithiocarbonates and sodium styrene sulfonate or 2,2,3,3,4,4,5,5-octafluoropentyl acrylate as comonomers. All these polymers exhibit surface-active properties in the wide range of pH.

The influence of the concentration of the monomer, initiator and polymeric RAFT agent, as well as the temperature and pH of aqueous phase on the 1) molecular-weight characteristics of the product formed; 2) the size and particle size distribution; 3) polymerization kinetics and limited conversions; 4) particle morphology was studied. The stabilizing ability of polymeric RAFT agent increased with increase of its hydrophobicity. The decrease of monomer concentration and simultaneous increase of polymeric RAFT agent concentration enhanced the control over molecular weight characteristics of block-copolymer formed. The stable dispersions of core-shell structured particles have been obtained at high monomer and low polymeric RAFT agent concentration.

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This work was supported by Russian Scientific Foundation (project No 15-13-30007).
Understanding different phenomena happening at donor-acceptor interfaces in bulk heterojunction solar cells (BHJSC) is of prime importance for high performant organic photovoltaic devices (OPV). The delicate balance between charge dissociation (CD), charge recombination (CR), and charge separation (CS) is one of these key processes. A deep understanding of these phenomena is still a challenge.

Aiming to shed more light on these phenomena, we initially focus our study on P3HT*-P(NDI2OD-T2)** based donor-acceptor BHJSC. Previous studies have reported on: (i) the importance of avoiding pre-aggregation in the case of P(NDI2OD-T2). (ii) presence of a very high donor-acceptor charge recombination ratio (70%), which was found to be the dominant factor degrading the solar cell performances in this D-A combination (iii) important role of crystallite orientation at the interface.[1-2] Upon substitution of P3HT and P(NDI2OD-T2) with other donor and acceptor polymers,[3] only small improvements have been obtained.

A detailed theoretical analysis based on DFT methods suggests that these results are due to different factors playing in opposite senses. An important reduction in electronic couplings corresponding to the CR seems to dominate the global effect. This last effect is found to originate from two principal factors: increase in the average distance between donor and acceptor at the interface, and from the larger space delocalization of the LUMO in the acceptor unities.

The theoretical analysis also focusses on some factors impacting the energy gradient (bending) at the D-A interface in these systems. The structural and electronic modifications upon replacing P3HT and P(NDI2OD-T2) with other polymers are shown to increase the energy gradient at the D-A interface, in turn increasing the driving force for the charge separation.

*poly(3-hexylthiophène)

**poly([n,n’-bis(2-octyldodecyl)-11naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5’-(2,2’-12 bithiophene))

References

PREPARATION AND CHARACTERIZATION OF HOT-PRESSED Li⁺ ION CONDUCTING PEO COMPOSITE ELECTROLYTES

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Preparation and characterization of hot-pressed Li⁺ ion conducting Polyethylene oxide (PEO) composite electrolytes are discussed in this paper. Lithium trifluoromethanesulfonate with linear formula CF₃SO₃Li is selected as Li⁺ ion source for polymer composite electrolyte processing. Polyethylene oxide as matrix for polymer electrolyte is selected, because of its cation solvatation and salt complexes formation partibility. Nano-sized fillers such as carbon nanotube (CNT) and graphene (GR) are introduced to polymeric composite to improve PEO electrolyte mechanical properties. The composites were prepared from PEO, CF₃SO₃Li, CNT and GR by solution casting and by hot-pressing method. Influence of CF₃SO₃Li, CNT and GR concentrations on the electrical, thermal and mechanical properties of PEO composite is investigated and discussed. The additives addition to the PEO matrix improves the electrical, thermal and mechanical properties of the composite. The crystallinity of the PEO decreases.
IMPROVING OF THE THERMAL STABILITY OF THE AMBIPOLAR MULTICHROMOPHORE FLUORENONE-BASED COMPOUNDS

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Organic light-emitting diodes (OLEDs) suggest a promising solution for the large-area, high-resolution flat panel displays and lighting sources ¹. Ambipolar charge transport in organic semiconductors is essential for the development of integrated microelectronic organic circuits and optoelectronic devices ². Donor-acceptor molecular architecture can provide a wide range of interesting optical, photophysical and electrochemical properties. However, the performance of the target optoelectronic devices proves to depend strongly on the stability of the used organic semiconductors.

In the current work we present the synthesis and characterization of the bipolar multichromophore fluorenone-based compounds. The dendritic molecules exhibit remarkably high initial degradation temperatures $T_{ID}$ (473–509 °C) and glass transition $T_g$ temperatures (238–327 °C), as well as good film forming ability. The obtained fluorescent dyes emit light in the yellow spectral region with the maxima in the range of 495–526 nm. The ionization potentials of the synthesized compounds were estimated by the electron photoemission spectrometry and found to be comparable (5.48 – 5.55 eV) and in good agreement with the data obtained from cyclic voltammetry measurements and DFT calculations. Balanced hole and electron charge mobilities, well exceeding $10^{-4}$ cm²/V·s, were observed for the target compounds with fluorenone nucleus. The effect of the nature of the chromophores on the thermal, photophysical and photoelectrical properties of the dendritic molecules was investigated.

References

CORE–SHELL MULTI-LIPOSOMAL CONTAINERS BASED ON BIODEGRADABLE POLYLACTIDE PARTICLES

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Bilayer lipid vesicles (liposomes) nowadays have found applications in medicine and biology including drug delivery. Liposomes are widely used as containers, that can be loaded with different bioactive compounds: drugs, polypeptides, proteins, nucleic acids. One could prepare multi-liposome assembly, for example via immobilization of several liposomes on a nano-sized colloid or solid carrier. It would help to increase the efficacy of liposome uptake by cells and therapeutic effect of a liposomal drug.

In this study we describe biodegradable multi-liposomal core–shell containers (MLC). They were made of a poly-L-lactide–polyethyleneoxyde–poly-L-lactide triblock-or poly-L-lactide–polyethyleneoxyde diblock-copolymer core covered by electrostatically adsorbed liposomes. Copolymer of poly-L-lactide and poly (ethylene glycol) was synthesized via ring opened polymerization of lactide in the presence of PEG, catalyzed by stannous octanoate. The average size of PLA particles that were used for constructing MLC was equal to 120–170 nm. A small negative charge of PLA particles was probably imparted due to dissociation of terminal groups of the copolymer. Liposomes were prepared from a mixture of electroneutral and negatively charged lipids with a molar fraction of negatively charged polar groups equal to 0.1. To make anionic liposomes bind to the negative PLA particles, they were modified by a cationic polymer, polylysine.

It was found that ternary PLA-polylysine-liposome complex carries number of liposomes forming multiliposomal container. Liposomes were loaded with different bioactive compounds. The liposomes retained their integrity after adsorption within 3 hours, which allows them to be used for encapsulating bioactive compounds. The multiliposomal containers eventually decomposed, by being attacked by a proteolytic complex Morikrase, which makes them promising for use in drug delivery.

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POLY(N-VINYLCAPROLACTAM) AS A CARRIER FOR ORGANIC SUBSTANCES

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Poly(N-vinylcaprolactam), PVCL, is a water soluble thermoresponsive polymer, the properties of which we have studied for years. It has started to attract interest in several laboratories because of its generally accepted biocompatibility and also because of the development of the synthesis methods.

PVCL is known to complex ionic surfactants and organic substances as phenols in aqueous solutions.[1,2] It shows potential as a carrier for various drugs.[3,4]

This presentation discusses the syntheses and the mechanisms of phase separation of block copolymers based on poly(dimethylaminoethylmethacrylate), PDMAMA, and PVCL. Both blocks show LCST but the behaviour of PDMAEMA is modulated by pH and ionic strength. The polymers have a tendency to aggregate in water even at room temperature owing to the interactions between the cationic repeating units and the VCL units.[5]

Recently we synthesized novel micro/nano gels of PVCL and decorated the gel surfaces with gold nanoparticles. Binding and release of 8-anilino-1-naphthalenesulfonic acid ammonium salt, 1,8-ANS, and (4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran, 4HP, have been studied as function of temperature by fluorescence spectroscopy. Thermal collapse of the gel particles can be induced by heating the AuNPs with uv-vis light.[6]

References

GREEN ALTERNATIVE BINDERS FOR HIGH VOLTAGE ELECTROCHEMICAL CAPACITORS AND LITHIUM-ION BATTERIES

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In contrast to electric double-layer capacitors (EDLC), Li-ion capacitors (LIC) offer higher capacitance, cell voltage, energy density and lower cost per watt-hour. LIC contains a negative electrode, which is similar to the lithium-ion battery (LIB) anode, and a positive electrode, which is similar to EDLC cathode. LIC and LIB performance depends significantly not only on the right choice of the active materials, but also on many electrode manufacturing parameters. In this work, different polymer binders have been studied for applications in positive and negative electrodes of LIC and LIB. The current work describes also some new approaches for the electrode binder optimization for LIC and LIB devices.

Since 1991, industry uses polyvinylidene fluoride (PVDF) as the most popular binder for LIB electrodes. This binder has a time-tested quality. In the traditional electrode production, a large amount of an organic solvent is used as a medium for electrodes casting on metallic collector foils. N-Methyl-2-pyrrolidone (NMP) is the solvent predominantly used. Using NMP is technologically undesirable because it has important disadvantages, such as a high cost and toxicity. Besides, being volatile, flammable, easily absorbed by the human skin, NMP is suspected to cause genetic and reproductive damages to humans. Nevertheless, it is difficult to replace NMP in electrode production techniques. This is because the process chain for electrode manufacturing is distinguished by its complexity and the large number of influencing factors. In the present work, we introduce an innovative slurry concept for the fabrication of LIB and LIC electrodes, which based on two following approaches:

I) Dimethyl sulfoxide (DMSO) was employed instead of NMP as an alternative eco-friendly solvent;

II) Aqueous-based technique for preparation of LIB and LIC electrodes was developed.

The electrodes, which made with DMSO as a solvent, have demonstrated similar coating properties and electrochemical characteristics. On the positive electrode side, some adhesion-related problems for activated carbon electrodes have been eliminated with usage of an etched aluminum foil and hot calendaring. Hence, this improved adhesion made remarkable difference in electrochemical performance of electrodes with different types of binders. As further efforts to change the binder type from organic to aqueous and to reduce the cost of the electrode making process, Solvay aqueous alternatives were employed as binders. LIC and LIB electrodes made from Solef® PVDF aqueous dispersions have revealed a superior electrode quality and a high electrochemical performance.

The obtained results enlighten the promising prospect of innovative slurry concept for the fabrication of LIB and LIC electrodes. These achievements have demonstrated the possibility to develop LIB and LIC environmentally friendly production processes and to facilitate the recycling devices.

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Microwave is the ultimate range for open space communication. The rapid growth of satellite data transmission in last decades, reinforced by the Internet traffic, makes inevitable the overcrowding of the spectral bands allocated to the different communication channels. In order to solve problem of electromagnetic compatibility, there is a real need for new materials to be used as coatings, shields and filters in future nanoelectronic devices.

Thanks to its high electrical conductivity, graphene presents a good shielding efficiency against GHz radiations [1]. Several graphene planes separated by thin polymer slabs (100 nm – 1 micron) add their conductivities arithmetically, because each of them conserves the intrinsic properties of isolated graphene. Maximum absorption of radiations of normal incidence at 30 GHz for free standing graphene/polymer (PMMA) sandwiches consisting on 4-6 graphene layers is achieved at the level 50%.

Nevertheless for plenty of possible graphene applications, the graphene quality is a topical issue. In this communication, we demonstrate experimentally as proved theoretically [2] that microwave performance of graphene/polymer sandwiches is robust against various graphene defects inherent to the CVD production method, such as microscopic holes, microscopic dots or grain boundaries. The absorption properties remain constant to first order in defect concentration when the heterostructure contains the optimum number of layers.

References

NEW GUANIDINE-CONTAINING NANOCOMPOSITES WITH CYTOTOXIC ACTIVITY

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The field of nanoscience has blossomed over the last twenty years and the need for nanotechnology will only increase as miniaturization becomes more important in areas such as computing, sensors, and biomedical applications [1]. Advances in this field largely depend on the ability to synthesize nanoparticles of various materials, sizes, and shapes, as well as to efficiently assemble them into complex architectures. The incorporation of nanoparticles into various matrices will extend their utility in material and biological applications. Such nanocomposites could exhibit novel useful properties. Our work is focused on incorporating of silver nanoparticles into matrice of new copolymers based on 2,2-diallyl-1,1,3,3-tetraethylguanidiniumchloride.

The copolymers of 2,2-diallyl-1,1,3,3-tetraethylguanidiniumchloride with N-substituted maleimides (N-phenylmaleimide, N-(n-carboxyphenyl)maleimide, N-(n-acetoxyphenyl)maleimide) have been obtained by free radical polymerization. 2,2-diallyl-1,1,3,3-tetraethylguanidiniumchloride copolymerizes with maleimides with formation of cis-, trans-stereoisomeric pyrrolidine structures in cyclolinear polymer chain.

Synthesis of silver nanocomposites was conducted by the reduction of AgNO₃ with NaBH₄ in solution of copolymer. Reaction proceeds via formation of the stable dark brown sols, from which nanocomposites were separated.

SEM results proves the obtaining of nanocomposites with regular narrow-dispersed distribution of silver nanoparticles in polymer matrice. Nanoparticles of spheric and elliptic forms were obtained.

Investigation showed that new nanocomposites have a significant cytotoxic activity and can be used for medical applications.

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References

ORGANIC MICROCAVITIES: FROM METAL LAYER TO OLED INTEGRATION

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We report on investigation of low-dimensional, photonic structures consisting of inorganic and organic dielectrics and metal. The use of organic material as a broadband emitter within a microcavity enables to explore the optical properties of such systems in a broad spectral range. In combination with a thin metal layer, hybrid plasmon-polariton modes (optical Tamm-states, [1]) arise in these structures and can be evaluated. Basing on the knowledge of the optical mode structure in such systems, OLEDs are implemented into a high quality microcavity consisting of two distributed Bragg reflectors (DBRs).

Our samples are prepared by high vacuum deposition of all layers. In a first step, the organic hostguest system Alq3:DCM as the active material is sandwiched in between two high-reflective SiO2/TiO2 DBRs. Additionally, a thin homogenous or laterally structured metal layer (Ag) could be prepared within the resonator. In a further step, a specific OLED design was developed to meet the requirements of optical, electrical and stability properties.

We show that low threshold room temperature lasing of different modes can be obtained at optical pumping including coherent emission from Tamm-states [2]. Creation of single in-plane structures leads to a discretisation of the dispersion while periodic in-plane structures produce complex dispersion. We discuss the influence of structure, material and preparation conditions on the emission properties of the OLEDs.

Fig. 1: Experimental angular-resolved emission spectra from organic MC (excitation: cw 405 nm)
(a) without metal layer; (b) with embedded un-patterned 40 nm Ag layer;
(c) with periodically-spaced silver stripes (period $a$ =10.1 μm)

Fig. 2: Electroluminescence of OLED in MC
The quality factors of the modes are 800 and 150

References
A hybrid polypropylene composite reinforced with man-made cellulose fibres of two selectively tailored interfaces was developed in the course of this study. In the developed hybrid, a part of fibres was compatibilised for a strong fibre-matrix interphase, which provided good mechanical properties, while the other part of fibres was anticompatibilised in order to obtain a weak interface, which improved the impact behaviour of the composite owing to dissipation of impact energy by fibre pull-out. The fibres with weak interface exhibit a synergistic effect with fully compatibilised fibres, which translates into good mechanical performance [1]. In relation to the composite reinforced with fully compatibilised man-made cellulose fibres, the manufactured hybrid displayed a 32% higher notched impact strength with merely a 5% reduced flexural strength and heat deflection temperature. The invented method of manufacturing hybrid composites with a dual-interface is a novel concept, which owing to its simplicity and use of standard processing equipment can be easily implemented in the plastic industry [2].

The authors would like to express their appreciation to Clariant Masterbatches, HSH Chemie Poland for supplying MAH grafted waxes and EKOTEX for supplying chopped fibers.

STUDIES ON THE POTENTIAL DONOR PROPERTIES OF DIPHENYLETHENYL - SUBSTITUTED BRIDGED - TRIPHENYLAMINES IN ORGANIC SOLAR CELLS

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Organic solar cells (OSC) have attracted much attention during the last decade due to their potential for fabricating light-weight, large-area, customized, flexible and low-cost solar panels [1]. Solar cells can be seen as absorbing layers sandwiched between selective contacts. These selective layers - hole and electron transport layers (HTL, ETL) - play an important role when designing high efficiency solar cells. As absorbing layers different combinations based on bilayer or heterojunction structures have been used.

One of the main parameter that characterizes the performance of OSCs is the open-circuit voltage (Voc). Voc values depend mainly from the difference between the HOMO level of the donor and the LUMO level of the acceptor. In this sense many efforts are devoted to synthetize new light absorbing materials with low HOMO level position and high light absorbing coefficients.

In this work we check the properties of small-molecules of compounds based on diphenylethynyl-substituted bridged-triphenylamines thermally evaporated using high-vacuum system as a potential donor in organic solar cells.

In particular OSCs based on a bilayer structure were fabricated with the following structure: glass/ITO/MoO₃/donor/C₇₀/BCP/Al, in which MoO₃ and bathocuproine (BCP) are the HTL and ETL, respectively. Donor materials, diphenylethynyl-substituted bridged-triphenylamines, were synthesized and used without further purification process. OSCs with these donors showed excellent performances, with JSC = 5.20 mA/cm², VOC = 0.78 V, FF = 46 % and η = 1.9 % for the best device.

Finally, the optoelectronic properties of OSCs based on these diphenylethynyl-substituted bridged-triphenylamines donor materials were compared with identical OSCs fabricated using the standard tetraphenyldibenzoperiflanthene (DBP) as a donor material [2].

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References

Flexible polyurethane (PUR) foams are widely used in industrial production of mattresses and seat cushions. In recent years, European ecological policy and the development of "green chemistry" resulted in the use of renewable raw materials also in the synthesis of polymeric materials including polyurethane foams. Flexible PUR foam formulations consist of two main components which are polyols and diisocyanates, as well as other compounds like catalysts, surfactants and blowing agents. Synthesis of porous composite materials using polyurethane matrix and fillers of natural origin allows to produce bio-foams with various mechanical properties. Among such fillers natural fibers, mainly consisted of cellulose and lignin, are used. Polyurethane foam synthesis by a continuous process, with the use of a mixing and dosing machine, is an intermediate step between and industrial scale production. The main difference lies in the process of combining two components of PUR system by a static-dynamic mixer, with precise and repeatable dispensing of exact amount of each component. In our study, three different ARBOCEL® fillers were applied. Foaming process analysis was conducted using FOAMAT® which measured changes in temperature, pressure, dielectric polarization, and the velocity of rising rate of the reaction mixtures in a function of the applied modified foam formulations. It was found that along with the fibers size, temperature in the foams core increases, dielectric polarization drops more dynamically which indicates fillers influence on the foaming process. Moreover, it was found that the semi-crystalline structure and small nano/micrometric dimensions of cellulose fibers have a significant impact on cell structure and selected mechanical properties of flexible polyurethane foams. Depending on the average fibers size, different effects have been observed. The results of ball rebound resilience and compression strength tests showed that in the case of foams of isocyanate index of 0.9, with the increase of fiber size, resilience increases along with hysteresis and comfort factor. Foams modified with filler with the longest fibers had also the higher hardness at maximal compression although at 40% compression, hardness of all modified materials was similar.

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WOOD-POLYPROPYLENE-COMPOSITES: INFLUENCE OF PARTICLE SIZE AND SHAPE ON MECHANICAL PROPERTIES

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Fillers and reinforcing materials from natural resources offer various opportunities for usage in plastics technology. However, unlike synthetic fillers, they have no constant properties, but rather differ from each other, depending on harvest year, growing area or type. Together with the different processing parameters this results in a significant influence on the mechanical properties of the final component. In this oral presentation, it will be shown which mechanical properties can be reached with WPC components. Finally, these studies will lead to a precise statement of the material behavior thus contributing to safe and reliable materials.

In this research project, the relation between particle geometry of biogenous fillers and the mechanical properties of the composite are analyzed. Different hard- and softwood flours, supplied by JRS (J. Rettenmaier & Söhne GmbH & Co. KG, Germany), used as fillers, are compounded with polypropylene using a twin screw extruder. With a fractionation by size of the fillers before the compounding process, blends with different average particle sizes are created and investigated. The used fillers derive from different plant resources, growing areas and are processed with different parameters. Furthermore the usage of a coupling agent is highly important, as it can significantly improve the mechanical properties of the composites. A maleic anhydride-polypropylene copolymer (MAPP) obtained by Clariant, Germany, was used as a coupling agent to improve the adhesion between wood fillers and the PP matrix.

The produced compounds are processed to test specimen using an injection molding machine to carry out mechanical tests to investigate the tensile, flexural and impact properties. The particle size distribution and particle shape in raw material, compound and finished component is determined with the dynamic image analysis using a Sympatec QICPIC and further optical examination methods.

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TEMPERATURE INFLUENCE ON CHEMICAL SENSOR-EFFECT OF POLYMER NANOSTRUCTURED CARBON COMPOSITES

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In our previous works [1-2] is discussed humidity influence on polymer nanostructured carbon composite (PNCC) VOC vapour sensor-effect. There were concluded PNCC is able to detect VOCs at elevated relative humidity. It was found that at the water-ethanol mixture ratio 70:30 changes the composite response mechanism to vapour: the contribution of proton conductivity of the water layer on the surface of PNCC sample overcomes the contribution of tunnelling currents inside of composite [2].

There were made PNCC from ethylene vinyl acetate copolymer (EVA) and extra-conductive highly structured carbon black (CB), which was used as electrically conducting filler with average particle size 30 nm. Particles specific surface: 950 m²/g and DBP (dibutyl phthalate) adsorption: 380 ml/100 g.

In order to continue explore surrounding environment influence we investigated VOC vapour sensoreffect of PNCC at various temperatures. It was done using sensor platform ((SP); Heraeus Sensor Technology) as PNCC substrate. SP is designed for the mounting on them layer like materials. All of them - temperature sensor (Pt 1000), a heater and interdigitated electrode structures (IDES) in platinum thin film - are integrated on a ceramic substrate. Heater and sensor are covered with an insulating glass layer. PNCC layers were coated onto the non-passivated electrode structures by using screen process or drop-coating. PNCC characterization and temperature influence on different VOC as well as on fuel vapour sensoreffect is going to be investigated and discussed.

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References:


NEW MODIFICATIONS OF POLYMERIC TAPE YARNS

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The application of additives is known as an effective way to develop the new modifications of polymeric materials, for example, the tape yarns for textile industry [1, 2]. In the current study, the applications of several additives for polyolefin tape yarns were examined. The polypropylene (PP) MOSTEN TB 003 granules (Unipetrol Co., Czech Republic) were used as main component. The new modifications of the yarns were developed applying together the following additives: UV 01017PP (Constab Co., Germany), Granic 422 (Constab Co., Germany) and Polycom JB 7100 (Omega Plasto Compounds Co., India).

In this stage of research, the variations in portions (wt%) of the one additive and PP component as well as the applications of fixed portions of other additives were used as key method to study the effects of the variable portions. To evaluate the new modifications, the qualitative and quantitative changes in properties were studied. The scanning electron microscopy (SEM) micrographs of the surfaces, the elemental analysis by means of the energy-dispersive X-ray spectroscopy (EDX), the colour changes, geometrical parameters (width, thickness), linear densities and tensile properties for different variants of tape yarns were examined.

Two examples of typical views from EDX analysis of the new tape yarns with different portions of additive Granic 422 (a – 3.00 wt% and b – 7.00 wt%) and PP component (a – 92.25 wt% and b – 88.25 wt%) are shown in greyscale version (see Fig.). In this additive, the particles of ultra fine calcium carbonate (CaCO₃) of 1.6 µm mean size were used. In the images, where the local signs of the presence of calcium (Ca) element are visible as bright patterns, the clear differences between the two structures are noticeably apparent.

Fig. EDX images of tape yarns with variable portions of components: a) PP – 92.25 wt%, UV 01017PP – 1.75 wt%, Granic 422 – 3.00 wt%, Polycom JB 7100 – 3.00 wt%; b) PP – 88.25 wt%, UV 01017PP – 1.75 wt%, Granic 422 – 7.00 wt%, Polycom JB 7100 – 3.00 wt%.

References:

BIODERIVED POLYURETHANE FOAMS BASED ON TUNG OIL: SYNTHESIS AND CHARACTERIZATION

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Flexible polyurethane foams (FP) belongs to a well-known class of polymeric materials that offers daily applications like cushioning and automotive seating, among others. Nowadays, the global production of FP uses polyols mainly derived from petrochemical raw materials. Consequently, the replacement of these components by more eco-friendly materials is challenging. In this sense, the chemical modification of vegetable oils is a promising alternative in the production of green polyols1.

Tung oil, a non-edible oil also called “China wood oil” is commonly used in wood finishing applications because of its drying properties. These properties are associated to its composition, due to its high content of unsaturated fatty acids. In particular, Δ-eleostearic acid, a fatty acid with three-conjugated double bonds accounts for around the 80% of the triglyceride composition of the tung oil. Through the chemical modification of tung oil it can be obtained multi-functional polyols, which can be used further as building blocks in the bio-based polyurethane synthesis. In this work, hydroxylated methyl esters (HMETO) and glycerol were obtained as main and sub products, respectively, of tung oil chemical modification, following a two-step procedure. First, fatty acid methyl esters (FAME) and glycerol (GLY) were obtained by means of alkaline transesterification. Then, the resultant FAME was modified by hydroxylation with performic acid generated in situ. In this way, hydroxyl groups (-OH) were added to the carbon chain. Infrared spectroscopy (FTIR), proton nuclear magnetic resonance (H1NMR) and different analytical procedures (iodine value, acid value and hydroxyl number) were used to characterize the tung oil and reaction products. The hydroxyl value of the HMETO was 163.2 mg KOH/g.

Polyurethane foams were based on a commercial polyether polyol and variable amounts of glycerol or hydroxylated methyl ester of tung oil (0, 10, 20 wt.% respect to the polyether polyol mass) as multifunctional bio-based polyols. The petroleum-based polyol presents low functionality (3) and high molecular weight (4800), as required for flexible foam. Water was chosen as chemical blowing agent and a multifunctional pre-polymer based on 4,4’-diphenylmethane diisocyanate (pMDI) with an equivalent weight of 133 g/eq was used as the isocyanate component.

The characterization of these foams, achieved by measuring the characteristic times during reaction and by termogravimetric analysis (TGÁ), scanning electronic microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and density measurements performed on the cured flexible foams, is reported and discussed. In brief, it was found that the obtained foams are not only a good alternative for applications where low weight, flexibility and insulating properties are desirable but also are more eco-friendly than the control foam prepared by using just the petroleum-based polyol.

References
Organic-inorganic composites for printing technologies are attractive for manifold applications in flexible electronic devices during the last decade. Transparent electrodes conduct electrical current and allow light to pass through. Such electrodes are required for photo-voltaic, electroluminescent devices, touch screens etc. Electrodes with high surface area are developed for supercapacitors and dye sensitized solar cells. The ideal electrode can be made from graphene. However, this process is expensive. One of the possible roots for the creation of printable flexible electrodes is based on organic-inorganic nanocomposites. Carbon nanomaterials are known to increase strongly the conductivity of polymers. The decoration of carbon nanomaterials with metallic conducting, magnetic, and luminescent materials can result in the development of polymer composites with new attractive properties.

In this talk our achievements on the creation approaches and physical properties of nanocomposites based on conducting polymer and graphene nanoplatelets are presented and analyzed. We showed that application of triple nanocomposite results in conductivity increase without transparency loosing. Good results are obtained with graphene-magnetic and graphene-luminescent polymer nanocomposites.
EFFECT OF THE SPACER ON THE THERMAL PROPERTIES OF BIPOLAR MOLECULAR MATERIALS

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Overall stability of the organic electronic devices, such as organic light emitting diodes (OLEDs), organic solar cells (OSCs), organic field effect transistors (OFETs) strongly depends on the stability of the organic electroactive compounds used¹. The important properties of organic electroactive materials are thermal stability and glass-forming ability. During the operational time of the electronic devices energy loss often occurs in the form of heat. Moreover, in the direct sunlight, the temperature of solar cells can reach almost 100 °C. In the design of new organic compounds the stability requirements are important along with the other requirements, like high fluorescence/phosphorescence quantum efficiency, charge carrier mobility, HOMO and LUMO energy levels, electrochemical stability, etc.

In the present study we investigated the influence of the phenylene spacer on the glass transition temperature and the thermal stability of bipolar electroactive molecular materials. Our aim was to achieve efficient and stable blue emitters. Incorporation of the different linkages between donor and acceptor moieties, like para- or meta-phenylene unit, not only changes the degree of conjugation, but also is responsible for the geometry of the molecules, and thus, for the thermal stability. The thermal characterization of the synthesized compounds was investigated by the means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The synthesis, optical, electrochemical properties will also be presented.

Reference
Renewable resources for polymer production have been widely studied in past decade. Main driving force behind these investigations is push towards replacement of petrochemical materials and introduction of sustainable solutions which are motivated by new government regulations and market demands. This paper describes study of Latvian State Institute of Wood Chemistry (IWC) in development of catalytically active, high functionality polyols for rigid polyurethane (PU) foam production.

Several bio-based polyols have been developed for PU material production and their production technology has been up-scaled to industrial scale. Main drawbacks of these polyols are following: high price compared to petrochemical materials and lack of primary hydroxyl groups, which decreases their reactivity [1]. In previous studies IWC has developed polyol synthesis by transesterification of rapeseed oil fatty acid triglycerides with triethanolamine (TEA) [2]. Obtained polyols had high reactivity, only primary hydroxyl groups and high catalytically activity due to presence of tertiary amine groups, but their functionality was too low (~2.25) to obtain excellent quality rigid PU foams.

In this study IWC uses well-known epoxy ring opening reaction [1] with different polyfunctional alcohols to obtain polyols with high reactivity and high functionality. Epoxidation of rapeseed oil was done by peroxycetic acid, which was obtained from reaction between hydrogen peroxide and acetic acid, in presence of ion-exchange resin catalyst. Conversion of 84% of rapeseed oil double bonds was achieved and afterwards epoxy rings were opened with polyfunctional alcohols TEA and diethylene glycol (DEG). Molar ratio of epoxy groups and polyfunctional alcohol 1/1.1 was used. DEG polyol is already produced on industrial scale and it was chosen as comparison material. After epoxy ring opening additional amount of TEA was added to carry out transesterification of triglyceride ester bonds in presence of zinc acetate catalyst. Three different molar ratios of fatty acid triglyceride and TEA were studied: 1/1.5; 1/2.0 and 1/2.5.

Following characteristics were determined for obtained polyols: hydroxyl value, acid value, viscosity, density and moisture. The structure of polyols were investigated by Fourier transform infrared (FTIR) spectroscopy and gel permeation chromatography (GPC). From GPC data average molecular weight (Mn), the weight average molecular weight (Mw), polydispersity index and average functionality of polyols was determined. Obtained polyols were used to produce rigid PU foam thermal insulation materials for which thermal conductivity, apparent density and compression strength was tested.

This study showed that it is possible to obtain good quality polyols and rigid PU foams that are comparable to petrochemical materials and conventional bio-based polyols. Obtained TEA polyols had much higher reactivity than DEG polyol. Also their OH value was higher 550±15 to 242±15 mgKOH/g. From FTIR spectra it was seen that full epoxy group conversion was achieved, but GPC data showed that oligomers with high Mw were obtained, especially in case of DEG polyol which’s Mn was 2542 g/mol compared to TEA polyol with Mn of 709 g/mol.

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References

NEW CARBAZOLE DERIVATIVES FOR LIGHT-EMITTING DEVICES: PHOTOPHYSICAL, PHOTOELECTRICAL AND ELECTROLUMINESCENT PROPERTIES

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A survey of literature reveals that carbazole derivatives have received much attention during the recent years due to their optical, electrochemical, thermal, charge-transporting properties, energy levels and applications in organic devices and material science. For example, carbazole-based compound tri(9-hexylcarbazol-3-yl)amine (THCA) has recently been used for the preparation of a novel double-layer exciplex-based OLED [1]. In addition, THCA has been applied for the formation of a “warm-white” OLED [2].

With the aim of realization of effective OLEDs, we have studied a new carbazole derivative 3,6-di(4,4’-dimethoxydiphenylamino)-9-(1-naphthyl)carbazole (1). The ionization potential of the solid films of 1 was estimated from electron photoemission spectra. The value of ionization potential (5.04 eV) of 1 shall facilitate the hole injection from the anode into the organic layer, accepting holes, as well as the charge transport of injected holes to the emitting layer in OLEDs. In order to develop a structure of the highly efficient OLED, we have investigated the charge-transporting properties of the emissive layers of 1. The solid films of 1 showed the hole mobility of 2.5×10−4 cm2·V−1·s−1 at electric field of 2.5×105 V/cm. The electroluminescent device ITO/CuI/1/Bphen/Ca/Al was fabricated by the means of the vacuum deposition of semiconductor layers and metal electrodes onto precleaned indium tin oxide (ITO) coated glass substrate under vacuum of 1×10−5 Torr. The electroluminescence spectrum of the fabricated OLED is characterized by two maxima at 490 nm and 528 nm. The designed OLED shows a low turn-on voltage of 4.0 V for electroluminescence (at 10 cd/m2). The fabricated device exhibits current efficiency values of 10.6 cd/A and the maximum brightness of 28000 cd/m2 (at 15 V).

Acknowledgment
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References
POSTERS
TEMPO-MEDIATED OXIDATION OF CELLULOSE NANOCRYSTALS: KINETICS AND ESR STUDY

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TEMPO-mediated oxidation has been known for more than two decades as a selective oxidation method for primary hydroxyl groups [1]. It also has been used to obtain polyuronic acids from the corresponding carbohydrates, having a very good yield and maintaining the crystallinity of the materials. It has been presented as a “green oxidation” because it only uses TEMPO in catalytic amounts, and larger quantities of NaClO and NaBr producing only NaCl and NaBrO. Also, NaOH is added as required to maintain the pH between 10 and 10.5 [2]. Normally, the amount of carboxyl groups is regulated with the amount of NaClO added, however, the evolution of the TEMPO concentration in the system has not been investigated.

In this work, we used cellulose nanocrystals (CNC) as reagent, obtaining high crystalline oxidized CNC, with a degree of oxidation (DO) of 26%. As TEMPO is a radical, it can be easily quantified using electron spin resonance (ESR) spectroscopy, and then the evolution of TEMPO concentration can be related to that of NaClO and the advance of the degree of oxidation, both determined by separate method such as iodometric and conductometric titration respectively. We performed two sets of experiments: one using the usually reported method (pH controlled by addition of aliquotes of NaOH solution) in which we only determined the initial and final concentrations of TEMPO, and related these values to the final DO obtained; and a second set of experiments in which we used a pH 10 buffer to continuously to fix the pH of the media. In this case, we quantified the TEMPO concentration and find a phenomenological kinetic simple model that fit the results. The data could be directly correlated to DO and NaClO concentration.


There is a growing interest in academic and industrial sectors in using materials and reactants based on the biomass. This trend is a response to the need of replace petroleum based materials and chemicals, but also to the novel properties that are arising from their development [1]. Natural renewable resources are available worldwide; products, by-products and wastes form agricultural and forest activities, as well as fisheries and food industries can be a source for these new materials, which in many cases are also biodegradable. Argentina is an high volume producer of these goods, which makes it particularly important to study this type of materials. Biomass is a source of polymers, chemicals and precursors, and also for fillers and reinforcements that can be used in the production of composites and more recently of nanocomposites.

Researchers at the Ecomaterials group at INTEMA have been working for more than twenty years on wood plastic and natural fiber composites, carbohydrate-based films and hybrid carbohydrate-protein films for food packaging, structural and functional composites based on vegetable oils, nanocellulose composite films, "smart" bio-based materials. Other areas (which will not be discussed in this presentation) are protein and multilayered films, coatings and adhesives and bacterial polyesters.

In the field of carbohydrates, chitosan has been considered in the preparation of strong films (by complexation with a protein derivative, such as caseinate) or in the electrospinning of nanostructured non-woven mats [2,3].

Vegetable oil-based materials have been extensively studied to prepare different type of materials such as alkydic type resins (from linseed oil), or polyurethanes (from castor oil and tung oil) and derived wood plastic composites with excellent compatibility and much improved properties. Cationically polymerized tung oil allowed the preparation of crosslinked networks with wide range of mechanical properties, with some of them displaying shape memory behavior [4].

Finally, nanocomposites prepared from functional nanoparticles (such as nanomagnetite) dispersed in a bio-based polymeric matrix or bio-nanoparticles (such as cellulose nanocrystals) dispersed in synthetic or bio-based polymeric matrices were studied, and the relation processing-structure-properties investigated [5].

References

AIR VORTEX ASSISTED ELECTROSPINNING UNIT FOR NANOYARN PRODUCTION

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Continuous production growth in textile and fiber industry during last decade has big influence for development of novel materials in “smart” clothing. In parallel, electrospinning, as a method for nanofiber preparation, is gaining popularity. High specific surface area of said fibers gives unlimited possibilities to use end-products in filtering materials, optoelectronics, energy harvesting/storage. Production of nanofibrous membranes is increasing and first steps have been done to produce even yarns but the production rate of such products is low.

The aim of this research is to investigate different approaches to nanofibrous yarn production. The different methods of yarn formation from the nanofibers were tested under various production conditions such as controlling humidity, using variety of polymer solutions, changing the potential of electrical field and polymer solution feed rate. Used polymers were PA6, PAN, PVOH.

The results indicated that under correct conditions (nozzle distance from the collector, solution viscosity, pumping rate, controlled climate) the yarn production was successfully carried out. The yarn production rate has reached with novel mechanism up to 66 cm/min. The twist level and fiber angle in the yarn are controllable.
IMPROVEMENT OF ANTIBACTERIAL ACTIVITY OF GRAPHENE OXIDE AND METAL PARTICLES NANOCOMPOSITES

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The most effective means to protect against bacterial invasion and to reduce the risk of dangerous infections are antibacterial components synthesis. Early it was determined that hybrid graphene oxide/silver/copper nanocomposites coatings have long-term bactericidal effect on wide spectrum of standard bacterial strains. Metal nanoparticles are known as an effective antimicrobial agent, while graphene oxide also shows high antibacterial activity. Our investigations demonstrated that nanocomposite shows synergistic mechanism of action. In this study the possibilities to use graphene oxide/metal nanoparticles composites for the inhibition of clinically important bacteria strains which have developed multiple resistances to antibiotics have been investigated. These bacteria due to the acquired resistance to many classes of antibiotics, the ability to obtain resistance to all antibiotics through mutations often cause dangerous infections in medical institutions of many countries. Hybrid graphene oxide and metallic (silver, copper, gold, etc.) nanostructures composite bactericidal efficiency was increased by using higher concentrated anisotropic shape nanoparticles colloids. Nanocomposite samples were characterized by TEM, SEM-EDX microscopy and UV-Vis spectrometry. The antibacterial activity was evaluated against multidrug-resistant bacteria strains P. aeruginosa and Acinetobacter spp. by solutions dilution method. Graphene oxide (GO) and metal nanoparticles composites (see Fig.) oxicity toward bacteria. Their ability of bacteria cells inhibition increases by increase nanoparticles concentration, nanoparticles shape (nanoplates, nanospheres or nanowires) and colloid type. Investigations show that created nanocomposites show excellent antibacterial activity against multidrug-resistant bacteria strains, such as P. aeruginosa producing BlaVIM gene and Acinetobacter spp.

Such hybrid nanocomposites can be applied on hospital installed equipment surface, to modify the filters, ensuring their antibacterial safety against pathogenic bacteria, especially to P. aeruginosa and Acinetobacter spp. colonization.

Acknowledgment

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PREPARATION AND CHARACTERIZATION OF NANOSTRUCTURED SUPERHYDROPHOBIC POLYDIMETHYLSILOXANE SURFACE

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Superhydrophobic materials and coatings play an important role in many applications, such as contamination prevention, biocompatibility, enhanced durability, etc [1]. The hydrophobicity can be varied by changing surface energy and roughness of the solid surface. The increase of surface roughness results in the increase in true surface area and, thus, leads to the increased nominal surface energy.

Polydimethylsiloxanes (PDMS) have found widespread application in many fields because of easy fabrication, non-toxicity, biocompatibility and biodurability. Although the surface of PDMS is naturally hydrophobic, a number of efforts have been made to modify PDMS and enhance its surface properties.

In this study PDMS surface hydrophobicity modification by two simple methods is presented. Superhydrophobic properties to PDMS surface were imparted by the deposition of plasma polymerized hexamethyldisilazane (pp-HMDS) film via arc-discharge using HMDS monomer vapour as precursor or by surface abrasive rubbing of silica nanoparticles coated with polymerized HMDS film deposited from the liquid phase via the microwaves activation. As deposited, HMDS films were characterized using SEM, AFM and FTIR methods. Changes in PDMS surface energy after modification were evaluated by means of contact angle (CA) measurements.

Unmodified PDMS surface was found to be hydrophobic with static CA value of 122°. After pp-HMDS film deposition dual-scale roughness originates on the PDMS surface. SEM and AFM analyses show that the pp-HMDS film is composed of the quasi-spherical nanoparticles stacked together to form branched network that provides superhydrophobicity to PDMS surface with CA value close to 170°. Increase of film deposition time results in large nanoparticle aggregate formation with the decrease of CA values. Meanwhile, abrasive rubbing of silica nanoparticles coated with polymerized HMDS film fabricates PDMS surface with slightly higher superhydrophobicity and self-cleaning ability. In both cases superhydrophobic behaviour of PDMS after modification with polymerized HMDS is attributed to the incorporation of the methyl groups and nanostructured surface formation.

References


Acknowledgment

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NANOCELLULOSE REINFORCED POLYURETHANE OBTAINED FROM HYDROXYLATED SOYBEAN OIL

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Polyurethane (PU) has become one of the most widely used plastics for various applications such as thermal insulation, automotive parts and seating materials. Polyols for PU production are derived mostly from petrochemical products but can be replaced by renewable materials. The use of renewable resources in materials has attracted great interest in both industrial and academic fields because of their environmental aspect and sustainability [1]. Nanocellulose is often being regarded as the next generation renewable reinforcement for the production of high performance composites. Cellulose nanowhiskers have been widely investigated as reinforcement in PUs. Therefore cellulose nanocrystals could be candidate for reinforcing PU composites [1-2].

In this research, the cellulose nanocrystals (CNC) were successfully obtained from microcrystalline cellulose and dispersed in a PU matrix. PU matrix was prepared from hydroxylated soybean oil Agrol (OH=120.8 mg KOH/g), tertiary amine catalyst and polymeric diphenyl diisocyanate. Nanocomposites containing 0.5, 1.0 and 2.0 wt\% CNC were prepared. Thermal properties and tensile strength of the resulting films were evaluated. Also, dynamic mechanical analysis (DMA), Fourier transform infra-red tests and X-ray diffraction tests were carried out.

Nanocellulose reinforced PU composite was successfully prepared with good CNS dispersion. As shown in Table 1, the glass transition temperature (T\textsubscript{g}) of the nanocomposites increased slightly.

<table>
<thead>
<tr>
<th>DMA glass transition temperature of nanocomposites</th>
<th>Tg, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNC content in nanocomposite, wt%</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>31</td>
</tr>
<tr>
<td>0.5</td>
<td>31</td>
</tr>
<tr>
<td>1.0</td>
<td>33</td>
</tr>
<tr>
<td>2.0</td>
<td>35</td>
</tr>
</tbody>
</table>

Increase of T\textsubscript{g} indicates a favourable fiber–matrix interaction and restriction of molecular mobility because of the strong association between CNC and the soft segment of the PU matrix [1]. Results of thermogravimetry showed that thermal stability of nanocomposites is not much affected by incorporation of CNC. Mechanical properties are further investigated.

Acknowledgements
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References
Hybridization usually improves interfacial interaction between the components and ensures higher performance characteristics of materials. Hybridization is also used as a tool for structure perfection of multi-phase polymer systems, including, nanocomposites, namely distribution of nanoscale fillers within polymer matrix is improved. Hybridization can be also used for substituting expensive polymer additives with cheaper ones, without losing much of performance characteristics of the composites. It has been shown [1] that in the presence of nanoclay in the polymer based (epoxy, polypropylene, polyethylene, polyamide 6, polyimide) composites percolation threshold is reduced and electrical conductivity, as well as elastic modulus is increased generally due to improved dispersion degree of the conductive nanofiller (graphene, SWCNT, MWCNT, CB) because of reduced re-agglomeration tendency during processing. It has been also shown that geometrically different carbonaceous nanostructures (graphene, SWCNT, MWCNT, ND, CB) prevent agglomeration within the polymer matrix (generally epoxy, styrene-butadienen rubber and high-engineering thermoplastics such as polyetherimides, polysulphones and polyethersulphones) by formation of a co-supporting network of the separate fillers leading to improved mechanical properties, as well as increased electrical and thermal conductivities.

Considering actuality of this topic the current research is devoted to investigation of multi-walled carbon nanotubes (MWCNT) and single layer graphene (SLG) modified polyvinylalcohol (PVOH) hybrid composites obtained via solvent based approach. Polymer nanocomposites have been manufactured by multi-step manufacturing process. Initially stable aqueous dispersions of MWCNTs and SLG have been obtained. Stability of the dispersions has been ensured by adding certain amount of suitable surfactant. Stable aqueous suspensions of carbonaceous nanofillers have been combined with a polymer solution in a suitable solvent. Desirable quality of mixing between the ingredients of the multi-component system has been ensured by choosing optimal conditions of mechanical agitation and ultrasound treatment (time, temperature, speed).

Structural as well as mechanical and dielectric relaxation characteristics of MWCNTs and SLG modified polymer nanocomposites have been investigated. The effects of addition of MWCNTs and SLG on the mechanical and dielectric characteristics of the investigated polymer hybrid composites have been cleared out on the background of structural investigations.

It is suggested that observed improvements of electrical conductivity as well as elastic stiffness of the investigated polymer hybrid composites are closely related to preferable dispersion pattern of MWCNT and SLG within the PVOH matrix.

Reference
Composites obtained with chitosan as a biocompatible polymeric matrix and a dispersed phase of iron oxide nanoparticles can be used in the development of valuable materials with potential applications in fields like biomedicine or biotechnology. Particularly, the interest in nanomagnetite based films is related with the fact that even embedded in a polymer matrix, these nanoparticles can be oriented using an external magnetic field. Some of the potential applications of these systems are as targeting drug carriers, hyperthermia local inductors for cancer therapy, pollutant removals, biosensors and magnetic cell separators\textsuperscript{1-2}. In this work, the physical, mechanic and magnetic characteristics of nanomagnetite-chitosan composite films obtained by a simple processing method are presented\textsuperscript{3}.

The films were prepared by casting of solutions containing chitosan, iron salts and occasionally glycerol (to evaluate the effect of a plasticizer). Once the films were dried, magnetite nanoparticles were precipitated by immersing the films in a concentrated sodium hydroxide solution. The films were finally washed with distilled water until neutral pH.

To estimate the nanoparticle size in the composites, DRX measurements were carried out and the results obtained were in agreement with those found by TEM observations. The last technique allowed also to determine that the nanoparticles precipitated in non-plasticized films have a narrow size distribution and are well dispersed into the chitosan matrix. The overall analysis of data obtained from thermogravimetric analysis, infrared spectroscopy and moisture sorption tests indicated that different but strong interactions between nanomagnetite particles and chitosan matrix took place. Consequently the nanocomposites are less thermally stable, but also less hydrophilic than the corresponding matrices. Additionally, the presence of magnetite causes important changes in the superficial microstructure of the films that led to different contact angles and to a more fragile but stiff behavior as particle concentration increases.

The curves of magnetization versus temperature demonstrated that super-paramagnetic behavior was obtained for composite films containing 5, 7, and 10 wt % magnetic nanoparticles (MNP), while in the less concentrated samples the diamagnetic contribution of the matrix is the dominant magnetic effect. Moreover, plasticized samples showed lower magnetization and higher coercitivity than unplasticized ones for the same nanomagnetite content.

References:
RIGID POLYURETHANE FOAMS BASED ON A RAPESEED OIL POLYOL AND THEIR MODIFICATIONS WITH GLYCEROL AND CELLULOSE

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Polyurethanes can offer a wide variety of properties that can be useful in several applications. In general, the reactives used for their production are derived from the petroleum industry [1]. The search of renewable resources as replacement of synthetic raw materials in the production of polymers has grewed considerably in the last decades, due to environmental aspects and interest in sustainable development. In particular, vegetable oils are interesting because of advantages such as wide availability at low cost. They consist of triglyceride molecules with three unsaturated fatty acid chains able to be chemically reacted in order to obtain monomers for the polymer industry [2]. Specifically, the reaction of the double bonds of triglycerides to incorporate hydroxyls groups by means of different reaction paths has been studied [3-5]. One of the most reported methods, is the reaction of the carbon-carbon insaturations to introduce hydroxyl groups through epoxidation with peroxiacids followed by oxirane ring-opening with different alcohols like diethylenglycol [5]. The structure of the resulting oil based polyol depends on the chemical modification method and the distribution and position of the carbon-carbon double bond in the fatty acid chain of the oil.

The aim of this work is synthesize a rapeseed oil based polyol to be posteriorly used in the production of polyurethane rigid foams using water as a reactive blowing agent. Commercial microcellulose was used as a filler while glycerol was used as a reactive modifier that allowed to increase the crosslinking density and to improve the mechanical properties of the foams. The characterization of the foams have included apparent density measurements, thermal conductivity tests, water absorption, morphological characterization and compression tests. The results showed that the rigidity and glass transition temperatures increase with the incorporation of MNC and glycerol to the foam formulation as well as the water absorption and the fragility of the cell walls of the foams. The considerable increase of foam compression strength, can be achieved by the modification of the polyurethane with 5 wt. % of glycerol.

References
LIQUID AND SOLID ANIONIC LIPOSOMES CONTAINING
CHOLESTEROL LOADED WITH BIOACTIVE COMPOUNDS IN
CONTACT WITH SPHERICAL POLYCATIONIC BRUSHES

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For last decades liposomes are widely used for the design and development of drug delivery systems. For these purposes they are used as drug carriers and are loaded with biologically active substances. One can increase the efficacy of liposome interaction with cells and therapeutic effect of a liposomal drug via immobilization of several liposomes on a nano-sized colloid particle. However, liposome binding with a solid surface is usually accompanied by their destruction and uncontrolled release of encapsulated agents. Therefore it is very important to construct the drug carrier devoid of the disadvantages. Recently, we have proposed to adsorb anionic liposomes on the surface of “spherical polycationic brushes”. This method allows a lot of liposomes with different contents to be concentrated within a rather small volume.

In this work we loaded small unilamellar solid and liquid liposomes with biologically active substances. The liposomes were composed of neutral, anionic lipids and cholesterol. It was shown that the phase state of the membrane and cholesterol integration into liposomes had a strong effect on the membrane permeability to small ions and organic molecules. The membrane permeability was studied by means of conductometry and fluorescence techniques. We found the composition and phase state of the membrane, wherein the liposomes retain their integrity after encapsulation of bioactive compound, which allows them to be used as a containers. These liposomes were added to polystyrene microspheres with grafted polycationic chains, i.e., “spherical polycationic brushes”. Polycation-liposome interaction was studied by means of microelectrophoresis and dynamic light scattering.

The results obtained should be taken into account for the design of liposomal drug carriers.

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PRODUCTION AND CHARACTERIZATION OF BIOPOLYOLS FROM BRAN AND STRAW OAT

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The feasibility of using crude glycerol to liquefy oat bran and straw for the production of biopolyols was investigated in this study. The method of liquefaction was the combination of two different methods, based on either acidic or basic catalysis, applied into two-step process using both types of catalyst. Biopolyols produced under preferential conditions showed hydroxyl numbers from 200 to 450 mg KOH/g and viscosities from 2 to 11 Pa*s. These results suggest that crude glycerol can be used as an alternative solvent for the liquefaction of lignocellulosic biomass such as bran and straw oat for the production of biopolyols.
APPLICATION OF CARBON MATERIALS TO PRODUCE OF FIREPROOF BIOPOLYMERS AND COMPOSITES

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The use of polymer materials (leather is a natural polymer) are increasing every year because of their remarkable combination of properties, low weights, and ease processing. However, polymer materials are highly flammable increasing their risk as fire hazards when used in practical applications. Consequently, improving polymer fire retardants is a major challenge for extending polymer use in most applications. Polymer nanocomposites have recently attracted extensive attention in materials science because they often exhibit properties quite different from those of their counterpart polymer microcomposites whose matrices contain the same inorganic components [1].

The development of fire retardants is subject to regulations. Halogen-free, recyclable, environmentally friendly flame-retardant systems that do not release toxic gases have recently become preferable. Polymer materials begin to burn while they are heating to temperatures at which thermal degradation begins. Inorganic fillers (hydroxides, carbonates) have used as fire retardants because they have suffered an endothermic decomposition at high temperature and release water and carbon dioxide. Nanofiller-based flame retardants show high flame-retardant efficiencies. Adding only a small amount of nanofiller can reduce the peak heat release rates (PHRRs) of polymer materials and thus reduce the speed at which flames spread throughout them. Further, the small amount of nanofiller does not reduce polymer processability and can improve the mechanical properties of polymers.

There are attempts of carbon nanotubes applications as a potentially new class of materials that can improve fire-resistant properties of composites [2]. The key factor determining carbon-based-nanocomposite flame retardancy is the formation of a surface network layer.

To provide fireproof properties of leather materials graphitized nanostructured carbon PUREBLACK® Carbon (Superior Graphite, USA) was used. TEM image of it, shown in Fig. [3]. Leather samples treated by carbon, hardly combust while entering into the flame, and quickly stop burning when taking them off. A layer of carbon material on the surface of collagen fibers acts as a barrier against the gaseous decomposition products of the polymer and against oxygen coming from the external environment and accelerates the process of decomposition. The carbon material is uniformly settling in the dermis of the leather without compromising its breathability and mechanical properties.

References
STRUCTURATION OF DERMA COLLAGEN BY MODIFIED DISPERSIONS OF MONTMORILLONITE

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Collagen is the main protein of the derma of animals. Collagen is characterized by a multi-level organization and has a hierarchical structure. The lowest level is the consistent position of amino-acid residues in the polypeptide chains, and top level – the dermis of an animal hide and skin. The spatial association of polypeptide chains in a triple helix is a macromolecule. Groups of adjacent and located parallel to 5 macromolecules form microfibrils, and their combination – a fibril, whose diameter does not exceed tenths of a micron. Fibrils respectively form the next level of the primary structure of fibers with diameters of about 5 microns in flooded condition. Further combining of the primary fibers in bundles corresponds to the aggregates with dimensions of 200 microns. The spatial organization of the fiber bundles shows the structure of the dermis. Every structural level forms a certain number of capillaries and pores. Taking this into consideration, the dermis as the porous material comprises pores of different sizes that vary in the range from 1 nm to 200 microns and form a micro- (rpore ≤ 1 nm), meso- (1 nm ≤ rpore ≤ 200 nm) and macroporous (rpore ≥ 200 nm) structure.

Collagen of derma is an amphoteric protein. Amphoteric of the collagen is caused by carboxyl, amine, peptide, hydroxyl and others groups. Therefore, bonds of different nature and location can be formed in the collagen structure.

During the processing of animal skins into natural leather, the destruction happens between some of the bonds in the structural elements of the collagen and the formation of new bonds by reaction with chemicals.

For effective formation of the collagen structure of derma it is necessary to achieve the structuring of its components at the levels of size. For this it is advisable to use materials with different functional groups and different sizes of particles. The dispersions of montmorillonite are presenting a practical interest because after the modification of the particle of dispersion they may change the surface charge and size. Targeted modification of montmorillonite will allow to effectively structuritation the derma collagen.

Bentonite clay was used (Dashukivski deposit, Ukraine) with minerals – montmorillonite. Previous modification of montmorillonite was performed with sodium carbonate in an amounts of 10 % by weight of dry mineral. Then in the modified montmorillonite dispersion (Na-MMT) chrome tanning agents were added (Cr-MMT), in terms of Cr2O3, with mechanical stirring at a speed of 1500 rev/min for 1 h at 20 °C.

Application of Cr-MMT made provision for production of chromium-tanned semi finished product containing 1,7-2,0 times less amount of chromium oxide (III) with two times smaller amount of chromium tanning agent required. The use of Hydroxy-Cr-MMT solutions enables efficient control over reaction between chromium compounds and functional collagen groups due to its reactive-plactisizing action. Resulted semi finished item exceeded control samples by its physical-mechanical properties. The technology developed may be characterised as of having better environmental efficiency and resource saving because of 3,2-4,6 times lower chromium oxide (III) content in spent solution.
NUMERICAL MODELLING AND EXPERIMENTAL STUDIES OF IMPACT BEHAVIOUR OF CARBON FIBRE REINFORCED METHYL METHACRYLATE COMPOSITE

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The carbon fiber-reinforced polymer composite laminates are very susceptible to low-velocity impact. The low-velocity transverse impact could cause various damages, such as matrix cracks, delamination and fiber breakage [1]. Such damages influence on the significant reductions of strength and stiffness of the materials and are difficult characterized. Hence, it is crucial to understand the mechanisms and mechanics of the impact damage in the composite laminates.

The goal of the present study was to investigate the low velocity impact behavior and damage patterns of carbon fiber reinforced methyl methacrylate (CF/MMA) composites. The process of low-velocity impact damage in composite was simulated using the finite element method and experimentally verified. Orthotropic plane stress conditions of homogenized continuum lamina were used to model composite structure. Evolution of damage was simulated by material model MAT58 based on Matzenmiller’s [2] damage mechanics model with four Hashin’s [3] failure criteria. Damage variables were determined performing calibration of numerical model according to the experimental results of three point bending test.

A low-velocity impact tests were performed on 3 mm thick 10-ply square CF/MMA plates ([0/90]5). The composite was impacted by a 25 kg hemispherical impactor at a velocity of 1.768 m/s, generating impact energy of 40 J. The impact-damaged composite specimens also were inspected experimentally by ultrasonic C-Scan method.

Detailed quantitative comparisons were carried out between delaminated areas simulated by the model and those characterized experimentally by ultrasonic C-Scan method. The results of the numerical analyses demonstrate good agreement with experimental data in the terms of contact force histories, peak force values, absorbed energy and projected damage area.

References:

INFLUENCE OF SILVER SELENIDE TREATMENT ON PROPERTIES OF DIFFERENT NATURE FIBERS

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The usage of electrical and electronic devices is expanding rapidly. Electromagnetic waves emitted from electronic equipment negatively affect human health and other electrical devices. The functional materials which may reduce negative environmental influence to human health are becoming even more important. This work was inspired by an increasing interest in new materials for flexible and efficient magnetoresistant thin layers. One way of it is textile materials chemical surface modification with the binary chalcogenide thin layers. In the past few years, significant progress has been made on polymer materials, and many new methods have been developed for the preparation of chalcogenides with desired properties and functions, such as the sol–gel approach, direct mixing processes, intercalation techniques and etc. The sorption–diffusion method for the preparation thin layers of metal chalcogenides in the surface of polymer is simple and promising. Using this method the layers of Cu₃S, CuₓSe and AgₓSe on the surface of polyamide PA 6 films [1,2] and PA 6 cloth [3] in two stages were formed.

By changing the conditions of chemical treatment process the fiber surface can be covered with a sparse (Fig. 2 a), thin (Fig. 2, b) or dense (Fig. 2, c) layer of silver selenide.

![Figure 2. Poliamide 6 fibres with sparse (a), solid thin (b) and dense (c) silver selenide layer after the treatment.](image)

However, improving the quality of silver selenide layer the duration of aggressive chemical treatment also increases and can cause fibres damage. For this reason, the influence of silver selenide modification process on the mechanical properties of different nature fibers was investigated. In case of natural fibers, the lowest difference of tensile strength after chosen method of modification with silver selenide was observed on wool fibre. In case of natural cellulose fibre the lowest difference of tensile strength was estimated on bamboo fibre (~20 %) and the highest – on flax fibre (~40 %). Influence on the elongation of fibre is visibly lower.

References:

The surface of the soil is mulched in order to protect from the growth of weeds, to preserve moisture and to maintain more constant temperature of the soil. Polyethylene (PE) films is currently the most widely used for this purpose. They preserve moisture, transmit the radiation of sun, help to maintain the enhanced temperature and effectively prevent the germination of weeds. The PE mulch is user-friendly, large area can be covered with PE film. However PE film as a mulch has some drawbacks. PE is obtained from non-renewable resources. PE films are non-biodegradable. After exploitation they have to be collected and recycled. Biodegradable films seem to be good alternative for PE mulch. After exploitation they can be inserted into soil where they are degraded by microorganisms. However the cost of biodegradable films is higher than that of PE films. The liquid mulch is also studied as an alternative for PE mulch. In the case of application of the liquid mulch the polymer solution is sprayed on the surface of soil. When the solvent evaporates the mulch film is formed. However this method of mulching is not widely used so far. The reason for this might be the technological problems related to the necessity of covering of the large areas of the surface of soil. The formation of uniform film is rather complicated task at the natural conditions when many different factors influence the process. The composites consisting of poly(vinyl alcohol), horn meal, rapeseed cake, glycerol and phosphogypsum are proposed in this presentation for the formation of small area mulch films on the surface of the substrate. Such mulch films can be used when the plants are cultivated in flower pots or containers. The mulch films proposed contain phosphorus, nitrogen calcium, potassium, sulphur which are useful nutrients for plants. Mechanical properties of the films, water vapour transmission rate, biodegradation in soil and their effect on the agrochemical properties of the soil were studied. The vegetative tests were performed. The composites were used for the formation of mulch films, which were used in the cultivation of the tomato sprouts in pots and showed considerable positive effect. It was established that the proposed mulch films retain moisture in the pots while the nutrients present in the films stimulate growth of the sprouts.

Acknowledgements. Financial support of this research by the Research Council of Lithuania (project No MIP-066/2015) is gratefully acknowledged.
EXPRESS PROCEDURE FOR EVALUATION OF DURABILITY OF COMPLEX SHAPE PULTRUDED COMPOSITE PROFILES

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Pultruded composite profiles of different shapes are increasingly applied in civil engineering for new building constructions and renovation of the existing ones. These materials pose a set of high specific mechanical characteristics, comparatively safe fracture modes, high corrosion resistance, easy handling, but sometimes are used not enough efficiently because of several issues. One of such issue is environmental effects on composite stability and durability. Pultruded profiles often have quite complex shapes of their cross-section that makes difficult analytical calculation of the environmental effects. The aim of this research is development of an analytical express procedure for evaluation of durability of complex shape pultruded composite profiles and reinforcing rods subjected to aggressive environmental factors.

The procedure includes next stages: (1) Express estimation of comparative aggressiveness of environmental factors; (2) Estimation of aggressive factor effects on the service characteristics of composite material; (3) Prediction of the dangerous influence of the environmental factors on composite profile. Moisture, high temperature, and thermal cycling are considered as the examples of aggressive environmental factors. The third stage includes the following principal steps: (3a) virtually splitting of a complex shape on simple ones; (3b) evaluation of environmental effect; (3c) virtually merging the environmental effect from the simple forms back to the complex one.

The procedure is illustrated on the thermal and moisture effects on I- and box-shape pultruded beams. Analytical estimation is compared with FEM calculations and proved with the experimental data for moisture effect. The investigation makes a contribution to the branches of advanced materials science and environmental sciences, civil engineering.

References

POLYISOPRENE – REDUCED THERMALLY EXFOLIATED GRAPHENE OXIDE COMPOSITE FOR SENSOR APPLICATION

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Polymer nanocomposites with carbon nanoparticle filling are interesting for their various applications. They have been researched as pressure sensors [1] as well as volatile organic vapour sensors [2].

Nanocomposites are made from a polymer matrix and carbon nanoparticles. Nowadays many commercial carbon nanoparticles are available, like carbon black (CB), single wall carbon nanotubes (SWCNT), multiwall carbon nanotubes (MWCNT), thermally exfoliated graphite (TEG), graphene and many variations of these fundamental types. Most of them have been reported to show sensor activity, when mixed in a nanocomposite as a single filler or as a mixture of various fillers.

In this work we propose an improved filler. The starting material is pre-exfoliated graphite – TEG. The process includes two stages – firstly TEG is oxidized and secondly the oxidized product – graphene oxide (GO) – is reduced to acquire reduced graphene oxide (RGO). Oxidation process was done using modified Hummer’s method [3] with potassium permanganate (KMnO₄) and sodium nitrate (NaNO₃) in sulphuric acid as the solvent and reduction was done using sodium borohydride (NaBH₄) with cobalt ion (CoCl₂·6H₂O) assistance [4].

Thermally exfoliated graphite undergoes oxidation more fully than commonly used graphite flakes, because of the pre-exfoliation. The synthesized graphene oxide has higher electrical resistance, because of oxygen functional groups which disrupt graphene plane sp² conjugation. After reducing graphene oxide the electrical conductivity increases significantly, because of the restored π-bonds. The oxidation of graphite with a subsequent reduction is believed to be the most promising way for large scale graphene-like materials production [4].

Polyisoprene RGO nanocomposite sensor effect for mechanical deformation as well as for volatile organic vapours is investigated.

References

EFFECT OF MELAMINE PHOSPHATE ON THE THERMAL STABILITY AND FLAMMABILITY OF BIO-BASED POLYURETHANES

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Melamine phosphate (MP) is halogen free intumescent flame retardants, in which the well-known phosphorus/nitrogen synergism is utilized. It is successfully used in thermoplastics and some thermosets.

In the present study, performed in the framework of the State Research Program 4.1 NatRes, the efficiency of MP as an intumescent additive to biobased polyurethane coatings, based on triethanolamine esters of tall oil fatty acids, was evaluated. For this purpose, the main parameters of the thermal stability and flammability of the polyurethane coating with addition of MP were compared with the characteristics of coatings with the most often used intumescent additives such as ammonium polyphosphate (APP) and APP in combination with melamine (Mel).

The synthesized polyol based on triethanolamine esters of tall oil fatty acids and isocyanate Voratec SD 100 (Dow Chemical) at the molar NCO/OH ratio = 1.1 were used for polyurethane coatings preparation. MP (Tianjin Aokatet Chemical Co., Ltd., China); APP, grade Exolit® AP 422 (Clariant International Ltd., BU Additives) and Melamine 99% ALDRICH (Sigma-Aldrich Co. LLC.) were used as intumescent additives. MP was preliminary mixed with the isocyanate, but APP and Mel – with the polyol.

Thermogravimetric analysis (TGA) of polyurethane coatings was performed using TGA/SDTA 851® METTLER TOLEDO. Combustion performance of the polyurethane coatings applied on 100×100×16 mm standard wood samples was studied using a FTT Cone Calorimeter (Fire Testing Technology Ltd.). Testing was performed according to ISO 5660 at a heat flux of 35 kW/m². Samples were measured in the horizontal position.

It has been found by TGA measurements that the char yield at 600°C for polyurethanes, containing MP, is lower than the char yield of polyurethanes, containing APP, since the content of phosphorus in MP is 2.6 times lower than that in APP. The much higher content of nitrogen in MP than in APP did not have a pronounced effect on the final results of polyurethanes’ thermal decomposition.

The relatively higher content of nitrogen in MP and its joint action with phosphorus manifested itself only in cone calorimeter tests. With increasing content of MP, the main flammability parameters of polyurethanes changed approximately as the parameters of the polyurethane with addition of APP. The parameters, characterizing the initial period of combustion of wood samples with the coating, decreased to a higher extent. In this, case, to attain better indices, the addition of 20% of MP was enough. Owing to the higher content of nitrogen, total smoke release upon the combustion of the samples with addition of MP was much lower. When using MP as a partial (up to 50% from the total amount of the fire retardant) substitute of APP, it is possible to considerably decrease the characteristic parameters of polyurethane flammability such as peak of heat release rate, total heat release and maximum average rate of heat emission.

References:

In the present conditions the strict requirements for goods of natural leather are required not only since the aspect of their functional, visual and hygienic properties. When the consumer is choosing the clothes, shoes or gloves, he also assesses the safety of used materials, which will affect the person during in use. The creating of modern leather goods which must conform to these requirements has not possible without improvement in existing technologies.

The antiquated treatment methods and inefficient chemical reagents that using in leather industry does not provide quality of products, the rational use of material and energy resources, and also impair the ecological situation, negative impact on human health. Especially it concerns tanning and liquid finishing process, during which the basic structure and consumer characteristics of leather are formed, and the wide range of chemical materials with varying spectrum of ecological safety (acids, salts, surfactants, mineral and organic tanning agents, dyes, act) are provided in existing technologies.

Promising decision of this problem is the improvement in existing technologies by applying soluble polymeric compounds of new generation that are perfectly combine with collagen and other applicable chemical reagents, provide leather with desired properties, do not exert a harmful impact on humans and environment [1,2]. As result of complex researches the authors are developed a resource saving technologies with application of polymeric materials based on unsaturated carboxylic acids (polymaleates and polyacrylates) on different stages of the production cycle: at the stage of chrome tanning in garment sheepskin technology, at the stage liquid finishing (dyeing) of chrome calf leather for upper of shoes. The positive impact of polymers on processes treatment, the semi-finished item and finished leather properties was found. The intensification of the process, filling, formation and hydrothermal derma stability have founded in tanning with polymer; the fullness, softness, the strength and evenness leather dyeing in a liquid finishing; and in all cases have further degree of the exhaust solutions. Was proved experimentally that the polymer processing for pelt before chrome tanning, as an alternative of traditional pickling, helps to reduce the process in four times, improved the exhaustion of tanning solution at 25 % and the consumer and hygienic properties of leather [3]. The positive results show the feasibility of the investigated polymeric materials in leather production, moreover, is considering the promising development of resource saving technologies with partial or complete replacement of tanning chromium compounds by alternative, eco-friendly tanning agents in order to obtain leather with the desired consumer properties.

References:
A NUMERICAL STUDY TO ANALYSE MECHANICAL PROPERTIES OF POLYMER COMPOSITES WITH SMART MICROCAPSULES FOR HIGH PERFORMING SENSING APPLICATIONS

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Recently microcapsules are applied in many advanced materials and composites [1-3]. The concept of the use of microcapsules as sensors for controlled release of high performance polymeric coatings is one of the most relevant. This concept is based on the combination of the active protection with sensing functionalities that indicate when the protective coating is damaged and the substrate is already under the risk. Such smart self-sensing composite structures capable to provide the information about the structural integrity. Making predictions of the mechanical behaviour and response of these self-sensing structures with microencapsulated active materials embedded into polymer matrices by numerical simulations is a good possibility to understand a real phenomenon that occurs at the micro level of the composites and cannot be implemented in the existing analytical models. This also allows to speed up the trial and error experimental testing.

One of the foremost progresses in contemporary structural components is the enhancement done on the materials to obtain the optimum behaviour relevant to its application. This is done through the exploitation of the materials’ microstructure.

The aim of this investigation is to determine the effective material properties of self-sensing composite structures using numerical homogenisation approaches based on finite element modelling of the composite microstructure.

Using experimentally obtained mechanical properties of both the polymer matrix and capsule shell material the representative volume elements (RVEs) of microstructure of self-sensing polymer composite was generated with the help of the ANSYS software. According to the deterministic theory of averaging [4], the components of the macroscopic stress tensors was defined as the suitable average over the volume occupied by the RVE of the microscopic stresses components. The macroscopic stress tensor was calculated as the appropriate volume averages of their corresponding local quantities.

References

CATIONIC POLYMERIZATION OF ISOBUTYLENE IN TOLUENE: TOWARDS WELL-DEFINED HIGH MOLECULAR WEIGHT POLYMERS AT ELEVATED TEMPERATURE

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Well-defined polyisobutenes (PIBs) are key intermediates for different kind of products such as lubricant and fuel additives¹, biomedical devices². Controlled/living cationic polymerization of isobutylene (IB) opens great possibilities to the synthesis of functionalized PIBs³. However, most of functional end groups were introduced into PIB through post-polymerization modifications of tert-chloride end group, which typically involved multistep procedures. Although controlled/living cationic polymerization has several disadvantages (low reaction temperatures, low monomer concentrations, the use of chlorinated solvents), its remains only one method which allows to synthesize di- and trifunctional PIBs⁴. Recently, it was shown, that cationic polymerization of IB initiated by complexes of Lewis acids (AlCl₃, FeCl₃, GaCl₃ and RAICl₂) with ether gave rise to well-defined monofunctional polymers with high content of exo-olefin end groups (>80%), but only low molecular weight polymers (Mₙ<3,500 g mol⁻¹) were typically obtained⁴. Therefore, the cost-effective synthesis of exo-olefin terminated PIB with medium molecular weight (Mₙ=5,000–50,000 g mol⁻¹) will be of great interest in order to broaden the application of conventional cationic polymerization towards synthesis of functional polymers.

In this work, the synthesis of well-defined exo-olefin-terminated PIBs with low- to medium-molecular-weight in toluene at relatively high reaction temperature (−20 °C) using ¹Bu₂AlCl or complexes of RAICl₂ (R=Et, ¹Bu) with ethers as co-initiators is reported. It was shown that ill-defined PIBs with tri- and tetra-substituted olefinic end groups were formed in the presence of RAICl₂ (R=Et, ¹Bu) and ¹Bu₁.₅AlCl₁.₅, while polymers with high content of exo-olefin end groups (90%), but in low yield (12%) were obtained with ¹Bu₂AlCl as co-initiator. Addition of external water as an initiator allowed increasing of IB conversion up to 80% and obtaining predominantly exo-olefin terminated PIBs with medium molecular weight (Mₙ=50,000 g mol⁻¹). Since ¹Bu₂AlCl was not active in the polymerization of IB when even low amounts of ether were added into the system (¹Bu₂AlCl:Bu₂O≥1:0.6 mol/mol), complexes of ¹BuAlCl₂ with ethers (Bu₂O, ¹Pr₂O) were used as co-initiators of isobutylene polymerization. It was shown that ¹BuAlCl₂·0.6O¹Pr₂ and ¹BuAlCl₂·0.6Bu₂O complexes afforded medium molecular weight PIBs (Mₙ>20,000 g mol⁻¹) in moderate yield (70%) and with high content of exo-olefin end groups (>85%).

Acknowledgements. This work was supported in part by BASF SE and Belarusian Republican Foundation for Fundamental Research (X15P-013).

References:

CATIONIC POLYMERIZATION OF ISOBUTYLENE INITIATED BY COMPLEXES OF ALKYLA LUMINUM DICHLORIDES WITH DIISOPROPYL ETHER: AN ACTIVATING EFFECT OF WATER

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The polyisobutylene (PIB) with high exo-olefin end groups content and $M_n \sim 1000$–3000 g/mol (highly reactive PIB (HR PIB)) is an important precursor to motor oil and fuel additives. In recent decades, several new methods based on using of complexes of Lewis acids with ethers have been reported for the synthesis of HR PIB [1, 2]. Among them, the best selectivity towards $\beta$-H abstraction showed complexes of alkylaluminum dichlorides ($\text{exo} > 90\%$). However, the main disadvantage of this method is low monomer conversion ($\leq 30\%$) [2].

In this work, the influence of water (0.016–0.1 M) on the cationic polymerization of isobutylene induced by complexes of alkylaluminum dichlorides ($\text{EtAlCl}_2$ or $\text{tBuAlCl}_2$) with diisopropyl ether ($\text{O}^{\text{iPr}}$) in $n$-hexane at high temperature (10 °C) and high monomer concentration (2.9–5.8 M) has been investigated. We showed that addition of $\text{H}_2\text{O}$ led to increase of yield of HR PIB with $\text{tBuAlCl}_2 \times 0.8\text{O}^{\text{iPr}}$ as co-initiator from 25–35% to 60–73 % (reaction time: 10 min), but the content of exo-olefin end groups decreased from 92 to 81%. The optimal concentration of water was 0.033 M.

The kinetic investigations revealed that the sequence of components addition influenced significantly both the reaction (fig. 1). Indeed, the content of exo-olefin end groups can be increase to 90%, if water was added into the system after 3 minutes since the start of polymerization. The addition of the catalytic complex or $\text{H}_2\text{O}$ into two shots allowed to further improve monomer conversion (>90% in 15–20 min) keeping at the same time good functionality ($\text{exo} > 88\%$).

FIGURE 1 Conversion vs. time plots for the isobutylene polymerization co-initiated by $\text{tBuAlCl}_2 \times 0.8\text{O}^{\text{iPr}}$ or $\text{BuAlCl}_2$ and separately added diisopropyl ether, respectively, in $n$-hexane at 10 °C without (1) or with (2, 3) externally added water: $[\text{tBuAlCl}_2]=22$ mM; $[\text{Pr}_2\text{O}]=18$ mM; $[\text{IB}]=5.8$ M. The sequence of components addition: (1) $n$-hexane, diisopropyl ether, $\text{BuAlCl}_2$, isobutylene; (2) $n$-hexane, diisopropyl ether, $\text{H}_2\text{O}$, isobutylene, $\text{tBuAlCl}_2$; (3) $n$-hexane, diisopropyl ether, $\text{H}_2\text{O}$, $\text{tBuAlCl}_2$, isobutylene. The concentration of water: (1) no water; (2), (3) $[\text{H}_2\text{O}]=0.033$ mM.

Acknowledgements. The authors thank BASF SE and Belarusian Republican Foundation for Fundamental Research (X15M-013) for the continuous financial support of this research.

References:

SYNTHESIS OF POLYMERIZABLE IONIC LIQUID MONOMER AND ITS CHARACTERIZATIONS

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The synthesis of polymerizable ionic liquid (PIL) is a challenging objective and has drawn an intense attraction for its uniqueness such as mechanical durability, excellent ionic conductivity and low glass transition temperature (Tg) which lead to employ in electrospinning process and other emerging technology for its potential application in various fields. Initially, the ionic liquid, 1-(6-hydroxyhexyl)-3-methylimidazolium bromide was synthesized using 1-methylimidazole and 6-bromo-1-hexanol. The reaction time was taken for 48h at room temperature with inert gas condition. The thin layer chromatography (TLC) tests were conducted at each step to verify the reactions. The synthesized compound was then kept in vacuumization for 12h at 1.1 mbar pressure. Eventually, it was observed that the ionic liquid compound forms after 48h reaction time. Alongside, it confirms the presence of starting materials, observed in TLC tests. In order to evacuate the starting materials and other unwanted gas or vapour, the synthesized ionic liquid was washed out for three times using toluene and kept again in vacuumization for 12h at 1.1 mbar. A high viscous transparent liquid was extracted which yields pure ionic liquid. Apart from that, the synthesis of ionic liquid was also performed using microwave treatment and heating process to stimulate the reaction and minimize the process time of the starting materials. Surprisingly, it was observed that the reaction was taking place within a fraction of second, thus confirms the formation of ionic liquid which proved by TLC test.

In the second step, acetonitrile and 2, 6-di-tert-butyl-p-cresol (BHT) were added in predefined quantity to the synthesized ionic liquid. Subsequently, methacryloyl chloride and acetonitrile mixture were added drop wise at 0 °C. The solution mixture was then kept at room temperature and stirred up mechanically for 48h in inert atmosphere. The probable reaction is likely to be found in the Figure 1. The reaction mixture was purified followed by washing with diethyl ether for three times and vacuumized for 12h. Finally, a high viscous yellowish liquid was yielded which believed to be monomer of polyionic liquid (PIL) and further proved by TLC and FTIR tests.

![Chemical Reaction](image)

Figure 1: Synthesis of PIL: Chemical reaction and yielded compound

Keywords: Synthesis, ionic liquid, thin layer chromatography, polyionic liquid, FTIR
RADICAL POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF SURFACE FUNCTIONALIZED DETONATION NANODIAMONDS FOR POLYMER NANOCOMPOSITES PRODUCTION

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Filling of a polymeric matrix by nanodispersed substances for obtaining of nanocomposites is a modern trend of polymeric materials producing with the wide range of improved properties. From the point of view of the polymer materials science the most promising way of achievement of the purpose is using of nanocarbons. Nowadays the various kinds of nanocarbons are known having a real possibility to be successfully used in practice of the materials science. These are fullerenes/fullerene soot, multiwall carbon nanotubes (MWNT), detonation nanodiamonds (DND)/ diamond blend (DB). It should be noted that using of DND and DB gradually grows in comparison with fullerenes and NT which were considered as the most perspective for the polymeric nanocomposites forming until recently.

One of the unsolved problems of DND effective application is the difficulty of homogeneous distribution of small and extra-small quantity of DND in a high-viscous polymer matrix. The main idea of synthesis of polymer-DND nano-composites is to do it directly in the course of polymerization. It allows to avoid filling through solution or melt. The bulk polymerization initiated by AIBN (60-70°C) of methyl methacrylate (MMA) was investigated. The most unexpected effect caused by the presence of DND is their obvious influence on kinetics and molecular mass characteristics of PMMA obtained (see the Table). In the case of perfluoroalkyl functionalized DND MM slightly decreases and polydispersity becomes more narrow. If the trimethylsilyl functionalized DND was used MM increased but polydispersity index also decreased.

Table – MM characteristics of PMMA obtained in the presence of functionalized DND

<table>
<thead>
<tr>
<th>Functional groups on DND surface</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without DND</td>
<td>608 000</td>
<td>3 304 000</td>
<td>5.4</td>
</tr>
<tr>
<td><img src="image1.png" alt="Fullerene" /></td>
<td>564 000</td>
<td>1 620 000</td>
<td>2.9</td>
</tr>
<tr>
<td><img src="image2.png" alt="Perfluoroalkyl DND" /></td>
<td>730 000</td>
<td>3 580 000</td>
<td>4.9</td>
</tr>
<tr>
<td><img src="image3.png" alt="Trimethylsilyl DND" /></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
THERMAL STABILITY OF STYRENE AND BUTYL ACRYLATE COPOLYMERS OF VARIOUS ARCHITECTURES SYNTHESIZED VIA A RAFT TECHNIQUE

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Controlled radical polymerization, in particular reversible addition–fragmentation chain transfer (RAFT) technique has significantly facilitated the synthesis of well-defined polymers with pre-determined architecture. At the same time, a detailed and systematic knowledge of their thermal stability, which is highly important for practical applications, e.g. for processing in most industrial processes, is not practically available. Recently it has been shown that linear polystyrene carrying a trithiocarbonate mid-chain functionality can undergo decomposition under continuous thermal treatment in a range of the temperatures $140 – 160 \, ^{\circ}C$. It was proposed that degradation mechanism is based on Chugaev-type cleavage reaction [1]. Previously we have demonstrated the easy root for synthesis of styrene/butyl acrylate copolymers of various architectures (block-, gradient and random) using dibenzyl trithiocarbonate (BTC) as a RAFT agent [2]. However their thermal stability hardly can be predicted basing on knowing literary data.

The aim of the present research was to reveal the correlation between the chain structure, namely between the monomer sequence order and the monomer nature bonded with trithiocarbonate group, and thermal stability of copolymers.

Thus, using BTC we have synthesized homopolymers – polystyrene, PS and poly(butyl acrylate), PBA carrying trithiocarbonate group, triblock-copolymers PS–PBA–PS and PS–PBA–PS, in which trithiocarbonate group was located in the middle of the inner block, and finally a range of copolymers of various compositions but close molecular weight and narrow MWD.

Each sample was put in an ampoule, degassed and sealed, then it was placed in air bath heated at preset temperature and was kept there for 6 h. Molecular weight characteristics of the polymers before and after heating were analyzed. Two independent experiments aiming at 1) establishing the location of trithiocarbonate group in each sample and 2) verification of ability of samples heated at different temperatures to serve as polymeric RAFT agents were carried out additionally.

These experiments allowed to conclude that poly(butyl acrylate) and triblock-copolymer with inner PBA block are characterized by higher thermal stability. The lesser thermal stability is characteristic for polystyrene and block-copolymer with inner PS blocks. While styrene/butyl acrylate copolymers are in the middle of this range, their thermal stability is decreased sequentially with growth of styrene content in copolymer.

References


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AMPHIPHILIC BLOCK-COPOLYMER SYNTHESIS USING POLYACRYLIC ACID TRITHIOCARBONATE AS A RAFT AGENT

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Generally, amphiphilic block-copolymers comprising from hydrophilic and hydrophobic blocks, which contain monomer units differing by chemical nature of functional groups, are used in formation of nano- and micro-structured polymer films. It is supposed that co-existence of dense hydrophobic areas and thin hydrophilic channels formed from the blocks bearing charged functional groups of hydrophilic block in polymer film allow to produce the systems possessing simultaneously the high mechanical strength and conductivity. Combination of these properties is of particular urgency for production of different membranes.

Aiming this, we have developed the procedure of the synthesis of amphiphilic block-copolymers basing on polyacrylic acid and on poly(alkyl acrylates), namely poly(butyl acrylate) and poly(2,2,3,3,4,4,5,5-octafluoropentyl acrylate) via a solution polymerization in non-selective solvent using RAFT (reversible addition–fragmentation chain transfer) technique. It was necessary to study the mechanism of block-copolymer formation in order to confirm the living nature of the process and to produce a range of block-copolymers, which will be used for formation of structured films by traditional technique – by deposing of polymer solution in common solvent and further annealing.

Polyacrylic acid trithiocarbonate (PAA-TC) carrying mid-chain trithiocarbonate group with $M_n = 9400$ Da and $M_w/M_n = 1.3$ was synthesized via a solution RAFT polymerization using dibenzyl trithiocarbonate (Bz–S–C(=S)–S–Bz). Its chain extension in DMF solution using [PAA-TC] = $6 \times 10^{-3}$ M led to formation of PAA with $M_n = 107\,200$ Da and $M_w/M_n = 1.22$, thus confirming the efficiency of PAA-TC as a RAFT agent at least in homopolymerization of acrylic acid.

When PAA-TC was used as a RAFT agent in butyl acrylate polymerization, then the degree of control depended on monomer (M) concentration in DMF solution: at [M] = 0.7 M at monomer conversion higher 90% $M_w/M_n = 1.3$, while at [M] = 2.6 M $M_w/M_n = 1.6$, which might come from worsening of thermodynamic quality of the solvent (DMF) due to addition of non-solvent – butyl acrylate. The additional introduction 2,2,3,3,4,4,5,5-octafluoropentyl acrylate to the reaction mixture also decrease thermodynamic quality of the solvent; in this case PAA-TC slowly consumed in the polymerization process, resulting in bimodal MWD of the products isolated up to 50% of monomer conversion and unimodal MWD at monomer conversion higher 70% ($M_w/M_n = 1.7$). However, in all the mentioned systems $M_n$ was noticeably low comparing to blank experiments, carried out in the absence of PAA-TC keeping other polymerization conditions the same.

Thus to synthesize amphiphilic block-copolymer comprising PAA block the dilute monomer solution is required.

This work was supported by Russian Scientific Foundation (project No 15-13-30007).
CHAIN TERMINATION ON TRANSITION METALS CATIONS IN RADICAL POLYMERIZATION OF ACRYLIC MONOMERS

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Synthesis of well defined functional polymers with predetermined molecular mass characteristics influencing strongly on their topology, composition, functionality and suitability for a number of applications is in the centre of attention of many scientific laboratories. Commonly using of copper and the other transition metals ions is associated with atom-transfer radical polymerization (ATRP) or retardation and even inhibition in conventional radical polymerization. However as it is shown in this study copper (II) and cerium (IV) ions can be effective molecular mass regulators (see the Table) in the fast polymerization of acrylic monomers: acrylic acid (AA) and acryl amide (AAm). It can be described by the following scheme:

\[
\begin{align*}
\text{Cu}^+\text{HSO}_4^- & \quad + \quad \text{H}_2\text{O}_2 \\
\rightarrow & \quad \text{Cu}^{2+}\text{SO}_4^{2-} \quad + \quad \text{H}_2\text{O} \quad + \quad \text{HO}^-
\end{align*}
\]

\[R = \text{OH, NH}_2\]

\[\text{Cu}^+\text{HSO}_4^- + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{2+}\text{SO}_4^{2-} + \text{H}_2\text{O} + \text{HO}^- + n \text{OH} \]

\[\text{R} = \text{OH, NH}_2\]

Table – Molecular mass of PAA and PAAm synthesized in the presence of Cu\textsuperscript{2+}.

<table>
<thead>
<tr>
<th>CuSO\textsubscript{4}\cdot5H\textsubscript{2}O, mass, % (relative to \text{monomer mass})</th>
<th>Acryl amide (M\textsubscript{n})</th>
<th>Acrylic acid (M\textsubscript{n})</th>
</tr>
</thead>
<tbody>
<tr>
<td>25% aqueous solution, initiatorH\textsubscript{2}O\textsubscript{2}, 90°C</td>
<td>25% solution CH\textsubscript{3}NO-H\textsubscript{2}O\textsubscript{2}, initiator AIBN, 90°C</td>
<td>25% aqueous solution, initiatorH\textsubscript{2}O\textsubscript{2}, 90°C</td>
</tr>
<tr>
<td>0</td>
<td>93000</td>
<td>81500</td>
</tr>
<tr>
<td>0.01</td>
<td>50500</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>42500</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>27000</td>
<td>24000</td>
</tr>
</tbody>
</table>

The scheme explains the decrease of molecular mass and the fact that any retardation is not observed in the systems containing copper (II) ions. Copper (I) ions forming in the chain termination reaction become a part of new redox initiation system so the kinetic chain does not terminate. Moreover generating of OH radicals catalyzed by copper (I) is probably faster than in reaction of thermal decomposition of hydrogen peroxide and copper ions can accelerate polymerization. Thus copper actually works like an ideal chain transfer agent terminating material chains but slightly influencing on polymerization kinetics.

The similar effect was observed in organic solvents and with other initiators (see the table). In ATRP this chain termination can cause forming of "dead" chains and lead to a poor control. The similar situation is observed in acrylic monomers polymerization in the presence of cerium (IV) ions. Obviously cerium (IV) causes chain termination and leads to decrease of polymer molecular mass according to the same scheme. But the transition Ce\textsuperscript{4+}→Ce\textsuperscript{3+} is irreversible and the influence of cerium ends when all amount of its cations is reacted. Therefore at low concentration of cerium the bimodal molecular mass distribution is obtained.
SYNTHESIS OF HIGHLY BRANCHED POLY(2-HYDROXYPROPYLENE IMINES)

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Polycondensation is one of the most widespread techniques used for the synthesis of polymers. Large potential of this method is predetermined by both impressive variety of the suitable monomers and wide range of the chemical reactions leading to the formation of macromolecules. Usually, linear polymers are obtained from bifunctional monomers, and branched or crosslinked polymers are obtained when at least one of the monomers has functionality higher than two [1, 2].

In this study, highly branched poly(2-hydroxypropylene imines) (PHPI) were synthesized by polycondensation and were characterized by SEC, $^1$H and $^{13}$C NMR spectroscopy, and DSC [3].

Polycondensation of equimolar amounts of 1,3-diamino-2-propanol (DAP) and 1,3-dibromo-2-propanol (DBP) was carried out in polar protic solvents methanol (MeOH), 2-propanol (ISP) and water (H$_2$O), and aprotic solvents N,N-dimethylacetamide (DMAC) and N,N-dimethylformamide (DMF) (scheme 1). Concentration of the monomers was 40 %, reaction temperature 80 °C, and duration 168 days. All reaction products were purified by ultrafiltration through 10 kDa membrane against water, and the solid polymers were isolated by freeze-drying.

![Scheme 1. Simplified scheme of polycondensation between DAP and DBP](image)

Yield of the purified PHPI was low (15-20%). Weight average molecular weight M$_w$ of the polymers synthesised in protic solvents varied from 8 to 12 kDa and was much lower than of those synthesized in polar aprotic solvents. Dispersity index M$_w$/M$_n$ of the ultrafiltrated PHPI remained large, about 2 for the samples synthesized in methanol and water, and nearly 5 for those synthesized in aprotic solvents. Analysis of high-molecular fractions of PHPI by $^{13}$C NMR spectroscopy revealed that these PHPI were highly branched polymers, with branching points being separated by approx. 1 to 3 repeating units. PHPI with the highest degree of branching were synthesized in DMF, while those with the lowest in MeOH. Irrespective of the degree of branching, PHPI were not crosslinked and well soluble in aqueous solutions. Glass transition temperature $T_g$ of PHPI was strongly dependent on the degree of branching being the highest for the polymers synthesized in DMF and DMAC.

References

KINETIC STUDY OF THE POLYCONDENSATION OF 1,3-DIAMINO-2-PROpanol WITH 1,3-DIBROMO-2-PROpanol

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Recently it has been reported that poly(hydroxyalkylene imines) may be synthesized via simple polycondensation reaction from 1,3-diamino-2-propanol and appropriate dibromide [1]. It was found, that these newly synthesized polymers are very efficient gene delivery in vitro and in vivo vehicles in a variety of different cell lines and outcompeted most of the widely used polymer or lipid based transfection reagents. Unfortunately, these polymers were synthesized under limited set of reaction conditions restricting possibilities to vary their molecular weight. Moreover, reaction kinetics and structure of such polymers were not studied thoroughly [1].

In the present study, we examined polycondensation of 1,3-diamino-2-propanol with 1,3-dibromo-2-propanol in a various polar solvents with the aim to synthesize poly(2-hydroxypropylene imine) with medium to high molecular weight. Simultaneously, an attempt was made to elucidate kinetics of polycondensation of this type of monomers and ascertain possibilities to control branching of the reaction products.

Polycondensation of equimolar amounts of 1,3-diamino-2-propanol and 1,3-dibromo-2-propanol was carried out in several polar protic (methanol, 2-propanol and water) and aprotic (N,N-dimethylacetamide and N,N-dimethylformamide) solvents. Polycondensation reaction kinetics was investigated using argentometric titration and SuperCRC isothermal microcalorimeter. Reaction products were analyzed using SEC, $^1$H and $^{13}$C NMR spectroscopy.

It was found that molecular weight of synthesized polymers is relatively low. $^{13}$C NMR analysis showed highly branched structure of polymers. Degree of branching was mainly dependent on the solvent’s ability to accept or donate protons to the nucleophilic amino groups. Irrespective of the degree of branching, polymers were not crosslinked and well soluble in aqueous solutions.

Calorimetric study revealed that polycondensation reaction, independently of the solvent used, starts immediately. The rate of the reaction differs, however, being the highest in aprotic solvents. Several kinetic models were applied to treat experimental heat flow curves and was concluded that Prout-Tompkins model [2], which is a simplified case of Sestak-Berggren generalized model, is adequately suitable for the mathematical description of polycondensation reaction investigated. The order of the reaction was calculated using differential method of Van't Hoff and was close to 2, which led to conclude that polycondensation of 1,3-diamino-2-propanol and 1,3-dibromo-2-propanol is a typical $S_N$2 reaction.

References:

SYNTHESIS BY RAFT AND MODIFICATION OF WELL-DEFINED p(t-BMA) PRECURSORS FOR ANIONIC MOLECULAR BRUSHES

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Because of pH-responsive properties, polymers and, especially, molecular brushes with negatively charged side chains are gaining more and more attention [1]. Molecular brushes can be synthesized via 3 main strategies: „grafting-onto“, „grafting-from“ and „grafting-through“. According to the first strategy, the side chains are grafted onto a pre-established multifunctional backbone by various coupling reactions using previously synthesized precursors [2, 3].

RAFT polymerization of t-BMA (tert-butyl methacrylate) yielding low dispersity precursors was carried out using especially functionalized RAFT chain transfer agents (CTA) (Fig. 1). The synthesis was performed in N-methyl-2-pyrrolidone at 65°C using various ratios of CTA to the initiator AIBN. Molecular weight, MWD and dispersity of the polymers were determined by SEC with triple detection. $M_n$ of the polymers varied from 3000 to 9000, dispersity being as low as 1.1.

Fig. 1. RAFT CTA used in the present study

Fig. 2. Aminolysis of p(t-BMA) precursors

Removal of trithiocarbonate groups was performed via 3 methods: reduction with sodium borohydride/triphenylphosphine and aminolysis with hydrazine or dimethylamine. The most promising results were obtained by aminolysis with dimethylamine at 40-fold excess of the latter to trithiocarbonate groups. No disulfide formation or other side reactions were observed (Fig. 2, SEC traces before and after aminolysis). Furthermore, UV absorbance spectra showed quantitative removal of trithiocarbonate groups (Fig. 2).

Well-defined p(t-BMA) precursors with suitable end-functional groups are intended to be used for further steps in obtaining anionic molecular brushes. The polymers synthesized with CTA1 are suitable for epoxy-thiol click reactions, while those synthesized with CTA2 are suitable for azide-alkyne click reactions.

Acknowledgements. Financial support from the Research Council of Lithuania under the project MIP-51/2012 is gratefully acknowledged.

References
SYNTHESIS OF HYDROPHILIC MULTIBLOCK COPOLYMERS BY ONE-POT RAFT COPOLYMERIZATION

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Because of facile response to external stimuli like pH and temperature, good solubility in organic solvents and open possibilities for further modification, the copolymers containing segments of poly(2-(dimethylamino)ethyl methacrylate) (pDMAEMA) are unique and promising. For example, pDMAEMA can be permanently quaternized forming polymers with upper critical solution temperature. Such polymeric materials have attracted considerable attention in a number of different applications, including drug and gene delivery [1], nanofiltration, and lenses [2]. Multiblock copolymers containing segments of pDMAEMA can be prepared by the methods of living radical polymerization like ATRP, NMP or RAFT by successive building of appropriate blocks, with or without isolation of intermediate products – homopolymers, diblock copolymers, etc.

Several linear multiblock copolymers containing 3 blocks of poly(2-hydroxyethyl methacrylate) (pHEMA) or poly(ethylene oxide) methyl ether methacrylate (PEOMEMA) and 2 or 4 blocks of pDMAEMA (5 or 7 blocks in total) were synthesized by the RAFT method using stepwise monomer addition approach. Difunctional RAFT chain transfer agent di(ethylene glycol) di(2-(1-butyl) sulfanylthiocarbonyl sulfanyl-4-cianopropionate) was synthesized by carbodiimide method to ensure chain propagation to two opposite directions [3]. The effects of various factors, such as concentration of the reaction components ([Monomer]0/[CTA]/[AIBN]), solvent, and pH of aqueous media on kinetics of RAFT polymerization was studied. Conversion of the monomers was monitored by 1H NMR spectroscopy, and molecular weight of multiblock copolymers was determined by SEC with triple detection. Trying to obtain “pure” blocks, polymerization was carried out up to very high conversions (> 95 mol.%), and then the next monomer was added. Block copolymerizations were carried out in different solvents like butanol, isopropanol, dioxane, N-metylpyrrolidone, toluene, DMSO and in mixtures of the above solvents with water. The preferred molar ratio of the reaction components was [M]/[CTA]/[AIBN]0 = 100/1/0.2. The use of NMP enabled to reach the highest monomer conversion (about 98 mol.%). Disperisty of the final multiblock copolymers was reasonably low (Ð about 1.60).

Multiblock copolymerization of DMAEMA and HEMA was rather well controllable until very high overall monomer conversion enabling to synthesize each block with degree of polymerization about 100, dispersity 1.6–1.8, and containing trithiocarbonate moieties at both ends of the chain. In multiblock copolymerization of DMAEMA and PEOMEMA, very high conversion of the monomers (ca 98 mol.%) was reached at higher concentration of the initiator only. Multiblock copolymers pDMAEMA-block-pPEOMEMA synthesised under these conditions were characterized by higher dispersity (D over 3).

Acknowledgements. Financial support from the Research Council of Lithuania under the project MIP-54/2015 is gratefully acknowledged.

References:

OBTAINING POLYURETHANE MICROCAPSULES USING INTERPHASES POLYMERIZATION

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Microencapsulation is a process in which around solid particles, liquids or molecular dispersions spherical shell from other material is made. Capsule membrane can be one or multi-walled, with varied thickness, porosity, mechanical strength or size. Application areas of microcapsules include agriculture, pharmacy, food, cosmetics, textiles, paints, adhesives and coatings, etc [1].

In this work in order to obtain self-healing coating materials that can autonomously extend the lifetime of the surface material, polyurethane microcapsules were formed. Microcapsules were synthesized by interfacial polymerization. For capsule shell forming polyl (glycerol or 1,3-propanediol) and toluene diisocyanate was used, while role of active agent performed isophorone diisocyanate. As a solvent cyclohexanone was taken, but as surfactant – gum arabic. In order to evaluate morphology and surface features of microcapsules scanning electron microscope SEM \textit{Tescan TS 5136 MM} with secondary electron detector and \textit{VEGA TC} computer software was used. To ensure isocyanate existence inside capsules, samples were tested using FT-IR spectroscopy.

![Fig. 1. Polyurethane microcapsules: a - filled with isophorone diisocyanate, b – without active agent](image)

Figure 1a shows with isophorone diisocyanate filled microcapsules. The presence of isocyanate inside the capsules is obvious - because of little shell wall damages isocyanate has reacted with air moisture and has become solid. The surface of capsules is smooth and shell wall thickness is small. The average size of these capsules are between 20 and 50 µm. In Figure 1b “unfilled” polyurethane microcapsules are shown. Contrary to what we were expecting, microcapsules are not empty but filled with lots of smaller capsules. It is seen that both outer and inner surfaces are rough. The size distribution is uneven and the size of capsules is between 1 and 100 µm.

With this work we have proved that it is possible to obtain spherical and good quality microcapsules using described above synthesis method. With isocyanate filled polyurethane capsules have the potential to be industrially used in adhesives and coatings as self-healing additives.

References

MICROWAVE SYNTHESIS OF POLYOLS FOR URETHANE MATERIALS

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All type of thermally driven chemical reactions can be accelerated by microwaves (MW). From the early 1980-ties, many investigations have been performed in the field of MW synthesis of different organic substances. It is possible significantly to decrease the synthesis reaction time from hours to minutes. Arrhenius equation (Eq.1) testifies that very low activation energy should be applied to start the chemical reaction [1].

\[ k = A e^{-E_a/RT} \]  

(Eq.1)

The main aim of the present investigation is connected with synthesis of polyols for urethane materials preparations. MW assisted reactions of glycolysis and transesterification were performed and compared with conventional synthesis. The investigation is focused on the utilization of bio-based rapeseed oil (RO) and recycled polyethylene terephthalate (PET) for the proposed MW synthesis. The clear PET bottle waste was depolymerized by the glycolysis reaction with diethylene glycol (DEG). The additives of adipine acid (ADA) and glycerol (GL) were used. The hydroxyl group containing polyol was transesterified from RO. Zinc acetate (ZnAc) catalysis was used for both reactions. Both polyols were also transesterified together.

The MW assisted synthesis was accomplished on the lab. scale 1 liter glass reactor equipped with MW generator, mechanical stirrer, argon flux and condenser. The frequency was 2450 MHz, power – 800 W. Considering the precise temperature control of the reaction bulk, the applied power was only 60%. The final MW synthesis time of the polyols was about 60 minutes, which was significantly shorter than 3-4 hours by synthesis process with conventional heating.

The synthesized polyols consisted from 34% renewable (RO) and 23% recycled (PET) components; they combined the advantages of aromatic and aliphatic structure blocks in the molecule backbone. The use of recycled and bio-based raw materials in the polyol synthesis can replace the petrochemical resources for polyol synthesis. The obtained polyol properties are summarized in the following table.

<table>
<thead>
<tr>
<th>No.</th>
<th>Property</th>
<th>Value</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Appearance</td>
<td>Homogeneous, viscous brown liquids</td>
<td>Visually</td>
</tr>
<tr>
<td>2</td>
<td>Acid number, mgKOH/g</td>
<td>6.5 ± 0.5</td>
<td>DIN 53402</td>
</tr>
<tr>
<td>3</td>
<td>Hydroxyl number, mgKOH/g</td>
<td>350 ± 10</td>
<td>DIN 53240</td>
</tr>
<tr>
<td>4</td>
<td>Viscosity, mPa s</td>
<td>780 ± 50</td>
<td>DIN 53015</td>
</tr>
<tr>
<td>5</td>
<td>Water content, wt.%</td>
<td>0.3 ± 0.1</td>
<td>DIN 51777</td>
</tr>
</tbody>
</table>

The utilization of processed innovative polyols for PU rigid foams fabrication was testified experimentally in the lab. The PU foams can be used for thermal insulation materials, considering the increasing demands for the energy efficiency in construction, especially.

Acknowledgements
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SYNTHESIS AND SOLUTION BEHAVIOUR OF ANIONIC PENTABLOCK BRUSH COPOLYMERS

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In the last decade, molecular brushes (or molecular bottle-brushes) have attracted considerable attention in a number of different applications such as drug delivery systems, tissue engineering, and biomimetic lubrication. Unique properties of molecular brushes are related to extended chain conformations, based on the intermolecular excluded volume interactions between densely grafted side chains [1].

In the preparation of pentablock brush copolymers, the first step included the synthesis of pentablock copolymers of 2-hydroxyethyl methacrylate (HEMA) and butyl methacrylate (BMA) by one-pot sequential monomer addition RAFT polymerization [2]. During the second step, pHEMA blocks of the pentablock copolymers were modified by attaching 2-bromopropionyl bromide (BPP) followed by nucleophilic substitution with sodium trithiocarbonate forming precursors of RAFT CTA on the polymeric backbone. Alternatively, polymeric backbones with multiple RAFT CTA were prepared by attaching 4-cyano-4-(butylsulfanylthiocarbonyl) sulfanyl pentanoic acid by carbodiimide method. Finally, in the third step, RAFT polymerization of acrylic acid (AA) or methacrylic acid (MMA) in the presence of pentablock copolymers decorated by multiple RAFT CTA was carried out resulting in anionic pentablock brush copolymers. Conversion of the monomers was monitored by gravimetric method, and molecular weight of pentablock and pentablock brush copolymers was determined by SEC with triple detection.

When conversion of AA or MAA was relatively low (20-40%), pentablock brush copolymers were characterized by reasonably low dispersity (Mw/Mn about 1.4). At higher conversions of these acidic monomers, partial crosslinking took place resulting in anionic pentablock brush copolymers with multimodal molecular weight distribution and large dispersity (Mw/Mn over 2). In order to avoid crosslinking or at least minimise it, a certain amount of low-molecular CTA of the same structure like on the “decorated” pentablock copolymers was added [3]. Addition of low-molecular CTA reduced dispersity of molecular brushes by 15-20 %.

Ionization behavior of anionic pentablock brushes copolymers in water was studied by potentiometric titration and dynamic light scattering (DLS). Pentablock copolymers with both pAA and pMAA side chains showed conformational changes during titration with alkaline solutions which were more evident for molecular brushes containing more hydrophobic side chains of pMAA.

Acknowledgements. Financial support from the Research Council of Lithuania under the project MIP-54/2015 is gratefully acknowledged.

References:

MATERIAL RECYCLING AND IMPROVEMENT ISSUES IN ADDITIVE MANUFACTURING

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This study explores options to truly make additive manufacturing an environmentally friendly production process. The focus is on eliminating the polyamide-12 (PA-12) waste generated in Selective Laser Sintering (SLS) process. Since the material properties of the polymer powder degrade when exposed to high heat in the SLS machine, not all of it can be re-introduced to the same process; only between 30 – 70% of it can be mixed with virgin powder and used in SLS again. Experiments conducted during this study have shown that there are no enormous differences in tensile properties between virgin and re-used PA-12 powder. This means that re-used PA-12 powder could still be suitable for being used in production. During this study recycled PA-12 powder was turned into a filament using a laboratory compounder. This filament was used in a Fused Deposition Modeling (FDM) printer to test the material’s FDM printability. This test proved that recycled PA-12 filament is FDM printable, but the material needs further modifications in order to provide printed parts with high quality. In addition, in this study attempts have been made to improve used PA-12 powder’s mechanical properties. Currently, three different blends are in the process of being developed – a blend that is softer and a blend that is harder than pure recycled PA-12, and a blend that is electrically conductive. The tensile testing outcomes of initial blends have been successful – the properties have changed in the desired direction. And the third blend showed some electrical conductivity. Ongoing studies are focused on making those improvements more significant. For making a softer blend, thermoplastic polyurethane (TPU) is used with recycled PA-12 powder, for making a harder and stiffer blend, aramid fibers are added and for electrical conductivity, graphite powder is mixed into recycled PA-12 powder. In addition to being environmentally friendly, the ultimate tangible goal of this study is to develop FDM printable filament blends with advanced properties that would improve the end user’s experience with FDM printed products made of those filaments. Some possible applications include medical devices and mechatronic equipment. In medical devices, such as prosthetic hands, a softer blend would provide a more secure grip and a harder blend would provide precise connection of details as well as precise movement of the hand. In mechatronic equipment, such as cases for electronic devices, some electrical conductivity would lead static electricity away.
RECYCLED PET FLAKES AND RAPESEED OIL AS FEEDSTOCK FOR RIGID POLYURETHANE FOAMS

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Among different poly(ethylene terephthalate) (PET) recycling techniques chemical recycling is the most favourable and depolymerizing PET using glycolysis offers following advantage such as lower reagent amounts, lower temperatures and pressure [1, 2]. To prevent some of the PET polyol drawbacks such as incompatibility with the physical blowing agents and high viscosity, vegetable oil based polyols are introduced in polyol system [3].

Three bio/recycled polyols using recycled PET and rapeseed oil (RO) were successfully synthesized using continuous two-step method. The first stage was synthesis of rapeseed oil triethanolamine (RO/TEA) polyol using transesterification reaction of RO with TEA at molar ratio 1 M of RO and 2.9 M of TEA. In the second stage the reaction temperature was risen to 240°C and depolymerisation of PET flakes was carried out using diethylene glycol (DEG) as glycolysis reagent for 4 hours. The molar ratios of PET to DEG were 1:2; 1:4 and 1:6. New polyols were named RO/PET polyols. The properties of synthesized RO/PET were compared to RO/TEA polyol and commercially available PET based polyol. The hydroxyl values and acid values of RO/PET polyols were in range from 233 – 368 mg KOH/g and from 2.3 - 3.2 mg KOH/g, respectively. The synthesized RO/PET polyols were investigated using FTIR spectroscopy. It was observed that with the increase of DEG molar ratio the RO/PET polyols showed increased hydroxyl numbers and decreased viscosity.

Rigid polyurethane (PUR) foams were prepared from RO/PET using unified apparent density of 40 - 45 kg/m³ and with an isocyanate index of 130. For comparison foams were also prepared from RO/TEA polyols and commercially available PET based polyol. For RO/PET polyols based foams the closed cell content was ~95% and thermal conductivity was in range from 19.49 to 21.50 mW/m·K. Water absorption experiments showed that the presence of PET in polyol increased moisture resistance. The thermal stability of rigid PUR foams increased with the increase of aromatic groups in the RO/PET polyols, also giving higher char residues. Rigid PUR foams obtained from RO/PET polyols showed higher compression strength than foams from RO/TEA. The highest compression strength was shown by PUR foams from RO/PET polyols using PET to DEG molar ratio 1:4. The results indicated that rigid PUR foams obtained from these polyols can be successfully used for preparing energy efficient thermal insulation material.

Acknowledgements
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References
The properties of electrospun fibrous membranes can be modified by adding different fillers. Conductive polymer, polyaniline (PANi), is one of these additives. Due to high conductivity and simplicity of synthesis the usage of PANi is increasing with its application as blended filler to produce membranes or biosensors for electromagnetic devices. The focus of this study is electrospinning of conductive membranes using PANi salt. There are studies on electrospinning of doped polyaniline (PANi) base blended with a polymer matrix. But there are no studies of producing conductive nanofibrous membranes by using polyaniline salt as conductive filler. Thus, in the present research, for the first time, polyaniline salt is dispersed in polymer solution to prepare conductive membranes by electrospinning. To improve the dispersion of PANi salt in polymer solution, for the first time, 5 wt% of ionic liquid (IL), butyl-methyl-imidazolium chloride, is added. The solution has been prepared by dispersing 3 wt% and 10 wt% of PANi salt blended with 10 wt% of polyacrylonitrile (PAN) in dimethylsulfoxide (DMSO). PAN is used as a matrix. The influence of the increasing PANi concentration up to 10% and of added IL on the conductivity and morphology of electrospun membranes has been researched. As expected, the added IL increases the conductivity of the membranes more considerably comparing with pure PANi as an additive. With adding 5 wt% of IL the conductivity of PANi membranes increases up to $0.9 \times 10^{-2}$ mS/cm whereas the membrane conductivity with the only added 10 wt% PANi is measured $0.08 \times 10^{-2}$ mS/cm. Using of IL has also improved the dispersion of PANi salt. The morphology of electrospun membranes has been estimated by SEM. The membranes with smoother, aligned fibers have been produced. During the study the conditions of electrospinning to produce conductive PANi membranes with limited concentration of 5 wt% IL and up to 10 wt% of PANi in PAN solution have been found out.
APPLICATION OF POLYMER ADDITIVES USING ELECTROSTATIC AND STERIC MECHANISMS OF SUSPENSIONS STABILIZATION FOR MODIFICATION OF CONCRETE MIXTURES PROPERTIES

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Nowadays in the industry of construction cement mixtures the special additives for modification of concrete properties are of great interest both from the practical and fundamental points of view. These are the substances (often polymers or oligomers) increasing mobility of cement mixtures at the same or even a smaller amount of water (water-reducing agents), increasing or decreasing air entrainment, changing kinetics of hydration etc. In this study the additives (see the pic.) on the base of lignosulfonates (LS), the sodium naphthalenesulfonate-formaldehyde condensate and copolymers of acrylic acid (AA) and methoxy poly(ethylene glycol) methacrylate (MPEGMA), using electrostatic and steric mechanisms of stabilization of concrete suspensions were investigated.

Dependence of some important characteristics of concrete on type of additive and the presence of the other modifier was investigated and the examples are shown in the table below. Uniqueness of polymers AA-MPEGMA is their long PEG radicals providing effective steric stabilization of dispersions instead of strictly limited electrostatic one, being enough hydrophilic for solubility in water. The mechanism of steric stabilization was estimated using the computer modeling of possible structures. It was established the protective PEG layer around of cement particles provides such colloidal systems with aggregate stability and, that is extremely important, not interfering in cement hydration.

Table – The influence of some additives on concrete mixtures properties

<table>
<thead>
<tr>
<th>Additive</th>
<th>Slump (mm)</th>
<th>Compressive strenght (MPa)</th>
<th>Air entrainment (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3 days</td>
<td>7 days</td>
</tr>
<tr>
<td>Control</td>
<td>4</td>
<td>14</td>
<td>16</td>
</tr>
<tr>
<td>LS</td>
<td>6</td>
<td>21</td>
<td>26</td>
</tr>
<tr>
<td>LS with strenght modifier</td>
<td>6</td>
<td>23</td>
<td>28</td>
</tr>
<tr>
<td>LS with sulphanole</td>
<td>8</td>
<td>30*</td>
<td>34**</td>
</tr>
<tr>
<td>LS with RO(CH2CH2O)nH</td>
<td>12</td>
<td>28*</td>
<td>33**</td>
</tr>
</tbody>
</table>

* – 7, ** – 14, *** – 28 days.
RESEARCH ON WEB STRUCTURE OF ELECTROSPUN NANOFIBRES

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Electrospinning is a process that employs electrostatic forces to produce nanofibres from polymer solution or melt. The diameter of these fibres depends on the polymer solvent and operating conditions. Sometimes the influence of these parameters is inconspicuous.

The web of electrospun nanofibres usually consists from fibres of different diameters. The reasons of such phenomena by various authors are explained in different ways. Some of them states that nanofibres stick on the web when they reach the web do not finally dried. The diameter of the fibre and the uniformity of structure are very important factors for determining the quality of nonwoven structure, because the web with small diameter of nanofibres and uniform structure have numerous applications in various fields such as filtration materials, biomedical applications and others.

In previous works we have analysed various webs created from nanofibres and found variety of nanofibres diameter distributions [2-5]. Because of this, it is impossible to compare the average values of nanofibre diameters. In this work we present our investigations of the last few years, some results of which have been published earlier in various journals [3-5]. The goal of this work is to present the possibilities of web evaluation by mathematical criteria and to describe distribution of nanofibres by well known mathematical distribution – compound distribution from few normal distributions [6]. The evaluation of diameter of nanofibres by average value and modal values of each normal distribution, also the percentage quantity of measurements of each distribution in this work is proposed also. According to this method, it is possible to compare different investigations when diameters of nanofibres distributed differently.

References

Adding conductive additives to the electrospinning solutions has been proven to increase the conductivity of the electrospun membranes. The aim of this study was to learn the effect of ionic liquids (ILs) on the polyacrylonitrile (PAN) membranes conductivity. Three different ionic liquids (1-butyl-methylimidazolium chloride \([C_4\text{MImCl}]\), 1-ethyl-3-methylimidazolium bromide \([C_2\text{MImBr}]\), and 1-ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide \([C_8\text{H}_{11}\text{F}_6\text{N}_3\text{O}_4\text{S}_2]\)) were used with concentration up to 10%. The influence of ILs in two solutions of PAN with concentration 8% and 10% in dimethylformamide (DMF) and dimethylsulfoxide (DMSO) was investigated. Concentration of ILs up to 10% has been found to be the optimum concentration to perform electrospinning. The results have shown that membranes conductivity significantly increases with increasing concentration of added different ILs. In the case of all three ionic liquids the highest conductivity of electrospun PAN membranes has been achieved with 10% of added ionic liquid. Most conductive membranes with conductivity measured 0.16 \(\mu\text{S}\) were produced from PAN solution with added 10% \(C_4\text{MImCl}\). \(C_8\text{H}_{11}\text{F}_6\text{N}_3\text{O}_4\text{S}_2\) has shown the lowest conductivity, 0.07 \(\mu\text{S}\), respectively, that can be explained by comparable small conductivity of this IL.
GLASS-FORMING CYANO SUBSTITUTED CARBAZOLE DERIVATIVES FOR OPTOELECTRONICS

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Organic charge transport materials are used in electrophotographic photoreceptors, light-emitting diodes, photovoltaic devices and other optoelectronic devices [1,2]. Much attention is recently paid to organic low-molar-mass compounds that form glasses above room temperature. However, low-molar-mass hole-transporting materials often suffer from poor thermal stability, and easy recrystallization, which limit their use in photoelectric devices.

Due to efficient hole transport and excellent thermal stabilities, electron-rich carbazole moiety is widely used in the design of hole-transporting and light-emitting materials [3]. On the other hand, cyano-substituted compounds show good optical and electrical properties due to their high electron affinities. Some cyano-substituted compounds have been reported which show unique enhanced emission rather than a fluorescence quenching in the solid state [4]. Our strategy for the synthesis of new series of carbazole derivatives containing cyano groups is outlined in Fig 1. The key step was Ullmann coupling reaction of 3- or 2-iodo-9-ethylcarbazole with 3- or 3,6-dicyanocarbazole.

![Fig. 1. Cyanom substituted carbazole based derivatives](image)

The chemical structures of the synthesized compounds were confirmed by $^1$H and $^{13}$C NMR, IR and mass spectroscopies. The thermal, optical, photophysical, electrochemical and photoelectrical properties of the synthesized compounds have been studied.

References:


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POLYETHERS CONTAINING 3,6-DIARYLCARBAZOLYL GROUPS AS POLYMERIC MATERIALS FOR HOLE TRANSPORTING LAYERS OF OLEDS

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Carbazolyl containing polymers and low-molar-mass derivatives are among the most widely studied materials for optoelectronic and electronic applications due to good film forming properties, high hole mobility in their layers and photoconductive properties [1, 2]. Some carbazole-based materials have been commercialized in a number of devices and processes (photocopying machines, laser printers, etc.) [3]. New electro-active polyethers are shown in Scheme 1.

The amorphous polymers demonstrate high thermal stability. The electron photoemission spectra of thin layers of the materials showed ionization potentials in the range of 5.47-5.69 eV. Hole-transporting properties of the polymeric materials were tested in the structures of organic light emitting diodes with Alq3 as the green emitter. The devices with the polymer P3 containing electro-active 3,6-di(4-biphenyl)carbazolyl groups exhibited the best overall performance with a maximum photometric efficiency of about 2.3 cd/A and maximum brightness exceeding 2630 cd/m².

Acknowledgements
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References
POLYMERIZABLE DERIVATIVES OF INDOLYL-BENZO[b]CARBAZOLE AS ELECTROACTIVE MATERIALS

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Low-molar-mass and polymer organic light emitting diodes have attracted considerable attention due to their great application potential in large area flat panel displays and solid state lighting [1]. In this work we employed efficient regioselective acid-catalysed reactions of 1H, 1-methyl- and 1-naphthylindole with o-phthalaldehyde [2]. New indolyl-benzo[b]carbazole derivatives (Scheme 1) were synthesized and investigated in order to identify correlations between the molecular structures of the compounds and their optical, electrochemical and photophysical properties. DFT calculations employing the B3LYP functional were performed in vacuum with the Spartan’14 program [3]. Neutral cationic and triplet state geometries of molecules were optimized from conformational analysis data using 6-31G (d,p) basis set as starting point.


The thermal, optical, photophysical, electrochemical and photoelectrical properties of the materials, as well as photo- and thermally activated polymerization of the monomer containing vinyl group monitored by FTIR will be reported.

Acknowledgements
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References
TWIN COMPOUNDS OF PHENYLVINYL SUBSTITUTED CARBAZOLES AS EFFICIENT MATERIALS FOR CHARGE TRANSPORTING LAYERS OF OLED DEVICES

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² State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

Carbazole-based polymers and low-molecular-weight derivatives are among the most studied materials for electronic applications due to their good electron donating properties and high hole mobility in their layers [1, 2]. Derivatives containing electronically isolated carbazole rings have also high triplet energies and are widely used as host materials for phosphorescent OLEDs [3, 4]. We will present twin derivatives containing two phenylvinyl substituted carbazole fragments, which were expected to show enhanced hole injection and transport properties and to be suitable as hole transporting materials for multilayer OLEDs. (Scheme 1).

The derivatives form homogeneous amorphous layers with glass transition temperatures of 74-119 °C. The electron photoemission spectra of the layers showed ionization potentials of 5.05-5.45 eV. The compounds were tested as hole-transporting layers in organic light emitting diodes using Alq₃ as the green emitter and electron transporting layer. The device based on a twin derivative containing 3-[2-(4-methylphenyl)vinyl]carbazolyl fragments exhibited the best overall performance with a maximal photometric efficiency of 2.34 cd/A and maximum brightness of about 7380 cd/m².

Acknowledgements
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References
Nanostructured CdSe layers with a highly effective surface area to volume ratio were electrodeposited potentiostatically onto the glass/ITO substrates. Overall thickness of the synthesized CdSe layers was about 400 nm. It was found, that the as-deposited CdSe layers exhibit nanocrystalline thin film structure where dense bottom layer with the thickness of about 200 nm is covered with the clusters formed from fibers with the fibers diameter around 30 nm (Fig. 1). The deposited CdSe layers were annealed under different ambients (air, argon and vacuum) at various temperatures for 30 min to stabilize the nanocrystalline structure and improve morphology. The influence of annealing conditions on morphology, phase composition and photoelectrochemical properties of the prepared layers was investigated. According to the Raman analysis, no additional phases were observed in the as-deposited and annealed nanocrystalline CdSe. It was found, that the optical and photoelectrochemical properties of electrodeposited CdSe was improved significantly for the layers annealed at 250 °C in pure argon atmosphere. On the other hand, annealing in the temperature range higher than 250 °C deteriorates the CdSe layers optical, electrical and morphological properties and accompanies with the recrystallization of CdSe. Also, hybrid photovoltaic (PV) structures on the basis of electrodeposited CdSe nanomatrix and poly(3-octylthiophene) (P3OT) conductive polymer functional layer were prepared and characterized. I-V measurements showed that the fabricated glass/ITO/CdSe/P3OT PV produces so far an open-circuit voltage (Voc) of 0.49 V under white light illumination of 100 mW/cm2 intensity.

Fig. 1. HR-SEM cross-sectional (left) and surface (right) images of electrodeposited CdSe film.
3,6-FUNCTIONALIZED 9-(1-NAPHTHYL)CARBAZOLE DERIVATIVES AS GLASS-FORMING ELECTROACTIVE MATERIALS

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Recently much attention is paid to organic low-molar-mass compounds that form glasses. To obtain sterically bulky molecular configurations different substituents are attached to carbazole framework to further expand the range of π-conjugated molecular structures and to acquire enough morphological stability when the compounds are deposited as thin films [1]. Compounds containing conjugated π-electron systems are of fundamental importance in many research areas including organic optoelectronics [2,3]. In this work we report on low-molecular-weight organic compounds consisting of a carbazole core with attached corresponding arylamino or heterocyclic side-arms at C-3,6 positions and naphthyl group at N-9 position of the carbazole unit. The derivatives of 9-(1-naphthyl)carbazole differently functionalized at C-3,6 positions (3-8) were synthesized by Ullmann-type coupling reaction from 9-(1-naphthyl)-3,6-diodocarbazole and the corresponding arylamine or carbazole derivative using powdered copper as a catalyst. All the compounds obtained were purified by column chromatography. They were indentified by 1H and 13C NMR, IR and mass spectrometries.

The synthesized compounds exhibit high thermal stability with 5% weight loss temperatures ranging from 385 to 442 °C. They are capable of glass formation with the glass transition temperatures ranging from 89 to 201 °C. The derivatives absorb electromagnetic radiation in the range of 225–425 nm. The ionization energies of the synthesized compounds range from 5.04 to 5.66 eV. Charge-transporting properties of the selected compounds were tested by time-of-flight technique. Hole drift mobilities in the amorphous layers of the materials reach 10⁻³ cm²/V s at high electric fields.

Acknowledgements
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References
POLYMERS WITH PENDENT HARMANE, PHENOXAZINE OR CARBAZOLE RINGS AS HOST MATERIALS FOR OLEDs

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Improvements in the performance of organic light emitting diodes (OLEDs) over the past decade have resulted in commercially available products. The efficiencies of OLED devices have advanced rapidly in recent years because of the development of efficient emitters as well as efficient phosphorescent guest molecules containing transition metals \cite{1,2}. Here, we present on new electroactive polymers containing electronically isolated pendent harmane, phenoxazine or carbazole rings. The fragments of aromatic heterocyclic compounds are attached to long and neural alkyl chains of the macromolecules and have not an electronic interaction. The polymers have high triplet energy and are suitable as polymeric hosts for large area OLED devices.

Monomers were prepared by a nucleophilic substitution reaction between the corresponding aromatic heterocyclic compound (harmane, 10H-phenoxazine, 9H-carbazole) and an excess of 4-vinylbenzyl chloride under basic conditions with a phase transfer catalyst. Homopolymers (Figure 1) were obtained by radical polymerization of the vinyl monomers in N-methyl-2-pyrrolidone solutions using 2,2’-azoisobutyronitrile as an initiator.

Figure 1. a–poly[1-methyl-9-(4-vinylbenzyl)pyrido[3,4-b]indole]; b–poly[10-(4-vinylbenzyl)phenoxazine]; c–poly[9-(4-vinylbenzyl)carbazole]

The thermal behaviour of the polymers was studied by DSC and TGA. The new polymers represent amorphous materials of high thermal stability with glass transition temperatures of 139-179°C. Ionization potentials of thin amorphous films of the materials were determined from electron photoemission spectra of the layers. The layers showed ionization potentials of about 5.6-6.0 eV.

The synthesised materials were tested as hosts in phosphorescent OLEDs with bis(2-phenylpyridine)(acetylacetonato)iridium(III) as the guest. The device with the host polymer containing pendent phenoxazinyl fragments exhibited the best overall performance (turn-on voltage: 2.8 V; maximum photometric efficiency: \(\sim 17 \text{ cd/A} \); maximum brightness: 2920 cd/m\(^2\)).

References:

DONOR-ACCEPTOR DERIVATIVES OF PHENOTHIAZINE AND CARBAZOLE AS SEMICONDUCTORS FOR OLEDs

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Nowadays in a rapid development of new technologies organic materials attracted an increased attention. Organic compounds exhibiting thermally activated delayed fluorescence (TADF) are of great interest because of their application in OLEDs.\(^1\) TADF is a promising approach for converting electricity into light at an internal quantum efficiency of nearly 100\%.\(^2\)

In this work TADF compounds based on a 10\(H\)-phenothiazine (Phen) as electron donor unit and a 9-ethyl-9\(H\)-carbazole (EtCz) as electron acceptor unit were developed.

![Molecular structures of synthesized compounds](image)

The molecular structures of the synthesized compounds were proved by X-ray analysis, also confirmed by \(^1\)H NMR, \(^13\)C NMR, IR spectroscopy and mass spectrometry. The thermal behavior of the synthesized compounds was examined using differential scanning calorimetry and thermal gravimetric analysis. The photophysical and optical properties were estimated.

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**References**

It is well known that external electromagnetic radiation have negative impacts on human health and wildlife. This is due to the fact that the external field acting on the protective aura human. The stronger the external field, the stronger this effect. It is particularly harmful influence is not the entire spectrum of the signal and the higher harmonic components, which fall in the range of association of biological macromolecular structures. The wavelength of the harmonic components is generally in the millimeter and centimeter range. Most affected by electromagnetic fields circulatory system, brain, eyes, immune and reproductive systems. It encourages the search for materials and technologies that can protect humans and wildlife from electromagnetic radiation, electromagnetic terrorism and weapon of directed energy.

We have synthesized and studied a fairly wide range of composite materials in terms of their potential to protect people from exposure to electromagnetic radiation. We investigated the transmission rate $\alpha$ of electromagnetic radiation such materials in the frequency range of 10 GHz. In addition, the electrical conductivity of the samples was studied and the mechanism of the screening action (preferential absorption or reflection of electromagnetic waves).

The main materials studied include two main groups:

1. PVC composites filled with various carbon-containing fillers (graphene, graphite, thermally expanded graphite, acetylene black, graphitized carbon black, carbon nanotubes) at concentrations ranging from 5 to 20%;
2. Carbon cloth - standard and modified by some of the nano-metal additives (e.g., nanoparticles of Cu).

The samples of materials were fixed between the horn antennas of transmitter and receiver of electromagnetic radiation at certain distances. Evaluating the effectiveness of the electromagnetic energy absorption was carried out by comparing the measured values of the transmittance and reflectance modules. The results showed that the shielding ability of the materials group (2) is significantly higher than the group of materials (1), which is probably due to the presence of internal skeleton conductivity material. A transmittance of the conventional carbon cloth is of about 20%, which is significantly less than that of the materials group (1). Modification of carbon cloth by nanometal particles (e.g., copper) reduces a transmittance up to 10-15% and thus provide a sufficiently effective protection against electromagnetic radiation.
IMPACT OF PECTIN ESTERIFICATION ON THE ANTIMICROBIAL ACTIVITY OF NISIN-LOADED PECTIN NANOPARTICLES

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Nisin is a small cationic peptide produced by Lactococcus lactis subsp. lactis and belongs to the class I bacteriocins named lantibiotics. Nisin exhibits a wide spectrum antimicrobial activity. It was approved by the US Food and Drug Administration for food application. Nisin was also recognized as a food additive in EU and was assigned the number E234 [1]. To enhance the stability and prolong the efficacy of antimicrobial peptide in food systems, the preparation of nisin-loaded pectin nanoparticles in the simple and low cost way based on the complexation method is presented.

For nanoparticle preparation, different types of pectin biopolymer were used. High methoxyl pectin (HMP, degree of esterification 60 %), low methoxyl pectin (LMP, degree of esterification ≤ 26%) and pectic acid (PecA) were chosen. Moreover, dodecyl pectins (DoPecA) with the degree of substitution of 5.4 and 25% were synthesized. Nisin loading efficiency was dependent on the pH value of solution, and on the pectin degree of esterification and the alkyl chain length of substituent. The antimicrobial activity of samples was analyzed by performing agar-diffusion assay and by applying the agar plate count method. All tested samples were active against Gram positive bacteria Arthrobacter sp. and Bacillus subtilis. However, the antimicrobial activity against both bacteria obviously depended on the pectin used for the preparation of particles. Nisin-loaded PecA nanoparticles demonstrated the greatest antimicrobial activity. Nisin-loaded DoPecA with the low degree of substitution of 5.4% showed the similar ability to inhibit bacteria growth. However, the conversion of carboxyl groups of galacturonic acid to methyl or to dodecyl esters decreased the antimicrobial properties of nisin-loaded nanoparticles. It appears plausible that the esterification of carboxyl groups influences the interaction of nisin-loaded nanoparticle with nisin receptor of Gram-positive bacteria cells.

Acknowledgements
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References
RHEOLOGICAL BEHAVIOUR OF CONCENTRATED AQUEOUS DISPERIONS OF TITANIA NANOPARTICLES STABILIZED BY CATIONIC COMB COPOLYMERS

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Titanium dioxide is one of the most important nanomaterials globally used due to its unique size-dependent properties such as mechanical, chemical, and optical stability; nontoxicity; low cost; and corrosion resistance. Physical and chemical properties of TiO₂ nanoparticles are affected not only by the molecular structure but also by their size, shape, organization, and surface properties. Because of their large surface area and high value of the Hamaker constant \( A = 5.35 \times 10^{-20} \, \text{J} \) for interactions across water, titanium dioxide nanoparticles have a high tendency to adhere and aggregate; therefore, the use of dispersants for the stabilization of TiO₂ dispersions in aqueous media is essential. Rheology is the most useful method to evaluate nanoparticles stability by measuring flow behavior of the dispersions. Rheological behaviour of alkaline concentrated titania nanoparticle dispersions stabilized by cationic linear and comb copolymers differing in charge density and length of PEO side chains was studied, and the data were compared with those of alkaline nano-sized dispersions of bare titania. Dynamic viscosity of alkaline (pH 10.0) concentrated dispersions of bare titania with solid loading 15-25 wt.% was rather high, about 1 Pa.s, and the dispersions exhibited shear-thinning flow behaviour. Alkaline concentrated titania nanoparticle dispersions treated by cationic comb copolymers acted as Newtonian fluids at low and medium shear rates (< 200 s⁻¹), and showed shear-thickening flow behaviour at higher shear rates. Dynamic viscosity of the dispersions with solid loading 15-25 wt% treated by cationic comb copolymers was very low, 2 to 30 mPa.s. The minimal viscosity (2-3 mPa.s) was characteristic for the dispersions treated by cationic comb copolymers with high density of the charged groups (65 mol %) and medium length of PEO side chains (22 repeating units of ethylene oxide).

Acknowledgement. Financial support from the Scientific Exchange Programme Sciex-NMS² (no. 13.030) is gratefully acknowledged.

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PURE BARK NANOPARTICLE GELS AND MIXTURES WITH CHITOSAN SOLUTIONS FOR IMPROVEMENT OF PAPER PROPERTIES

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At present, wood bark, which remains after wood processing, is commonly used as a fuel. However, it would be more economically attractive to use it in composites with other materials for improving their properties. We have found that lignocellulosic materials can be used for reinforcing of paper. In the present work, the possibility of using bark nanoparticle gels for improving paper properties was investigated.

Nanoparticle gels were obtained from grey and black alder bark. Unextracted bark and that extracted in biorefinery, left after polyphenol isolation, was used. The bark was destructed by a thermocatalytic destruction method, developed in our laboratory, and then dispersed in water medium in a ball mill. At sufficient concentrations, gel-like dispersions were obtained, which contained nanoparticles. It was established that the nanoparticles had the size ~300 nm. The effect of nanoparticle gels on the properties of paper sheets was investigated by introducing the dissolved gels in paper furnish and by covering both sides of paper sheets with nanoparticle gel coatings. The coatings were produced using pure nanoparticle gels and in mixtures with chitosan solutions.

It has been established that, in the case of introducing the bark nanoparticle gel in the paper furnish, the nanoparticles improve the mechanical properties of paper. The effect of improvement is greater for nanoparticles from extracted bark and depends of the filler content. At a filler content of 20%, in the case of unextracted and extracted grey alder bark, the tensile index in a dry state increases by 28 and 44%, respectively, and burst index by 78 and 91%, respectively. In the case of unextracted and extracted black alder bark, tensile index in a dry state increases by 30 and 40% and burst index by 19 and 25%. At 20% of unextracted and extracted grey alder bark, tensile index in a wet state increases by 21 and 42%, but in the case of black alder bark by 67 and 73%.

For coatings made from bark nanoparticle gels, tensile strength in a dry state and burst strength increase with increasing coating thickness. For the coating with a thickness of 34.5 µm, prepared from the 6% extracted black alder nanoparticle gel, tensile strength and burst strength grow by 12.6 and 27.7%, respectively. However, tensile strength in a wet state decreases with increasing coating thickness. Coatings from bark nanoparticle gels increase also the Gurley air resistance. Such coatings increase the Gurley air resistance by 35% compared with that of uncoated paper sheets. Coatings made from mixtures of alder bark nanoparticle gels with chitosan solutions essentially improve the mechanical properties and air resistance of paper sheets. Thus, in the case of mixtures, which contain 70% of chitosan solution and 30% of the unextracted black alder nanoparticle gel of the same concentration at a coating thickness of 20 µm, tensile strength in a dry and wet state and burst strength increase by factors of 1.5, 3.4 and 2, respectively, while air resistance increases by the factor 425. Mechanical characteristics and air resistance decrease with increasing nanoparticle gel content in the mixture.

Therefore, bark nanoparticle gels can be used to improve paper properties by introducing them in paper furnish and by using coatings from pure gels or in mixtures with chitosan.

Acknowledgement: The study was financed by the Latvian State Programme “Res Prod” and from the EU Project “Investigation of ecofriendly molded paper fibre materials for their use in food packing with additives from renewable resources”.

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EFFECTS OF NANOPARTICLES ON THE ELASTIC MODULUS IN THE POLY (VINYL ALCOHOL)/POLY (VINYL ACETATE) BLENDS BY THE RESPONSE SURFACE METHODOLOGY

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Poly vinyl alcohol (PVA), is the largest synthetic water-soluble polymer produced in the world based on volume. It is produced commercially by the hydrolysis of poly vinyl acetate (PVAc). Composites prepared by blending of comparatively rigid poly vinyl alcohol (PVA) with rather compliant poly vinyl acetate (PVAc) show attractive strength-deformation characteristics which change significantly with PVA/PVAc proportions. To improve mechanical and other properties PVA is blended with different synthetic polymers.

The aim of this study was to evaluate the influence of nanoparticles on the elastic modulus of PVA/PVAc blends by using response surface methodology (RSM). RSM include approximate model and the plan of experiments where the response has to be evaluated. A 3 level Full Factorial Design was employed for designing the plan of experiment.

Three design variables (montmorillonite clay (MMT), microcrystalline cellulose (MC) and PVA/PVAc ratio) and 27 experiments were selected for study. In the each point of plan of experiment PVA and PVAc composite films were prepared and tested. The specimens were prepared by casting two-component water-based system blends: a solution of the rigid PVA and emulsion of compliant plasticized PVAc. Natural fillers - montmorillonite clay (MMT) and microcrystalline cellulose (MC) were added to PVA/PVAc blends. Diethylene glycol was used as plasticizer for both polymer components. The tensile tests were carried out by a Zwick/Roell universal testing, according to EN ISO 527. The mathematical relationship of elasticity response on the corresponding factors is expressed by the second-order polynomial expression.

It was concluded that adding nanofillers to the PVA/PVAc compositions will have an enormous effect on the tensile properties. The higher values of the elastic modulus show systems with equal content of polymers in the blend. Regardless of PVA/PVAc content relationships, the higher modulus values present systems that contain both fillers. For PVA/PVAc systems with a constant amount of MC, modulus values increases proportionally to the increase of the amount of MMT.

Acknowledgement

This work has been supported by the European Social Fund within the project 2013/0017/1DP /1.1.1.2.0/13/APIA/VIAA/06.
Damage Identification in Polymer Composite Beams Using Spatial Continuous Wavelet Transform and Mode Shape Curvature Squares

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Composite materials possess superior stiffness and strength properties as compared to the conventional materials, therefore composites are exploited in a variety of engineering applications, such as aircraft, automobiles, sporting goods and electronics. On the other hand, mechanical properties of composites may be heavily deteriorated by the presence of damage which may grow as a combination of such failure modes as matrix cracking, fibre pull-out, fibre fracture, fibre-matrix debonding and delamination between plies. Damage of any structure may cause failure, leading to tragic consequences but it is especially true for engineering structures, such as buildings, bridges, dams, stadiums, tunnels, automotive and aerospace facilities. As a result, non-destructive structural health monitoring (SHM) methods have become an important research area in civil, mechanical and aerospace communities.

Numerous vibration-based methods for damage detection are proposed. These methods are based on the fact that dynamic characteristics, namely, natural frequencies, mode shapes and damping are directly related to the stiffness of the structure. Therefore, changes in these characteristics will also indicate changes in stiffness. Many studies have shown that mode shapes and corresponding mode shape transformations are highly sensitive to damage and can be used for damage detection and quantification. However, the major drawback of those methods is a need for the data of healthy structure, which sometimes can be difficult or even impossible to obtain. To overcome this shortcoming, wavelet transform technique is suggested as one of solutions. It originated in 1980’s and was mainly used for signal singularity detection, signal denoising, image compression to name a few. Later in 1990’s wavelet transform technique was used on vibrational data for damage detection for the first time. Wavelet transform is simply a mathematical tool to transform the original signal into a different domain where additional data analysis becomes possible, therefore damage-affected signal portion is revealed.

In this paper a method based on wavelet transform technique for damage detection and localization in beam structure is described and compared to well-known mode shape curvature squares (MSCS) method. MSCS method is based on a principle that the mode shape curvature of a healthy structure has a smooth surface and it can be interpolated with Fourier series approximation. Damage index is defined as the absolute difference between the measured curvature of the damaged structure and smoothed approximation representing the healthy structure. Applicability and effectiveness of the proposed algorithms are demonstrated experimentally on carbon/epoxy polymer composite beams containing single mill-cut damage.
CHARACTERIZATION OF BIODEGRADABLE POLYMER AND CALCIUM PHOSPHATE NANOCOMPOSITE FOR ORTHOPAEDIC APPLICATION

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Bioresorbable materials are widely used for bone fixation and repair applications overcoming the need of a second surgery for implant removal after the bone heals in comparison with metallic implants. Hydroxyapatite (HAp) and tricalcium phosphate (TCP) are one of the most used implant materials in the reconstructive surgery to repair damaged hard tissues¹. Calcium phosphates (CaP) have excellent biomaterial properties due to their similarity to the inorganic component of the bone matrix. However, their clinical applications are restricted because of inherent brittleness and poor shape ability². To capitalize the advantages and overcome drawbacks of CaP, it is combined with biodegradable polymer (e.g. polylactic acid, polycaprolactone) to generate biocomposite material. Calcium phosphate and biodegradable polymer composites have received a great deal of interest in orthopedic and dental applications, which is attributed to their good osteoconductivity, biodegradability and high mechanical strengths.

CaP powder was prepared by wet chemical precipitation synthesis method from calcium oxide and orthophosphoric acid solution³. Biodegradable polymer and calcium phosphates composites were manufactured using novel liquid/solid suspension technology. Polymer and CaP composites with various CaP contents (ranging from 90 wt% up to 50 wt%) were obtained. Fourier-transform infrared spectroscopy (FT-IR) was used to determine the various functional groups in the composite samples. Compressive strength of fabricated composites was measured at ambient temperature. The crosshead was run at 0.05 mm/min. The wettability of the composite material was examined by the static sessile drop method. The degradation behavior was performed according to the ISO 10993-14 “Biological evaluation of medical devices”.

Composite strength can be adjusted by varying polymer amount in the composite. Highest compression strength of 120 MPa is achieved for composites with 10 wt% polymer. The wetting ability of composite is promising for the cell adhesion. Increasing polymer weight fraction in composite from 10 wt% to 50 wt%, the contact angle increases from 10° to 70°. In vitro evaluation of composite showed that the dissolution of the CaP component is not strongly affected by the presence of biodegradable polymer, at least not at short immersion time.

Acknowledgements: This work has been supported by the M-ERA.NET within the project “Tough, Strong and Resorbable Orthopaedic Implants” (GoIMPLANT).

References:

MODIFICATION OF CARBON NANOTUBES WITH IONIC LIQUIDS AND CHARACTERIZATION OF MECHANICAL AND THERMAL PROPERTIES OF POLYETHYLENE BASED NANOCOMPOSITES

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In recent years increasing attention is devoted to the development of conductive nanofiller (generally single-wall carbon nanotubes, multi-wall carbon nanotubes (MWCNTs) and graphene) containing thermoplastic and thermosetting polymer nanocomposites for broad range applications in electrotechnics, electronics, energetics, transport, structural engineering, medicine and elsewhere. At the development of these multiphase systems especial attention is devoted to the improvement of interfacial interaction between the carbonaceous nanofiller and polymer matrix. This is an important prerequisite for development of high-performance materials for the above mentioned application areas. Consequently this research is devoted to functionalization of MWCNTs with surface active imidazolium ionic liquid (IL) incorporating hexadecyl moieties for enhancing the dispersion of the nanofiller in the of polyethylene (PE) matrix. ILs with different hydrocarbon chain lengths have been used. Initially IL-MWCNT-PE masterbatches have been obtained by using solvent based approach. Consequently masterbatches have been melt compounded with PE matrix ensuring that the nanofiller concentration ranges from 0 to 10 wt.%

Rheological, mechanical, dielectric and thermal properties of the developed PE composites have been investigated by using rotational viscometry, stress-strain analysis, dynamic mechanical thermal analysis, broadband dielectric spectroscopy, differential scanning calorimetry, thermogravimetric analysis and laser flash analysis. The results of analysis showed an increase of mechanical properties, electrical conductivity, thermal conductivity and thermal stability of IL-MWCNT-PE composites along with raising the nanofiller content in the polymer matrix.
TRIPLE COMPOSITE CONTAINING LIGHTLY CROSS-LINKED POLYCATIONIC GEL, STAR-SHAPED POLY(ACRYLIC ACID), AND CATIONIC SURFACTANT

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To date, the interactions of lightly cross-linked charged gels with oppositely charged species have been studied thoroughly. These reactions result in the formation of new compounds, interpolyelectrolyte complexes. It was found recently that lightly cross-linked cationic network, poly(N,N-diallyl-N,N-dimethylammonium chloride), can sorb star-like poly(acrylic acid) with formation of interpolyelectrolyte complex in the whole gel volume.

In the present work, more complicated ternary systems including interpolyelectrolyte complex of cationic gel with star-like polyanion, and positively charged surfactant were studied. It was shown that interpolyelectrolyte complex is able to sorb positively charged surfactant. This process is accompanied with formation of a new complex between star-like polyanion and cationic surfactants in the gel volume, here, the charged network fragments are released from the interaction with oppositely charged polyelectrolyte, and the significant increase of the sample swelling ability is observed. The structure of triple component composite formed was studied with X-ray scattering technique. Thus, one can obtain the polymer-colloidal composite, having a matrix of swollen charged gel filled with polymer-surfactant complex particles.

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VULCANIZATION AND PROPERTIES OF EBONITE COATINGS FILLED WITH DEGRADED POLYETHYLENETEREPHTHALATE

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Increase of polymer packaging production results in accumulation of nondegradable waste, which causes environmental problems. A considerable amount in the whole bulk of polymer packaging is taken by polyethyleneterephthalate (PET) [1].

The paper is aimed at studying the possibilities of using powdered destructant PET (bulk density 368 kg/m 3), obtained by its chemical decomposition in water-ammonia liquor as a filler of fluidal ebonite composites used for obtaining protective coatings.

Oligobutadienediol (OBD) with \( M_r = 4638 \) g/mol, Brookfield viscosity of 26.9 Pa·s (25°C) and containing 0.421 mmol/g of hydroxyl was used as a cohesive base for ebonite composites. Composite precure was performed with «PM-200» diisocyanate.

Vulcanization into the state of ebonite was performed with sulfur in the quantity of 50 weight parts for 100 weight parts of OBD with accelerators diphenylguanidine and 2-mercaptobenzothiazole at 150°C in a hot air bath under atmospheric pressure.

Optimally vulcanized ebonite filled with degraded PET is characterized by tensile up to 100 MPa, adhesion to iron >5 MPa when tearing off and chemical resistance in 20% sulfuric and hydrochloric acids (mass variation 0.02% and 0.04% correspondingly).

The results of the carried out research have shown the possibility of using chemically degraded PET as a filler of ebonite compositions for protective coatings of high strength, adhesion and chemical resistance.

References:

CELLULOSE ACETATE FIBER MATS FOR ACTIVE FOOD PACKAGING APPLICATIONS

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²Department of Environmental Technologies, Kaunas University of Technology, Kaunas, Lithuania
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Over the past decades, active food packaging materials, including those containing antimicrobial agents or antioxidants, have been developed and have become a center of interest [1]. In active releasing systems components migrate from the packaging material to the packed food with the aim to extend shelf-life or improve the quality of the packed food [2]. One of the most common approaches is based on the release of volatile antimicrobial agents from the packaging material such as essential oils, or other non-volatile antimicrobial agents, such as silver ions. This is due to the increasing number of health-conscious consumers who prefer minimally processed foods [1].

Food science research has increasingly focused on using polymer nanofibers in the area of active packaging. Electrospinning is an interesting technique for the production of fibers for food packaging applications. It has a great advantage of producing fibers with a large surface area/volume ratio. The electrospinning process is simple, and the required equipment is affordable. Further, since e-spun fibers offers a high surface/volume ratio, only a small amount of polymer sample is needed to produce a fiber mat. Electrospun fibers may be given additional functionality by incorporating functional compounds such as essential oils or silver.

The objective of this research was to produce e-spun fiber mats containing bioactive components and to investigate their antioxidant properties as well as the effectiveness of the mats on inhibition against some foodborne pathogens.

Acknowledgement

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References

Starch is a natural polymer with the advantages of being renewable, biodegradable, and abundant, also of relatively low cost. It is used in many food and industrial products [1]. The starches can be modified physically and chemically [2]. In this work cationic starch (CS) flocculant based on native wheat starch was obtained by two steps, first step was chemical modification by semi-dry method and the second one – physical modification of cationic starch by extrusion process. CS was obtained by etherification with EPTMAC in presence of NaOH [3]. The granular morphology was preserved. The nitrogen content in CS was estimated by the Kjeldahl method and degree of substitution was obtained 0.26. Such CS was processed by mechanical treatment using shear forces and temperature. Extrusion of CS mixture (21% water content and 30% of sorbitol by dry mass of CS) was done with twin screw extruder (Kraus Maffei, Berstorff, Germany) at the same flow rate, only the temperature differs from 80 to 110 °C. Characteristics and the flocculation efficiency of modified starch after gelatinization treatment (CS_gel) or/and extrusion (CS_extr80-110) were examined (Table).

Table. Characteristics and flocculation efficiency of modified cationic starch

<table>
<thead>
<tr>
<th>Sample</th>
<th>Extrusion temp., °C</th>
<th>A, %</th>
<th>d, nm</th>
<th>PI</th>
<th>Flocculation efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C_{min} (mg/g)</td>
</tr>
<tr>
<td>CS_gel</td>
<td>-</td>
<td>13±0.8</td>
<td>-</td>
<td>-</td>
<td>17</td>
</tr>
<tr>
<td>CS_extr80</td>
<td>80</td>
<td>37±1.8</td>
<td>837±80</td>
<td>0.360</td>
<td>7</td>
</tr>
<tr>
<td>CS_extr90</td>
<td>90</td>
<td>40±2.3</td>
<td>673±162</td>
<td>0.293</td>
<td>5</td>
</tr>
<tr>
<td>CS_extr100</td>
<td>100</td>
<td>55±2.2</td>
<td>464±9</td>
<td>0.218</td>
<td>4.3</td>
</tr>
<tr>
<td>CS_extr110</td>
<td>110</td>
<td>65±4.7</td>
<td>521±49</td>
<td>0.281</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Particle size (d) was measured using a DelsaNano C instrument and flocculation experiment was done using model kaolin suspension – the residual turbidity was measured [3]. From obtained results we see that with increasing temperature on extrusion process the availability for polyanions (A, %) of cationic groups on CS increases from 37 to 65% meanwhile the size of particles decreases. Also the flocculation efficiency is higher, minimum required dose (C_{min}, mg/g) declines – the flocculant dose of CS_extr110 is 5 times less than CS_gel, with higher temperature and flocculation window (W) is still broad – decreases only 3 times.

Acknowledgement

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References:
ADSORPTION OF VANILLIC ACID ON CATIONIC CROSS-LINKED STARCHES

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Polyphenols (PPH) are naturally occurring compounds found largely in the fruits, vegetables, cereals and herbs. They are classified into different groups according to the number of phenol rings and structural elements that bind these rings. The main classes include phenolic acids, flavonoids, stilbenes and lignans [1]. PPH have recently attracted great interest in the functional foods, nutraceutical and pharmaceutical industries, due to their potential health benefits to human. However, the effectiveness of PPH depends on preserving the stability, bioactivity and bioavailability of active ingredients. One of the ways to protect the anionic PPH could be the formation of complexes with polymers having cationic groups. As adsorbents of anionic compounds [2, 3], cationic cross-linked (CCS) starches could be used to form a complex with anionic PPH such as vanillic acid (VA). In this case, the adsorption occurred due to electrostatic interaction between the positively charged groups of the adsorbent and anions of the adsorbates.

The aim of present work was to investigate the equilibrium adsorption of VA on CCS with quaternary ammonium groups; to evaluate VA released from complexes. The equilibrium adsorption of VA on CCS derivatives containing quaternary ammonium groups was investigated at temperatures of 30 oC, 40 oC, 60 oC. The Langmuir, Freundlich, Dubinin–Radushkevich and Temkin adsorption models were applied to describe the adsorption isotherms of VA (Table 1). The thermodynamic parameters of the adsorption were calculated. The release of adsorbed VA into the buffer solutions was also evaluated.

Table 1. Influence of temperature on parameters of adsorption models for adsorption of VA on CCS

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Q_L, mmol/g</th>
<th>K_L, l/mol</th>
<th>E_F, mol/ekv</th>
<th>R^2</th>
<th>K_F, l/mol</th>
<th>E_DDR, kJ/mol</th>
<th>R^2</th>
<th>ΔE_T, kJ/mol</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.651</td>
<td>3441</td>
<td>0.34</td>
<td>0.9844</td>
<td>2.42</td>
<td>8.9·10^{-3}, 0.9916</td>
<td>11.3</td>
<td>0.9963</td>
<td>33.0</td>
</tr>
<tr>
<td>40</td>
<td>0.794</td>
<td>2115</td>
<td>0.43</td>
<td>0.9869</td>
<td>2.83</td>
<td>5.4·10^{-3}, 0.9896</td>
<td>11.6</td>
<td>0.9890</td>
<td>27.5</td>
</tr>
<tr>
<td>60</td>
<td>0.703</td>
<td>1663</td>
<td>0.38</td>
<td>0.9934</td>
<td>3.00</td>
<td>4.2·10^{-3}, 0.9920</td>
<td>12.7</td>
<td>0.9900</td>
<td>32.2</td>
</tr>
<tr>
<td>30</td>
<td>-</td>
<td>-</td>
<td>0.89</td>
<td>0.9386</td>
<td>0.9821</td>
<td>5.8, 0.9757, 5.1</td>
<td>0.9875</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>-</td>
<td>-</td>
<td>1.06</td>
<td>0.1575</td>
<td>0.9938</td>
<td>6.4, 0.9933, 6.0</td>
<td>0.9894</td>
<td></td>
<td></td>
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<tr>
<td>60</td>
<td>-</td>
<td>-</td>
<td>0.69</td>
<td>1.7676</td>
<td>0.9916</td>
<td>6.4, 0.9903, 4.5</td>
<td>0.9754</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Acknowledgment. The authors are grateful to the Research Council of Lithuania for the financial support of the project MIP-055/2015.

References
INVESTIGATION OF LONG-LASTING TEXTILE RELAXATION RATE

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Mechanical behaviour of various polymer materials (textiles, leather, films and etc.) is one of main important properties for their usage. The main problem in stress relaxation investigation is a very long time of measurements for each kind of textiles especially if users need to know behaviour of textile in long time usage. Usually researches investigate not very long-lasting relaxation, but only relax till some hours, but the long-lasting relaxation for usage is very important also. On the other hand, an investigation of such long-lasting relaxations takes from researches a high time and is not popular due to that.

After analysing of known investigations it can be noted that dependence of relative stress relaxation \( \frac{P}{P_0} \), which characterizes a rate of relaxation, on logarithm of the time \( \log(t) \) is not linear. This phenomenon complicates a long-term stress relaxation prediction by short time investigations [1-2]. Earlier it was found, that the curve of stress relaxation properties can be divided into two linear curves. The point in which stress relaxation behaviour change character was named as break-point of relaxation. In this paper we try to prove the existing of such break-point of stress relaxation and to describe definite time of break-point for polyester multifilament 29.4 tex yarns.

The stress relaxation tests were provided on Zwick/Roell universal testing machine operated by the programme testXpert® at the gauge length was 500 mm. The tensile speed – 500 mm/min, all the testing time \( t = 200 000 \) s. The relaxation process of materials was investigated by fixed elongation method, i.e. the test specimens were stretched up to 10 % and stresses have been measured.

![Figure 1. Describing of relaxation process of polyester yarn: 1 – described by one straight line, 2 – described by two straight lines (21 - line of first part (\( \log(t)\leq2 \)), 22 – line of second part (\( \log(t)\geq2+5.3 \)))](image)

Long-lasting relative stress relaxation \( \frac{P}{P_0} \) of polyester yarns can not be described as linear dependence on logarithm of the time \( \log(t) \). After 100 seconds the rate of relaxation changes and becomes lower. The method of describing of stress relaxation by two linear dependences with break-point very well describe process of long-lasting relaxation and can be used for practical prediction of residuals stresses after very long time of relaxation (Fig.1). Our experiments confirms that the rate of relaxation is not constant and after some time changes.

References:

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THERMOPLASTIC CELLULOSE ACETATE FILMS FOR ACTIVE FOOD PACKAGING APPLICATIONS

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About 50% of Europe’s food is packed in plastic packaging [1]. After their intended use, plastic packaging materials are often contaminated by foodstuff, so recycling these materials is impracticable and most of the times economically not convenient [2]. Packaging materials can be manufactured from synthetic polymers, although the use of polymers will be more desirable when they do not cause a negative environmental impact due to disposal. The environmental impact of plastic waste is an area of growing concern. Biodegradable plastics offer a possible alternative to the traditional non-biodegradable plastics, especially in short life-time application and when their recycling is difficult and/or not economical [3]. Bio-based polymers are moving into the mainstream and the polymers that are biodegradable or based on renewable “feedstock” may soon be competing with commodity plastics. Therefore, bioplastic demand is on the rise and is expected to grow.

Cellulose is attracting interest as a substitute for petroleum feedstock in making plastic in the commercial market [4]. Cellulose derivatives like cellulose acetate are produced through esterification of cellulose and could be used to make plastic packaging materials. The main drawback of cellulose acetate is that the melt processing temperature exceed decomposition temperature. This dictates that cellulose acetate needs to be plasticized.

The objective of the present research was to develop thermoplastic cellulose acetate packaging material incorporated with antimicrobial agents (active films). Biodegradable, thermoplastic and active cellulose acetate films were fabricated using eco-friendly and food-grade plasticizers. The effect of different plasticizers on the flow properties of a polymer melt, mechanical properties and thermal properties of the bioplastic films have been evaluated.

Acknowledgement. The authors are grateful to the Research Council of Lithuania and National Paying Agency under the Ministry of Agriculture for financial support of the project MT1131.

References

POLYVINYL ALCOHOL – POLYVINYLACETATE COMPOSITE FILMS FROM WATER SYSTEMS: FORMATION, STRENGTH-DEFORMATION CHARACTERISTICS, FRACTURE

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The object of investigation was thin (< 200 μm) films, formed by casting from water based mixtures of polyvinyl alcohol (PVA) water solution and polyvinyl acetate (PVAc) water suspension. So starting systems essentially was suspensions of plasticized PVAc particles (1-5 μm in diameter) in PVA water solution. Systems with full range of PVAc volume fraction \( \phi_{PVAc} \) were studied.

Kinetic relationships of several parameters which characterize film formation in drying process (water removing, decrease of volume and thickness of drying layer, viscosity growth of PVA solution, reducing of distance between PVAc particles etc.) were compared and scrutinized.

It was found that up to \( \phi_{PVAc} = 0.7 \) the structure of composite is simply not deformed PVAc particles, which are more or less evenly distributed in PVA matrix. The main factor which restrains coalescence of PVAc particles is high viscosity of PVA water solution at the final stage of composite structure formation.

At higher \( \phi_{PVAc} \) values PVAc particles come in more close contact and change the shape. The same complex of interfacial forces, which determines structure formation in pure PVAc water suspensions, plays now crucial role. The difference is that instead of water there is the PVA water solution, whose surface tension and viscosity significantly changes during the drying process. Nevertheless PVA stays to be the continuous matrix in the final structure.

In tensile deformation conditions systems PVA-PVAc behaves as being PVA matrix composites in a whole range of PVAc content, up to \( \phi_{PVAc} \leq 0.9 \).

The dependence of composite tensile elastic modulus \( E_{COMP} \) on \( \phi_{PVAc} \) is very close to additive one: \( E_{COMP} = E_{PVA} - (E_{PVA} - E_{PVAc}) \phi_{PVAc} \). Composite essentially is a rigid PVA frame \( (E_{PVA} = 2.3 \text{ MPa}) \) containing included much more compliant PVAc particles \( (E_{PVAc} = 0.3 \text{ MPa}) \).

Use of Kerner approach, based on the self-consistency idea [1], for the analysis of \( E_{COMP}(\phi_{PVAc}) \) relation, confirms the continuity of PVA matrix.

Correlation analysis of characteristics, obtained from stress–strain relations for composites with various PVAc content (values of yield, maximum and ultimate stress, respective elongation values and others) shows that fracture of composites starts with break of less deformable load-bearing PVA frame at comparatively small elongation and continues with significant deformation of PVAc component. This feature becomes more pronounced with increase of PVAc content.

The results of this study led to a slight change in the data interpretation of the work [2].

References:
THE OXYPROPYLATION OF LIGNIN FRACTIONS, ISOLATED BY
SEQUENTIAL FRACTIONATION OF WHEAT STRAW LIGNIN
AND CHARACTERISTICS OF LIGNOPOLYOLS OBTAINED

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Lignin is a three-dimensional amorphous biopolymer formed by three major
monolignols (p-coumaryl, coniferyl and sinapyl alcohols) with different ratios, linked
together by various types of ether and carbon-carbon bonds. Native lignin in biomass has a
complex structure with a high degree of condensation and heterogeneity. The structure of
lignin and its physical-chemical properties strongly depend on plant origin and methods of
lignin isolation. This is the reasons why utilization of lignin in high value-added products
is so difficult [1]. Due to the heterogenous feature of lignin, it’s very difficult to control
and standardize the properties and qualities of the derived products from lignin; thus
several techniques have to be used to increase the uniformity of lignins. Lignin can be
fractionated into sub-fractions by gel permeation chromatography, ultrafiltration, selective
precipitation, etc. However, these methods have high cost in large scales. The successive
fractionation of lignin with increasing hydrogen-bonding capacity solvents is an alternative
method for obtaining more uniform lignin fractions.

In this work the wheat straw Biolignin™ was successive fractionated with three
organic solvents: ethyl acetate, methylethylketone and methylethylketone/water mixture. It
was established that separated fractions of lignin are characterized by lower condensation
indices, reduced thermostability and lower content of hydroxyl groups in comparison with
parent lignins. Lignin fractions, isolated by sequential fractionation were used for
productions of liquid lignopolyols with lignin constituent content up 40 % via
oxypropylation reaction. The oxypropylation of parent and fractionated lignins was
realized in laboratory high pressure 1 L PARR reactor. The influence of lignin fraction
type and lignin/propylene oxide ratio on the viscosity, hydroxyl values of lignopolyols
obtained the content of polypropylene oxides and copolymers in them were studied. The
lignopolyols were successfully used for rigid polyurethane foams production.

ACKNOWLEDGEMENT
The financial support from 7th FP Collaborative project BIOCORE Contract 241566 is gratefully
acknowledged.

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EFFECTS OF HEMP FIBERS PRE-PROCESSING AND CONTENT ON LINEAR LOW DENSITY POLYETHYLENE MATRIX COMPOSITE PROPERTIES

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Research focused on improving physical and mechanical properties of LLDPE composites reinforced with hemp fibres. As the previous studies show, due to their polar and hydrophilic nature, natural fibres show poor compatibility with hydrophobic polymers. This incompatibility could lead to weak interfacial adhesion as well as to the non-uniform dispersion of fibres within the composite. To overcome incompatibility several strategies have been tested to enhance the adhesion between the lignocellulosic fillers and the polymer matrix. These strategies generally involve fibres modifications by physical or chemical methods.

Chemical modification of natural fibres used in this study involves various chemical treatments in order to reduce the content of hydroxyl groups and/or introduce cross-linking between the filler fibres and the polymeric matrix. 2% sodium hydroxide treatment, grafting with 5% maleic anhydride in combination with the sol-gel [1-2] fibers pre-processing were used to obtain twelve composite variants.

Surfaces of modified fibers and composites with fibres content in a range from 30 wt.% to 50 wt.% were evaluated visually and by atomic force and scanning electron microscopy. Influences of hemp fibres content and fibres pre-processing method on melt flow index, composites mechanical properties, water sorption and surface microhardness have been investigated.

Melt-flow indexes of variants fall in a range from very low (0.1 for samples with un-processed fibres) till very high (24.4 for samples with silica sol pre-treated fibres). Hemp fibres pre-treatment with alkali leads to the reduction of LLDPE composite tensile strength and Young’s modulus, cross-linking by 5 wt.% MAPE allows to improve composite tensile strength.

Natural fibres have a tendency to absorb water, but research results show that it is possible to decrease the amount of absorbed water thanks to chemical pre-processing of fibres; it has a positive impact on total composite exploitation results. Water sorption after 438 h varies in range 8.28 (30 wt.% sample with un-processed fibres) to 21.65 (50 wt.% sample with un-processed fibres) and increases with the increase of the fibre content from 30 to 50 wt.%.

Surface microhardness ratio of composites is decreased by chemical pre-processing of fibres and varies in range 51.20 (30 wt.% sample with un-processed fibres) to 344.77 (50wt.% sample with silica sol pre-treated fibres).

References:

INVESTIGATION OF COMPOSITE MATERIAL PROPERTIES, BASED ON SCRAP TIRES AND POLYURETHANE-TYPE BINDER, UNDER DIFFERENT CROSSLINKING CONDITIONS

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It is a common knowledge that the most promising way of scrap tires reuse is in combination with polymer binder and production of composite materials [1-3].

The authors have previously conducted studies of composition and technology of manufacturing composite material using mechanically grinded scrap tires and polyurethane type binder. It was found that mechanical properties of the composite material are highly dependent not only on the composition of material and the type of polymer binder used, but also on specific technological parameters such as moulding pressure, formation time, relative air humidity, temperature etc. [4-6].

The objective of this paper is to additional investigation of selected properties of the composite material based on scrap tires and polyurethane type polymer binder with defined reactivity (~NCO group content 2.4%) under specific circumstances, potentially affecting polymer binder and therefore composite material properties, - water content in the rubber crumb. It is well known [7] that environmental moisture content directly affects the hardening degree of polyurethane polymers containing isocyanate groups, due to degree of change of polymer crosslinking.

The Shore C hardness (ISO 7619, ISO 868), apparent density AD (LVS EN 1602), compressive stress at 10% deformation $\sigma_{10}$ and compression modulus of elasticity E (EN 826) in correlation with the composition (wt.%) of composite material were investigated. Special attention was turned to investigation of volume components of the composite material, with different content of the polymer binder and presence of water in rubber crumb.

Obtained results showed that mentioned above properties of the composite material are highly dependent on rubber crumb treatment with water. It was estimated, that rubber treatment with water leads to increase of Shore C hardness, tensile strength and compression modulus of elasticity of composite material due to intensification of crosslinking and hardening processes of polyurethane binder, independently from the content of the polymer binder in the composite material.

Purposful selection and mutual combination of technological parameters, including moisture content in rubber crumb, can ensure predictable mechanical properties of the composite material based on scrap tires and polyurethane-type binder.

References
SOME EXPLOITATION PROPERTIES OF WOOD PLASTIC COMPOSITES (WPC) BASED ON HIGH DENSITY POLYETHYLENE (HDPE) AND PLYWOOD PRODUCTION WASTE

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During last 20-30 years many researchers have paid attention to studies of exploitation properties of wood polyolefine composites (WPC) [1]. The most useful from the wide selection of polyolefines are high density polyethylene (HDPE) or polypropylene, but as reinforcement of WPC different waste materials comprising lignocellulose fibres often are used. Such materials also are a lot of waste which arises for example in plywood production industry. In this work for reinforcing of HDPE we approbated one of the waste product- plywood sanding dust (PSD), which contain wood fibres fractions with different length (l). The main fraction (68%) are fibres with length l=0.25-0.5 mm. Our previous studies [2] showed that PSD is promising filler for PP reinforcing. Additions of the PSD up to 40 wt.% increases tensile and flexural modulus, but decreases deformation ability of PP matrix, impact strength, water resistance and fluidity of composite melts. Modification of composites with interfacial modifier maleated polypropylene (MAPP up to 5–7 wt.%) considerably improve all the above-mentioned properties. Very popular matrix for preparing WPC also are different types of recycled HDPE [3]. The goal of this study is to determine PSD influence (30, 40, 50, 60 wt.%) on virgin HDPE (type Liten PND 33-300, MFI=15.58g/10min.) containing WPC physical-mechanical and other exploitation properties. As interfacial modifier Licocene PP MA-7452 (1,3,5 wt.%) and polyvinylbutiral (PVB 5,10 wt.%) were used. Composites were prepared by mixing on two rolls mill, then cooled, granulated and pressed in 1 mm thick sheets for microhardness measurements by Vikers M-41. Flexural and impact strength tests were done for standard specimens (EN ISO 178 and ASTM D 256 M respectively), bars produced by injection moulding. Melt fluidity (melt flow index-MFI) was estimated by standard ASTM D 1238. Water resistance measurements were done according to standard ASTM D 570-88. From our studies as optimal composition of the composite containing PSD was chosen HDPE+50 wt.% PSD (A) what showed the best physical mechanical properties. Additions of the MAPP and PVB to HDPE+50 wt.% PSD considerably improve all exploitation properties of this composite. Flexural strength increase up to 28.98 MPa (3 wt.% MAPP) and modulus up to 2161.5 MPa (10 wt.% PVB). Impact strength properties was optimal at 3 wt.% MAPP concentration. At the same time these composites melts maintain rather good fluidity (MFI values are 2.65 and 2.4 g/10 min.). The greatest microhardness shows composites containing 50 wt.% PSD (112.96 MPa) and 50 wt.% PSD + 3wt. % MAPP (155.26 MPa). Additions of interfacial modifier (3-5 wt.% MAPP) also promote the increase of water resistance. SEM pictures shows positive influence of the MAPP on strengthening of the investigated composites.

References


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THE COATING WITH REDUCED FLAMMABILITY FOR LINEN FABRICS

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Over the last decade’s flax fabrics are reverting as draperies, curtains and other interior materials. The necessity for reduced flammability of such textiles has been increased by governmental legislations in many countries [1]. It is noticeable, that hazards may occur by fires as the combined effects of smoke and toxic gases. Standards and codes of human safety based on recognized general requirements of fire protection are obligatory for lot of textile materials used in building, transport, construction, home and protection garments [2]. All fabrics will burn with some being more combustible than others. The burning rates can be reduced with flame retardants (FR), applied through treatment [3] with chemicals, such as inorganic salts, mix of ammonium polyphosphates, halogen donators, expandable graphite (intumescent) etc. [1]. The choice of every individual FR and kind of treatment depends on requirements for produced material. The antimony compounds can be safely used for the textile treatment without causing a risk to human health and the environment [4].

The aim of this research is investigation of burning characteristics of Latvian local linen /the raw linen (178 g/m²) and the bleached linen (190 g/m²)/ fabrics without and with continuous coating, containing commercial printing paste Printperfect EX-TS, pigment Bezaprint GELB (both producer CHT BEZEMA) and diantimony trioxide (Sb₂O₃) as the flame-retardant additive. The flat screen method for coating of fabrics was used. The drying of coating at 100 °C 7 min, the thermal treating at 150 °C duaring 5 min. The fabrics burning characteristics were tested with the vertical and the horizontal method, in accordance LVS EN ISO 15025:2003, before and after 5 washing cycles. The abrasion resistance was determined on Taber Rotary Platform abraser, according LVS EN ISO 5470-1:2001.

The results of the burning tests show, that uncoated raw and bleached linen fabrics burn down completely. The use of investigated coatings decreases the linen fabrics flammability ~ 2 times. The positive coating effect remains after 5 washing cycles. The abrasion resistance of coatings depends on the coating thickness.

The coating with commercial printing paste Printperfect EX-TS with antimony trioxide as flame-retardant additive is applicable for linen technical textiles.

References
THE "GHOSTING" DEFECT AS THE RESULT OF INTERACTION OF THE PAPER AND PRINTING INKS, ITS PRECLUSION POSSESSIBILITIES IN THE SHEET-FED OFFSET PRINTING TECHNOLOGY

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The "ghosting" defect occurs frequently, both in the sheet and web offset printing. It increases the costs of production and negatively influences the quality of the printed products, which brings to customer complaints and their refusal to pay. This brings losses of several million EUR to the printing companies. “Ghosting” defect can be described as an increase in lightness or tonal change on one side of a print which corresponds to the motif printed on the reverse side. For the study of this problem, the printing company Livonia Print provided the material technical basis and implementation of the research results in the manufacturing process.

"Ghosting" defect in sheet-fed printing originates through the interaction of paper, the printing ink, printing-press, print-related technological parameters and printed motif.

The summarization of source material manufacturers information on paper, ink and varnish samples studied at Livonia Print Ltd. The measurement of the necessary parameters and microclimate for the sheet offset printing in the printing company. The determination of the test printing realization’s schedule, the preparation of the materials and technological equipments and test printing. The study of samples and realization of measurements for the printed sheet in the Institute of Wood Chemistry, in the laboratory of the incorporated company KvadraPak, the analysis of the results.

For the study of the ghosting defect there were selected 7 grades 130g/m² papers used in Livonia Print production’s manufacturing of the different manufacturers with different coating and with differences in furnish composition, using 4 printing inks, printing-presses – Heidelberg Speedmaster SM-102-8P and XL-106-10P, resulting in 77 printed samples of the required measurements and research.

There was carried out an acquisition of the results of technical measurements for the source materials, laboratorial study of the interaction of the physical and chemical properties, paper, inks and varnish for the experimentally printed sheets, determination of the physical and chemical changes comparing to conditions of the references. Separate ink/paper combinations differently present the “ghosting” defect. Its increase is observed at the increase of the thickness of the printing ink layers, as well as on print of both sides of sheets, when ink drying on sheet one side can affect the lower side of the paper. The origin of the “ghosting” defect in the sheet offset printing could be catalysed by the different existing drying speeds of paper printing inks. The conclusions will become the basis for the output of the recommendations packet for the manufacturers of the printing and publishing industry.

Acknowledgements
LIDA ERDF project "New Technology Development Ltd."Livonia Print" offset to fill the gaps" (Project JPA / 2.1.2.2.4 / 13/13/001); "Livonia Print" Ltd.
INFLUENCE OF MONOMER ON STRUCTURE, PROCESSING AND APPLICATION CHARACTERISTICS OF UV CURABLE URETHANE ACRYLATE COMPOSITE COATINGS

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Increased interest in the esthetical natural nail coatings have encouraged more in-depth studies particularly of UV curable coatings: their formation, processing, structure, use characteristics and removing [1, 2]. Typical requirement for nail coatings is good adhesion, but preferably for the short time of functioning (usual 2–4 weeks) [3, 4].

The objective of this study is to explore some of mentioned above aspects for UV curable system composed of urethane acrylate oligomers and diverse monomer types. The main composite ingredients (oligomers, monomers, photoinitiator) were selected to confirm the requirements of EU Cosmetic Regulation. For the film forming properties the base oligomer – tri-functional urethane acrylate oligomer were chosen. Hexa-functional urethane acrylate oligomer was added as adhesion promoter. For the initiation of radical photopolymerization reactions ethyl - 2,4,6 – Trimethylbenzoylphenylphosphinate photoiniciator was applied. Four different monomers: tertiobutyl cyclohexyl acrylate (TBCHA), ethylene glycol dimethacrylate (EGDMA), tetrahydrofurfuryl acrylate (THFA) and hydroxypropyl methacrylate (HPMA) have been tested.

200 µm film was cured under UV lamp with Luminous intensity 130mw and λ_max = 405nm for 30s. Coatings before curing were covered with PE film to prevent the inhibition influence of oxygen present in the air. After curing, PE film was removed. Tests for cured films were performed immediately after cure and 72 h after cure to assure complete polymerization.

Viscosity and flow ability experiments for uncured mixture allowed finding of two optimal monomer concentrations for further coating tests (30% and 40%). Degree of conversion, strength-deformation characteristic (tensile modulus of elasticity E, elongation at break ε_B), micro hardness HV, surface gloss G and adhesion loss A were studied for cured films. Correlation E, ε_B, HV, G and A values is discussed.

Specific coating application requires comparatively high coating flexibility and stability of mechanical characteristics. This can be achieved with 30% of monomer TBCHA, what shows the ε_B = 0.23 – 0.24, E = 670-710 MPa and comparatively constant properties in 72 hours (ΔE = 1.3%, Δε_B=6.0%). A composition with 30% of TBCHA reaches the fastest coating destruction achieving adhesion loss within 3 min. This composition could be recommended as natural nail coatings.

References

BACTERIAL CELLULOSE GEL FILMS: STUDY OF THE MORPHOLOGICAL STRUCTURE

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An increased interest to the properties and technology of bacterial cellulose (BC) is caused by it’s perspective application in pharmacology, medicine, cosmetics and food production - well developed fields in Latvia.

The main aim of the SEM studies was to determine and describe BC morphological microstructure elements, which are characteristic for all BC samples under study, and the peculiarities observed for them.

Scanning electron microscope (SEM) Vega TS5136 was used.

BC gel films were obtained using acetic acid bacteria (Acetobacter xylinum, Gluconoacetobacter hansenii) grown in culture media with varied carbon sources (glucose, fructose, etc.) and different cultivation conditions (statistical and dynamic regimes, temperature and times).

BC samples for SEM studies were taken from BC gel films, which had been treated with alkali (2-4% NaOH solution), washed with water and dried with different methods (lyophilic, inclusion, air temperature). 56 samples were analysed in total.

Obtained dried BC gel films were transparent, even and smooth. The films’ thickness was 0.1-0.3 mm depending on the bacteria growth conditions. The BC gel film is found to be a multi-layer composition. The number of layers varied from 5 to 32. The thickness of individual layers is about 0.2-1.5 µm. Each individual layer of the composition consists of cellulose fibrils (CF) and contains an amorphous substance as well. CF is the product of bacterial synthesis, which contains threadlike elements with the length up to 70 µm and a width of 50-200 nm. CF forms a parallel-netlike microstructure, which is the framework of the individual layers of the gel film. Gel films, which are formed in the glucose and fructose culture medium, contain CF with a relatively even width – 100-150 nm. By using apple juice and whey, the CF width becomes more uneven and varies from 50 to 250 nm. During the lyophilic drying, the CF network becomes looser. The amorphous substances that are not released after the gel-film’s alkali treatment and drying, forms a fine film-type layer, which covers CF. This probably represents microorganisms’ remains, their metabolites, and residual media components.

During the drying, the amorphous substances can form a compact continuous layer.

A comparison of the gel films formed in different culture media showed that the amount of the amorphous substance considerably increased in the case of apple juice and whey. The CF network has almost fully submerged into the amorphous layer.

The observed comparatively great amount of non-cellulose components in the BC gel film probably can impair the properties of BC products designed for application in medicine and cosmetology and therefore should be studied further.
PILOT SCALE PRODUCTION OF RIGID POLYURETHANE FOAMS FROM LIGNOPOLYOL FOR THERMOINSULATION APPLICATIONS

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Lignin, the most abundant natural phenolic polymer, is by-product from the pulp and paper industry and biorefineries. Lignin is mainly used as low-value fuel for heat and power production although it is a source for renewable aromatics, enriched by OH groups and therefore can be used in rigid polyurethane (PUR) foam production [1]. The synthesis of Lignopolyol by oxypropylation of wheat straw lignin was developed [2] and rigid PUR foams containing lignin was obtained in lab scale [3]. The goal of our work was to study production of rigid PUR foams obtained from Lignopolyol by semi-industrial scale 2-component spraying machine.

Rigid PUR foam formulation was developed to obtain thermal insulation material from Lignopolyol by spraying method. Rigid PUR foams with lignin content 7.6% was obtained. Characteristics of produced foams are shown in following Table.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent density</td>
<td>36 kg/m$^3$</td>
</tr>
<tr>
<td>Closed cell content</td>
<td>96 vol.%</td>
</tr>
<tr>
<td>Water absorption (7 days)</td>
<td>2.9 vol.%</td>
</tr>
<tr>
<td>Shrinkage after 24 hours</td>
<td>0.2 %</td>
</tr>
<tr>
<td>Compression strength</td>
<td>0.21 MPa</td>
</tr>
<tr>
<td>Thermal conductivity (initial)</td>
<td>18.5 mW/m·K</td>
</tr>
<tr>
<td>Thermal conductivity (after 1 month)</td>
<td>19.5 mW/m·K</td>
</tr>
<tr>
<td>Thermal conductivity (after 1 year)</td>
<td>24.0 mW/m·K</td>
</tr>
</tbody>
</table>

Both, lower thermal conductivity and water absorption of sprayed rigid PUR foams on the basis of Lignopolyol in comparison with lab sample of lignin free and Lignopolyol based foams was detected. Up-scaling did not affect compression strength, modulus of elasticity and dimensional stability. It should be emphasized relatively minimum heat insulating properties decrease in long term storage of foams.

Lignin has a great potential as raw material for rigid PUR foams as thermal insulation material. The modification of lignin by propylene oxide allows production of highly reactive Lignopolyols which can completely substitute commercially available polyether in PUR foam formulation.

Acknowledgements
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References
WETTABILITY OF MODIFIED LIGNOCELLULOSES AS A FILLER FOR POLYMER COMPOSITES

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The contact angle (CA) of lignocellulosic powder allows predicting important properties of a filled polymer composite material such as its wettability, adhesion, adsorption, etc. The contact angle and the surface free energy can be measured by the Washburn method, which is used to determine the capillary constant calculated from the penetration rate of a liquid into the compacted lignocellulosic powder, and by the Wilhelmy method based on measuring interface surface tension of the filled polymer composites. The aim of the work was to evaluate the wettability of the initial and the modified wood microparticles as well as the composite samples consisting of recycled polypropylene and the lignocellulosic microparticles, using contact angle, water sorption and Zeta potential (ζ) measurements. The contact angle was determined with a tensiometer Kruss 100M. The capillary constant (K) for each lignocellulosic powder was determined in n-heptane. The surface free energy was calculated using the approach suggested by Owens-Wendt-Kaeble. The Zeta potential of the microparticles was measured with a dynamic light scattering device Zetasizer Nano SZ. For the modification, at first, the hardwood lignocelluloses were treated with low temperature acid hydrolysis under mild conditions [1]. Then, the fractionated hydrolysed microparticles were modified to introduce the new functional groups at their surface. It was found that the hydrolysis and the modification of the lignocellulosic particles differently affect on their water wettability. While the hydrolysis of the lignocelluloses led to the increase in the negative Z potential values of the particles and the decrease in their contact angles, the modification essentially decreased the negative charge of the lignocellulosic microparticles and remarkably enhanced their contact angles in water.

The composite samples were prepared from the raw blends composed from recycled polypropylene and the lignocellulosic microparticles in the wide range of a filling degree (10-50%) by the extrusion and the moulding method using HAAKE MiniLab II and MiniJet device. The composites containing the modified microparticles were characterised by the enhanced advancing and receding contact angles, which did not dramatically decrease with the growth of the filling degree, as well as by a smaller contact angle hysteresis in comparison with the same indexes of the composites filled with the hydrolysed microparticles. All the factors indicated the improvement of the wettability of the modified lignocellulosic microparticles towards the polymer matrix. This conclusion was supported by better physico-mechanical properties of the composites filled with the modified microparticles in comparison with the same properties of the composites containing the initial and hydrolysed wood particles.

Reference

WOODY BIOMASS REMOVAL FROM WASTEWATER WITH NEW COMPOSITE COAGULANT BASED ON POLYETHYLENIMINE

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Keeping in mind the volume of the polluted effluents formed annually at woodworking enterprises and the zero waste policy for rational use of bioresources, it is very important to extract quantitatively and qualitatively the formed biomass from the effluents to achieve more its rational utilization. The effective removing of biomass will allow to return the purified wastewater in the basic technological cycle. The formed sewage sludge of woodworking wastewater as a product of the coagulation can be used successfully for soil improvement and for producing building materials or sorbents.

The plywood production wastewater generated at hydrothermal treatment of hardwood is dramatically polluted with biomass consisting of hemicelluloses, low molecular lignin and tannin fragments, wood extractives. The coagulation is one of the cheapest processes for obtaining the biomass from such type of wastewater. The aim of this work was to increase the efficiency of the coagulation process of plywood production wastewater by developing a new composite coagulant based on PEI (CCPEI). The composite coagulant represented a polymeric complex formed with PEI macromolecules and colloid particles having the reactive functional groups. The effect of the content of PEI in the coagulant, the CCPEI dosage and the pH value of the coagulation process on the biomass removal was studied.

The optimum content of PEI in the coagulant, the CCPEI dosage and the pH value of the coagulation process on the biomass removal was studied. The optimum content of PEI in the composite coagulant didn’t exceed 35%; the optimum coagulation pH values and the CCPEI dosage varied in the range of 6-7 and 75-100 mg/L, respectively. The removal of the total biomass and lignin with CCPEI was 98% and 65%, respectively, while these values for PEI were lower. The efficiency of the lignin removal from the wastewater, depending on the content of PEI in CCPEI at the different pH values, is shown in Fig.1.

Fig.1. Lignin removal from the model wastewater depending on PEI content in CCPEI at different pH

Thus, it was established that the new composite coagulant has exhibited better biomass and lignin removal efficiency from the woodworking wastewater in comparison with PEI.
NOVEL ALKYD - LINSEED OIL EMULSION FORMULATIONS FOR WOOD COATINGS

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All water-borne coatings need surfactants in order to reduce the free energy of the various interfaces of the system, thus providing kinetic stability to the formulation. Surfactants are used as binder emulsifier and as pigment dispersant, they are needed to improve wetting on low energy substrates, to control foaming during application and processing, and to prevent film defects caused by surface tension gradients (Hellgren A.-C et al, 1999). The purpose of this experiment was to obtain a water-based emulsion, suitable as a coating for wood protection and, at the same time, reduce or eliminate the presence of co-solvent, which is usually always present also in water-based coatings. The main components of this emulsion are linseed oil and an alkyd, mixed in a 1:2 ratio, and water. Alkyd and linseed oil together constitute 15% in concentration of the formulation, water is 80%. The first step of our experiment was to find a valid dispersing agent, capable to give a stable emulsion. Several surfactants, obtained from different producers were tested, the main factors considered were the nature of the surfactant and its HLB. The majority of surfactants used in coatings formulations are standard anionic and nonionic amphiphiles, such as fatty alcohol sulfates, alkylaryl sulfonates and alcohol ethoxylates. Cationic and amphoteric surfactants are rarely used. In our experiment only nonionic surfactants were used, and results confirmed that the most suitable surfactants are ethoxylated nonionic types, with a high HLB values comprised between 12.5 and 14.4, while surfactants based on gemini technology showed a poor efficiency, due to scarce solubility in water, which led to separation of phases. The components were mixed using an ultrasonic homogenizer to facilitate the dissolution of oil in water. A good achievement was the elimination of co-solvent, which is usually always present also in water-based coatings. Once the optimal emulsion composition was obtained, tests were carried out to compare the efficiency of three driers Co, Ca and Zr in the formation of film from water emulsion. Each drier was tested singularly, and added to the emulsion at the same concentration (0,10%). In an aluminum plate, 2 g of emulsion were put and let dry at room temperature to test which drier was faster in the formation of film. Quite a number of studies have been reported comparing the efficiency of different combinations of driers in both water-borne and solvent-borne alkyd paints (Van Gorkum et al., 2005), according to our results, Zr and Ca, respectively categorized as secondary drier and auxiliary drier, used alone, are not effective in promoting the cross-linking reactions in the film formation: even after a week the oil is not dried yet and it has an oily, viscous consistence. Co, which is a primary drier, has confirmed to be the most effective drier: the formation of the film is visible after 24 hours, but it’s not complete, it takes about 2 days to the complete evaporation of water.

References

PREPARATION AND CHARACTERIZATION OF POLY(URETHANE-UREA) MICROCAPSULES WITH DIFFERENT DIAMINES, DIISOCYANATES AND POLY(VINYL ALCOHOL)

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Microencapsulation enclose particles of solids, droplets of liquids, or gases in an inert shell that act as a protective barrier from external environments [1]. In fact, all the interest of microcapsules resides in the membrane. The shell can be formed by chemical or physical process [2]. Polyurethanes and polyurea polymers are emerging as useful biomaterials for biomedical applications because of their synthetic versatility, excellent mechanical properties and good biocompatibility [3].

In the present paper, we report on the preparation by the interfacial polyaddition technique in W/O emulsion of poly(urethane-urea) microcapsules (PUUMC) derived from poly(vinyl alcohol) (PVA) and three different diisocyanates: 1,6-hexamethylene diisocyanate (HMDI), toluene-2,4-diisocyanate (TDI) and 4,4’-methylene diphenyl diisocyanate (MDI) and three diamines (DA): 1,2-diaminoethane (EDA), 1,3-diaminopropane (PDA) and 1,4-diaminobutane (BDA). The maltogenic α-amylase (MG) from Bacillus stearothermophilus was encapsulated in PUUMC. The aqueous phase was PVA solution in water and the oil phase was surfactant Span 85® solution in butyl acetate. After emulsification, diisocyanate and diamine were added to the reaction mixture. Encapsulation of MG was carried out by two ways: during or after formation of PUUMC.

The structure of shell of capsules has been proven by chemical analytical methods and by FT-IR spectra. The surface area (19–86 m²/g), pore size (14–30 nm) and volume (0.12–0.44 cm³/g) of shell of microcapsules were determined by using BET and BJH methods. These parameters mostly depended on reactivity of initial components. Size and morphology of the PUUMC were evaluated by optical and scanning electron microscopy. The TGA measurements were performed to determine the thermal stabilities of shell of PUUMC as well as their compositional properties. DTGA curves show the two stage decomposition profile. The first peak in the DTGA curve indicates the decomposition of urethane and urea linkages. The second decomposition stage of PUUMC indicates degradation of polyene residues of the main chains of PUUMC.

Capsules with encapsulated MG were studied as enzyme delivery systems. MG release depends on used diisocyanate and diamine for synthesis of capsules. The efficiency of immobilization of MG during the synthesis of capsules was higher than efficiency of immobilization after their synthesis in all cases. The highest efficiency of immobilization of MG was 98 % during the synthesis of capsules from PVA, HMDI and EDA, when their initial molar ratio was 1:9:3.

References:
MODIFIED SILYL-TERMINATED POLYETHER POLYMER BLENDS WITH BISPHENOL A DIGLYCIDYL ETHER EPOXY FOR ADHESIVE APPLICATIONS

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Epoxy resins have been used successfully as adhesives for many years. Despite many advantages of epoxy resins like high strength, chemical and heat resistance, in many applications they lack flexibility. During service under dynamic stress and variable environment this may lead to cracking and even failure of the adhesive joint. To improve epoxy resin adhesive performance they can be modified with other polymers. In this work modified silyl-terminated polyether polymer (MS Polymer) was used as elastic matrix material in various mixing ratio with epoxy resin.

In the MS Polymer/epoxy blend A component consists from MS Polymer, amine catalyst, aminosilane and additional fillers. B component is based on bisphenol A diglycidyl ether (DGEBPA) epoxy resin with tin catalyst, water and fillers. When epoxy resin is mixed together with MS Polymer at the right ratio they form heterogenic matrix/domain structure which consists of the epoxy domains functioning as hard segments in elastic MS Polymer matrix [1]. When A and B components are mixed together, curing happens by epoxy reacting with amine catalyst, at the same time MS Polymer reacting with water. Aminosilane links MS Polymer with epoxy.

Tensile stress-strain characteristics according to DIN 53504 were determined by using Zwick/Roell Z010 universal testing machine.

Fracture surfaces of brittle-broken test specimens were observed by using Mira/LMU field emission scanning electron microscope (TESCAN a.s.).

MS Polymer/epoxy blends show gradual decrease in Young’s modulus E and tensile strength $\sigma_B$ by increasing MS Polymer ratio from 30 to 70%. At the same time tensile deformation $\varepsilon_B$ starts to show considerable values at MS Polymer/epoxy ratio equal or higher than 45/55. By increasing MS Polymer content to 70% increase of $\varepsilon_B$ above 60% is observed.

By considering morphology as well as the results of mechanical tests MS Polymer/epoxy ratio 60/40 was considered as the most suitable for adhesive formulation.

Acknowledgements

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References

RHEOLOGICAL, MECHANICAL AND ADHESION PROPERTIES OF TWO COMPONENT ADHESIVE BASED ON MODIFIED SILYL-TERMINATED POLYETHER POLYMER AND EPOXY RESIN

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Today an increasing interest in two component adhesive products can be sensed in the market. The driving force requesting more specific adhesive materials is automotive industry for bonding of light-weight structures or challenging designs. These requirements from industry make to seek for new raw material types to formulate adhesive systems with higher strength, broad superior adhesion spectrum and other demanding properties.

The combination of epoxy resin with modified silyl-terminated polyether polymer (MS Polymer) is supposed to deliver a two component adhesive that shows superior strength compared to pure MS Polymer based adhesives, while combining all the other positive features from both polymer resin types. In two component adhesive formulation MS Polymer and epoxy hardener are main ingredients of one component and epoxy, MS Polymer catalyst and water are main ingredients of other component. Depending on the amount of methoxysilyl groups various MS Polymer types, namely, di-functional MS Polymers (DMS) and tri-functional MS Polymers (TMS), were used.

Rheological characteristics were measured by using Bohlin CVO 100 rheometer. Instrument was equipped with 20 mm diameter spindle in plate-plate geometry with gap size 1000 μm. Tests at 23 °C were performed in oscillatory shear mode at frequency 1.5 Hz and strain 0.15. Dynamic storage G’ and loss moduli G” were recorded as functions of the reaction time.

Adhesive and tensile stress-strain characteristics were determined by using Zwick/Roell Z010 universal testing machine. Tensile tests were made according to DIN 53504. Lap shear tests were made according to EN 1465. Samples were tested after 1, 7, 14, 21 and 28 days of curing.

Cross-over modulus or gel point (t_gel) of DMS based systems was considerably different from that characteristic for TMS based systems. Since TMS polymers have additional methoxysilyl group, their t_gel ranges from 20 to 29 min, which is considerably lower than t_gel of DMS polymers, ranging from 110 to 175 min.

Stress-strain characteristics for cured MS Polymer/epoxy adhesive samples with different MS Polymer types show that, depending on MS Polymer grade, tensile stress at break σ_B can reach values over 2 MPa. Adhesive formulations containing these MS Polymer grades, however, offer lower ultimate elongations. Such strength and elongation variations, depending on MS Polymer type, may distinct potential use of the adhesive by choosing the suitable MS Polymer type.

Lap shear strength experiments to stainless steel, Al and PVC substrates have been also performed. Increase in adhesive strength was gradually rising along with progression of cure as confirmed by testing samples after 1, 14, 21 and 28 days after bonding. After 24 hours of curing the highest adhesive strength to stainless steel and PVC substrates was achieved with SAX 530 and SAX 520 MS Polymer adhesive formulations.

Acknowledgements
This work was supported by EU-Project No 2013/0070/2DP/2.1.1.1.0/13/APIA/VIAA/004
CHARACTERISTICS OF MODIFIED LIGNOCELLULOSIC FILLERS WITH FT-IR AND TITRATION METHOD

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With the aim to predict the effect of modified lignocellulosic fillers on properties of wood-polymer composites (WPC), the functional groups composition of the initial and the modified lignocellulosic particles were investigated with Fourier transform infrared spectroscopy (FT-IR) and conductometric titration in aqueous media. As lignocelluloses, by-products in the form of sawdust and bark of various wood species (pine, birch, grey alder, etc.) were used. For their modification, the desoxyamination (DEEPA) and oxyammonolysis reactions were employed. Our study has revealed that, on the average, from 2.5% to 3.8% of nitrogen may be introduced in the lignocelluloses matrix (0.6-0.9 amino groups per one phenyl propane unit) (Table 1).

It is supposed that the different amount of the introduced amino groups in hardwood and softwood is gained by the various content of lignin and wood resins [1]. With increasing the lignin content and decreasing the content of the resin, the amount of the introduced amino groups grows.

Table 1. Nitrogen content in the lignocelluloses depending on tree species

<table>
<thead>
<tr>
<th>Tree species</th>
<th>With all synthesis mixture</th>
<th>Active component DEEPA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yield of N-polymer (%)</td>
<td>N-content in N-polymer (%)</td>
</tr>
<tr>
<td>Pine</td>
<td>76</td>
<td>3.04</td>
</tr>
<tr>
<td>Grey alder</td>
<td>57</td>
<td>1.37</td>
</tr>
</tbody>
</table>

As the FT-IR spectra shown that the increase of absorption in the region 1690-1640 cm\(^{-1}\) with a maximum at 1666 cm\(^{-1}\) and the increase of absorption in the region 1600-1520 cm\(^{-1}\) with a maximum at 1556 cm\(^{-1}\) were associated with the presence of C-N stretching, and C-N-H bending vibrations in the formed amide I and amide II bonds in the modified lignocelluloses. The increase of absorption at 1640 cm\(^{-1}\) indicated the formation of the salt bonds in the lignin macromolecules of the lignocellulosic matrix due to the participation of the formed carboxylic groups in the reaction with the N-containing modifier. The presence of the new carboxylic groups in the lignocellulosic matrix during the modification was confirmed by the conductometric titration curves.

At the same time, the analysis of the main absorption bands of lignin in the spectra of the modified lignocellulosic microparticles did not indicate the destruction of the aromatic rings of lignin during the modification process.

References:

SURFACE ACTIVITY OF POLYELECTROLYTE COMPLEX NANOPARTICLES FROM LIGNIN AND CHITOSAN AND THEIR APPLICATION IN WOOD-POLYMER COMPOSITES

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It is known that alkali lignin and lignosulphonates possess surface active properties due to their amphiphilic chemical nature. They are often used for controlling the stability and rheological properties of various dispersing systems. Compared with traditional surfactants, knowledge of the behaviour of lignin and their modified products at the air-water interface is more limited. The purpose of this study was to investigate surface films, formed with polyelectrolyte complex nanoparticles (PECNs) from alkali lignin (Lig) and chitosan (Ch) at the air-water interface depending on the molecular mass of Ch, pH values of the reaction mixtures and the time of the polyelectrolyte interaction, using Langmuir technique. A non-stoichiometric polyelectrolyte complex consisting of alkali lignin (M_w = 4160) and chitosan (DD = 75-78%, M_w = 178–400 kDa) was obtained by mixing both polyelectrolytes in aqueous solutions at the defined concentrations and the defined charge ratio (n_-/n_+ <1) [1]. The sizes of the obtained water-soluble PECNs varied in the range of 60-90 nm and were significantly smaller than the sizes of the chitosan particles. This was in accordance with the obtained viscosimetric results: the values of reduced viscosity for chitosan and PECNs solutions were changed in the range of 0.8–1.2 g/dl and 0.03–0.08 g/dl, respectively, within a pH interval of 4-8. Surface pressure - area isotherms were obtained at room temperature using a KSV NIMA Langmuir through double-barrier device at a barrier speed of 10 mm/min. Before measurements, the reaction mixtures lignin/chitosan were stored in the through for 24-72 h before the (π-A) isotherms were measured. Due to the more hydrophobic structure and the compact forms of the formed PECNs, that favoured their orientation and interaction via hydrogen and hydrophobic linkages at the interface, their initial and final surface film pressure was characterised by higher values in comparison with the case of the films formed with the alkali lignin and chitosan. The high values of the final surface pressure and modulus of surface elasticity at pH 4-6 indicated that the cohesion interaction in the surface films formed with the PECNs were strong and stable. The applied method of monomolecular layers has shown that, with increasing the molecular mass of Ch, the two-dimensional pressure isotherms π-A displaced towards higher values of the surface pressure. The ultimate two-dimensional pressure registered at the maximum compression of the monolayer achieved 32-34 mN/m for the PECNs formed with a high molecular mass Ch for 72 h of storage at room temperature.

It was found [1] that, in the wood-polymer composites, PECNs composed from lignin and chitosan can perform the role of a regulator of the interfacial tension (compatibiliser). Owing to the presence of hydrophobic and hydrophilic domains in the PEC structure, it is simultaneously well compatible with the PP matrix and wood filler that promotes the homogenisation of the composite material and determines its optimum mechanical, hydrophobic and technological properties.

References
SYNTHESIS OF BLOCK COPOLYMERS BASED ON STYRENE, ISOBUTYLENE, AND D,L-LACTIDE BY LIVING CATIONIC AND ANIONIC RING-OPENING POLYMERIZATION

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The ability of block copolymers, comprising blocks of different chemical nature, to form morphologically ordered structures is widely used to create science intensive materials of high quality$^1$. The main strategy of obtaining of such materials is based on the usage of functionalized macroinitiators. This work is devoted to the synthesis of functionalized polystyrene or poly(isobutylene-block-styrene) via controlled/living cationic polymerization and their use as macroinitiators in the ring-opening polymerization (ROP) of D,L-lactide.

Functionalized polystyrenes have been synthesized in a single step by a controlled/living cationic polymerization of styrene using CumCl/TiCl$_4$/pyridine initiating system in CH$_2$Cl$_2$/n-hexane mixture at $-78^\circ$C followed by quantitative end-capping of living polystyrene chains with 4-phenoxy-1-butanol$^2$ (Scheme 1). A number of well-defined hydroxyl-terminated polystyrene macroinitiators with controlled molecular weight ($M_n$=4300–17700), narrow molecular weight distribution ($M_w/M_n$≤1.9), and quantitative functionality ($F_n$>95%) have been obtained. Similarly, hydroxyl-terminated poly(isobutylene-block-styrene) macroinitiators with controlled molecular weight ($M_n$=18900–29500), narrow molecular weight distribution ($M_w/M_n$≤1.7), and quantitative functionality ($F_n$>80%) have been obtained. Further, PSt-OH was used for ROP D,L-lactide.

A number of poly(styrene-block-D,L-lactide) block copolymers with controlled length of poly(D,L-lactide) ($M_n$=12000–17000) and narrow molecular weight distribution ($M_w/M_n$ ≤ 1.70) have been synthesized. Further research directed to the synthesis of poly(isobutylene-block-styrene-block-D,L-lactide) copolymers is currently in progress.

Acknowledgements. This work was supported in part by Belarusian Republican Foundation for Fundamental Research (project X15PM-041).

References:

CONTROLLED RING-OPENING HOMO- AND COPOLYMERIZATION OF CYCLIC ESTERS BY IMINOPHENOLATE ZINC COMPLEXES: EFFECT OF THE IMINO SUBSTITUENTS ON THE CATALYTIC ACTIVITY

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During the past 2 decades biodegradable (co)polymers from lactones or lactides due to their good mechanical properties have received increasing interest for use in biomedical applications such as surgical sutures, drug delivery systems, tissue engineering scaffolds and in the production of environment friendly polymer materials. Nowadays a particular attention is paid to the synthesis of functionalized polyesters due to the possibility to use them as building blocks, macromonomers or macrorinitiators for obtaining more complex macromolecular architectures (star-shape, graft copolymers and etc.).

In this work, new zinc complexes with phenoxy-imine ligands modified by unsaturated alcohol (1a-1c, Scheme 1) or simple amido derivatives N(TMS)2 (2a-2b, Scheme 1) were tested as catalysts in the ring-opening polymerization of ε-caprolactone and D,L-lactide in bulk at different temperatures.

The influence of ligands structures, substituents in ligands and polymerization conditions (temperature, catalysts concentration) on catalysts activity have been studied in detail. The complexes 1a-1c demonstrated quite high activity affording polyesters with acceptable content of vinyl end groups (Fₙ up to 65%), controlled molecular weight (Mₙ~1000–80000 g/mol) and narrow molecular weight distribution (Mₘ/Mₙ≤1.7). Compounds 1a, 1b initiate ring-opening polymerization of ε-caprolactone at mild reaction temperatures (65…80 °C), while complex 1c is required to use higher temperatures (100…130 °C) to provide high catalyst activity. Both complexes 2a, 2b were found to be active catalysts for the ROP of ε-caprolactone and D,L-lactide (reaction temperature 100–130°C), providing polymers with expected molecular weight (Mₙ~1000–40000 g/mol) and narrow molecular weight distribution (Mₘ/Mₙ≤1.9).

Acknowledgment. We thank Belarusian Republican Foundation for Fundamental Research (X15PM-002) for financial support.
NEW TRITERPENE-CONTAINING COPOLYMERS: SYNTHESIS AND BIOLOGICAL PROPERTIES

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Triterpene derivatives of lupane type are of significant interest due to the broad spectrum of their biological properties and availability of nature compound – betulin. Betulin and its derivatives can be used as medical drugs. Betulinic and betulonic acids have proved to possess antitumoral and antiviral activities [1-3]. That is why triterpene introduction into soluble polymer matrix is undoubtedly of present interest.

It was found that betulin reacts with vinylacetic and vinylbenzoic acids with formation of 28-O-ethers of betulin (Scheme).

![Scheme. Synthesis of 28-O-ethers of betulin.](image)

These ethers of betulin were found to be not homopolymerized but copolymerized with N-vinylpyrrolidone (VP), vinylacetate (VA), acrylonitrile (AN) in the presence of free-radical initiators.

It was determined that at copolymerization of new ethers of betulin with VP and AN in the conditions of free-radical initiation the copolymers are characterized by statistical distribution of monomer units. The peculiarity of the copolymerization of new ethers of betulin with AN is a high tendency of the comonomer units toward alternation in the polymer chain.

The structure of new copolymers was identified by IR, $^1$H and $^{13}$C NMR spectroscopy. The copolymers obtained are soluble in organic solvents owing to the absence of intermolecular crosslinks.

Investigation of biological properties of copolymers shows that new copolymers possess cytotoxic activity and can be used in medicine and biotechnology.

Acknowledgements

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References

KINETICS AND MECHANISM OF N-VINYL SUCCINIMIDE BULK HOMOPOLYMERIZATION IN THE PRESENCE OF DIBENZYL TRITHIOCARBONATE

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\textsuperscript{3}Lomonosov Moscow State University, Moscow, Russia

(Co)polymers based on N-vinyl succinimide (VSI) cause intense interest due to possibility of application as hydrophilic non-toxic materials in medicine. Such copolymers can be easily modified by alkaline hydrolysis resulting in conversion of VSI units to the N-vinyl succinimidic acid (VSA) units with carboxylic groups attached to the main chain via \(-\text{NH}–\text{C(O)}–\text{CH}_2–\text{CH}_2–\) spacer permit to bind low molecular compounds including medicinal products to the polymers, leading to various advantages of such polymeric drug conjugates, for instance, their prolonged action \textit{in vivo}.

Obtaining soluble VSI homopolymer and copolymers with high composition homogeneity by polymerization in bulk is impossible using conventional radical polymerization because of the chain transfer reaction to VSI cycle methylene protons leading to cross-linked product and, in the case of copolymerization, a great difference of VSI and other vinyl monomers reactivity ratios. All these problems can be solved by using reversible chain transfer (or RAFT technique of radical polymerization). Poly(VSI) was synthesized using dibenzyl trithiocarbonate (BTC) as a RAFT agent. The presence of BTC redistributes the probabilities of elementary reactions of growing macroradicals: propagation, transfer to RAFT agent, transfer to polymer, termination. It minimizes the role of chain transfer to polymer and termination and leads to obtaining soluble non-crosslinked polymer with molecular mass well controlled, depending on the \([\text{monomer}] / [\text{BTC}]\) ratio, and growing in the course of polymerization. The poly(VSI) samples were synthesized in this way with molecular masses (Mn) of 4500-68000. To find where CS\textsubscript{3} group situates in polymer chains an additional experiment was realized. Poly(VSI) \((1.3 \times 10^{-4} \text{ mole/l})\) was heated in inert solvent (benzene) with excess of azobisisobutyronitrile (AIBN) as a source of radicals \((3 \times 10^{-1} \text{ mole/l})\) at 80°C during 24 h. If trithiocarbonate group is located in the middle of the polymeric chain after heating with AIBN in the absence of monomer the molecular mass of the polymer should decrease in half. If it is located on the tail, molecular mass should remain practically the same. In this case molecular mass of poly(VSI) samples changed correspondingly: from 7000 to 5300 and from 48000 to 40000. It evidences that the chains grow with the different rates on both side of trithiocarbonate group. Chain length dependence on the elementary reactions rates, molecular mobility of propagating radicals, reactivity of the radicals have to be considered to explain the forming of such asymmetrical microstructure.

Chain transfer constant \(C_{tr}\) to BTC was calculated using NMR spectroscopy data of BTC current concentration during the reaction: \(C_{tr} \approx 19\). It makes possible to classify BTC as a relatively effective in VSI polymerization (according to E.Chernikova's classification such RAFT agents should be characterized by chain transfer constant in diapason \(1 \leq C_{tr} \leq 50\)).

The possibility of further chain growth and block polymers synthesis on the base of poly(VSI)-trithiocarbonate obtained in VSI homopolymerization in the presence of BTC was also investigated as an additional evidence of polymer chains "reviveness".

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KINETICS AND MECHANISM OF PROPYL ACRYLATE RAFT POLYMERIZATION IN THE PRESENCE OF DIBENZYL TRITHIOCARBONATE

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Reversible addition-fragmentation chain transfer (RAFT) polymerization is one of the techniques of controlled radical polymerization having the most perspectives in the wide range of practical applications due to its unique combination of easy realization with ability to synthesize polymers of various macromolecular architectures. There are no references to propyl acrylate (PA) RAFT polymerization. We suggest that combination of data collected in RAFT polymerization studies of alkyl acrylates with various chain length of alkyl radical could make possible to establish a connection of main polymerization parameters (chain transfer constant $C_{tr}$ to a RAFT agent, kinetics, chain microstructure – location of trithiocarbonate group in polymer chains if polymerization in the presence of trithiocarbonates as RAFT agents is considered) with the monomer structure.

In this study the results of investigation of PA polymerization in the presence of dibenzyl trithiocarbonate (BTC) are presented. The following aspects have been considered:

- influence of BTC on polymerization kinetics, mechanism and reasons of retardation;
- molecular mass (MM) growth with conversion (as an example, the change of MM and polydispersity index of poly(PA) in the course of polymerization is shown at the picture below) and its dependence on [BTC];
- location of trithiocarbonate groups in polymers obtained at various monomer conversions;
- possibility of further chain growth and block polymers synthesis on the base of poly(PA)-trithiocarbonates obtained in PA homopolymerization in the presence of BTC.

Pic. – a: Normalized GPC curves of poly(PA) at various monomer conversions (shown above the curves), b: dependence of MM and polydispersity index (shown at the points) of poly(PA) on monomer conversion. Straight line – theoretical dependence. Polymerization in bulk, 80°C, [AIBN]=10⁻³, [BTC]=0.2 mole/l.
WHAT CAN AND SHOULD BE DONE WHEN RAFT POLYMERIZATION IN THE PRESENCE OF TRITHIOCARBONATES IS INVESTIGATED

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RAFT polymerization is a most promising technics of controlled radical polymerization nowadays because of its simple practical realization and the wide range of macromolecular architectures that can be synthesized by using it. Well known mechanism of RAFT polymerization is accepted by the most of scientists, however many particular, but important for understanding facts observed in experiment, questions is widely discussed, and there is no single opinion about them. It concerns, first of all, whether the real reactions correspond with the formal scheme. Secondly, what is the reason of retardation and even inhibition often observed in RAFT polymerization but which are not intrinsic to the RAFT mechanism. Thirdly, how the microstructure of polymer obtained can be described taking into account growing the chain in the course of the whole period of polymerization.

In the presence of trithiocarbonates as RAFT agents the scheme is more complicated. The chain growing is possible to the both side from trithiocarbonate group CS\textsubscript{3}, and as it has been shown in our recent studies with different rates. This can lead to forming of polymer of a specific chain structure with CS\textsubscript{3}-group situated a) in the middle of chain (growing with the equal rates), b) close to one of the ends of chain (growing with different rates), c) at the end of chain (growing only to one side). We have proposed to name the structures as symmetrical, asymmetrical and terminal one.

The main kinetics parameter of RAFT polymerization is the chain transfer constant (C\textsubscript{tr}) to RAFT agent, and, in the case of polymerization in the presence of trithiocarbonates as RAFT agents, to poly(RAFT)\textsubscript{1} –monosubstituted trithiocarbonate obtaining on the first stage of the reaction. We propose, by the some examples, how using NMR spectroscopy to find them both, which is not a routine task especially for C\textsubscript{tr} to poly(RAFT)\textsubscript{1}.

Thus, among the standard procedures which must be done in any investigation of each new polymerization system: 1) observing a dependence of polymer molecular mass characteristics on monomer conversion and its accordance with theoretical one; 2) proving of possibility of further chain growth and block polymers synthesis on the base of polymer obtained in the presence of initial RAFT agent,

the following can and should be done due to NMR spectroscopy means:

3) Monitoring of the initial RAFT agent and poly(RAFT)\textsubscript{1} current concentrations during polymerization which is a powerful tool of its kinetics and mechanism investigation.

4) It is necessary to examine accordance of polymerization system studied with the conventional scheme, possible side reactions, and as a result to make a suitable choice of initiator, RAFT agent and the most appropriate polymerization increment to avoid incorrect calculation of C\textsubscript{tr} especially to poly(RAFT)\textsubscript{1}.

5) Gradient microstructure of copolymers obtaining in RAFT polymerization can be described by finding the monomers conversions at each polymerization increment. Together with information about location of trithiocarbonate fragment in polymer chains and molecular mass characteristics it gives a realistic estimate of the copolymer structure.

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SURFACE ACTIVITY OF ACRYLIC SUBSTANCES IN AQUEOUS SOLUTIONS: FROM MONOMERS TO POLYMERS

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The reactions between components of reaction mixture in radical polymerization and their influence on mechanism and kinetics of polymerization are of great interest in the recent time. First of all these are any association of monomers, selective sorbtion, possibility of template mechanism of polymerization due to forming of arranged structures. Polymerization of surface-active monomers which can form micelles in solution is a particular case of these reactions. It is obvious that in polymerization of water-soluble monomers their adsorption on the "solution-air" interface occurs and can influence on kinetics and structure of polymers obtained. Systematic studying of adsorption of some well known monomers like acrylic acid, methacrylic acid, acryl amid, methacrylamide and their derivatives must establish the relations between monomers surface activity and their polymerization particular features.

The experimental surface tension isotherms and their analysis are used for investigation of adsorption on the "solution-air" interface. In this study surface tension was determined by maximum bubble pressure method relating to the group of dynamic methods. Further it was assumed the dependence of surface tension on solution concentration is better described by the following equation:

$$\Delta \sigma = b \frac{ax}{1 + ax}$$

when $\Delta \sigma \equiv \sigma_o - \sigma$, $\sigma_o$ and $\sigma$ – the surface tension of solvent and solution, $a$ and $b$ – constants, $x$ – solution concentration (mole fraction). Equation (1) together with Gibbs one leads to the adsorption isotherm with a maximum:

$$\Gamma = \frac{b \frac{ax}{RT (1 + ax)^2}}{}$$

Maximum adsorption, area covered by each molecule in the adsorption layer and the thickness of the adsorption layer were calculated for acrylic and methacrylic acids and methoxy poly(ethylene glycol) methacrylates with poly(ethylene glycol) radicals of various lengths.

The other item of the study is how surface activity changes at the transformation of monomers to polymers. The surface activity of poly(acrylic acid) PAA and poly(acryl amide) (PAAm) in aqueous solutions was studied. The surface tension isotherms of PAA and PAAm with various molecular mass have no deep differences but the decrease of the surface tension a little higher for the relatively high molecular PAA. We think that it occurs because of more effective adsorption on the solution-air phases boundary of high molecular samples. When surface activity of polymers are studied the following factors have to be considered: hydrophilic-hydrophobic balance, molecular mass, microstructure and macromolecular architecture of polymers, the presence of ionogenic groups ionized or capable of dissociation, the rate of ionization, the nature of counter-ions, flexibility of polymeric chains.
Production of polyol esters is performed via transesterification / esterification of vegetable oils / free fatty acids with multi-functional branched alcohols, for instance, trimethylolpropane, neopentyl glycol or pentaerythritol. There is one fourth of carbon atom in them, which gives high chemical stability to these molecules [1].

Neopentyl glycol oleate is one of the most widely used in the family of polyol esters. Synthetic esters are recognized as environmentally friendly lubricants, having excellent technical properties together with ecological benefits. They are readily biodegradable in aqueous media and nontoxic. Such esters are high quality lubricants having potential in industry and transport applications: hydraulics, metal working fluids, gear lubricants, chain saw lubricants [2].

The aim of this study was using biotechnological methods synthesize polyol esters, which could be used as bio-lubricants.

Polyol esters were synthesized in solvent-free systems. Enzyme Novozym 435, i.e. enzyme is obtained from genetically modified Candida antarctica species, immobilized on acrylic resin, was used as biocatalyst. Esterification process was carried out at varied reaction conditions such as alcohol to acid molar ratio (1:1–1:7), biocatalyst concentration (1–13%), and temperature (20–70 °C). The optimal conditions of process of esterification of polyol esters have been determined. The process shall be executed at 70 °C temperature, the optimal molar ratio between neopentyl glycol and oleic acid in the reaction media should be 1:3, and the concentration of enzyme is 7 % of the mixture mass. The process of esterification shall be executed in 2 stages for 7 hours each.
SYNTHESIS, PROPERTIES AND POLYMERIZATION OF VINYL-FUNCTIONALIZED PHENANTHROIMIDAZOLE

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Efficient solid-state emission of organic materials is essential for their application in optoelectronic devices. The molecular design and development of new chromophores that emit visible light in the solid state with high efficiency are strongly desired for the development and advanced applications of organic light emitting diodes with superior performance [1]. Phenanthroimidazole derivatives are recognized as efficient emitting and/or charge transporting materials for various applications [2]. In this presentation we report on the synthesis and self-polymerization of new phenanthroimidazole-based monomer. Synthetic route to monomer M1 is outlined in Scheme 1.


The structures of the synthesized compounds 1, 2 and M1 were confirmed by $^1$H NMR, $^{13}$C NMR, IR spectroscopy and mass spectrometry. The thermal properties of monomer M1 and the polymer were investigated by the differential scanning calorimetry and thermogravimetry. Optical and photophysical properties were studied by UV and fluorescence spectroscopies. The polymerization kinetics was investigated by DSC and real time FT-IR technique. The average molecular weights were determined by GPC technique.

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References
SYNTHESIS AND SELF-POLYMERIZATION OF 1,8-NAPHTHALIMIDE-BASED VINYL MONOMER

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High electron-affinity of 1,8-naphthalimides determines the possibility of their use as electron-transporting media, and the imide nitrogen makes 1,8-naphthalimides easy to functionalize [1]. They exhibit good photochemical stability and high luminescence quantum yields [2]. The aim of this work was the synthesis and investigation of vinyl monomer containing 1,8-naphthalimide moiety and demonstration of the possibility of its self-polymerization.

1,8-Naphthalimide-based vinyl monomer 2 was synthesized by two step synthetic route. The first step (a) was condensation of 4-bromo-1,8-naphthalic anhydride with dodecylamine. The target monomer 2 was prepared by Suzuki coupling reaction (step b) between 4-vinylbenzeneboronic acid and compound 1 (Scheme 1).

![Scheme 1. Synthesis of compound 2](image)

The structures of the synthesized compounds were proved by 1H and 13C NMR, IR and mass spectrometries. The thermal, optical, electrochemical and photophysical properties of the synthesized compound were investigated. The possibility of self-polymerization of the synthesized monomer was demonstrated by differential scanning calorimetry. The DSC heating scan of compound 2 showed endothermic melting signal at 126 °C and exothermic peak of self-polymerization at 177 °C. By performing the DSC scans at the different heating rates, integrating exothermic peaks and measuring the temperature at 50% conversion, the activation energy of the process was estimated using Ozawa method [3]. The activation energy of self-polymerization of compound 2 was found to be 152 kJ/mol. Glass transition temperature of the obtained polymer was observed at 136 °C.

References

BRIDGED-TRIPHENYLAMINES WITH EXTENDED \( \pi \)-CONJUGATED SYSTEMS AS EFFECTIVE ORGANIC SEMICONDUCTORS

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Derivatives of triphenylamines with extended \( \pi \)-electron systems have received particular attention due to their diverse potential applications as electroactive materials for optoelectronics [1]. The advantage of an enhanced \( \pi \)-conjugation is obtained due to the relatively planar structure of the bridged-triphenylamines [2]. Such molecular is planarity inherent for achieving molecular ordering which may give rise to interesting electronic and/or optical properties.

In this work we report on synthesis and studies of bridged-triphenylamine derivatives with enhanced conjugated \( \pi \)-electron systems i.e. bridged-triphenylamines possessing phenylethenyl moieties.

The synthesized compounds were identified by IR, \(^1\)H NMR, \(^{13}\)C NMR spectoscopies and mass spectrometry. The synthesized compounds were found to constitute glass-forming molecular materials with glass transition temperatures in the range of 50-130 °C as characterized by differential scanning calorimetry. Absorption spectra of the dilute solutions of the compounds in tetrahydrofuran are similar. The absorption intensity maxima are in the range of 270-410 nm. The ionization potentials of the synthesized compounds estimated by cyclic voltammetry range from 4.94 to 5.09 eV. The compounds are electrochemically stable.

Acknowledgements
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References
HIDE UNHAIRING PECULIARITIES USING SODIUM ALUMINATE AS ALKALINE AGENT

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In leather industry, unhairing is a heavy pollution operation [1]. The conventional lime-sulphide process produces a large amount of lime silt polluted by sulphides and protein degradation products which are toxic to health and difficult to dispose. Therefore, it seems worthwhile to look for alternative unhairing system which could replace insoluble lime and diminish the eco-toxicological parameters [2]. Sodium aluminate is an important commercial inorganic chemical [3]. It works as an effective source of aluminium hydroxide for many industrial and technical applications. Also, this alkaline has good solubility in water. So, it was done assumption that sludge formation after unhairing process will be eliminated using this alkali instead of lime. The most important step is to establish sodium aluminate action on hide derma. The preliminary results have shown that acceptable unhairing could be achieved under such conditions (% from leather mass): H₂O – 100%; NaAlO₂ – 2.0%; temperature – 20ºC; Na₂S – 0.9%; duration – 24 h. The control group was processed by conventional method using Ca(OH)₂. It was established that sodium aluminate has weaker effect on the derma collagen than lime. The amount of collagenous proteins removed from hide was accordingly 0.09 (sodium aluminate) and 0.28 g/kg (lime). The results have shown that additional derma is opening up and epidermis removing after such unhairing is required.

Figure. Unhaired hide surface images (×100 times): a – with NaAlO₂; b – with Ca(OH)₂ (control)

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References
Over the past two decades, scientists have shown significant scientific and technological interest in polymer–inorganic nanocomposites. The incorporation of inorganic nanoparticles into polymer matrices can result in novel high-performance materials that find applications in many industrial fields.

CdSe nanoparticles have received a lot of attention because of their unique optical and electronic properties [1]. This work is devoted to thin CdSe films deposition on various polymers substrates. The combined CBD-SILAR method has been elaborated. This method requires comparatively mild conditions and relatively low-toxic Cd(II) and Se(II) precursors. As selenium precursors aqueous solutions of SeO$_2$, H$_2$SeO$_3$, Na$_2$SeO$_3$ and Na$_2$SeSO$_3$ were used. The reducing agent was Na$_2$SO$_3$. Synthesis parameters such as a deposition temperature, exposure time and selenium precursor concentration were optimized. Principal route of this combined CBD-SILAR method is presented in Figure.

In the first step of the process, the anions present in the selenium precursor solution are adsorbed on the surface of the polymer substrate and form the Helmholtz electric double layer [2]. Adsorbed layer on polymer is composed of two layers: the inner consist of negatively charged Se$^{2-}$ and the outer of positively charged Na$^+$. Recently, we have found that the adsorbed selenide partially oxidised to elemental Se in environmental [3]. The excess of adsorbed Na$^+$, Se$^{2-}$, SeO$_3^{2-}$, SO$_3^{2-}$ and SO$_4^{2-}$ ions was rinsed away from the diffusion layer. Further the polymer plate is transferred in the Cd(II) precursor solution. Cd$^{2+}$ reacts with adsorbed ions and a solid CdSe is formed on the surface. The reactions and factors affecting the CdSe forming mechanism were also discussed. The influence of selenium precursor nature on the structural, morphological, optical and electrical properties of the deposited CdSe films was determined. This method is also suitable for other metal selenide films such as the CuSe, Ag$_2$Se and In$_2$Se$_3$ deposition on polymer substrate.

References
GLYCEROL-BASED POLYMERIC COMPOSITES FILLED WITH
INDUSTRIAL WASTE MATERIALS

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The replacement of petroleum-derived plastics and composites by bio-based materials obtained from inexpensive, renewable, natural resources has the potential to greatly impact the industries of plastics, coatings, and composites [1]. Glycerol, the by-product of biodiesel refining, is a promising candidate which can be used as monomer in the synthesis of polymers as it is or after chemical modification [2]. Cationic photopolymerization of glycerol diglycidyl ether was chosen for the production of the glycerol-based polymeric composites because of its important advantages such as the absence of inhibition by oxygen, low shrinkage, good adhesion, and good mechanical properties of the UV-cured materials [3].

The composites were obtained by photopolymerization of glycerol diglycidyl ether batches with the different industrial wastes, i.e. rapeseed cake, phosphogypsum, and horn meal. The mixture of triarylsulfonium hexafluoroantimonates was used as photoinitiator. The (5-20)% concentration of the fillers was used in the batches. The chemical structures of the photocross-linked products were confirmed by IR spectroscopy. The yield of the insoluble fraction of the polymeric composites obtained after Soxhlet extraction in chloroform for 72 h was in the range of (96-99)%. It was established by thermogravimetrical analysis that the thermal degradation temperatures at the weight loss of 10 % of the polymeric composites were in the range of (175-292)°C. The differential scanning calorimetry measurements revealed that all the photocross-linked polymeric composites were the amorphous materials with the glass transition temperatures in the range of (21-38)°C. Their tensile strength ranged from 25.02 MPa to 117.59 MPa. The elongation at break was found to be in the range of (5.36-13.77)%. The Young modulus ranged from 47.5 MPa to 110.5 MPa.

The composites of glycerol-based thermoset with the industrial waste fillers were found to be biodegradable in natural environment. The combination of mechanical, thermal, swelling properties, and biodegradability of the formed composites show their suitability for the production of the environmentally degradable-ecocompatible products.

Acknowledgement

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References:
Composite materials, such as carbon-fibre-reinforced polymers, are used extensively in the fabrication of high-performance structures for a variety of engineering applications such as aircraft, automobiles, sporting goods, and electronics. Composite laminates often show considerable advantages of stiffness and strength over homogeneous materials, and this is particularly evident when these properties are considered on a unit weight basis. However, these advantages are counterbalanced by lower damage tolerance levels. External mechanical loads, repeated cyclic stresses, and impact lead to damage in laminated composites due to their low delamination resistance. Damage in a structure may cause failure leading to tragic consequences and therefore structural health monitoring and damage detection in civil, mechanical, and aerospace engineering structures has become one of the most important keys in maintaining the integrity and safety of a structure.

Several methods have been developed for structural health monitoring of composite structures using fibre optic sensors, piezoelectric sensors, and self-sensing approaches. In this paper, the self-sensing damage detection method based on the electrical resistance measurement of laminated composites is proposed. The basic idea of the method is that damage such as fibre fracture or delamination between plies will cause a decrease in the electrical conductivity in the damaged region leading to a resistance or voltage change. For the measurement of electrical properties of laminated composites, the two-probe and four-probe methods are employed. The two-probe method is based on the definition of resistance according to Ohm’s law when two electrodes are used to measure the electrical resistance. The four-probe method is an alternative to the two-probe method. A current is passed through the outer probes and induces a voltage in the inner voltage probes. Based on the measured voltage and current, the resistance between the voltage contacts is then measured.

In the present study, 2-D numerical analysis of strip-type specimens of laminated composites with and without damage are considered and numerical investigation is carried out by using the finite element program ANSYS. The surface and oblique resistances are numerically calculated according to the two-probe and four-probe methods. Electrical conductivity of the composite laminate in the longitudinal direction is given constant, while electrical conductivity in the through-thickness direction is used as a variable in the parametric study. The resistance change for each case due to delamination is estimated by comparing the obtained resistance with the corresponding value of the specimen without delamination. Applicability and effectiveness of the proposed method are investigated by using various locations and lengths of a delaminated crack in the specimen.
1-BUTYL-3-METHYLIMIDAZOLIUM CHLORIDE ASSISTED COAXIAL ELECTROSPINNING OF STRYRENE-ARCYLONITRILE COPOLYMER

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Electrospinning is a spinning process that uses electrostatic force to draw thin fibers from a polymer solution [1]. Coaxial electrospinning is used to maintain fibers with core-sheath structure. These fibers have large surface area, high mechanical strength and porous structure. Core-sheath fibers are used in lithium ion batteries and they are applied in electrochemical fields and are also used for storing energy [2]. The purpose of this research was to find out 1-butyl-3-methylimidazolium chloride’s ([Bmim]Cl) influence on core-sheath fiber’s morphology that was electrospun during coaxial electrospinning. SEM pictures of the fibers were taken and solution parameters like electrical conductivity, viscosity and surface tension were measured to analyze their impact on the fiber morphology.

Firstly, it was examined if it was possible to perform coaxial electrospinning with [Bmim]Cl. Pure [Bmim]Cl was used in the inner layer and in the outer layer was styrene-acrylonitrile (SAN) in dimethyl sulfoxide (DMSO) solution at different concentrations. It was found that coaxial electrospinning is possible with pure ionic liquid in inner layer, but the process itself is unstable. Cylindrical shape of fibers was achieved. Furthermore, the diameter of fiber increased with the increase on polymer’s solution concentration.

Secondly, for coaxial electrospinning was used in the inner layer [Bmim]Cl+DMSO at different concentrations and in the outer layer was 13% SAN in DMSO solution. It was found that the fibers were beaded and their structure was ribbon-like. Finally, to achieve fibers with cylindrical shape, solution of [Bmim]Cl in 1,2-dichloroethane (1,2-DCE) at different concentrations was used in the inner layer and in the outer layer was used 20% SAN in DMSO solution. However there were less beads in the fibers, the fiber diameter was not uniform.

Coaxial electrospinning’s stability with using [Bmim]Cl in the inner layer and cylindrical shape was achieved using 85% [Bmim]Cl in 1,2-DCE solution in the inner layer and 20% SAN in DMSO solution in the outer layer.

Acknowledgements
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References
POLYMER-SAND PRODUCTS BASED ON THE MIXED AND HEAVILY CONTAMINATED THERMOPLASTIC WASTE

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An alternative method of recycling the mixed and contaminated polyolefin waste (PE, PP) in industry is the production technology of polymer-sand products, which does not require deep cleaning and sorting of raw materials. Such polymer-sand products have a low physical-mechanical properties, low softening temperature, high flammability, low ultraviolet radiation resistance which limits their use. On the basis of the conducted exploratory research for obtaining polymer-sand products with improved mechanical and operational characteristics polyethylene terephthalate was used as a polymer matrix. A considerable number of PET waste is heavily contaminated and mixed with other polymers (PVC, PA, polyolefins) materials which are advisable to be processed by means of filling with sand and they are the ideal basis for creating polymer-sand products.

For research were used: PE-15803-020 of «Polymir» production (PE), ExxonMobil™ LLDPE LL 4004EL Wire&Cable (LLDPE), stretch, PET 8200, secondary waste of pneumatic moulding of PET in the form of flakes(R-PET), polyethylene terephthalate glycol-modified (PETG), polycarbonate TRIREX (PC), graft copolymer of polyethylene with maleic anhydride (PE-g-MA), synthesized in laboratory conditions; silane Dynasylan® AMEO Evonik Industries AG Inorganic Materials and rivers and without impurities. For the experiment, each polymer was ground by a rotary grinders into a powder to obtain a homogeneous system of polymer-sand and was subjected to drying in order to prevent degradation of the polymer. The sand used was of a particle size from 0.2 mm to 1 mm, dried to constant mass. The sand was modified by pre-treatment of a 1% solution of silane with subsequent drying.

Polymer-sand products were obtained in two ways. In the first case, a polymeric matrix and a filler were mixed in the cold state and subjected to heat treatment in a muffle furnace at 250 C for 15 minutes, then the resulting system was stirred in a blade mixer with heating and the samples were obtained by pressing. In the second case, the polymer matrix was pre-melted in an extruder and mixed with hot sand in a paddle mixer. The identified mechanical properties of the obtained specimen are density, Tensile strength at break, strength at compression, strength at flexure and thermal resistance, the MFI, the quality of mixing. The obtained data of mechanical properties is presented in the table.

Table -Mechanical properties of obtained polymer-sand compositions

<table>
<thead>
<tr>
<th>№</th>
<th>The structure of composition</th>
<th>The content of polymer, %</th>
<th>The content of sand, %</th>
<th>Tensile strength at break, σb, MPa</th>
<th>Strength at compression, σc, MPa</th>
<th>Strength at flexure, σf, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PE</td>
<td>80</td>
<td>15-25</td>
<td>25-30</td>
<td>17-25</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>R-PET</td>
<td>80</td>
<td>45-50</td>
<td>80-95</td>
<td>35-40</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>PETG</td>
<td>80</td>
<td>45-55</td>
<td>90-105</td>
<td>30-35</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>PETG/PE-g-MA10/10</td>
<td>80</td>
<td>45-55</td>
<td>80-85</td>
<td>30-35</td>
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<tr>
<td>5</td>
<td>PETG/PC 15/5,0</td>
<td>80</td>
<td>55-65</td>
<td>115-120</td>
<td>65-70</td>
<td></td>
</tr>
</tbody>
</table>

The best physical-mechanical properties have the polymer compositions based on PETG and PETG with the addition of PC.

SCOTS PINE BARK BASED POLYOLS FOR POLYURETHANE FOAMS PRODUCTION

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Elaboration of sustainable processes with the most profitable utilization of all products obtained in the technological cycle is the basic position of modern biorefinery concept. Bark comprises about 13 – 21\% of dry weight of typical log \cite{1}. Most of bark is used for energy production. On the other side, bark is a renewable biomass that has a large potential as a raw material for synthesizing of bio-based polyols suitable for rigid polyurethane (PUR) foam making. In this work the process of Scots pine (\textit{Pinus Silvestris}) bark oxypropylation and the properties of polyols obtained were studied. Scots pine bark was oxypropylated in laboratory scale high pressure PARR reactor using different bark content (10- 30\%) in reaction mixture and different alkali catalyst content (2 -10 \% from bark weight). Finally, the reaction products were neutralized with acetic acid. Polyols obtained from bark were characterised by methods of wet chemistry, FTIR spectroscopy and viscometry. The viscosity of polyols was increased with increasing the bark content in the reaction mixture and varied in the range of 380 – 280 000 mPa·s. The increasing of KOH content from 2 to 5\%, at bark content 10\% - 20\% in reaction mixture leaded to a drastic decreasing of the viscosity of polyols. With further increasing of the catalyst content, the viscosity remained the similar. At bark content 30\% in reaction mixture viscosity remained the similar independently of catalyst content. The hydroxyl value of polyols from all bark substrates was increased with increasing of bark content in the reaction mixture and varied in the range of 220 – 475 mg KOH/g. The minor influence of catalyst content on hydroxyl value of polyols was established.

The high reactivity of bark based polyols with 4,4-diphenyl diisocyanate (MDI) in the pure dioxane media in the presence of dibytin dilayrate as catalyst was established by kinetic methods. The reaction proceeded in argon atmosphere at 25 °C, NCO group content was ~0,3 mol/l and NCO/OH molar ratio equal 1.0.

The water content in all polyols under study did not exceed 0,2\% that meet the requirements for polyols suitable for PUR production. PUR foams from bark based polyols were obtained. The parameters of foaming process as well as the density and closed cell content in foams were determined.

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Reference

BUILDING OF CURING KINETIC MODELS FOR A SIMULATION OF PULTRUSION PROCESSES

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Pultrusion process is a continuous and efficient process producing composite profiles with a constant cross-section. During pultrusion, the fibre reinforcements are saturated with the resin in a resin tank and then continuously pulled through a heated die by a puller. Inside the die, the resin gradually cures and solidifies to form a composite part with the same cross-section profile as in the die. After exit from the die the finished product is cut to the desired length by saw integrated to the pultrusion tool. An effective set up of pultrusion process is not possible without a numerical analysis of the technological process when the curing kinetic model for a matrix material should be developed separately.

Curing of thermoset resin is an exothermal chemical reaction, where the curing kinetic is characterized by the degree of cure. Using differential scanning calorimetry (DSC) results, the degree of cure is determined as the ratio of the amount of heat evolved during the reaction up to present time to the total heat of reaction. Traditionally dependencies of the degree of cure on time are approximated by using the Arrhenius relationship multiplied by a simple mathematical function that depends on the resin properties and varies with the resin reaction model.

Physical parameters of the Arrhenius relationship - activation energy and frequency factor are determined by using an experimental data. In this case at least 3 DSC tests at different heating rates (usually 1…10°C/min) are required. There are many methods for a determination of Arrhenius relationship’s parameters. The most widely applied are the Kissinger method [1] and ASTM E 698 procedure [2] based on the Ozawa method. As a simple mathematical function, n-th order, Prout-Tompkins [3] and Kamal-Sourour models [4] are more frequently used for a formulation of the curing kinetic models. The ordinary least squares method is applied in this case to approximate the experimental curves of the degree of cure and to determine non-physical coefficients of a simple mathematical function.

The proposed methodology for a building of the curing kinetic models was validated by using DSC tests results presented in paper [5] and was realized as the Microsoft Excel tool. The best precision was obtained with the Kamal-Sourour model but the n-th order model gave the worst result. Finally the developed methodology was applied successfully for a building of the curing kinetic models of resins with high microwave absorption properties to be used in the advanced pultrusion processes.

The authors gratefully acknowledge the support of European Commission, FRAMEWORK 7 program, contract no. NMP2-SL-2013-609149, project “Development of an Innovative Manufacturing Process for the In-Line Coating of Pultruded Composites (COALINE)”.

References

The main aim of this study was to find the proper method for producing polystyrene ion exchangers by electrospinning. Polystyrene fibrous membranes were prepared by using the method included crosslinking by UV-radiation during the electrospinning and followed by functionalization of electrospun membranes. The solution for electropsinning was prepared from styrene and divinylbenzene (DVB) as a crosslinking agent with added binder polymer and initiator, azobisisobutyronitrile. The functionalization with di-2-ethyl-hexyl-phosphoric acid (D$_2$EHPA) was performed by using mechanical stirring. The effect of temperature and duration of process on the functionalization was investigated.
STUDY OF FORMATION OF CADMIUM SULFIDE – CADMIUM SELENIDE LAYERS ON POLYAMIDE

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Thin CdS, CdSe and Cd(S,Se) semiconductor films are of particular interest for the fabrication of large area photodiode arrays, solar selective coatings, solar cells, photoconductors, sensors etc. [1]. Deposition of these films by vacuum evaporation, sputtering and chemical methods such as chemical vapour deposition, spray pyrolysis, electrodeposition, anodization, electroconversion, electroless, dip growth, successive ionic adsorption and reaction, chemical bath deposition and solution-gas interface techniques are well known [1-3]. Selection of the films deposition method first of all is specified by structural, mechanical and physical parameters, which should have thin film sample. Cadmium chalcogenide thin films preparations by chemical methods are currently attracting considerable attention as it is relatively inexpensive, simple and convenient for large area deposition. Compared with other methods, it allows carrying out the deposition at temperatures below 100ºC on substrates of different nature, using different combinations of substances.

A new sorption-diffusion way of formation of metals chalcogenide layers on dielectric surfaces was found and developed. This way is attractive from technological point of view because only two solutions have to be used. The method consists of two stages. Since a PA as semi hydrophilic polymer is capable of adsorbing ions of various electrolytes from aqueous solutions, in the first stage – chalcogenization of the polymer – PA films were treated 120 min with the solution of selenopentathionate, K₂SeS₄O₆ (0.05 mol/dm³ acidified with the addition of 0.1 mol/dm³ HCl 50 °C), the anion of which contain selenium and sulphur atoms of low oxidation state, O₃S–S–Se–S–SO₃⁻. In the second stage, the chalcogenized PA was treated with a solution of Cd(II) salt (15 min at 80°C) and the layers of CdₓS–CdᵧSe were formed in the surface of a PA. CdₓS–CdᵧSe films were obtained from the following cadmium-containing salts: cadmium chloride (CdCl₂·2.5H₂O), cadmium acetate (Cd(CH₃COO)₂·2H₂O) and cadmium sulfate (CdSO₄·8H₂O). The concentrations of these solutions were 0.1 mol/dm³ (pH ~ 11.2). Triethanolamine (7.4 mol/dm³) was used as a complexing agent. pH of Cd(II) salts solutions were adjust using sodium hydroxide (0.1 mol/dm³) and aqueous ammonia (13.4 mol/dm³).

CdₓS–CdᵧSe layers on PA films surface formed were characterized by atomic absorption spectrometry, X-ray diffraction, X-ray photoelectron spectroscopy, atomic force microscopy and scanning electron microscopy methods.

The objective of this work is to provide a comprehensive study on the effect of Cd sources on the physical properties CdₓS–CdᵧSe thin films.

References

STRUCTURE AND MECHANICAL PROPERTIES OF KOMBUCHA BIOFILM

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Properties of bacterial materials are attractive for a wide range of applications, e.g. in chemical, paper, food, medicine and other fields of industry [1]. Biomaterials capture the increased attention of designers due to environmental concerns. Several sustainable design and fashion projects were performed during the last year therefore is the lack of scientific investigation in the field of deformation behaviour of this kind materials.

Fermentation of sugared tea with tea fungus yields kombucha tea and microbial biofilm. Bacterial components of kombucha produce gel like membrane - biological material of cellulose network. Stable and solid cellulose sheet forms when gel like membrane is dried. Kombucha biofilm grows well and quickly at room temperature with minimal specialized equipment and it is readily degradable. This biofilm has potential as a natural easy produced material for sustainable products.

The aim of this research – to investigate the influence of bacterial biofilm sheet formation parameters on the structure and mechanical properties of material. Kombucha biofilm has a microfibrillar structure which determines it’s physical and mechanical properties. When gel like membrane is air dried it shrinks in the thickness direction when planar dimensions of the sample remain constant (the variation of sample dimensions before and after drying is 1.7-2.5 %). It was estimated about 90 % of sample thickness loss during membrane drying: the average thickness of dried biofilm is 0.73 mm when average thickness of produced biomaterial membrane - 8.45 mm. Kombucha hydrogels are characterised by low density and high water content. To form solid sheet of elastic material with high tensile strength (Table 1) the membrane looses 88 % of weight during drying process.

Table 1. Tensile properties of the biofilm

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (σ), MPa</th>
<th>Tensile strain (ε), %</th>
<th>E modulus (initial)</th>
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<tr>
<td>F1</td>
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<td>18</td>
<td>0.2842</td>
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<tr>
<td>F2</td>
<td>99</td>
<td>33</td>
<td>0.2182</td>
</tr>
</tbody>
</table>

Fig. 1. Samples of kombucha biofilm which colour was changed

Some possibilities to modify biomaterial colour, surface pattern and dimensions is analysed. The colour and texture of biofilm can be altered by using natural dyes and powder additives (Fig. 1).

References:

THE CONVENIENT SYNTHESIS OF CARBAZOLE SUBSTITUTED PYRIDINES AND THEIR PHOTOPHYSICAL PROPERTIES

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Organic light-emitting diodes (OLEDs) are an important application area of the organic semiconductor materials. The intensive research is currently carried out which aims to increase the efficiency of OLEDs. Thermally activated delayed fluorescence (TADF) is one of the efficiency-enhancing effects recently widely employed in OLEDs. In TADF processes, all triplet excitons can be theoretically converted into emissive singlet excitons by thermal activation, leading to nearly 100 % internal quantum efficiency in the device. Nowadays, the design and synthesis of new highly efficient blue emitters with TADF effect is an important practical issue. On the other hand, due to demands of industry, synthetic pathway to such compounds must be simple and cheap.

With this aim we synthesized a series of carbazole substituted pyridines 3—5 in one step, starting from the commercially available carbazole derivatives 1 and pentachloropyridine 2. The photophysical properties of the synthesized compounds 3—5 were studied. For compounds 3a—5a X-ray diffraction experiments and DFT calculations were done.

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References
COMPLEXES OF SCHIFF BASES WITH COPPER IN ATRP OF HYDROPHYLIC MONOMERS

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Atom transfer radical polymerization (ATRP) is the most popular method of catalytic reversible deactivation radical polymerization (RDRP), where an alkyl halide (R-Hal) is activated by a transition metal catalyst present in a lower oxidation state (Cu(I)/L), generating alkyl radical (R·) and the transition metal complex in a higher oxidation state (Cu(II)/L). Typically, bipyridine, tris(2-pyridyl methyl)amine, and tris[2-(dimethylamino)ethyl]amine are used as ligands in ATRP under various conditions of generation of the activator (AGET, ARGET, ICAR, SARA, ISARA, and eATRP). Schiff bases are an important class of ligands that coordinate to copper ions via azomethine nitrogen. They have wide applications in dye industry, analytical chemistry, catalysis, and biological systems. Schiff bases are prepared by condensing active carbonyl compounds with an amine under mild conditions. The most promising Schiff bases are those derived from salicylaldehyde, since they show photochromism and thermochromism in the solid state [1, 2].

Hydrophilic monomer 2-hydroxyethyl methacrylate (HEMA) and cationic monomer [2-(methacryloyloxy)ethyl]trimethyl ammonium chloride (METAC) were polymerized in aqueous solutions by ISARA ATRP using various redox systems and ligands. Molecular weight and dispersity of the polymers were determined by size exclusion chromatography with tipple detection. Schiff bases were prepared by condensing salicylaldehyde with di- or tetrafunctional amines. The best control over polymerization of METAC was realized using Me₆TREN as a ligand. Contrarily, polymerization of HEMA was efficiently controlled by Schiff bases. The most effective SRI were the oxidized form of ascorbic acid and iron (III) chloride.

The prepared polymers with molecular weight Mn up to 50 000 and low dispersity (D ≤ 1.5) were used as macroinitiators for the synthesis of diblock copolymers. PMETAC and PHEMA were efficient macroinitiators determining successful chain extension by the blocks of METAC and HEMA, respectively. A set of hydrophilic diblock copolymers with various length of the blocks and molecular weight Mn ranging from 50 000 to 100 000 was prepared and studied. Surface tension of the prepared diblock copolymers in water was measured by Kruss tensiometer using the methods of bubble, ring and plate.

References:

NEW DERIVATIVES OF 1,3,5-TRIAZINE AND CARBAZOLE AS LIGHT EMITTING MATERIALS FOR SOLUTION-PROCESSED OLEDs

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In this work, the newly synthesized compounds 2,4,6-tris(4-(3,6-di-tert-butylcarbazol-9-yl)phenyl)-1,3,5-triazine (1) and 2,4,6-tris(4-((9-hexyl-carbazol-3-yl)ethynyl)phenyl)-1,3,5-triazine (2) were investigated as light emitting materials in the organic light emitting diodes (OLEDs). These compounds possess good charge transporting properties. Hole mobilities of 3.3·10^-3 and 3.4·10^-3 cm^2 V^-1 s^-1 were observed at zero field strength for 1 and 2 respectively. Moreover, the quantum yields of 30% were found for the solid films of 1 and 2.

The experimental devices ITO/PEDOT:PSS/PVK:PBD (40 wt %): 1 (3 wt %)/LiF/Al (device I) and ITO/PEDOT:PSS/PVK:PBD (40 wt %): 2 (3 wt %)/LiF/Al (device II) were fabricated on ITO-coated glass substrate by spin-coating technique, where poly 3,4-ethylenedioxythiophene:poly styrenesulfonate (PEDOT:PSS) was used for hole transport layer (HTL), poly N-vinyl carbazole (PVK) and 2-(4-tetr-butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole (PBD) were used as host materials.

The electroluminescence (EL) spectra of the fabricated devices were recorded. The EL maxima of the devices I and II were observed at 463 nm and 515 nm respectively. These observations confirm that the emission observed was from 1 or 2, since PVK:PBD based devices have emission maxima at 433 nm [1, 2]. This fact indicates effective energy transfer from the PVK:PBD matrix to the electroluminescence dopants 1 or 2. The current density-voltage characteristics and luminance-voltage characteristics of the experimental devices were recorded. The turn-on voltage (V_on) of the device I was found to be 8 V for electroluminescence of 5.24 cd/m^2. In the case of device II the V_on was observed at 9.5 V for electroluminescence of 1.5 cd/m^2. The highest value of brightness of 1342 and 1221 cd/m^2 at 18 V for the devices I and II respectively were observed with the maxima of current efficiency in the range 0.1-0.55 cd/A. Commission Internationale de l’Eclairage (CIE 1931) chromaticity coordinates (x, y) of the devices I and II were found to be (0.15, 0.13) and (0.21, 0.33), respectively.

References
CHARACTERIZATION OF BARK EXTRACT FROM DECIDUOUS TREES WITH EMPHASIS ON THEIR ANTIOXIDANT ACTIVITY

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The bark of deciduous tree species growing in the Europe, in particular, in Latvia, is scarcely explored as a source for obtaining of valuable extractives products. The composition of their bark extractives was not yet studied systematically. High portion of flavonoids polymers - proanthocyanidins, better known as condensed tannins (CT) in polyphenolic pool of bark makes it a prospective raw material not only for medicine and veterinary but also for industrial application. Such condensed tannins as „quebracho” are produced commercially from wood and bark of acacia (Schinopsis sp.) trees and are often used as a raw material for the industrial production.

At present, demand for natural antioxidants is increasing, primarily due to the uncertain safety of synthetic compounds, for example, BHA, BHT, Irganox etc. The aim of the present work was screening of some widely spread in Latvia and Europe deciduous tree species: grey alder (Alnus incana), black alder (Alnus glutinosa), ash tree (Fraxinus excelsior), and goat willow (Salix caprea) as a potential source for obtaining of hydrophilic extract enriched with proanthocyanidins and their testing as a polymeric antioxidant for polymer compositions (poly-urethane, PU, elastomers).

The barks of deciduous trees were sequentially extracted (Accelerated Solvent Extractor ASE 350, Dionex) using solvents of increasing polarity. The data about total content of both lipophilic and hydrophilic compounds were obtained using sequentially extraction with hexane and aqueous ethanol. The highest yields of hydrophilic extractives were found for ash tree and goat willow (23.6% and 23.8%, respectively). The higher total contents of polyphenols were found also for black alder and goat willow bark (0.18 GAE/g and 0.12 GAE/g, respectively). Hydrophilic extract from the both alder species contained high amount (up to 7% on bark dry mass) of condensed tannins or oligomeric proanthocyanidins (PAC), whereas PAC content of extract from ash tree was negligible. The main component of ethanol-water extract from alder bark was identified using MALDI–TOF MS and 13C NMR spectroscopy as a B-type oligomeric proanthocyanidins with the catechin units polymerization degree of 5. In tests with free radicals (ABTS**, DPPH*, O2•−) and the ORAC (oxygen radical absorbance capacity) assay, the high radical scavenging capacities of the hydrophilic extracts enriched with PAC were demonstrated. The antioxidant efficiency of the hydrophilic extracts and proanthocyanidins from alder bark was tested by their influence on thermo-oxidative destruction of model polyurethane elastomers. The TGA data clearly revealed the high antioxidant effect of the hydrophilic extracts from alders and goat willow barks. The hydrophilic extracts enriched with proanthocyanidins have good potential as a technical antioxidant for polyurethanes, with the most prominent activity for the hydrophilic extract from black alder bark.

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THE EFFECT OF INTRODUCTION OF DIFFERENT TYPES OF CLAY ON THE ELASTIC PROPERTIES OF PC/ABS BLEND

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A variant of stepwise calculation of the elastic constants of a polymer composite, containing platelike multilayer clay particles as filler, has been suggested. First, the elastic characteristics of particles in the form of multilayer stacks with interlaminar galleries, enlarged by the intercalation of polymer, were determined according to the elasticity relations for layered media. Then, using the Mori-Tanaka theory of an equivalent medium, the elastic constants of the transversely isotropic representative structural element of a composite with a coplanar arrangement of platelike clay particles were calculated. Finally, the elastic constants of a composite with randomly oriented particles were found by using the method of orientational averaging of elastic properties of the structural element of the composite.

The effect of the number of monolayers in clay particles on the elastic constants of a composite was analyzed. It was found that, at the same mass content of filler an increased number of monolayers in particles leads to a considerable decrease in the elastic rigidity of the composite.

The results of the theoretical analysis are compared with experimental data for the elastic modulus of PC/ABS/clay composites with different types of clay: Del 43B, Del 67G, and Del LVF.
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