BALTIC POLYMER SYMPOSIUM 2018

PROGRAMME AND PROCEEDINGS

Jurmala,
Latvia
September 12-14

Organised by

Institute of Polymer Materials,
Riga Technical University

Latvian State Institute of Wood Chemistry

Institute of Technical Physics,
Riga Technical University

General sponsor

SIA "TENACHEM"

Baltic Polymer Symposium 2018
BPS 2018

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CONFERENCE AGENDA

12th of September

16.00 - 18.00	Registration in the hotel “SemaraH Hotel Lielupe SPA & Conferences” *(Bulduru pr. 64/68, Jūrmala)*
19.00	WELCOM PARTY in the hotel “SemaraH Hotel Lielupe SPA & Conferences”

13th of September

9.00-9.30	Registration in the hotel “SemaraH Hotel Lielupe SPA & Conferences”	
9.30-10.00	OPENING Prof. M.Kalnins; Prof.T.Juhna	
	SESSION 1 Chairman: M.Kalnins	
10.00-10.30	PLENARY **A. Dėdinaitė[1,2] ,P. M. Claesson[1,2]** **SYNERGIES IN LUBRICATION** [1]KTH Royal Institute of Technology, School of Engineering Sciences in Chemistry, Biotechnology and Health, Department of Chemistry, Surface and Corrosion Science, Stockholm, Sweden [2] RISE Research Institutes of Sweden, Materials and Surfaces, Stockholm, Sweden	16
10.30-11.00	PLENARY **A.Jiménez, M. Ramos, M. del Carmen Garrigós** **ENCAPSULATION STRATEGIES IN MULTIFUNCTIONAL BIOMATERIALS. AN OVERVIEW** University of Alicante. Department of Analytical Chemistry, Nutrition & Food Sciences. Alicante. Spain	17
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11.15-11.30	**I. Krasonu[1], E, Tarassova[1], S. Malmberg[2], V. Vassiljeva[1], A. Krumme[1]** **PREPARATION OF FIBROUS ELECTROSPUN MEMBRANES WITH ACTIVATED CARBON FILLER** [1]Department of Materials and Environmental Technology, Tallinn University of Technology, Tallinn, Estonia [2]Skeleton Technologies OÜ	19
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	SESSION 2 Chairman: J.V.Grazulevicius	
11.50-12.20	PLENARY **J.H.Lee** **EFFICIENCY ENHANCEMENT AND LIFETIME ELONGATION IN ORGANIC/HYBRID ELECTROLUMINESCENCE DEVICE WITH BLUE EMISSION** Graduate Institute of Photonics and Optoelectronics, and Department of Electrical Engineering, National Taiwan University	20
12.20-12.35	**P.M. Claesson,[1,2] Y. He,[1] G. Li,[1] J.Pan[1], I. Dobryden[1]** **LOCAL SURFACE NANOMECHANICAL AND WEAR PROPERTIES** [1]KTH Royal Institute of Technology, School of Engineering Sciences in Chemistry, Biotechnology and Health, Department of Chemistry, Surface and Corrosion Science, Stockholm, Sweden [2]RISE – Research Institute of Sweden, Chemistry Materials and Surfaces, Stockholm, Sweden	21
12.35-12.50	**M. Feldmann** **SUSTAINABLE COMPOSITES BASED ON POLYAMIDES REINFORCED WITH RECYCLED CARBON FIBERS - MICRO-STRUCTURE AND FATIGUE PERFORMANCE** Kassel/Germany	22
12.50-13.05	**J. Jonikaitė-Švėgždienė, A. Kudrešova, Š. Paukštis, R. Makuška** **POLYSTYRENE-BASED COIL-BRUSH COPOLYMERS: SYNTHESIS, PROPERTIES AND SELF-ASSEMBLY** Department of Polymer Chemistry, Vilnius University, Vilnius, Lithuania	23
13.05- 13.20	**M. Kirpluks, E. Vanags, A. Abolins, U .Cabulis** **TALL OIL FATTY ACID EPOXIDATION USING NOVEL HETEROGENEOUS PHASE CATALYSTS** Polymer Laboratory, Latvian State Institute of Wood Chemistry, Riga, Latvia	24
13.20-13.35	**A. A. Gosteva[1], G. F. Kolbina[1], G. M. Pavlov[1, 2]** **FLOW BIREFRINGENCE OF POLYMERS WITH BIOLOGICAL APPLICATIONS** [1]Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia [2]Physical Faculty, Saint Petersburg State University, St. Petersburg , Russia	25
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14.35-14.50	**S. V. Kostjuk[1,2], I. A. Berezianko[1,2], I. V. Vasilenko[1], D. I. Shiman[1]** **CATIONIC POLYMERIZATION OF ISOBUTYLENE USING IONIC LIQUIDS AS CATALYSTS: EFFECT OF IONIC LIQUID NATURE, CATALYST AGING, AND SONICATION** [1] Research Institute for Physical Chemical Problems of the Belarusian State University, Belarus [2] Department of Chemistry, Belarusian State University, Belarus	26
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15.05-15.20	**D.V. Vishnevetsky, A.N. Adamyan, P.M.Pakhomov and S.D.Khizhnyak** **HYDROGELS BASED ON L-CYSTEINE, SILVER NITRATE AND POLYVINYL ALCOHOL** Physical Chemistry Department, Tver State University, Tver, Russia	28
15.20-15.35	**R. Berzins, R. Merijs Meri, J. Zicans** **DIFFERENT EPOXIDE COUMPOUND INFLUENCE ON TWO-COMPONENT SILYTERMINATED POLYMER/EPOXIDE SYSTEMS MECHANICAL, RHEOLOGICAL AND ADHESION PROPERTIES** Institute of Polymer Materials, Faculty of Materials Sciences and Applied Chemistry, Riga Technical University, Latvia	29

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15.50-16.05	**A. Druktienyte[1], V. Navikaite-Snipaitiene[1], D.Cizeikiene[2], P. Pavelas Danilovas[1]** **TRANSFORMING GRAIN HUSKS INTO HIGHER-ADDED VALUE PRODUCTS** [1]Department of Polymer Chemistry and Technology, Kaunas University of Technology, Kaunas, Lithuania [2]Department of Food Science and Technology, Kaunas University of Technology, Kaunas, Lithuania	31
16.05-16.20	**S.D. Khizhnyak, A.N. Adamyan, Ya.V. Andrianova, T.V. Perevozova, P.M. Pakhomov** **PECULIARITIES OF SUPRAMOLECULAR HYDROGELS BASED ON SULPHUR CONTAINING AMINO ACID AND SILVER SALTS** Tver State University, Tver, Russia	32
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19.00	GALA DINNER in the National Library of Latvia *(Mūkusalas street 3, Riga)*

14th of September

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9.40-10.10	PLENARY **M. Arulepp[1], J. Leis[1,2]** **CDC CAPABILITIES IN DIFFERENT SUPERCAPACITOR APPLICATIONS** [1]Skeleton Technologies OÜ, Tartu, Estonia [2]Institute of Chemistry, University of Tartu, Tartu, Estonia	33
10.10-10.25	**I. Dobryden[1], X. Liu[2], Y. Boluk[3], P. M. Claesson[1,4]** **AFM FORCE AND NANOMECHANICAL STUDY OF POLYMER ADSORPTION ON CELLULOSE NANOCRYSTALS** [1] KTH Royal Institute of Technology, School of Chemical Sciences and Engineering, Department of Chemistry, Surface and Corrosion Science, Stockholm, Sweden [2] Key Laboratory of Applied Surface and Colloid Chemistry of Ministry of Education, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, China [3] University of Alberta, Department of Civil and Environmental Engineering, Edmonton, Canada [4] RISE Research Institutes of Sweden, Division of Bioscience and Materials, Stockholm, Sweden	34
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10.40-10.55	**P. Franciszczak[1], A. Bledzki[1], K. Kalnins[2], G. Japins[2], R.Merijs-Meri [3], J.Zicans[3]** **HIGH IMPACT STRENGTH PP-PET FIBRE COMPOSITES FOR INJECTION MOULDING** [1]Institute of Materials Science, Faculty of Mechanical Engineering and Mechatronics, West Pomeranian University of Technology Szczecin, Szczecin, Poland [2] Institute of Materials and Structures, Riga Technical University,Riga, Latvia [3] Institute of Polymer Materials, Faculty of Material Science and Applied Chemistry, Riga Technical University, Riga, Latvia	36

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12.15-12.30	**G. Sakale, G. Revalde, S. Stepina, I. Klemenoks, S. Guzlena, M. Knite** **INFLUENCE OF POLYMER MATRIX MATERIAL AND NANOSTRUCTURED FILLER ON COMPOSITE CHEMICAL SENSING PROPERTIES** Institute of Technical Physics, Faculty of Materials Science and Applied Chemistry, Riga Technical University, Riga, Latvia	40
12.30-12.45	**S. Malmberg [1,3], M. Arulepp[3], N. Savest [1], M. Käärik[2], A. Krumme[1]** **REASERCH AND DEVELOPMENT OF NANOSTRACTURED ELECTROSPUN SUPERCAPACITORS** [1]Department of Materials and Environmental Technology, Tallinn University of Technology, Tallinn, Estonia [2]Chair of Molecular technology, Institute of chemistry, University of Tartu,Tartu, Estonia [3]Skeleton Technologies OÜ, Lubja, Estonia	41
12.45-13.00	**L. Lapčinskis[1], I. Cīrulis[1], P. Lesničenoks[2], A. Ābele[3], M. Knite[1], A.Šutka[4]** **DESIGN OF WIDER POTENTIAL WINDOW PVA HYDROGEL ELECTROLYTES FOR SUPERCAPACITORS** [1]Institute of Technical Physics, Riga Technical University, Riga, Latvia [2]Institute of Solid State Physics, University of Latvia, Riga, Latvia [3]Institute of Polymer Materials, Riga Technical University, Riga, Latvia [4]Research Laboratory of Functional Materials Technologies, Riga Technical University, Latvia	42
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14.45-15.00	**H. Beneš[1], M. Perchacz[1], R.K. Donato[2], S. Livi[3], D. Popelková[1], P. Ecorchard [4]** **ROLES OF PHYSICAL AND COVALENT INTERACTIONS IN EPOXY NANOCOMPOSITES** [1]Institute of Macromolecular Chemistry AS CR, v.v.i., Prague, Czech Republic [2]MackGraphe – Graphene and Nanomaterials Research Center, Mackenzie Presbyterian University, São Paulo, Brazil [3]Université de Lyon, INSA Lyon, CNRS, Ingénierie des Matériaux Polymères, Villeurbanne, France [4]Institute of Inorganic Chemistry AS CR, v.v.i., Řež, Czech Republic	46
15.00-15.15	**R. Butkutė, L. Pečiulytė, R. Lygaitis, G. Buika, J. V. Gražulevičius** **PHENANTHROIMIDAZOLE‑BASED MONOMERS: SYNTHESIS, PROPERTIES AND SELF‑POLYMERIZATION** Department of Polymer Chemistry and Technology, Kaunas University of Technology, Kaunas, Lithuania	47
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POSTER SESSION

13th of September

1.	**T. Krivorotova, G. Lipinskaite, R. Makuska** **CONTROLLED SYNTHESIS OF ANIONIC AMPHIPHILIC GLYCOPOLYMER BOTTLE-BRUSHES** Faculty of Chemistry and Geosciences, Vilnius University, Vilnius, Lithuania	50
2.	**P. Radzevicius, M. Steponaviciute, T. Krivorotova, R. Makuska** **SELF-ASSEMBLY IN AQUEOUS SOLUTIONS OF THERMORESPONSIVE PENTABLOCK COPOLYMERS SYNTHESIZED BY ONE-POT RAFT POLYMERIZATION** Department of Polymer Chemistry, Vilnius University, Vilnius, Lithuania	51
3.	**E.V.Chernikova[1], A.V.Plutalova[1], K.O.Mineeva[1], N.S.Gubina[1], N.I.Osipova[2], Yu.V.Levina [2], S.D.Zaitsev [3]** **DIRECT SYNTHESIS OF AMPHIPHILIC RANDOM, BLOCK AND BLOCK-RANDOM COPOLYMERS OF ACRYLIC ACID AND STYRENE OR n-BUTYL ACRYLATE VIA RAFT SOLUTION POLYMERIZATION** [1]Polymer Department, Faculty of Chemistry, Lomonosov Moscow State University, Moscow, Russia [2] Lomonosov Institute of Fine Chemical Technologies, Russian Technological University – MIREA, Moscow, Russia [3]Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod, Russia	52
4.	**E.V.Chernikova[1], N.S.Serkhacheva[2], V.V.Ogay[2], A.V.Smirnov[2], N.N.Prokopov[2]** **POLYMERIZATION-INDUCED SELF-ASSEMBLY: SEEDED RAFT POLYMERIZATION FOR THE SYNTHESIS OF ABC AMPHIPHILIC BLOCK COPOLYMERS** [1]Polymer Department, Faculty of Chemistry, Lomonosov Moscow State University, Moscow, Russia [2] Lomonosov Institute of Fine Chemical Technologies, Russian Technological University – MIREA, Moscow, Russia	53
5.	**A.I.Gostev[1], E.V.Sivtsov[1], A.V.Dobrodumov[2]** **COPOLYMERIZATION OF N-VINYL SUCCINIMIDE WITH VINYL ACETATE IN THE PRESENCE OF DIBENZYL TRITHIOCARBONATE** [1] Saint-Petersburg State Institute of Technology, Saint-Petersburg, Russia [2] Institute of Macromolecular Compounds of RAS, Saint-Petersburg, Russia	54
6.	**P.M.Pakhomov, S.D. Khizhnyak, V.E. Sitnikova** **CHARACTERIZATION OF THE MORPHOLOGY OF POLYMER COMPOSITES AND MEMBRANES BY OPTICAL SPECTROSCOPY** Physical Chemistry Department, Tver State University, Tver, Russia	55
7.	**M. Cekaviciute, J. Simokaitiene, K. Baucyte, D. Volyniuk, J.V. Grazulevicius** **GLASS-FORMING ENAMINES AS HOLE-TRANSPORTING MATERIALS FOR OPTOELECTRONICS** Department of Polymer Chemistry and Technology, Kaunas University of Technology, Kaunas, Lithuania	56
8	**M. Lebedevaite[1], S. Kasetaite[1], J. Ostrauskaite[1], E. Skliutas[2], M. Malinauskas[2]** **SOYBEAN OIL-BASED PHOTOSENSITIVE RESIN FOR OPTICAL 3D PRINTING** [1] Department of Polymer Chemistry and Technology, Kaunas University of Technology, Kaunas, Lithuania [2] Laser Research Center, Vilnius University, Vilnius, Lithuania	57
9	**G. Krucaite[1], D. Tavgeniene[1], U. Baranauskyte[1], B. Zhang[2], S Grigalevicius[1]** **POLYETHERS CONTAINING CARBAZOLE-BENZOTHIADIAZOLE CHROMOPHORES AS SOLUTION PROCESSED MATERIALS FOR HOLE TRANSPORTING LAYERS OF OLEDS** [1] Department of Polymer Chemistry and Technology, Kaunas University of Technology, Kaunas, Lithuania [2] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, China	58
10	**D. Tavgeniene[1], S. Grigalevicius[1], D. K. Dubey[2], M. Singh[2], S. Sahoo[2], J. H. Jou[2]** **POLYMERIC HOLE-TRANSPORTING NETWORK AS A MIXED HOST FOR EFFICIENT SOLUTION-PROCESSED RED ORGANIC LIGHT EMITTING DIODES** [1]Department of Polymer Chemistry and Technology, Kaunas University of Technology, Kaunas, Lithuania [2]Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan	59
11	**M. Auguścik[1], J. Ryszkowska[1], L. Szczepkowski[2]** **COMPOSITE OF VISCOELASTIC POLYURETHANE FOAMS WITH DIFFERENT HERBAL FILLERS** [1]Warsaw University of Technology, Faculty of Materials Science and Engineering, Warsaw [2]FAMPUR Adam Przekurat Company, Bydgoszcz	60

33.	**A. Aniskevich, S. Stankevich, J. Sevcenko** **PREDICTION METHOD OF ELECTRICAL CONDUCTIVITY OF NANO-MODIFIED GLASS FIBRE REINFORCED PLASTICS** Institute for Mechanics of Materials, University of Latvia, Riga, Latvia	84
34.	**P. Akishin[1], E. Barkanov[1], N. L. Miazza[2], S. Galvez[2]** **METHODOLOGY FOR THE BUILDING OF CURING KINETIC MODELS** [1]Institute of Materials and Structures, Riga Technical University, Riga, Latvia [2]AIMPLAS, Paterna, Spain	85
35.	**G. Japins, K. Kalnins, O.Ozolins, E. Skukis** **INVESTIGATION OF THE RESIDUAL STRENGTH OF CFRP ALUMINIUM HONEYCOMB SANDWICH PANELS** Institute of Materials and Structures, Riga Technical University, Riga, Latvia	86
36.	**S. Gaidukovs[1], A. Medvids[2], P. Onufrijevs[2], L. Grase[3], J. Brunavs[4]** **DEVELOPMENT OF UV-CURED EPOXY RESIN BASED ON MARINELINE® FORMULATION FOR APPLICATIONS AS EFFICIENT REPAIR SYSTEM OF BOAT TANKS' PROTECTIVE COATING** [1]Institute of Polymer Materials, Faculty of Materials Science and Applied Chemistry, Riga Technical University, Latvia [2]Institute of Technical Physics, Faculty of Materials Science and Applied Chemistry, Riga Technical University, Latvia [3]Institute of Silicate Materials, Faculty of Materials Science and Applied Chemistry, Riga Technical University, Latvia [4]Jūras Servisa Centrs Ltd, Riga, Latvia	87

14th of September

1.	**E.V.Sivtsov, A.I.Gostev, O.M.Nesterova, V.A. Ostrovskii** **RAFT POLYMERIZATION OF N-HETEROCYCLIC VINYL MONOMERS IN THE PRESENCE OF DIBENZYL TRITHIOCARBONATE** Saint-Petersburg State Institute of Technology, Saint-Petersburg, Russia	88
2.	**E.A.Lysenko [1], K.O.Mineeva [1], N.I.Osipova [2], N.S.Serkhacheva [2], E.V.Chernikova [1]** **PHYSICO-CHEMICAL PROPERTIES OF AMPHIPHILIC STYRENE/ACRYLIC ACID COPOLYMERS IN POLAR SOLVENTS – FINE ADJUSTMENT VIA RAFT COPOLYMERIZATION** [1]Polymer Department, Faculty of Chemistry, M.V. Lomonosov Moscow State University, Moscow, Russia [2]Lomonosov Institute of Fine Chemical Technologies, Russian Technological University – MIREA, Moscow, Russia	89
3.	**R. Keruckiene, M. Guzauskas, J. V. Grazulevicius** **SYNTHESIS AND PROPERTIES OF *meta*-SUBSTITUTED ELECTROACTIVE BENZOPHENONE DERIVATIVES** Department of Polymer Chemistry and Technology, Kaunas University of Technology, Kaunas, Lithuania	90
4.	**V.S. Laguseva, S.D. Khizhnyak, A.I. Ivanova, P.M.Pakhomov** **KINETIC FEATURES OF FORMATION OF SUPRAMOLECULAR HYDROGELS BASED ON L-CYSTEINE, SILVER NITRATE AND METAL HALIDES** Physical Chemistry Department, Tver State University, Tver, Russia	91
5.	**D.V. Vishnevetsky, A.E. Solov'eva, P.M. Pakhomov S.D. Khizhnyak** **SELF-ORGANIZATION PROCESSES IN THE MIXED AQUEOUS SOLUTIONS OF L-CYSTEINE, SILVER NITRATE AND POLYETHYLENE GLYCOL** Physical Chemistry Department, Tver State University, Tver, Russia	92
6.	**V. Klimkevicius, M. Kavaliauskaite, A. Babiceva, V. Garina, R. Makuska** **SYNTHESIS AND STUDY OF THERMORESPONSIVE AMPHIPHILIC COPOLYMERS** Department of Polymer Chemistry, Vilnius University, Vilnius, Lithuania	93

SYNERGIES IN LUBRICATION

A. Dėdinaitė[1,2], P.M. Claesson[1,2]

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[2] RISE Research Institutes of Sweden, Materials and Surfaces, Stockholm, Sweden

William Hunter, the surgeon, wrote "The fabric of the joints in the human body is a subject so much the more entertaining, as it must strike every one that considers it attentively with an idea of fine mechanical composition. Wherever the motion of one bone upon another is requisite, there we find an excellent apparatus for rendering that motion safe and free." (Source: Philosophical Transacions of the Royal Society, vol. 42, no. 470, p. 514 - 521, 1743). Now, 275 years past Hunter's time, we can not express our admiration to the function of the synovial joint better. We appreciate though that much of its function is owing to the synergistic action of the many components of the synovial joint acting as lubricants in an aqueous environment. Oil-based lubricants are widely used in technology. Contrary, living organisms have developed water-based lubrication systems that work in boundary lubrication regime. What are these magic lubricating biological molecules? Perhaps, the magic is in their combinations?

In this paper we focus on water-based lubrication in the boundary-lubrication regime, and particularly on lubrication synergies. We aim at understanding how molecules work in synergy to provide superior lubrication. On the one hand, we discuss the intermolecular synergies where the combination of different molecules prove to be beneficial. For example, we address the case where the cartilage oligomeric matrix protein anchors and structures lubricin on the surface such that lubricins ability to lubricate the hydrophobic surface increases tenfold. On the other hand, we discuss the intramolecular synergies where either Nature, or the scientist, skilfully combines antagonistic properties in one molecule to achieve synergistic lubrication. As an example of this approch, we can mention recombinant mucins: molecules with an immunoglobulin foot and mucinous brush. While the foot provides molecular anchoring on the surface, the brush yields surface lubrication via its extensive hydration.

References:

1. *An, J., Dėdinaitė, A., Nilsson, A., Holgersson, J., Claesson, P.M.* Comparison of a Brush-with-Anchor and Train-of-Brushes Mucin on Poly(methyl methacrylate) surfaces: Adsorption, Surface Forces, and Friction // Biomacrmolecules, 2014, v. 15, no.4, P. 1515 – 1525
2. *Raj, A., Wang, M., Liu, C., Ali, L., Karlsson, N.G., Claesson, P.M., Dėdinaitė, A*. Molecular synergy in biolubrication: The role of cartilage oligomeric matrix protein (COMP) in surface-structuring of lubricin // Journal of Colloid and Interface Science, 2017, v. 495, P. 200 – 206.
3. *Dėdinaitė, A. and Claesson, P.M.* Synergies in Lubrication // Physical Chemistry Chemical Physics, 2017, v. 19, no 35, P. 23677 – 23689.

ENCAPSULATION STRATEGIES IN MULTIFUNCTIONAL BIOMATERIALS. AN OVERVIEW

A.Jiménez, M. Ramos, M. del Carmen Garrigós

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Encapsulation provides a significant protection for active and functional compounds against drastic conditions, such as oxidation and thermal degradation, thereby contributing to increase the shelf-life of the encapsulated active ingredients and permitting the application to functional biocomposites with enhanced thermal degradation. Micro and nano-encapsulation technologies have emerged as promising alternatives to control the release of essential oils and other compounds with specific functionalities, such as antioxidant, antimicrobial and others, onto material surfaces and to increase stability against environmental factors particularly to high temperatures. The use of encapsulation strategies to protect the intrinsic volatile functional molecules is getting some space in research since it is an innovative procedure to get thermal resistance while preserving the valuable functionalities provided by essential oils and other volatile compounds [1,2]. Furthermore, encapsulation was also shown to promote a controlled release of the encapsulated compounds; to change the physical properties of the initial material; and to improve the bioavailability of the encapsulated compounds, which is useful in selected applications such as biomedical [3] and active food packaging [4]. Micro- and nano-encapsulation certainly represents a viable and efficient approach to increase the physical and thermal stability of the active substances even after the use of aggressive processing methodologies for biocomposites. Encapsulation techniques are based on the formation of a physical barrier between the external media and sensitive active compounds to be protected against thermal degradation, oxidation and changes in moisture and pH, resulting all of them in loss of functionalities. Encapsulated micro and nano-particles can be produced by spray-drying, spray-cooling/ chilling, coacervation, gelation, solvent evaporation, electrospinning extrusion methods and supercritical fluid expansion among others. The large amount of techniques available for encapsulation results in a clear increase in versatility of these systems where differences between encapsulating agents are essential to ensure that the active principles contained in the microcapsules are protected in an efficient way and could resist high temperatures during processing after their incorporation to polymer-based matrices. In addition, microencapsulation and nanoencapsulation are advocated to enhance stability [5] and are normally tested as functionalization tools to obtain active molecules to be further integrated into polymer matrices. Protection against degradation of the valuable bioactive molecules by nanoclays and other matrices (even hydrophobic molecules) is one of the favourite approaches to permit the stabilisation of these active compounds. The reason of this behaviour was proved to be the hindrance from the contact with the atmospheric oxygen because the active molecules were incorporated in the interlayer space [6].

The main goal of this lecture is to provide a general overview of the encapsulation at the micro and nanoscale focusing on the use of the encapsulated materials in the formulation of specific multifunctional biocomposites with multiple applications in key industrial sectors such as biomedical and active food packaging, among others.

References:

1. S. Sarkar; B. Kim; *Polym Degrad Stab.* **2017**, *138*, 72.
2. Y. Fan; Y. Liu; L. Gao; Y. Zhang; J. Yi; *Food Chem*. **2018**, *261*, 283.
3. M. Fabbri: G. Guidotti; M. Soccio; N. Lotti; M. Govoni; E. Giordano; N. Gazzano; R. Gamberini; B. Rimini; A. Munari; *Polym. Degrad. Stab.* **2018**, *153*, 53.
4. K. Munhuweyi; O.J. Caleb; A.J. van Reenen; U.L. Opara; *LWT-Food Sci. Tech.* **2018**, *87*, 413.
5. D.B. Rodriguez-Amaya, *Current Opinion in Food Science*, **2016**, *7*, 20.
6. Y. Kohno, M. Inagawa, S. Ikoma, M. Shibata, R. Matsushima, C. Fukuhara, Y. Tomita, Y. Maeda, K. Kobayashi. *Applied Clay Science*, **2011**, *54*, 202.

BIPOLAR MOLECULAR MATERIALS FOR ORGANIC LIGHT-EMITTING DIODES

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Star-shaped derivative of triazine and carbazole 2,4,6-tris(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)-1,3,5-triazine was found to be effective blue TADF emitter. OLED containing this emitter dispersed in bis[2-(diphenylphosphino)phenyl] ether oxide with emission peak at 475 nm was fabricated [1]. Turn-on voltage of the device was found to be 5-6 V with a maximum external quantum efficiency (EQE) of 9.5%.

Derivative of 3-(trifluoromethyl)benzonitrile and 3,3'-bicarbazole was found to exhibit both TADF and exciplex-forming properties. Warm-white OLED based on this material showed EQE of ca. 20 %.

The derivative of acridan and dicyanobenzene was found to be efficient TADF-type emitter exhibiting aggregation induced emission enhancement. Green OLED fabricated using this emitter exhibited maximum current, power efficiency and EQE of 68 cd/m^2, 62 lm/W and 22.5 %, respectively.

By utilization of the derivatives cyanophenyl and ditertbutylcarbazolyl substituted triphenylbenzene with the different substitution pattern as host and guest of the emissive layer, deep-blue OLED based on triplet-triplet annihilation with EQE of 14.1% was fabricated.

A series of carbazole-quinoxaline-carbazole derivatives exhibiting TADF and mechanochromic luminescence properties were synthesized and studied. Green-blue to green-yellow TADF OLEDs fabricated by solution processing demonstrated EQE up to 10.9% and luminance of 16760 cd m^{-2}.

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References:

1. *Matulaitis T., Imbrasas P., Kukhta N.A., Baronas P., Buciunas T., Banevicius D., Kazlauskas K., Grazulevicius J.V., Jursenas S.* Impact of Donor Substitution Pattern on the TADF Properties in the Carbazolyl-Substituted Triazine Derivatives // J. Phys. Chem. C., – 2017. – 121. –P. 23618–23625.
2. *Kukhta N., Matulaitis T., Volyniuk D., Ivaniuk K., Turyk P., Stakhira P., Grazulevicius J.V., Monkman A.P.* Deep-Blue High-Efficiency TTA OLED Using Para- and Meta-Conjugated Cyanotriphenylbenzene and Carbazole Derivatives as Emitter and Host // J. Phys. Chem. Lett., – 2017, – 8, –P. 6199– 6205.

PREPARATION OF FIBROUS ELECTROSPUN MEMBRANES WITH ACTIVATED CARBON FILLER

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Suspensions electrospinning applied to produce fibrous polymer membrane heavily filled with activated carbon (AC) particles. Continuous phase of suspension is a solution of polyacrylonitrile (PAN) in polar solvent and dispersed phase is suspended in non-polar solvent AC particles. Ionic liquid 1-ethyl-3-methylimidazolium acetate (EmimAc) added to both phases to improve electrospinning and enhance electrical conductivity of electrospun mat. These types of mambranes developed as electrode materials for energy storage devices.

Typically compounding of AC with polymer significantly decrease accessibility of particle surface. Thus polymer-AC electrodes have to balance between electric and mechanical properties, but not combine both properties. Fibrous mats combine high macroscopic porosity and ion permeability with high mechanical strength and low weight. Phase separation in suspension prevents formation of uniform polymer layer on the surface of carbon particles during electrospinning of fibers. Electrospun fibers with diameter near to 100 nm show ultimate mechanical strength, and uncoated AC particles have high electric capacity.

In this study we obtain electrospun membranes with up to 60wt.% of activated carbon in it, AC particles are connected between each other by PAN nanofibers, and covered with PAN nanfibrous fine mesh.

EFFICIENCY ENHANCEMENT AND LIFETIME ELONGATION IN ORGANIC/HYBRID ELECTROLUMINESCENCE DEVICE WITH BLUE EMISSION

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In this presentation, we will demonstrate the improvement of efficiency and lifetime in organic light-emitting diode (OLED) and quantum-dot light-emitting diode (QLED) with blue emission, which is an important bottleneck for OLED/QLED development. Improvements in different blue OLEDs, including phosphorescent, thermally-delayed delayed fluorescence (TADF), triplet-triplet annihilation (TTA) emitters from viewpoints of materials and devices will be introduced. Pros and cons of these technologies will be also compared. >30% and >50% external quantum efficiency (EQE) was achieved in phosphorescent OLED without and with light-extraction techniques. Half-lifetime of the blue TTA-OLED >50000 hours was achieved with 1000 cd/m2 initial luminance. Besides, efficiency and lifetime improvements of blue QLED will be also presented

LOCAL SURFACE NANOMECHANICAL AND WEAR PROPERTIES

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Designated Atomic Force Microscopy, AFM, operational modes utilize fast collection of tip-surface force curves for extracting local surface mechanical properties, and AFM is also suitable for investigating local friction and wear. This presentation discusses these possibilities with focus on polymer coatings with applications for corrosion protection. Situations with and without added nanoparticles will be discussed. In nanocomposites particle-polymer interactions will influence the properties of the matrix polymer next to the particle surface, providing different physicochemical properties than in the bulk matrix. To evaluate the properties of this interphase region remains a challenge. In this presentation we will discuss how different AFM methods can be utilized to probe the surface nanomechanical properties of nanocomposite surfaces, including the interphase region [1-3]. If time permits we will also show data for soft hydrogels that are particularly challenging to investigate due to softness and viscoelasticity.

The local wear of organic coating will be discussed, and we will follow the development with increasing load. At low loads we find smooth friction and a smooth wear scar. As the load is increased stick-slip becomes prominent leading to formation of ripple structures in the worn area due to plastic deformation. The characteristic stick-slip length is very similar to the resulting ripple spacing as evaluated by 2D Fourier analysis. At even higher loads abrasive wear becomes dominant.

Nanomechanical mapping of surfaces of polymers, nanocomposites and hydrogels provide new insight into how the microstructure affects surface mechanical properties, including wear, which is of importance for the design and performance of such materials.

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References:

1. *Huang H., Dobryden I., Ihmer N., Johansson M., Ma H., Pan J. and Claesson P.M.* Temperature-dependent surface nanomechanical properties of a thermoplastic nanocomposite// J. Colloid Interface Sci. - 2017. - Vol 494 - P. 204-214.
2. *Huang H., Dobryden I., Thorén P.A., Ejenstam L., Pan J., Fielden M.L., Haviland D.B. and Claesson P.M.* Local surface mechanical properties of PDMS-silica nanocomposite probed with Intermodulation AFM//Compos. Sci. Technol.- 2017. – Vol. 150 -P. 111-119.
3. *Claesson P.M., Dobryden I., Li G., He Y., Huang H., Thorén P.A. and Haviland D.* From force curves to surface nanomechanical properties// Phys. Chem. Chem. Phys. – 2017. - Vol. 19 – P. 23642-23657.

SUSTAINABLE COMPOSITES BASED ON POLYAMIDES REINFORCED WITH RECYCLED CARBON FIBERS - MICRO-STRUCTURE AND FATIGUE PERFORMANCE

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Sustainability becomes more in more important in plastics products. Up to now the focus is mostly on paganing and single-use products. The combination of bio-based engineering plastics like polyamide with carbon fibers allows to achieve outstanding properties in short fiber reinforced composites for injection molding applications. In this field of application fatigue strength become more and more important for short fiber composites. Carbon fibers are widely used in aerospace parts. The valuable production waste is in the focus of raw material recycling. After pyrolysis the commercially available recycled long fibers are ready for compounding via twin-screw extruder.

Different bio-based polyamides from the type x.10 were compounded with 30wt% recycled carbon fibers. The micro structure and fiber length was evaluated by using high-resolution tomography (voxel size under 1µm) and Dynamic-Image-Analysis. Different mechanical tests were done to characterize the quasi-static, impact and cyclic dynamic performance of the composites.

The carbon fiber composites show a significant increase of Youngs' Modulus and tensile strengths compared to the neat polyamides. Besides the short carbon fibers (mean value around 80µm), larger impurities from the carbon fiber recycling process were observed. Due to this, the tensile strengths of these sustainable composites are lower compared to composites with unused carbon fibers and approximately on the level of glass fiber reinforced polyamides. The fatigue strengths range between 65 and 70% of the quasi-static strength of the same composite. The conditioning state (dry, wet or heat-aged) has a significant influence on the properties of the composites.

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POLYSTYRENE-BASED COIL-BRUSH COPOLYMERS: SYNTHESIS, PROPERTIES AND SELF-ASSEMBLY

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The interest in synthesis and investigation of precisely constructed ionic molecular brushes (brush polyelectrolytes) of various topologies is increasing. Due to the specific geometry and ionisable groups, they possess unique physicochemical properties and can be applied in various fields of science, medicine or industry as drug nanocarriers, dispersants, surfactants, nano-reactors, materials for tissue engineering, stimuli-responsive coatings, biosensors or smart surfaces [1, 2]. Subject to the nature of the monomers and macromolecular structure, these polymers respond to different external stimuli, such as pH, solvent, temperature or ionic strength. Among all fascinating characteristics, the most attractive is brush copolymers ability to self-assemble into various nano-scaled morphologies, including spherical micelle, cylinder, vesicle, and lamellae.

The main task of the present work was elaboration of the synthetic procedures for the preparation of polystyrene-backbone-based diblock and triblock coil-brush copolymers by RAFT polymerization, and comparative study of micellization behavior of such coil-brush copolymers of various architecture.

First, polystyrene (pSt) was synthesized by RAFT polymerization mediated by three especially developed RAFT chain transfer agents (CTA) with different location of trithiocarbonate (TTC) groups. In all the cases, polymers with low dispersity index (Đ 1.10-1.18) and reasonably high degree of polymerization (DP up to 135) were obtained. In the second step, previously synthesized pSt was used as macroCTA to mediate RAFT polymerization of vinylbenzyl chloride (VBC) to yield diblock and triblock copolymers with different position of the blocks. In the third step, previously synthesized random, diblock and triblock copolymers were modified to the derivatives with multiple TTC groups (pSt-*co*-pVBC-TTC). Finally, RAFT polymerization of acrylic acid (AA) in the presence of pSt-*co*-pVBC-TTC was done, and the target random, diblock (coil-brush) and triblock (brush-coil-brush or coil-brush-coil) anionic copolymers with relatively short (DP 6-25) and rather long (DP 30-50) pAA side chains were synthesized [3].

The films of polystyrene-based anionic brush copolymers are hydrophilic (water contact angle between 15º and 45º). The best wettability is characteristic for the films prepared using brush-coil-brush copolymers with long pAA side chains. The micellization and aggregation behaviour of polystyrene-based coil-brush copolymers in dioxane/water mixtures depends on structure of the copolymers and the length of pAA side chains. Coil-brush and brush-coil-brush copolymers tend to form spherical micelles (D_h 20–100 nm) and micellar aggregates (D_h 300-1000 nm), especially, when pAA side chains are short.

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

References:

1. *Verduzco R., Liv X., Pesek S. L., and Stein G. E.* Structure, function, self-assembly, and applications of bottlebrush copolymers // Chem. Soc. Rev. – 2015. – Vol. 44 – P. 2405–2420.
2. *Moad G.* RAFT polymerization to form stimuli-responsive polymers // Polym. Chem. – 2017. – Vol. 8 – P. 177–219.
3. *Jonikaite-Svegzdiene J., Kudresova A., Paukstis S., Skapas M., Makuska R.* Synthesis and self-assembly of polystyrene-based diblock and triblock coil-brush copolymers // Polym. Chem. – 2017. – Vol. 8 – P. 5621–5632.

TALL OIL FATTY ACID EPOXIDATION USING NOVEL HETEROGENEOUS PHASE CATALYSTS

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The development of advanced new materials and technologies for bio-based products is immensely needed as the world is facing an ever-increasing variety of challenges due to increasing public concern about global sustainability. The potential of the available bio-resources in value-added sectors still needs to be maximised and new approaches through the more complete deployment of the twelve principles of Green Chemistry have to be delivered. Bio-based products and technologies should be more atom efficient, achieve higher yields, generate less waste and utilize less energy, hazardous conditions and chemicals. Advanced biocatalysts like heterogeneous phase ion exchange resin provide such solution.

Various plant oils have been proposed as a replacement feedstock for bio-based polyurethane production. Unfortunately, most vegetable oils, like rapeseed oil, soybean oil and sunflower oil are considered as first generation renewable materials, because their production has to compete with food production [1]. Tall oil is a by-product of the wood pulping process and it can be considered as cheap raw material for polyol production [2]. This study demonstrates how it is possible to introduce oxirane rings into fatty acids of tall oil and subsequently synthesize polyols with high functionality.

Epoxidation of fatty acids as one of the steps for polyol production is done with peracetic acid which is obtained in situ from hydrogen peroxide and acetic acid. A high conversion rate to oxirane – 80% has been reported for fatty acid methyl esters. Before epoxidation of the tall oil, the methyl esters of the fatty acids have to be synthesised, which increases the total costs of polyol production. In this study, neat fatty acids were epoxidized to propose more cost-effective process.

Different catalyst influence, H2SO4 and ion exchange resin Amberlite IR120 and acetic acid content influence on epoxidation kinetic were studied. Epoxidation process was followed as change of conversion to oxirane as well as by change of iodine value, which was determined from a change of 3008 cm-1 absorption band in FTIR. Obtained epoxidized tall oil contained up to 2.31 mmol/g of epoxy groups which is 41,9 % of theoretically possible oxirane oxygen yield. Epoxidized tall oil was further used to synthesise polyols with high functionality by oxirane ring opening and simultaneous carboxylic group esterification with polyfunctional alcohols. Novel polyols were used to develop rigid PU foams with an apparent density of 40±1 kg/m3 and their common characteristics, like thermal conductivity, closed cell content and mechanical properties were analysed.

References:

1. Zhang C, Garrison TF, Madbouly SA, Kessler MR. Recent advances in vegetable oil-based polymers and their composites // Prog. Polym. Sci. – 2017. - Vol. 71 – P. 91-143.
2. Balo F. Feasibility Study of ‘Green’ Insulation Materials Including Tall Oil: Environmental, Economical and Thermal Properties // Energy and Buildings. – 2014. – Vol. 86, - P. 161–175.

FLOW BIREFRINGENCE OF POLYMERS WITH BIOLOGICAL APPLICATIONS

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The development of the synthesis of polymers with given properties requires as well a detailed study of their properties at the molecular level. Community of the chemist-synthetics and the physicists-researchers establishes of connections between the structures of a monomer unit of a macromolecule, the properties of polymers and materials based on them in their common synchronized work. Investigations of the optical properties of polymers at the molecular level by flow birefringence are the most sensitive both to the structure of the monomeric unit of the macromolecule and to the conformation of its chain.

In the present work, the Maxwell effect of alkylated copolymers based on N-vinyl amides was studied. The influence of hydrophobic alkyl side groups on the size of macromolecules and their conformation in aqueous solutions is discussed.

Also in the paper the Maxwell effect in solutions of macromolecules of poly-N-vinyl succinimide in benzyl alcohol and dimethylformamide was studied. A comparison of the results of optical characteristics with analogous characteristics of poly-N-vinylpyrrolidone is carried out. The chemical structures the both polymers are very similar.

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CATIONIC POLYMERIZATION OF ISOBUTYLENE USING IONIC LIQUIDS AS CATALYSTS: EFFECT OF IONIC LIQUID NATURE, CATALYST AGING, AND SONICATION

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Low molecular weight polyisobutylene possessing *exo*-olefin terminal group (highly reactive polyisobutylene, HR PIB) is a key intermediate in the manufacturing of motor oil and fuel additives.[1] Recently, a number of new methods for the synthesis of HR PIB have been reported.[2,3] Among them, the complexes of $AlCl_3$ and $RAlCl_2$ with ethers are the most promising catalysts for the synthesis of HR PIB due to their low cost and high activity.[2,3] However, the application of complexes of $AlCl_3$ in *n*-hexane (industrially relevant solvent) is limited due to their low solubility in this solvent, while the complexes of $RAlCl_2$ results in HR PIB with relatively high polydispersity ($M_w/M_n=3.0 – 4.5$). In this work, we present new catalysts for the synthesis of HR PIB based on the acidic chlorometallate ionic liquids in the presence of diisopropyl ether.

A series of imidazole-based acidic (χLA)>0.6) ionic liquids (RmimCl-LA, where R=Et or Bu, LA= $AlCl_3$, $AlBr_3$, $^iBuAlCl_2$, $FeCl_3$, $GaCl_3$, and BBr_3) has been tested in the cationic polymerization of isobutylene. Among different ILs tested, emimCl-$AlCl_3$, emimCl-$FeCl_3$ and emimCl-$GaCl_3$ showed best results in terms of monomer conversion, *exo*-olefin content and polydispersity.[4,5] It was shown that reaction rate depended strongly on the rate of partial hydrolysis of corresponding ionic liquid and increased in the following order: emimCl-$FeCl_3$<emimCl-$GaCl_3$<emimCl-$AlCl_3$. It was demonstrated that emimCl-$FeCl_3$ is the most promising catalyst for the synthesis of HR PIB with desired low molecular weight ($Mn<2500$ g mol^{-1}) and polydispersity ($M_w/M_n<2.5$) and high content of exo-olefin end groups (>85%). However, due to poor dispergation of emimCl-$FeCl_3$ in *n*-hexane as well as its high stability toward hydrolysis, the catalyst aging and/or sonication of reaction mixture is required in order to provide acceptable polymerization rate. Finally, the use of ILs as catalysts for the synthesis of HR PIB allows overcoming the main disadvantage of complexes of alkylaluminum dichlorides with ethers that is high polydispersity of the synthesized polymers ($M_w/M_n=3.5 – 4.5$).[4,5] It is evident that ILs-based initiating systems show great potential for industrial applications and can be a good alternative to the currently used BF_3-based systems.

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References:

1. *Mach H. and Rath P.* Highly Reactive Polyisobutene as a Component of a New Generation of Lubricant and Fuel Additives // Lubr. Sci. – 1999. – Vol. 11-2. – P. 175–185.
2. *Kostjuk S. V.* Recent Progress in the Lewis Acids Co-initiated Cationic Polymerization of Isobutylene and 1,3-Dienes // RSC Advances. – 2015. – Vol. 5. – P. 13125–13144.
3. *Kostjuk S. V., Yeong H. Y. and Voit B.* Cationic Polymerization of Isobutylene at Room Temperature // J. Polym. Sci. Part A: Polym. Chem. – 2013. – Vol. 51. – P. 471–486.
4. *Vasilenko I. V., Berezianko I. A., Shiman D. I. and Kostjuk S. V.* New Catalyst for the Synthesis of Highly Reactive Polyisobutylene: Chloroaluminate Imidazole-Based Ionic Liquid in the Presence of Diisopropyl Ether // Polym. Chem. – 2016. – Vol.7. – P. 5615–5619.
5. *Berezianko I.A., Vasilenko I. V. and Kostjuk S. V.* Acidic Imidazole-Based Ionic Liquids in the Presence of Diisopropyl Ether as Catalysts for the Synthesis of Highly Reactive Polyisobutylene: Effect of Ionic Liquid Nature, Catalyst Aging, and Sonication // Polymer. – 2018. Vol. 145. – P. 382–390.

BIO-BASED POLYOLS FOR RIGID POLYURETHANE FOAMS

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The main components of rigid polyurethane foams are polyols and isocyanates. Nowadays, efforts are being made to replace petrochemical polyols with those based on renewable raw materials in order to obtain bio-based and low cost polyurethane materials. Typical polyols contain 2–8 reactive hydroxyl groups and have average molecular weight from 300 to 10,000 g/mol. The two types of petrochemical polyols, polyether and polyester polyols, are materials most often used in the synthesis of foams [1,2].

Nowadays, various methods are used to obtain bio-polyols from renewable raw materials, for the application in polyurethane foams. Recently, research efforts are aimed to apply vegetable oil derivatives. The unsaturated vegetable oils, having double bonds but without hydroxyl groups, can be transformed into polyols using various chemical reactions. Two basic types of reactions are mostly described: transesterification and transamination involving esteric groups and converting double bonds into hydroxyl groups [3]. In the first case, monoglicerydes or other hydroxyl derivatives of different functionalities are obtained in the transesterification reaction of oils with glycols, glycerol, sorbitol, and sucrose or transamidization reaction usually with, for example, diethanolamine. Bio-polyols are also produced via the hydrolysis of natural triglycerides from vegetable or animal resources [2].

Moreover, sucrose, the most important starter of polyether polyols for rigid foams, is produced exclusively by extraction from natural resources. Tetrahydrofuran, a cyclic monomer used in the synthesis of poly(tetramethylene ether)glycols, can be produced from furfural, which is in turn obtained by the reaction of acid hydrolysis of pentosanes existing in many agricultural wastes. A very interesting natural starting material to prepare polyols for rigid foams is lignin, available in large quantities from the wood and cellulose industry [2].

In this presentation, different methods of bio-polyol synthesis will be shown and the used properties of such polyols will be compared taking into account their potential use to produce rigid polyurethanes foams for the applications in cryogenic temperatures.

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References:

1. Materiały Poliuretanowe / Ed. by *A. Prociak A., G. Rokicki, J. Ryszkowska* – Warszawa: *Państwowe* Wydawnictwa Naukowe PWN, 2014.
2. *Prociak A.* Bio-based polyurethane foams // In: Biofoams - Science and Applications of Bio-Based Cellular and Porous Materials / Ed. By S. Iannace and C.B. Park. - CRC Press, Boca Raton, 2016. - P. 267-285.
3. *Kirpluks M., Cabulis U., Kurańska M. and Prociak A.* Three different approaches for polyol synthesis from rapeseed oil // Key Eng. Mater. - 2013. Vol. 559 – P. 69–74.

HYDROGELS BASED ON L-CYSTEINE, SILVER NITRATE AND POLYVINYL ALCOHOL

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Obtaining and studying of the properties of supramolecular structures based on sulfur-containing amino acids and silver salts has more than a decade of experience [1]. The result of these studies was the discovery of a new gel-forming system consisting of the amino acid L-cysteine and some silver salts [2-5]. A disadvantage of supramolecular hydrogels is their low viscosity and strength properties. To increase the viscosity of the hydrogel, for example, a water-soluble polymer can be introduced into it. But it is still not clear whether supramolecular hydrogels will be compatable with a polymer solution. Thus, the aim of this work is to study the process of self-organization in mixed aqueous solutions of polyvinyl alcohol (PVA), L-cysteine and silver nitrate.

Good compatibility of aqueous solution of PVA with cysteine silver solution (CSS) was established. Using a set of methods (viscometry, UV - and IR-spectroscopy, pH-metry and dynamic light scattering), self-organization processes in aqueous solution of PVA, L-cysteine and silver nitrate under the action of sodium sulfate were investigated.

It was shown that the macromolecules of PVA interacts with the supramolecules of CSS by the formation of hydrogen bonds. At the same time, the increase in the concentration of PVA led to an increase in the viscosity of hydrogels, more pronounced thixotropic properties, an increase in the intensity of the main absorption bands in the UV spectrum, responsible for the formation of supramolecular structures in the CSS, an increase in the pH values, an increase in the average hydrodynamic particle sizes and a drop in the electrical conductivity of the system.

The study of the morphology of obtained hydrogels by scanning electron microscopy (SEM) revealed the formation of a regular macroporous structure. It was found that by changing the concentration of PVA in the solution, it is possible to adjust both the density of the spatial gel network and the porosity of the xerogel. For the highest concentration of PVA in the solution, the formation of a superporous xerogel structure was found. The possibilities of using of the obtained objects as bioactive compositions for encapsulation of various substances are discussed.

The work is performed under financial support of the Ministry of Education and Science of the Russian Federation in the frame of realizing of the State task in the field of the scientific activity (project N4.5508.2017/BP. This work is performed by means of the Equipment Center for collective Use of Tver State University.

References:

1. *L.O. Andersson //* J. of Polym. Sci., - 1972, - Vol. 10, - P. 1963.
2. *P. M. Pakhomov., S. D. Khizhnyak, et. al. //* Colloid Journal, - 2004, - Vol. 66, No 1 - P. 65.
3. *P. M. Pakhomov, S. S. Abramchuk, et. al.* // Nanotechnologies in Russia, - 2010, - Vol. 5, No 3–4 - P. 209.
4. *P. M. Pakhomov, M. M. Ovchinnikov, et. al. //* Polymer Science, Ser. A, - 2011, - Vol. 53, No 9 - P. 820.
5. *O. A. Baranova, N. I. Kuz'min, et. al.* // Fibre Chemistry, - 2011, - Vol. 43, No 1 - P. 90.

DIFFERENT EPOXIDE COUMPOUND INFLUENCE ON TWO-COMPONENT SILYTERMINATED POLYMER/EPOXIDE SYSTEMS MECHANICAL, RHEOLOGICAL AND ADHESION PROPERTIES

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Sealants and adhesives market is constantly growing because of new composite material development and increasing material requirements. Despite wide range of adhesives, still there are only some materials (polyurethane type) which can simultaneously provide good adhesion to various substrates and high material tensile strength (>3 MPa) and elongation (>100%). Previous publications [1-2] showed that some of silyl-terminated polymer/epoxy resin two-component systems (STP/EP) possessed the above properties. In these publications the effects of systems composition and various compatibilizers on the tensile, rheological and adhesion properties of the two-component materials were studied.
This contribution focuses on how different epoxy resins (bisphenol A epoxy resin, bisphenol A/F epoxy resin, modified bisphenol A epoxy resin, modified bisphenol A/F epoxy resin, reactive epoxy diluents) influence the multicomponent systems (containing from polymers, plasticizer, fillers, drying agents, adhesion promoters) tensile, rheological and adhesion properties. Results showed that epoxy resin has significant effect on materials tensile properties even in small concentrations. Changing different epoxy resins yielded multi-component materials with broad range of properties - tensile strength from 0,49 MPa until 4,06 MPa, elongation at break from 1196% until 284% - which were concluded to be sufficient for potential use of the materials in broad range of applications, starting from construction to automotive sectors.

References:

1. *Berzins R., Merijs Meri R., Zicans J*. Two Component Silyl-Terminated Polyether/Epoxy Resin Systems Mechanical and Rheological Properties// Solid State Phenomena-2017.- 267-P. 28-34.
2. *Bērziņš R., Merijs-Meri R., Zicāns J.* Amine Containing Compatibilizers Effect on Two Component Silyl-Terminated Polyether/ Epoxy Resin System Mechanical and Rheological Properties//Proceedings of the Estonian Academy of Sciences-2018.- in Press-P.1-8.

NANOCOMPOSITES OF COPOLYFLUORENES WITH CDSE/CDS/ZNS QUANTUM DOTS

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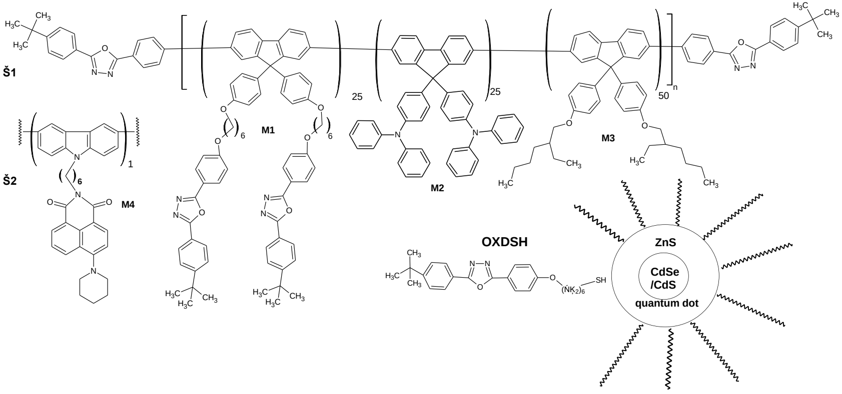
Semiconductor nanocrystals - quantum dots (QDs) - attract great attention due to their unique optical and electronic properties. Most applications require a combination of QDs with polymeric materials that play the role of a matrix and in some cases contribute to the stabilization of QD nanoparticles. In this regard, to create light-emitting diodes with improved characteristics a significant task is the creation of hybrid materials: QDs with conjugated polymers such copolyfluorenes (CPFs).



New CPFs emitting stable blue and cian light (P1 and P2) were obtained. Electron- (M1) and hole-transport (M2) monomers were introduced to the structure to balance flows of charges. P2 have the same structure as P1 but M4 (cian luminophore) was added.

New substance – derivative of oxadiazole (OXDSH) was obtained. Its structure as well as that of the monomers were confirmed by ^{1}H NMR spectroscopy. OXDSH was used as a ligand for QDs (TOPO) modification. QY of QDs slightly decreased after modification. At the UV spectra of QDs a band from ligand was found.

NCs of P1 and P2 with QDs were obtained. It was shown that fluorescence (FL) of NCs didn’t depend from the ligand type of QDs whereas EL depended significantly. Both bands from CPFs and QDs were observed at FL spectra. NCs with QD (TOPO) had very low EL. Their voltage of onset luminescence was about 30 V. Only band from QDs were observed in the spectra. In accordance with hypothetical energy diagram we supposed that in this system QDs acted as a deep trap and TOPO hindered of charge injection to QDs. NCs of CPFs with QD (OXDPO) exhibited EL with the spectra similar to FL. However EL of such NCs was worse than EL of pure CPFs (brightness was 2000 and 10300 cd/m^2 for P1 and P2 correspondently).

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TRANSFORMING GRAIN HUSKS INTO HIGHER-ADDED VALUE PRODUCTS

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Today's modern society, with its high population density, sophisticated industries and intensive methods of agriculture, produces wastes in constantly increasing scale [1]. Grain husks produced from harvesting are mostly used as a fuel, producing energy through direct combustion. However, rather than burning, such agricultural waste can be used to produce higher-added value products. Grain husk is a lignocellulosic waste, composed of cellulose fibers, hemicellulose, lignin, and can be converted to microfibers (Fig.1). This study explores the feasibility of using such lignocellulosic waste and cellulosic fibers from grain husks in the production of biocomposites.

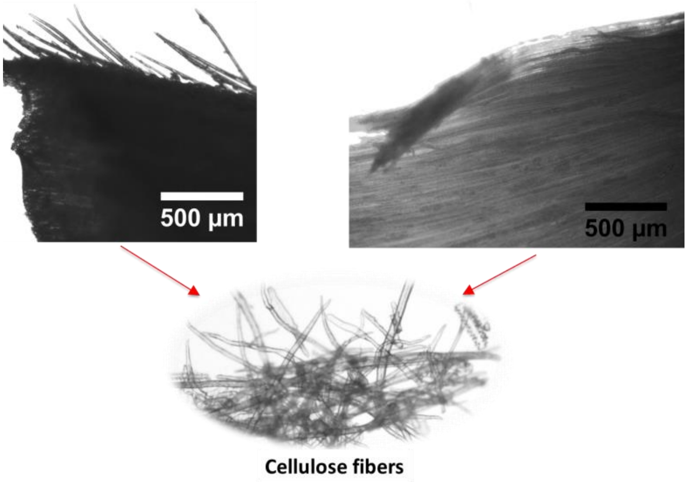

Fig.1. Cellulose fibers from grain husks

Acknowledgement. The authors are grateful to the Research Council of Lithuania for financial support of the project HyBiCo (S-M-ERA.NET-17-3).

Reference:

1. *Antoniolli Z. I., Steffen G. P., Steffen, R. B.* Rice husk and cattle manure used as substrate for the Eisenia fetida Savigny (1826) multiplication // Ciência e Agrotecnologia, Lavras, v.33, n.3, May./Jun. 2009, P.824-830.

PECULIARITIES OF SUPRAMOLECULAR HYDROGELS BASED ON SULPHUR CONTAINING AMINO ACID AND SILVER SALTS

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Nanostructured materials represent a novel class of materials which attract considerable attention of researchers in different branches of science and engineering: electronics, optics, catalysis and biomedicine. The most interesting among them are supramolecular hydrogels, which are characterized by presence not only strong bonds between the molecular fragments, but also more weak interactions realized through the coordination, π-π, dipole-dipole, van der Waals interactions, hydrogen bonding.

The work is focused on synthesis of novel supramolecular nanostructured hydrogels based on sulfur containing amino acid L-cysteine (L-Cys) and silver salts ($AgNO_3$, $AgNO_2$, $AgCH_3COO$, $AgClO_4$) and on study of gelation mechanism by means of rheological tests, UV and FTIR spectroscopy, dynamic light scattering (DLS), Nanoparticle Tracking Analysis (NTA), transmission electron microscopy (TEM). The main features of the hydrogels obtained by the authors are low concentration of the dissolved substances (~0.01%), thixotropy, biological activity of the initial components. It is established that structure and properties of the hydrogels are varied essentially in dependence on concentration of the initial components, molar ratio and a type of the silver salt. It is found out that just after mixing of the initial components silver mercaptide molecules are formed in the solution that is confirmed by FTIR spectroscopic study. According to UV-vis spectroscopy self-assembly of the silver mercaptide molecules via non-covalent bonding leads to the formation of supramolecular polymeric chains ($\text{--Ag-S(R)--Ag-S(R)--}_n$), and as a result gel precursor is obtained. Gelation in L-Cys based systems is induced by addition of electrolyte solution (for example, sulfate, chloride of various metals) into the precursor. Stability of the hydrogels over time depends mainly on a type and concentration of the electrolyte. According to DLS data, size distribution of the aggregates is varied in dependence on time, concentrations, molar ratio of the components, type of silver salt and temperature. NTA technique allowed us to provide real time monitoring of the subtle changes in the characteristics of particle populations and to characterize size distribution and concentration of the ultra low concentration samples. TEM images of the L-Cys based hydrogels demonstrate the fibrous structure of three dimensional network depending in a great extent on a type of electrolyte.

Scientific significance of the work is the study of gelation mechanism in supramolecular aqueous systems based on low molecular weight compounds. Practical importance is connected with the possibility to apply the systems with high antimicrobial activity as matrices for creation of highly efficient pharmaceutical formulations.

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This work is performed by means of the Equipment Center for collective Use of Tver State University.

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CDC CAPABILITIES IN DIFFERENT SUPERCAPACITOR APPLICATIONS

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Supercapacitors, also known as ultracapacitors, are well known energy storage devices since last century. They have wide field of applications, from small electronic devices up to light weight vehicles and heavy transportation. The main advantages of supercapacitors over the secondary batteries are high power density (~100 $kWkg^{-1}$), very long cycle-life (~10^6 cycles) and low temperature dependency of characteristics. The electrodes of supercapacitors are usually made of high-surface area carbon, which are saturated with aqueous or non-aqueous electrolyte. The capacitor charge is stored by physical adsorption of electrolyte ions in the micropores of carbon electrode. The fact that no chemical processes are accompanied in charge storage, gives the main advantages for the supercapacitors.

The carbide-derived carbon (CDC) is widely studied as the supercapacitor electrode material. The wide range of precursor carbides (TiC, SiC, Mo_2C, Al_4C_3, *etc*.) together with variable synthesis conditions allows to make carbon materials with very different structures and properties. Variability of different CDC structures also includes the high-surface area ultra-microporous carbon, which peak pore size can be exactly fitted to host the specific electrolyte ions. Possibility to nano-tune the CDC porosity and pore size distribution increases significantly the electric double-layer capacitance of respective supercapacitor electrodes, which in some cases exceeds even 100 Fcm^{-3}. This makes the CDC almost ideal electrode material for the research of different components and chemistries of energy storage devices related to variable applications.

AFM FORCE AND NANOMECHANICAL STUDY OF POLYMER ADSORPTION ON CELLULOSE NANOCRYSTALS

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The cellulose nanocrystals (CNC) are known to affect specific rheological properties in certain polymer solution, even in small added amounts, and can cause a substantial increase of the low-shear rate viscosity. Moreover, CNC can be used as a good rheology modifier for aqueous systems in many applications. Thus, for such systems, particle-polymer interactions will play a key role and affect the flow behavior. Also, adding of polymer chains into colloidal suspensions requires fundamental understanding and investigation if the polymers are adsorbed or not onto surfaces. Here we utilize atomic force microscopy (AFM) methods, such as nanomechanical, wear and force spectroscopy to directly probe polymer adsorption onto CNC thin films on silica surface in aqueous medium. Three polymers were investigated, such as neutral non-ionic poly(ethylene oxide) (PEO), anionic polyelectrolyte carboxymethyl cellulose (CMC) and cationic polyethylenimine (PEI). The AFM nanomechanical measurements showed changes in the CNC film stiffness after polymer adsorption for all three studied polymers. The polymer adsorption onto such CNC films was further verified and investigated with quartz crystal microbalance (QCM) measurements.

SELF-REINFORCED POLYMER-VENEER-COMPOSITES – CHARACTERISTICS UNDER IMPACT LOAD

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Self-reinforced thermoplastics offer interesting possibilities for technical applications. They combine exceptional mechanical properties, in particular excellent impact behavior, with an impressive lightweight construction potential. Additionally, they have good recycling qualities. Due to its low weight and comparatively high strength, wood has a high lightweight construction potential, too. In addition, wood impresses with its low carbon footprint.

Three-layered composites were manufactured out of self-reinforced plastics (PURE®, polypropylene) and wood veneer (European beech, *Fagus sylvatica*) in a hot compaction process. The outer layers each consist of wood veneer, the middle layer of eight layers self-reinforced thermoplastic fabric. Of particular interest for composites manufactured out of wood and plastics, is to know how they behave under impact stress. To investigate the behavior of the manufactured composites under impact stress, instrumented dart drop tests (penetration and impact mode) were conducted. With the composites produced, it was possible to increase the maximum force in the dart drop test (penetration mode) by almost 300% up to 4200 N in comparison to plywood (European beech) of comparable dimensions.

The manufacturing of composites based on self-reinforced thermoplastics and wood veneer offers new interesting opportunities. Both, the self-reinforced polypropylene and the veneer show independently exceptional mechanical properties and, due to their low weight, a high lightweight construction potential. The combination of this materials leads to an innovative composite with interesting characteristics. Here, the excellent quasi-static and impact properties of the composite are to be mentioned. In addition, self-reinforced thermoplastic fabrics are also produced based on bio-based thermoplastics, such as PLA. This results in the possibility of producing a fully bio-based composite with outstanding mechanical properties.

HIGH IMPACT STRENGTH PP-PET FIBRE COMPOSITES FOR INJECTION MOULDING

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The present study evaluates the use of short PET fibres as a reinforcement of polypropylene matrix. The main application of the developed composite compound are injection moulded goods. An earlier study found that the main drawback of PET fibres is their loss of mechanical performance after exposure to elevated temperature, which occurs during compounding and injection moulding [1]. For this reason the thermostable grade of PET fibres was selected for manufacturing of a composite, which was carried out at the lowest possible temperature. That gave considerable increase in terms of a composite's impact strength. Its strength was from two- to three times higher than that of its counterpart reinforced with the same weight content of glass fibres.

The study was done within the framework of the m-era.net project "High performance short-fibre biobased hybrid composites for injection moulding" (HyBiCo) funded by the National Centre for Research and Development, Poland (NCBiR) and State Education Development Agency Republic of Latvia (VIAA).

Reference:

1. *Franciszczak P., Merijs-Meri R., Kalniņš K., Błędzki A.K., Zicans J.* Short-fibre hybrid polypropylene composites reinforced with PET and Rayon fibres – Effects of SSP and interphase tailoring"// Composite Structures – 2017 – 181-P. 121-137

STUDY OF PRINTING PASTE COMPOSITION FOR NATURAL AND SYNTHETIC TEXTILES

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Textile printing is the most diverse and important of the methods used for introducing colour and design to textiles. It is a process, which combines a design idea, one or more colorants, and a textile substrate, using a technique for applying the printing paste with some precision.

The composition of dye-based printing paste is a complex combination of multiply constituents [1]. Among water, dye, thickener and pH buffers, the paste contains fixation agents and other auxiliaries. One of the most important components of printing paste, especially for reactive dye printing of cellulose-containing textiles, is urea, which is used as a swelling agent during the steaming process, dye solubilizing and disaggregation agent. However, because of high nitrogen content, it can cause environmental problems. Thus, investigation in the field of optimization of textiles printing technology is of current importance.

In continuation of the investigation of twill weave 50% cotton/ 50% polyester blended fabric one-step one-bath dyeing technology elaboration using a single dye class [2], the present study covers 100% cotton (100 g/m^2 surface density, and 0.11 mm average thickness) and 100% polyester (125 g/m^2 surface density, and 0.2 mm average thickness) fabric printing pastes' recipe elaboration for direct printing technique. The main goal of the research is to avoid the application of conventionally used constituent – urea, replacing it with polyethylene glycol ($M_w = 400$).

In this study, reactive dye-based printing paste for cotton fabric contained of water, reactive dye, sodium alginate thickener, sodium bicarbonate, sodium 3-nitrobenzenesulphonate, urea/ polyethylene glycol. Disperse dye-based printing paste for polyester fabric included water, disperse dye, dispersing agent, sodium alginate thickener, sodium 3-nitrobenzenesulphonate, urea/ tiourea/ polyethylene glycol and glycerine. Prior to printing, both cotton and polyester fabrics were pre-treated. For printing at the laboratory level, a screen printing technology was applied, following by drying at 100-105°C for 10 min and thermal fixation at 190°C for 1 min (for polyester fabric), scouring at 40-45°C for 15 min in non-ionic surfactant liquor (1-2 g/L) and drying.

Colour measurements of printed and non-printed area's cross-staining were determined according to national and international standards. Organoleptic estimation of printing quality was evaluated, using 5-point scale for stiffness, spread homogeneity, penetration, sharpness of contours and colour yield. Results of colour fastness to rubbing, washing and artificial light were also attained. Achieved results are promising as an alternative cost-effective and less environmentally hazardous printing paste option.

References:

1. Dyeing and screen-printing on textiles / *J. Kinnersly-Taylor* – London: A & C Black, 2011. – 191 p.
2. *Borisova A.* Chemical processing of cellulose-containing blended textiles // Latvian Patent – 2016. – LV15098B.

3D-PRINTED THZ PASSIVE COMPONENTS

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The recent growing interest in terahertz science and technology is due to its many important applications in physics, astronomy, chemistry, biology, and medicine, including THz imaging, spectroscopy, tomography, medical diagnosis, health monitoring, environmental control, chemical and biological identification, and future communication networks. According to the recently published "The 2017 terahertz science and technology roadmap" among the most important challenges are passive components, i.e., filters, polarizers, collimators, lenses and waveguides.

The first realization of three-dimensional (3D) "optical black hole" in microwave frequencies was presented recently on the basis of carbon hollow spheres [1,2]. Carbon-based cellular periodic structures of 100-300 microns cells might, from our point of view, offer interesting alternative for perfect absorption' applications, as they will demonstrate resonant behavior in THz-infrared frequencies and therefore possibly might block electromagnetic energy in particular space spot [3,4].

Alternatively, lossy photonic crystals comprising nanocarbon based polymer composite skeleton of particular sophisticated cellular or layered geometry could be realized by additive technologies. Having a precise control of the structure and geometry of the 3D template, we will come to regular conductive cellular structure with pre-defined electromagnetic response.

The possibility to achieve perfect absorption of THz radiation by 3D-printed cellular or layered structures will be discussed in this communication along with different ways to tune the electromagnetic response.

A series of passive components for THz applications such as shields, filters, frequency-selective surfaces, perfect absorbers and sensors will be proposed on the basis of 3D printed polymer meshes and sandwiches.

References:

1. *D. Bychanok,S. Li, A. Sanchez-Sanchez, G. Gorokhov, P. Kuzhir, F.Y. Ogrin, A. Pasc, T. Ballweg, K.Mandel, A. Szczurek, V. Fierro, and A. Celzard*, Hollow carbon spheres in microwaves: bio inspired absorbing coating // Appl.Phys.Lett. 108, 013701 (2016)
2. *D. Bychanok, S. Li, G. Gorokhov, 1 K. Piasotski, 1 D. Meisak, P. Kuzhir, E.A. Burgess, C.P. Gallagher, F.Y. Ogrin, A.P. Hibbins, A. Pasc, A. Sanchez-Sanchez, V. Fierro, and A. Celzard*, Fully carbon metasurface: absorbing coating in microwaves // J. Appl. Phys. 121(16):165103 (2017)
3. *Andrzej Szczurek; Alberto Ortona; Luca Ferrari; Ehsan Rezaei; Ghouti Medjahdi; Vanessa Fierro; Dzmitry Bychanok; Polina Kuzhir; Alain Celzard*, Carbon periodic cellular architectures // Carbon, 88, 70–85 *(*2015)
4. *M. Letellier, J. Macutkevic, P. Kuzhir, J. Banys, V. Fierro, A. Celzard*, Electromagnetic properties of model vitreous carbon foams // Carbon, 122, 217-227 (2017)

BIOCOMPATIBLE COMPOSITE MATERIALS FOR TISSUE ENGINEERING BASED ON POLYESTERS AND NANOCRYSTALLINE CELLULOSE

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Currently, the development of new biocompatible materials and the creation on their basis of biodegradable products for tissue engineering are some of the leading areas of research and commercialization1). The main emphasis of the researchers focuses on the search of technologies for creating biofunctional materials of biological and/or artificial origin, including functional cells of organs and tissues, or stimulating the regeneration of the corresponding cells in the implantation zone. The most promising biodegradable and biocompatible materials for regenerative medicine are polyesters2,3). However, their hydrophobic properties impair the adhesion of cells on the surface of the materials based on them, and therefore reduce the use of such polymers.

Thus, the aim of this work was the development of biocompatible composite materials based on polylactide and polycaprolactone filled with nanocrystalline cellulose to increase their hydrophilicity and cell adhesion. In this research, poly-D,L-lactide, poly-L-lactide and poly-ε-caprolactone were synthesized and characterized by Ostwald capillary viscosimetry and gel-permeation chromatography. These polymers were used to prepare the films containing the different amount of nanocrystalline cellulose. The morphology of the resulting films was studied by X-ray phase analysis, SEM, AFM, optical and polarization microscopy. The thermo-mechanical and physico-chemical properties of films (tensile strength, modulus of elasticity, yield strength, index of thermal stability, glass transition temperature, etc.) were investigated and compared with these determined for the non-filled films. Additionally, the biocompatibility and the cell adhesion on the surface of the developed materials were also explored.

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References:

1. *Chiellini E. and Solaro R.* Biodegradable polymeric materials // Adv Mater. – 1996. – Vol. 8 – P. 305-313.
2. *Albertsson A.C and Varma I.K.* Aliphatic polyesters: Synthesis, properties and applications // Adv. Polym. Sci. – 2002. – Vol. 157 – P. 1–40.
3. *Jerome C. and Lecomte P.* Recent advances in the synthesis of aliphatic polyesters by ring-opening polymerization // Adv. Drug Deliv. Rev. – 2008. – Vol. 60, No. 9 – P. 1056-1076.

INFLUENCE OF POLYMER MATRIX MATERIAL AND NANOSTRUCTURED FILLER ON COMPOSITE CHEMICAL SENSING PROPERTIES

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In this work hybrid polymer nanocomposites with carbonaceous fillers like carbon nanoparticles and carbon nanotubes for their application in volatile organic compound (VOC) vapour detection were studied and results were compared with composites that were mede in previous studies.

As matrix materials were used ethylene vinyl acetate copolymer (EVA; with 40% vinyl acetate content) and poliisoprene (Pi). And as conducting nanoparticle were used extra electroconductive, highly structured carbon black (CB; Printex XE2). CB has following characteristics: mean particle size 30 nm, dibutyl phthalate (DBP) absorption - 380 ml/100 g, specific surface area - 950 m2/g). Also there were used two types of CNT as filler material as well. First type of CNT was purchased from Sigma Aldrich; the outer diameter of tubes is in range from 40 to 60 nm, inner diameter is in range from 5 to 10 nm, length 0.5-500 µm, and aspect ratio 12500. These comparatively long CNT further will be designated as CNTl. Second type of CNT were obtained from CheapTubes; outer diameter is in range of 50-80 nm, inner diameter is from 5 to 15 nm, length 0.5-2 µm, maximal aspect ratio 40. Further these short CNT will be designated as CNTs.

Electroconductive properties of the nanoparticle's network, formed within hybrid polymer nanocomposite, were investigated. VOC sensing properties of the hybrid composites were investigated using toluene (on basis of previous researches). It was found that the simultaneous incorporation of both types of carbonaceous materials, carbon black and carbon nanotubes, leads to a higher sensitivity to toluene if Pi matrix is used. Thus, the hybrid polymer composites show promising gas sensing properties in comparison with composites, where only one filler is used.

Acknowledgment. This work was supported by ESF Grant No.1DP/1.1.1.2.0/13/APIA/VIAA/030 and by National research program IMIS^2.

REASERCH AND DEVELOPMENT OF NANOSTRACTURED ELECTROSPUN SUPERCAPACITORS

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The aim of present study is research and development of nanofibrous electrospun electrodes for the supercapacitors. Electrodes of carbon rich nanofibers are developed by utilizing conductive and non-conductive polymers, ionic liquids and compacting process. Physical properties and electrochemical behavior of produced double-layer capacitors are evaluated.

To reach stated goals nanofibrous electrode mats of polyacrylontrile (PAN) in dimethylformamide (DMF) solution with carbon rich mixture of carbide derived carbon (CDC) and carbon black (CB) were prepared. The ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF4) was added.

The porosity parameters of electrospun electrodes were evaluated by using low temperature N_2 adsorption method. Electrochemical characteristics of produced electrodes with triethylmethylammonium tetrafluoroborate in acetonitrile (TEMA/AN) electrolyte, were studied by cyclic voltammetry and constant current charge/discharge methods. The effects of various contents of CDC to capacitance and compacting of produced electrodes are discussed.

Results of experimental work showed that with electrodespun fibrous mats in thickness range of 10-20 μm it is possible achive electrical double layer capacitance up to 114 F/g.

DESIGN OF WIDER POTENTIAL WINDOW PVA HYDROGEL ELECTROLYTES FOR SUPERCAPACITORS

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Narrow operational voltage window can be considered as one of the greatest limitations for aqueous polymer electrolytes. It has been reported that this window could be made wider by using hydrogel electrolytes employing alkali metal salts as ion source [1, 2]. Using freeze-thaw hydrogel preparation method we have synthesized four electrolytic polyvinyl alcohol (PVA) hydrogels. Ion conductivity of these hydrogels has been achieved using H_3PO_4, KOH, Na_2SO_4 and K_2SO_4. Cyclic voltammetry (CV) data shows that operational voltage windows for PVA/Na_2SO_4 and PVA/K_2SO_4 samples are respectively 4.6 V and 4.4 V compared to 3.6 V and 3.2 V obtained for PVA/H_3PO_4 and PVA/KOH hydrogels. CV curves and chronopotentiometry measurements have been used to calculate capacitance and characterise the amount of energy stored in different charging processes. It was also seen that when Na_2SO_4 salt was used as ion source the compression Young modulus of hydrogel increased 2 times in comparison to pure PVA hydrogel. Differential scanning calorimetry results suggest that it may be due to increased crystallinity of PVA/Na_2SO_4 hydrogel.

Financial support of project "Hybrid energy harvesting systems" is greatly appreciated.

References:

1. *Batisse N., Raymundo-Piñero E.* A self-standing hydrogel neutral electrolyte for high voltage and safe flexible supercapacitors// J. Power Sources – 2017. – Vol. 348 – P. 168-174.
2. Materials for Sustainable Energy Applications: Conversion, Storage, Transmission, and Consumption / Ed. by *David Munoz-Rojas, Xavier Moya*, CRC Press, 2017. – 425 p.

TEHACHEM – TOGETHER, WE BUILD THE FUTURE

M. Lahovskis

General manager, TENACHEM Ltd, Dobele, Latvia

TENACHEM Ltd. – one of the leading European manufacturers of sealants for the glass industry, the largest construction sealant producer in the Baltics. TENACHEM shares top 5 among leading producers of insulating glass sealants in the world and currently is exporting 95% of its products to 40 countries worldwide. In next 3 years TENACHEM target markets are Germany and Great Britain. TENACHEM manufactures and delivers to customers around the world ~12-14 000 tons of production annually.

TENACHEM is a member of the Soudal Group from 2015. The Soudal Group is the largest independent European manufacturer of sealants, adhesives and polyurethane foams for professional and private users. This Belgian family business, founded in 1966, has developed into an international player and expert in chemical construction specialities. The group has 19 production branches on 4 continents, sales offices in 44 different countries and employs over 2,800 people worldwide. In 2017, Soudal has achieved a turnover of € 755 million, which is an increase of € 85 million or 12,7% compared to 2016.

Soudal group annual R&D budget is more than 5 million EUR. A long-term vision for innovation – with substantial investment in R&D – and adaptations to local market requirements have resulted in the success of the Soudal Group. Soudal continually innovates and develops new products for the construction, industry and retail markets. TENACHEM takes part in innovations as an important knowledge and production center and it is developing as the center of excellence for glass sealants of the Soudal Group. TENACHEM invests more than EUR 0,2 million in research and development every year by developing new products and innovative and competitive solutions for its customers. TENACHEM laboratory team works in close collaboration with Soudal group R&D department to develop products which meet environmental requirements and respond to customer needs. TENACHEM employs 14 skilled and highly qualified chemists and is continuously looking for new colleagues as the team is expanding. TENACHEM human capital lasts years has grown both in number as well as in quality.

TENACHEM research directions: two component hydroxyl terminated polybutadiene kinetic reaction research with methylene diphenyl diisocyanate in presence of different organo-metallic catalytical and additive systems for applications in insulating glass manufacturing; two component Thiokol based oxidative polycondensation reaction research with presence of different sulphur donor chain extenders and amine based deprotonating agents for applications in insulating glass manufacturing; rheological properties modelling research of polydisperse heterogenic matrix for component homogenisation at static mixer environment; one component silane terminated polyether polymer integration in polydisperse matrix with presence of adhesion promoters and rheological additives.

TENACHEM team is working on the following active research project - material characteristics improvement project – insulating glass edge sealing composite material development and adaptation for exploitation in aggressive climatic conditions with high thermal and hydrolytic resistance of adhesion bond after prolonged UV, thermal and hydrolytic exposure (implementation time 2016-2019).

HYDRODYNAMIC STUDY OF WATER SOLUTIONS OF POLYELECTROLYTES BASED ON N-METHYL-N-VINYLACETAMIDE

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Nowadays, intensive efforts are being made to synthesize and investigate carrier polymers, molecular containers for targeted transport of various biologically active substances [1]. Such biologically active substances are often hydrophobic meanwhile the efficiency of their therapeutic application is determined by the targeted delivery to the living organism. Accordingly, it is promising to search for molecular systems combining hydrophobic and hydrophilic fragments that would be sufficiently labile to be used to deliver medicines. Alkylation of hydrophilic charged copolymers of N-methyl-N-vinylacetamide and N-methyl-N-vinylamine hydrochloride (MVAA-MVAH) leads to the formation of amphiphilic copolymers with a specified length of the lateral radicals. Such macromolecules have hydrophilic backbone and some number hydrophobic side radicals and possibly may form hydrophobic internal domains in macromolecular coils. The methods of molecular hydrodynamics: velocity sedimentation, translational diffusion, and viscometry, have been used in the current research. The investigation has been performed in a following sequence: homopolymer N-methyl-N-vinylacetamide (PMVAA) → copolymer MVAA-MVAH obtained by partial hydrolysis of PMVAA → alkylated MVAA-MVAH copolymer. The studied macromolecules are charged; therefore they were characterized under suppressed polyelectrolyte effects in 0.2 M NaCl solutions. Hydrodynamic and conformational characteristics, molecular masses were estimated. In order to trace the change of sizes and properties of linear polyelectrolytes in a wide range of ionic strength (from pure water (10-6M) to 6M NaCl) [2], the viscous flow of dilute solutions was studied for determination of the intrinsic viscosity of polyions [3].

Acknowledgements. The reported study was funded by RFBR according to the research project № 18-33-00432.

References:

1. *Vilar G., Tulla-Puche J. and Albericio F.* Polymers and Drug Delivery Systems // Current Drug Delivery. – 2012. –Vol. 9, No. 4 – P. 367–394.
2. *Pavlov G. M., Gubarev A. S., Zaitseva I. I. and Sibileva M. A.* On the Intrinsic Viscosity Determination of Polyelectrolyte Chains in Aqueous Salt-Free Solution // J. Appl. Chem. – 2006. – Vol. 79, No. 9 – P. 1423–1428.
3. *Pavlov G. M., Dommes O. A., Okatova O. V., Gavrilova I. I. and Panarin E. F.* Spectrum of Hydrodynamic Volumes and Sizes of Macromolecules of Linear Polyelectrolytes versus their Charge Density in Salt-Free Aqueous Solutions // Phys. Chem. Chem. Phys. – 2018. – Vol. 20 – P. 9975–9983.

SYNTHESIS NEW POLYMERS WITH BIQUINOLINE UNITS IN THE MAIN CHAIN AND METAL-POLYMER COMPLEXES BASED ON

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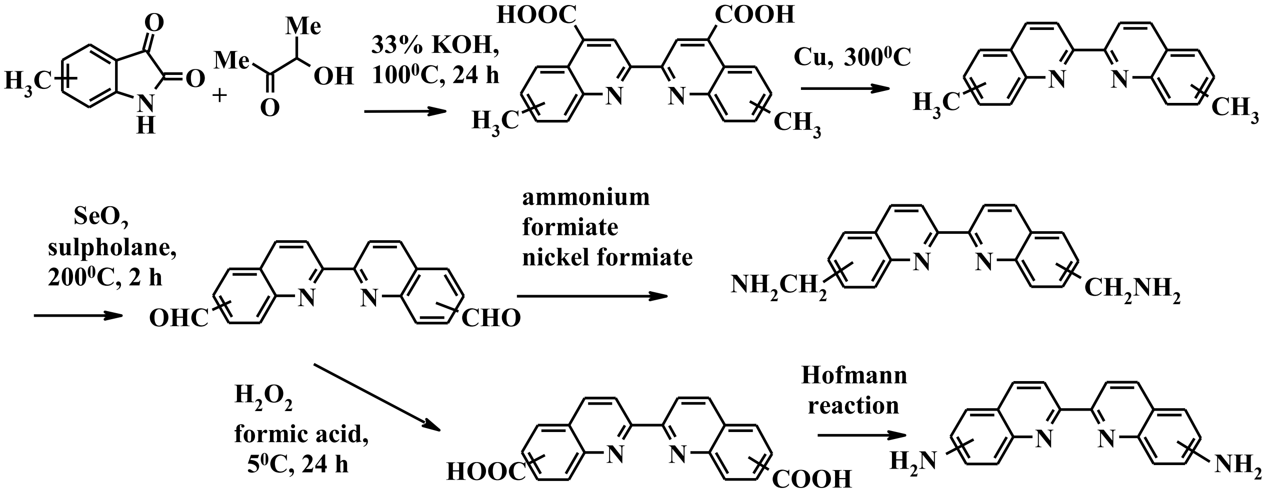
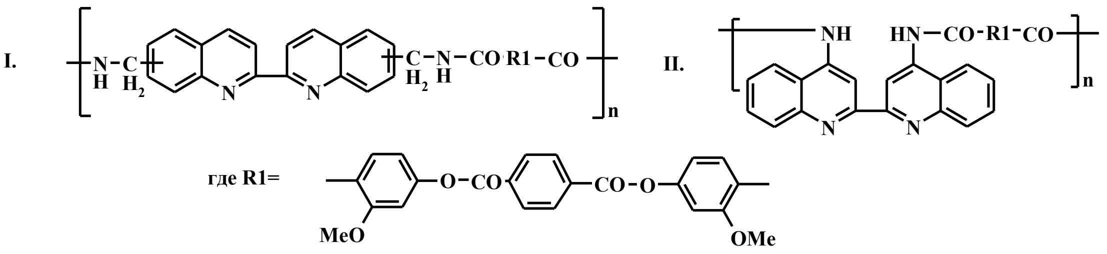
Metal-polymer complexes of transition metals are promising compounds for the creation of high-performance electro-optic devices, sensors, photochemical, electrocatalytic systems, and gas separation and pervaporation membranes. The functionalization is achieved by introducing into the main copolymer chain units containing biquinoline group capable of forming coordination bonds with cuprous salts. The purpose of this study was to obtain new biquinoline containing monomers - diildimetanames and diamines, synthesis of heat-resistant functionalized polymers on therefrom, synthesis a metal-polymer complexes with CuCl and study their properties.
Synthesis of monomers -$6,6^{/}$, $7,7^{/}$, and $8,8^{/}$-2,2-bihinolin diildimetanamines-and-2,2-biquinoline-$4,4^{/}$-diamine:

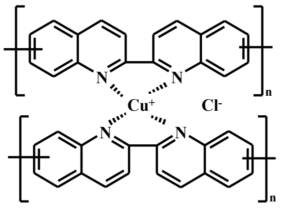


On the basis of these monomers, by low-temperature polycondensation, new polyamides with 10% biquinoline units and polymer-metal complexes with CuCl based on were synthesised.

The structure of biquinoline-containing polymers:



The structure of metal polymer unit:



ROLES OF PHYSICAL AND COVALENT INTERACTIONS IN EPOXY NANOCOMPOSITES

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In this contribution, the importance of interfacial interactions between inorganic nanofillers and epoxy matrix for preparation of high-performance composite nanomaterials is demonstrated on epoxy-nanosilica and epoxy-titanate nanotube systems.

Ionic bonding with simultaneous multiple hydrogen-bonding might be created on the epoxy-silica interphase by applying imidazolium-based ionic liquids (ILs) [1]. We have recently studied the IL-driven sol-gel process of (3-glycidyloxypropyl)trimethoxysilane (GPS) using two imidazolium-based ILs bearing chloride or methanesulfonate anion, which led to a formation of differently shaped IL−silica species applicable as reinforcing additives into the epoxy−amine network [1]. The epoxy-silica interfacial interaction might be further strengthened by using task-specific ILs bearing one or more carboxylic groups and providing *in-situ* covalent bonding during epoxy−amine polyaddition.

Titanate nanotubes present a cheaper and more versatile alternative to carbon nanotubes for the functional epoxy-based hybrid nanomaterials, since the polar and hydroxylated surface of titanate nanotubes allows for more efficient and industrially scalable modifications. Wa have functionalized titanate nanotubes by means of a low-molecular-weight bisphosphonate, a branched polyethyleneimine and polydopamine to provide active hydrogen functionalities for bonding with epoxy precursors during thermally-induced crosslinking. The functionalized nanotubes promoted interfacial interactions with the matrix via either covalent or/and physical bonding, which resulted in homogenous nanofiller dispersions enabling to substantially reinforce the epoxy−amine network.

Acknowledgement. Financial support of the Czech Science Foundation (project 17-08273S) is gratefully appreciated.

References:

1. *Donato, K. Z.; Matějka, L.; Mauler, R. S.; Donato, R. K.* Recent applications of ionic liquids in the sol-gel process for polymer–silica nanocomposites with ionic interfaces // Colloids Interfaces – 2017. - Vol. 1, No. 1 - P. 5.
2. *Perchacz, M.; Donato, R. K.; Seixas, L.; Zhigunov, A.; Konefał, R.; Serkis-Rozeń, M.; Beneš, H.* Ionic Liquid-Silica Precursors via Solvent-Free Sol–Gel Process and Their Application in Epoxy-Amine Network: A Theoretical/Experimental Study // ASC Appl. Mater. Interfaces - 2017. – Vol. 9, No. 19 – P. 16474−16487.

PHENANTHROIMIDAZOLE-BASED MONOMERS: SYNTHESIS, PROPERTIES AND SELF-POLYMERIZATION

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The approach to fabricate multilayer organic electronics devices using cross-linkable materials, which are coated from the solution and can be transformed into a covalently cross-linked film upon the application of heat or irradiation with ultraviolet light, was widely employed [1]. Such insoluble films usually exhibit high enough thermal stability which allows them to withstand the heat used to dry the film during the upper-layer processing. Photocross-linking is a convenient method; however, this technique may lead to quenching of excitons and/or trapping of charge carriers due to the presence of residues of photoinitiators [2]. Thermally cross-linkable materials are advantageous from this point of view because they do not require initiators [3]. Vinyl benzyl ether moieties have recently attracted attention as thermally cross-linkable groups useful for the fabrication of cross-linked hole-transporting layers of OLEDs [4] and in organic photovoltaic devices [5].

Phenanthroimidazole-based monomers with reactive vinyl groups were synthesized, and their thermal, optical, photophysical and electrochemical properties were investigated. The monomers exhibited high thermal stability with 5% weight loss temperatures (Td) ranging from 378 to 409 °C. Thermal degradation of the polymerization products apparently takes place in this temperature range. The solutions of the monomers exhibit emission peaks in the range from 388 to 398 nm. In the solid state, the emission of these molecules shows red shift which is coherent with the similar red shifts of the corresponding absorption spectra. Ionization potential values of the compounds estimated by cyclic voltammetry were found to be close and varied in the range from 5.44 to 5.63 eV. Solid-state ionization potentials estimated by photoelectron emission spectrometry varied in the range from 5.54 to 5.66 eV. Self-polymerization of the synthesized monomers was demonstrated by differential scanning calorimetry. The number average molecular weights of the polymerization products of monomers containing substituents at phenyl rings linked to C-2 and N-1 positions of imidazole ring were found to be 100,100 and 196,000, respectively. The apparent activation energy and pre-exponential factor of self-polymerization were found to be dependent on conversion degree. The values of activation energy for self-polymerization of monomers varied in the range from 78.7 to 136.0 kJ/mol (estimated by Ozawa method) and from 78.3 to 139.0 kJ/mol (estimated by Kissinger method).

References:

1. *Zuniga CA, Barlow S, Marder SR.*Approaches to solution-processed multilayer organic light-emitting diodes based on cross-linking// Chem Mater.-2011.- 23-P.658–681.
2. *Evans TR*. Singlet quenching mechanisms// J Am Chem Soc.-1971.- 93-P.2081–2082.
3. *Klärner G, Lee JI, Lee VY et al*. Cross-linkable polymers based on dialkylfluorenes// Chem Mater.-1999.- 11-P.1800–1805.
4. *Cheng Y-J, Liu MS, Zhang Y et al*. Thermally cross-linkable hole-transporting materials on conducting polymer: synthesis, characterization, and applications for polymer light-emitting devices//Chem Mater.-2008.- 20-P.413–422.
5. *Sun Y, Chien SC, Yip HL et al*. Chemically doped and cross-linked hole-transporting materials as an efficient anode buffer layer for polymer solar cells// Chem Mater.-2011- 23-P.5006–5015.

BIO-COMPONENTS FROM WASTE FOR POROUS POYURETHANE MATERIALS PREPARATION

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The synthesis of polyurethanes based on natural components and waste is one the most important fields in the current world research. The aim of this work was to evaluate the influence of municipal waste in form of used cooking oil on the properties of open cell polyurethane foams. The used cooking oil was modified by epoxidation and oxirane ring-opening process using diethylene glycol. Open cell foams were successfully prepared by using 2-components (polol premix and isocyanate) polyurethane systems. Different bio-polyols from municipal waste (up to 100wt%) to prepare various polyol premixes. A reference polyurethane system was prepared using only a petrochemical polyol. The effects of bio-polyols on the foaming process, cellular structure and selected properties of the foams such as the apparent density, compressive strength as well as water absorbance and dimensional stability were described. The modification of the polyurethane system with bio-polyols slowed down the reaction of the polymer matrix formation independently on hydroxyl value of bio-polyol. The polyurethane systems modified with bio-polyols had a lower maximum temperature and exhibited a slower decrease of the dielectric polarization during the foaming process. The apparent density of the polyurethane foams were in the range 12-18 kg/m^3 Modification of reference system with bio-polyols had significant effect on the decrease of thermal conductivity from 45 to 38 mW/m·K, as well as the increase of compressive strength at 10% of deformation from 29 to 52 kPa. The application of used cooking oil hydroxyl derivatives allows obtaining rigid polyurethane foams characterized by good dimensional stability as well as beneficial properties for using in construction industry as heat insulating materials.

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References:

1. *Marcovich N.E., Kuraska M., Prociak A., Malewska E., Kulpa K.* Open cell semi-rigid polyurethane foams synthesized using palmoil-based bio-polyol // Ind. Crop. Prod. – 2017. – Vol. 102 – P. 88-96.
2. *Prociak A., Malewska E., Kurańska E., Bąk S., Budny P.* Flexible polyurethane foams synthesized with palm oil-based bio-polyols obtained with the use of different oxirane ring opener// Ind. Crop. Prod. – 2018. – Vol. 115 – P. 69-77.
3. *Prociak A., Kurańska M., Malewska E.* Porous polyurethane plastics synthetized using bio-polyols from renewable raw materials // Polimery – 2017 – Vol. 62 – P.521-531.

POSTER SESSION

CONTROLLED SYNTHESIS OF ANIONIC AMPHIPHILIC GLYCOPOLYMER BOTTLE-BRUSHES

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Synthesis of glycopolymers has been widely reported in the last two decades. An increasing investigation of chondroitin sulphate (ChS) as a component of drug/gene delivery systems has been raised [1]. More importantly, particular properties of ChS endow it with the ability of site specific drug/gene delivery. The brush-like amphiphilic synthetic copolymers are capable of self-assembling into nano-sized carriers. Fortunately, advances in controlled radical polymerization allow precise control over polymeric structures and molecular weight making the synthesis of well-defined glycopolymers possible.

In the present study we report controlled synthesis of glycopolymer bottle-brushes based on triblock copolymers containing either poly(polypropylene oxide) methacrylate (PPOMA) (M_n 375 g/mol) or poly(lauryl methacrylate) (LMA) as terminal blocks, and random copolymer of 2-aminoethyl methacrylate (AEMA) and poly(ethylene oxide) methacrylate (PEOMA, M_n 300 g/mol) as a middle block. Anionic amphiphilic glycopolymer brushes, prepared by “one-pot” RAFT polymerization and reductive amination without protection of functional groups, are intended to be used as models mimicking adsorption and lubrication of natural bottle-brushes.

In the first step, a hydrophobic block of either PPOMA or LMA was synthesized by RAFT polymerization using 4-cyanopentanoic acid ditiobenzoate as a RAFT CTA. Trying to obtain “pure” blocks, polymerizations were carried out up to 57 % of PPGMA and 82 % of LMA and the first blocks were isolated which were subsequently acted as a RAFT chain transfer macroagent in one-pot sequential monomer addition RAFT polymerization [2]. In the second step of “one-pot” RAFT polymerization, a copolymeric block containing the units with primary aminogroups was attached. Finally, the third block was either of PPOMA or LMA again resulting in triblock copolymers with terminal hydrophobic blocks. AEMA units present in the middle block are intended for the attachment of ChS, while PEOMA as a spacer units and for improvement of solubility of the triblock copolymers in organic solvents.

Because of the units of PPOMA and/or PEOMA, the triblock copolymers have a shape of molecular brushes. These molecular brushes were converted to anionic bottle-brushes by the attachment of ChS from bovine tracea and its hydrolyzed analogs via reductive amination. ChS is sulphated glycosaminoglycan with pKa 2,8 in 0.1 M NaCl. The attachment of ChS moities to triblock brush copolymers was confirmed by ^{1}H NMR spectra and SEC chromatography, and composition of the anionic glycopolymer bottle-brushes was determined by potentiometric titration. It was determined that the degree of substitution of primary aminogroups of the copolymers was 6–7 % when using non-hydrolized ChS, and 2–3 % when using hydrolized ChS. pKa of the glycopolymer bottle-brushes carrying hydrolized ChS is aboute 2, while of that carrying non-hydrolyzed ChS aboute 3.

References:

1. *Zhao L, Liu M., Wang J., Zhai G*. Chondroitin sulfate-based nanocarriers for drug/gene delivery // Carb. Polym. – 2015. – Vol. 133 – P. 391–399.
2. *Radzevicius P., Krivorotova T., Makuska R.* Synthesis by one-pot RAFT polymerization and properties of amphiphilic pentablock copolymers with repeating blocks of poly(2-hydroxyethyl methacrylate) and poly(butyl methacrylate) // Eur. Polym. J. – 2017. – Vol. 87 – P. 69-83.

SELF-ASSEMBLY IN AQUEOUS SOLUTIONS OF THERMORESPONSIVE PENTABLOCK COPOLYMERS SYNTHESIZED BY ONE-POT RAFT POLYMERIZATION

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Block copolymers are composed of two or more chemically distinct polymer chains covalently bond into a single molecule. The nature and sequence of polymer blocks define functional properties of multiblock copolymers, such as their ability to microphase separation in bulk or in solution [1]. Among block copolymers, water-soluble pH- and temperature-responsive materials are of particular interest, since they are able to respond in a physiological environment and they are promising materials for various bioapplications. Such copolymers often contain a block with constituting units of 2-(dimethylamino)ethyl methacrylate (DMAEMA). pDMAEMA exhibits reversible temperature response, and its aqueous solutions possess a lower critical solution temperature (LCST). DMAEMA has been successfully copolymerized with 2-hydroxyethyl methacrylate (HEMA) which is a neutral monomer with high chemical and hydrolytic stability. Block copolymers of pDMAEMA and pHEMA are of varying hydrophilicity subject to pH and temperature, which imparts certain micellization behaviour [2].

In the current work, a series of hydrophilic pentablock copolymers composed of pHEMA and pDMAEMA blocks, were successfully synthesized by three-step one-pot RAFT polymerization in the presence of difunctional RAFT CTA. *N*-Methyl-2-pyrrolidone (NMP) was the best solvent enabling to achieve near full (>97 %) monomer conversion during building of the blocks and synthesize well-defined pentablock copolymers with almost pure blocks of low dispersity. Two types of pentablock copolymers with central block of either pHEMA or pDMAEMA were synthesized, and thermoresponsive self-assembly of these copolymers in aqueous solutions was studied (Fig. 1).

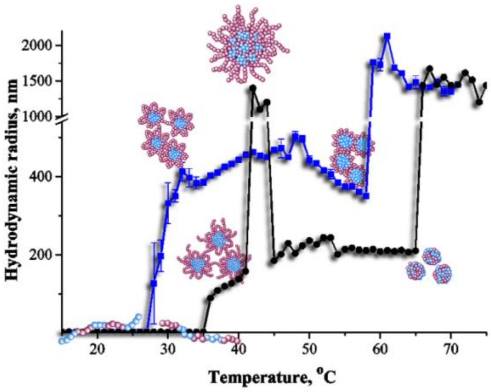

Fig. 1. Changes in hydrodynamic radius of the particles of the pentablock copolymers H_{77}-D_{79}-H_{50}-D_{79}-H_{77} (1) and D_{72}-H_{78}-D_{49}-H_{78}-D_{72} (2) during heating.

Acknowledgements. Financial support from the Research Council of Lithuania under the project MIP-054/2015 is gratefully acknowledged.

References:

1. K. Hales and D. J. Pochan. Using polyelectrolyte block copolymers to tune nanostructure assembly // Curr. Opin. Colloid. In. – 2006 – Vol. 11 – P. 330-336.
2. P. Radzevicius, M. Steponaviciute, T. Krivorotova, R. Makuska. Double thermoresponsive pentablock copolymers: synthesis by one-pot RAFT polymerization and self-assembly in aqueous solutions // **Polym. Chem.** – 2017. – Vol. 8 – P. 7217-7228.

DIRECT SYNTHESIS OF AMPHIPHILIC RANDOM, BLOCK AND BLOCK-RANDOM COPOLYMERS OF ACRYLIC ACID AND STYRENE OR n-BUTYL ACRYLATE VIA RAFT SOLUTION POLYMERIZATION

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Controlled synthesis of the polymers of complex architecture with given properties is one of the urgent tasks of polymer chemistry. Among them, block copolymers of various architectures, in particular, amphiphilic block copolymers attract special interest due to their ability to microphase segregation in bulk and to self-assembling in a selective solvent. Reversible addition–fragmentation chain transfer (RAFT) polymerization is one of the most versatile techniques for such kind of the synthesis due to the tolerance to the functional groups of the monomers, wide range of the appropriate solvents and mild temperature conditions.

The aim of the present research is to study the relative monomer reactivity in copolymerization of acrylic acid (AA) of styrene (S) and acrylic acid with n-butyl acrylate (BA) mediated by symmetrical trithiocarbonates (RSC(=S)SR) in the solvents of various polarity.

Copolymerization was conducted in 1,4-dioxane and N,N-dimethylformamide at 80^{o}C in the presence of dibenzyl trithiocarbonate (R=$PhCH_2$) and polymeric RAFT agents based on poly(acrylic acid), polystyrene and poly(n-butyl acrylate), containing trithiocarbonate group within the polymeric chain. Independently from the solvent and the chemical nature of the RAFT agent, the copolymerization is found to proceed via the living mechanism. The number average molecular weight increases linearly with growth of the monomer conversion, while dispersity of the molecular weights remains lower than 1.5.

The copolymer composition depends from the nature of the solvent, the nature of the RAFT agent and the polymerization degree of the polymeric RAFT agent. The increase of the solvent polarity in both systems AA – S and AA – BA results in the growth of the differences between monomer relative reactivities. In its turn, in the polar solvent, DMF, the hydrophilic polymericRAFT agent causes the decrease of AA reactivity, while the hydrophobic RAFT agent causes its increase. These observations are similar to the known features of conventional radical copolymerization of monomers of different polarity (bootstrap effect).

Thus, the bootstrap effect in combination with RAFT mechanism allow governing the block copolymer structure.

Independently polymeric RAFT agents were used in block copolymerization, and triblock copolymers PAA-block-PBA-block-PAA and PBA-block-PAA-block-PBA with narrow molecular weight distribution are successfully synthesized both in 1,4-dioxane and DMF.

This research was financially supported by Russian Foundation for Basic Researches (project 17-03-00131).

POLYMERIZATION-INDUCED SELF-ASSEMBLY: SEEDED RAFT POLYMERIZATION FOR THE SYNTHESIS OF ABC AMPHIPHILIC BLOCK COPOLYMERS

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Recently the combination of heterophase polymerization with reversible deactivation radical polymerization have made a breakthrough in the controlled synthesis of block copolymers. As a result, a new approach has been developed that provides the formation of AB or ABA block copolymers, mainly amphiphilic block copolymers, self-assembled into core-shell particles with given morphology directly in the course of the synthesis. The living nature of the process allows further chain extension and formation of ABC block copolymers, in which the further fine tuning of the morphology of the particles is possible. In the typical protocol, the monofunctional RAFT agents are used based on dithiobenzoates and non-symmetrical trithiocarbonates. We have shown previously that symmetrical trithiocarbonates can be also applied for the dispersion and emulsifier-free emulsion polymerization of alkyl acrylates.

The aim of the present research was to develop the conditions of dispersion and then seeded RAFT-based polymerization mediated by symmetrical trithiocarbonates to produce ABC block copolymers based on acrylic acid (AA), n-butyl acrylate (BA), and N-isopropyl acrylamide (NIPAM).

PAA containing trithiocarbonate group within the chain (M_n = 9600 g/mol) was synthesized using dibenzyl trithiocarbonate. Dispersion polymerization of BA was conducted in the water/ethanol mixture at 65 ^{o}C. The following parameters were studied: the monomer/medium volume ratio, the PAA molar concentration, AIBN/PAA molar ratio aiming at the synthesis of narrow dispersed triblock copolymers PAA-block-PBA-block-PAA at high monomer conversion. It was shown that the increase of AIBN concentration resulted in the growth of the polymerization rate and to slight loose of the control over MWD. Meanwhile, in all the systems number average molecular weight increased linearly with growth of the monomer conversion, while the dispersity depended on the polymerization conditions. The increase of PAA concentration led to decrease of both MW and particle size. The optimal system was then chosen and used in dispersion and emulsion seeded polymerization of NIPAM aiming at production of PAA-block-PBA-block-PNIPAM-block-PBA-block-PAA. The incorporation of NIPAM into the polymeric chain was confirmed by SEC and NMR spectroscopy.

This research was financially supported by Russian Foundation for Basic Researches (project 18-33-00386).

COPOLYMERIZATION OF N-VINYL SUCCINIMIDE WITH VINYL ACETATE IN THE PRESENCE OF DIBENZYL TRITHIOCARBONATE

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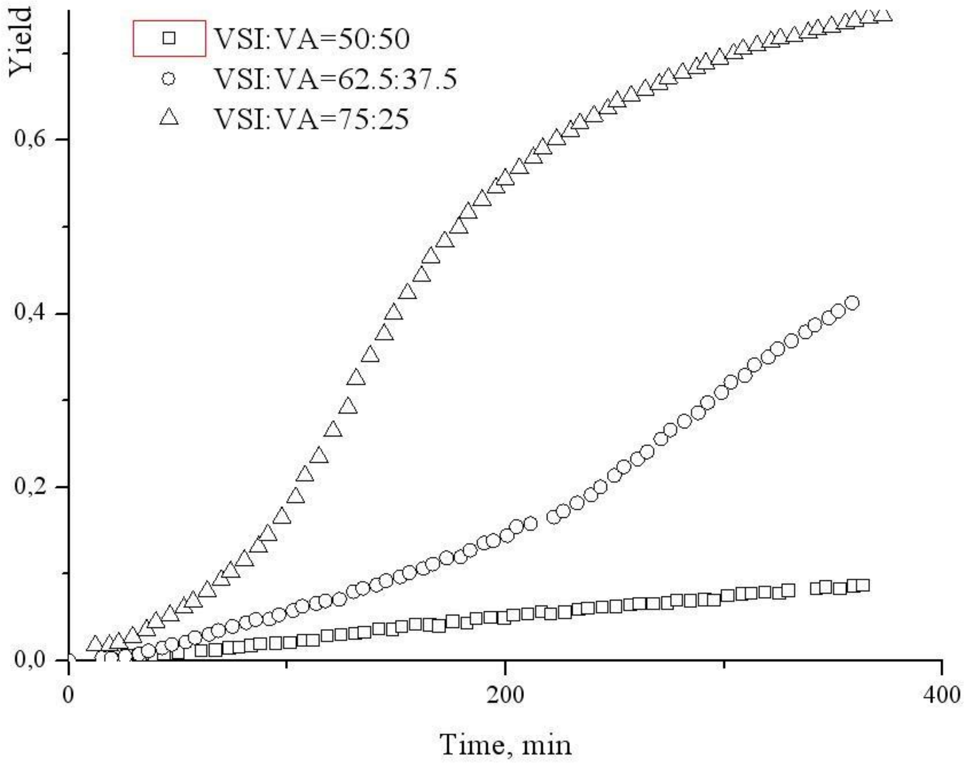
Copolymers of N-vinyl succinimide (VSI) with vinyl acetate (VA) are precursors to obtain water soluble non-toxic copolymers of N-vinyl amidosuccinic acid with vinyl alcohol obtained easily via alkali hydrolysis. The last are eminently suitable for binding on them various low-molecular substances like physiologically active ones. It is clear that RAFT polymerization for this purpose can be fruitful because of good control of molecular mass characteristics and the possibility to synthesize compositionally homogeneous copolymers from monomers of different reactivity.

In the present study kinetic of polymerization of VSI with VA in the presence of trithiocarbonate (BTC) as a RAFT agent has been investigated using continual NMR spectrometry monitoring of the reaction mass. In spite of absolutely inactivity of VA in BTC mediated polymerization its copolymerization with VSI can be successfully carried out as it is shown at the Picture. But there are certain limitation concerning VA content in copolymer which cannot be high enough.

The copolymers obtained have been transformed to water soluble matrix and processed by electro spinning to material for wounds and burns dressing.



Picture. The dependence of copolymer yield on reaction time: [BTC]=$5 \cdot 10^{-3}$, [AIBN]=10^{-3} mol/l, bulk copolymerization, Ar atmosphere, 70°C.

This work was supported by Russian Foundation for Basic Researches (project No 14-03-00155a)

CHARACTERIZATION OF THE MORPHOLOGY OF POLYMER COMPOSITES AND MEMBRANES BY OPTICAL SPECTROSCOPY

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At present, a significant number of methods for studying the morphology of polymeric materials are known, differing in informativeness, sensitivity, scale, and range of applicability. Unfortunately, most methods are used exclusively for analyzing the surface of a sample, it is much more difficult to obtain information on the structure of the internal regions of the sample. In connection with this, the development of an accessible non-destructive express method for analyzing the morphology of the interior regions of a polymer is an urgent task.

In this paper, a spectroscopic method has been proposed by the authors to study the morphology of "turbid media" (porous and filled composite polymer materials) [1-7]. The essence of our spectroscopic approach is to isolate and analyze the component associated with the attenuation of the radiation incident on the sample due to its scattering in the optical wavelength range (UV, visible and IR ranges) on the pores or filler particles. After appropriate processing of the scattering and absorption spectra, the porosity or degree of filling of the polymer material, the distribution of scattering particles (pores or filler particles) in size, anisometry, and the orientation of the anisometric scattering particles in the bulk of the polymer matrix can be estimated using the proposed approach.

The method was tested in the study of various porous polymer materials: track membranes, xerogels, etc., as well as composite materials based on various polymers with different types of fillers.

In the course of the research it was established that the optical spectra of porous and filled polymeric materials carry valuable information on the morphology of the object. The obtained information on the structure of the analyzed materials was confirmed by their analysis by independent methods of optical and electron microscopy.

The work is performed under financial support of the Ministry of Education and Science of the Russian Federation in the frame of realizing of the State task in the field of the scientific activity (project N4.5508.2017/BP. This work is performed by means of the Equipment Center for collective Use of Tver State University.

References:

1. *Pakhomov P.M., Kruglova E.V., Khizhnyak S.D.* IR spectroscopy study of polymer porosity // Polym. Sci. (Russia). − 2000. – Vol. 42B, No. 5-6 − P. 169−174.
2. *Pakhomov P.M., Malanin M.N., Kruglova E.V., Khizhnyak S.D.* IR spectroscopic study of track membranes based on poly(ethyleneterephthalate). // Polym. Sci. (Russia). − 2001. Vol.43B, No. 3-4 − P. 120−123.
3. *Pakhomov P.M., Malanin M.N., Khizhnyak S.D.* IR spectroscopic technique for studying polymer porosity // Polym. Sci. (Russia). − 2005. – Vol. 47B, No. 5-6 − P. 194−199.
4. *Khizhnyak S.D., Malanin M.N., Pakhomov P.M., Eichhorn K.-J.* IR spectroscopic study of polymer blends and composites: a new approach. // Polym. Sci. − 2008. – Vol. 50B, No. 5–6. – P. 158–164.
5. *Pakhomov P.M., Khizhnyak S.D., Zharov S.Yu., Eichhorn K.-J.* A new spectroscopic approach to characterization of porous and filled polymeric materials // Fibre Chemistry. – 2008. – Vol. 40, No. 3. – P. 253–265.
6. *Sitnikova V.E., Khizhnyak S.D., Moskalyuk O.A., Tsobkallo E.S., Yudin V.E. and Pakhomov P.M.* Optical spectroscopy characterization of carbon nanofiber orientation in polypropylene film. A new approach // Fibre Chemistry. – 2015. – Vol. 47, No. 3. – P. 220–226.
7. *Pakhomov P.M., Khizhnyak S.D., and Sitnikova V.E.* IR spectroscopy for the analysis of scattering polymeric materials. // J. of Appl. Spectroscopy. – 2017. – Vol. 84, No. 5. – P. 837–842.

GLASS-FORMING ENAMINES AS HOLE-TRANSPORTING MATERIALS FOR OPTOELECTRONICS

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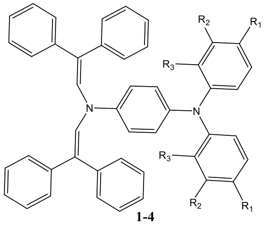
Charge mobility is important characteristic of organic materials used in (opto)electronic devices. For instance, charge carrier transport directly affects the switching rate of organic field effect transistors (OFETs), and turn-on voltage of organic light emitting diodes (OLEDs) [1]. Charge mobility also influences efficiency of organic and hybrid photovoltaic devices [2].

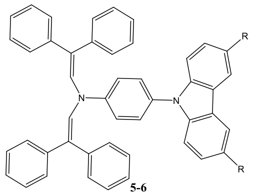
Aromatic amines possessing diphenylethenyl fragments are poorly examined as hole-transporting materials. Aromatic enamines represent a class of efficient p-type semiconductors [3]. Enamines represent a group of electron donating molecules having two substituted ethylene moieties at nitrogen atom and exhibit god hole-transporting properties [4].

In this work, we report on the synthesis and properties of glass forming charge transporting enamines containing carbazole or triphenylamine moieties.



1-4

	R_1	R_2	R_3
1	H	H	H
2	$-OCH_3$	H	H
3	H	$-OCH_3$	H
4	H	H	$-OCH_3$



5-6

	R_1
5	H
6	$-C(CH_3)_3$

Enamines 1-6 were synthesized by condensation reaction between appropriate primary amine and acetaldehyde in the presence of (+/-)camphor sulfonic acid. The synthesized compounds were identified by mass-, IR- and ^{1}H, ^{13}C NMR spectrometries.

The compounds were found to be thermally stable and capable of forming of molecular glasses with glass transition temperatures in the range of 87-147 ºC. Ionization potentials of the enamines estimated by cyclic voltammetry range from 4.76 to 5.70 eV. The synthesized compounds were found to be electrochemically stable. The layers of the compounds show high hole mobility reaching 10^{-3} cm^2/Vs at high electric fields.

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References:

1. *Coropceanu, V., Cornil J., da Silva Filho D.A., Olivier Y., Silbey R., and Bredas J.-L.*Charge transport in organic semiconductors // Chem. Rev. – 2007. – Vol. 107 – P. 926–952.
2. *Daskeviciene M., Paek S., Wang Z., Malinaustas T., Jokubauskaite G., Rakstys K., Cho T. K., Magomedov A., Jankauskas V., Ahmad S., Snaith H. J., Getautis, V., Nazeeruddin K.* Carbazole-based enamine: Low-cost and efficient hole transporting material for perovskite solar cells // Nano Energy. 2017. – Vol. 32, – P. 551–557.
3. *Sinicropi J.A., Cowdery-Corvan J.R., Magin E.H., Borsenberger P.M.* Hole transport in N,N'-bis(2,2-diphenylvinyl)-N,N'-diphenylbenzidine-doped polymers. // Proc. SPIE – Int. Soc. Opt. Eng., 1996. – P. 192–201.
4. *Puodziukynaite E., Burbulis E., Grazulevicius J. V., Getautis V., and Jankauskas V.* Carbazole-based bis(enamines) as effective charge-transporting amorphous molecular materials // Synth. Met. – 2008. – Vol. 158 – P. 993–998.

SOYBEAN OIL-BASED PHOTOSENSITIVE RESIN FOR OPTICAL 3D PRINTING

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Photopolymerization is commonly used to form thin films, varnishes, paints and adhesives.[1)] Optical 3D printing uses photopolymerization process to form 3D polymeric objects from photosensitive monomers. Commercial resins for optical 3D printing are usually systems, containing acrylate-, epoxy- or vinyl ester-based monomers derived from petrochemical feedstock.[2)] However, the use of polymeric materials derived from renewable raw materials for optical 3D printing is still little studied, though highly promising as it offers sustainable additive manufacturing technology.

In this work, acrylated epoxidized soybean oil was used as the main bio-based monomer, due to ready availability, inherent biodegradability, limited toxicity, and existence of modifiable functional groups. However, the mechanical properties of acrylated soybean oil homopolymer are rather weak. For this reason the use of aromatic comonomers is needed. Vanillin dimethacrylate was chosen as aromatic hardening agent of acrylated soybean oil, because among the bio-based phenol derivatives, vanillin is the major aromatic compound produced commercially from lignin which is the second most abundant biopolymer after cellulose. Myrsene was chosen as bio-based reactive diluent to increase the homogeneity of the reaction mixture and decrease its viscosity. Myrsene is an oily liquid extracted from the essential oils of many plants. In industry it is mainly obtained from the pyrolysis of β-pinene, which is produced from the distillation of pine tree oil and is already used in many industrial processes.[3)]

Photocross-linked polymers were obtain from three above mentioned monomers using 2,2dimethoxy–2phenylacetophenone as photoinitiator and without any organic solvent in the system. For comparison, analogous studies have been carried out with the synthetic stable aromatic compound divinylbenzene, often used as a synthetic cross-linking agent in polymer synthesis, which replaced vanillin dimethacrylate.

It was determined that photopolymerization rate and properties of the cross-linked polymers depended on the amount of myrcene in composition. Better viscosity and homogenisation of the system was obtained with increasing amount of myrcene, while the reduction of polymerization rate, worse mechanical and thermal properties were observed in such case. It was determined that the replacement of divinylbenzene by vanillin dimethacrylate in the system led to the higher photopolymerization rate, higher amount of polymer insoluble fraction, better mechanical and thermal properties of polymers.

Acknowledgements. Financial support from the Research Council of Lithuania (project No. S-LAT-17-2) is gratefully acknowledged.

References:

1. *Bauer F.* Progr. in Org. Coat.- 2014.- 77.-P.1085-1094.
2. *Barner-Kowollik C., Bastemeyer M., Blasco E., Delaittre G., Müller P., Richter B., Wegener M.* 2017-56-P.15828–15845.
3. *Robles-Dutenhefner P.A., Speziali M. G.*, Sousa E.M.B., dos Santos E.N., Gusevskaya E.V. Appl. Catal. A: General.- 2005.-295-P. 52-58.

POLYETHERS CONTAINING CARBAZOLE-BENZOTHIADIAZOLE CHROMOPHORES AS SOLUTION PROCESSED MATERIALS FOR HOLE TRANSPORTING LAYERS OF OLEDS

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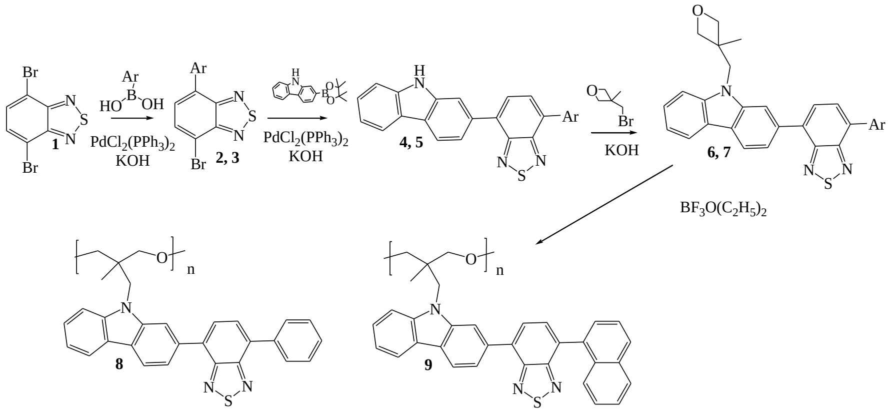
Solution processed derivatives containing substituted carbazole fragments are among the most studied materials for organic electronics due to their good chemical and environmental stability, and high positive charge mobility in their layers [1, 2,]. In addition, derivatives containing electronically isolated carbazole rings have high triplet energies and are widely used as host materials for electro-phosphorescent devices (PhOLEDs) [3].

The synthesis of polymers (**8-9**) containing electronically isolated 4-(carbazol-2-yl)-7-arylbenzo[c]-1,2,5-thiazole fragments was carried out by a multi-step synthetic route as shown in Scheme 1.



Scheme 1

The amorphous polymers have high thermal stability as well as very high glass transition temperatures (154 °C and 163 °C). It was observed that layers of polymers have rather high and similar values of ionization potential of about 5.9 eV. The investigations demonstrate that the thin electroactive films of the polymers are suitable as hole injection/ transport layers for OLEDs. Therefore, the polymers have been tested as hole transporting materials in bilayer OLEDs with Alq_3 as the emitter. The devices containing HTL of the synthesized materials exhibited turn-on voltages of 5.2 – 6.2 V, photometric efficiencies of about 1.6 – 2.5 cd/A and a maximum brightness of 300 – 1510 cd/m^2 at 23 V.

Acknowledgements. This research was funded by a grant No. S-MIP-17-64 from the Research Council of Lithuania.

References:

1. *Lengvinaite S., Grazulevicius J.V., Grigalevicius S., Zhang B., Jang Y., Xie Z., Wang L.* Cross-linkable aromatic amines as materials for insoluble hole-transporting layers in light-emitting devices// Synth. Met. –2008–Vol. 158, No.7– P. 213–218.
2. *Souharce B., Kudla C.J., Forster M., Steiger J., Anselmann R., Thiem H., Scherf U*. Amorphous carbazole-based (Co)polymers for OFET application// Macromolecular Rapid Communications. –2009–Vol. 30, No.14– P. 2158–1262.
3. *Tao Y., Yang C., Qin J*. Organic host materials for phosphorescent organic light-emitting diodes// Chem Soc Rev –2011–Vol. 10, P. 2943–2970.

POLYMERIC HOLE-TRANSPORTING NETWORK AS A MIXED HOST FOR EFFICIENT SOLUTION-PROCESSED RED ORGANIC LIGHT EMITTING DIODES

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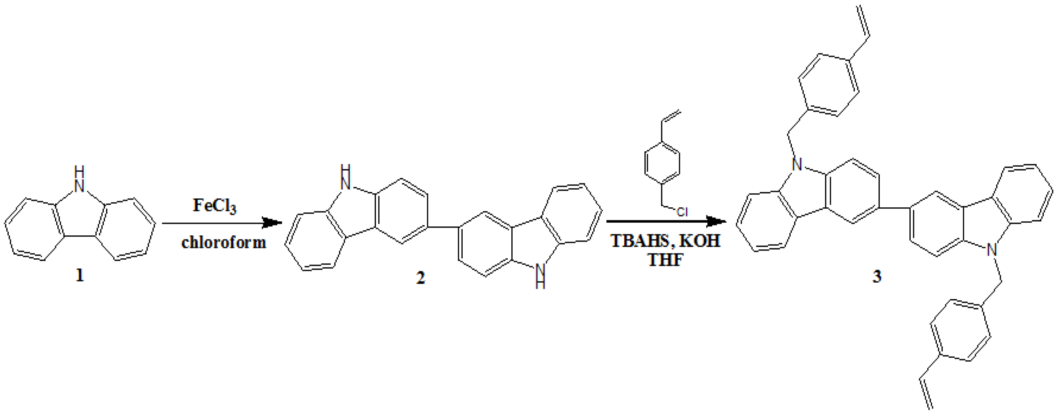
Fabrication of multilayer organic light-emitting diodes through the solution process presents challenges, especially regarding dissolution of the first layer during deposition of a second layer. Here, we have demonstrated highly efficient solution processed red organic light emitting diodes utilizing a novel electron confining cross linkable small molecules of 9,9′-bis(4-vinylphenylmethylen)[3,3′]bicarbazole (**3**) as a hole transporting and co-host material. Synthesis of the material **3** was carried out according to synthetic route shown in Scheme 1.



Scheme 1

The measured energy level suggests that compound **3** facilitates the injection of the hole and effectively blocks electron to realize high efficiency, especially at high luminance. Compared with the corresponding single host device, the luminance of the mixed host device was enhanced from 8,351 cd·m^{-2} to 15,200 cd·m^{-2}, an increment of 82%; power efficiency and current efficiency also show an increment of 25% and 20 % at 100 cd m^{-2}, respectively. The use of crosslinked material improved film integrity and hence device brightness. The enhanced charge carrier balance and broadened exciton recombination zone due to the mixed host contribute to the improvement of device performance.

Acknowledgements. The OLED materials were developed in the frame of project funded by the Research Council of Lithuania (grant No. S-MIP-17-64).

References:

1. *Jou J. H., Li T. H., Kumar S., An C. C., Agrawal A., Chen S. Z., Fang P. H., Krucaite G., Grigalevicius S., Grazulevicius J. V., and Sung C. F.* Enabling high-efficiency organic light-emitting diodes with a cross-linkable electron confining hole transporting material // Org. Electron. – 2015. – Vol. 24 – P. 254−262.
2. *Jou J. H., Kumar S., Agrawal A., Li T. H., and Sahoo S.* Approaches for fabricating high efficiency organic light emitting diodes // J Mater. Chem C. – 2015. – Vol. 3 – P. 2974−3002.

COMPOSITE OF VISCOELASTIC POLYURETHANE FOAMS WITH DIFFERENT HERBAL FILLERS

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Green tea has in its composition a unique set of polyphenols with various activities and catechins, strong antioxidants, tannins, alkaloids, lipids, amino acids, theine, vitamins and microelements. Rich composition makes that scientists are still discovering new properties and applications of green tea. The use of green tea as a natural filler for a composite with a viscoelastic polyurethane foam can give interesting results in improving the biocompatibility and other properties of materials for use as pillows, mattresses and underlay. Thanks to obtaining antiseptic properties and the effects of alleviating inflammation, such materials could be used in hospital rooms, public transport, nursing homes and others.

The aim of the research was to produce viscoelastic foams modified with a filler in the form of green tea with two particle sizes, with assumed functional properties. The matrix of the composite was a viscoelastic, open cell foam, described in the patent PL407875-A1. The properties of materials with different filling and with ground or unground green tea were compared. The obtained materials were tested for physical (density), mechanical (compression), thermal (thermogravimetric analysis, differential scanning calorimetry) and the assessment of resistance to environmental factors (material resistance to washing, rinsing filler particles). In addition, the structure of materials and the filler were characterized using a scanning microscope.

As part of the work, we managed to create foams with different filling with green ground and unground tea, with interesting colors and aromas. Foam filling of up to 20% filler retain good mechanical properties, a preferred density and structure. More preferred properties of the compression test and the test showed the permanent deformation of the ground filler materials, and the preferred density of the unground. Also, the cellular structure is more homogeneous in foams with green unbleached tea. To fully characterize the possibility of using materials to a predetermined application should be carried out basic biological research materials, and also check their performance in terms of possible trigger an allergic reaction.

PROPERTIES OF POLYURETHANE COATINGS BASED ON LINSEED OIL PHOSPHATE ESTER POLYOLS AND EXPANDABLE GRAPHITE

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To decrease the flammability of bio-based polyurethanes (PUs), different types of phosphorus-containing polyols were used. Even more significant results can be achieved if, in PU coatings, phosphorus-containing polyols are used together with expandable graphite (EG) [1]. In the present study, the effect of EG on the properties of PU coatings based on two kinds of phosphate ester polyol was studied.

Synthesizing polyols, phosphorylation of epoxidized linseed oil with phosphoric acid was performed in the presence of isopropyl alcohol (IPA polyol) or diethylene glycol butyl ether (DGBE polyol). The obtained polyols were characterized by Fourier Transform Infrared (FTIR) and ^{31}P Nuclear Magnetic Resonance (NMR) spectroscopy. For filling of PU coatings, two grades of EG (EG-290 and EG-096 from SINOGRAF SA, Poland), which differed in particle size and expansion volume, were used.

The properties of neat PU coatings based on two polyols, and those filled with different content of EG (up to 25 wt%) were studied using thermal gravimetric analysis (TGA), and tensile and flammability tests. TGA of polyurethane coatings in a nitrogen atmosphere was performed using TGA/SDTA 851^{e} METTLER TOLEDO. The tensile test of PU coatings was performed on a universal testing machine Zwick/Roell DO–FB0.5TS (500 N) according to ASTM D 882-10. 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/m^2.

It was found that the tensile modulus of PU coatings consistently increased, but tensile strength and elongation at break decreased, when the content of EG increased up to 25 wt%. The char residue in the TGA test of all coatings gradually increased with the addition of intumescent flame retardants, reaching the maximum values at their content of 25 wt%. As the IPA polyol contained not only phosphate mono- and diesters, as DGBE polyol, but also phosphate triester and pyrophosphate monoester, IPA neat and filled coatings had higher tensile characteristics and char residue in the TGA test. Also, the flame retardancy of IPA filled coatings, compared with that of DGBE coatings, was higher.

With increasing of EG content, the main flammability parameters of wood samples with PU coatings, including peak of heat release rate, total heat release, mean effective heat of combustion and total smoke release, gradually decreased and reached their minimum values at 25 wt% of EG. The decrease in flammability parameters was higher for coatings filled with EG-290. The coatings based on IPA polyol and filled with 25 wt% of EG-290 showed the best flame retardant properties.

Acknowledgements. The present study was supported by the National Research Programme "Forest and earth entrails resources: research and sustainable utilization – new products and technologies" (ResProd) Project No. 3 "Biomaterials and products from forest resources with versatile applicability".

Reference:

1. *Chen X-Y., Huang Z-H., Xi X-Q., Li J., Fan X-Y., Wang Z.* Synergistic effect of carbon and phosphorus flame retardants in rigid polyurethane foams // Fire Mater. – 2018. - Vol. 42, No. 4 – P. 447–453.

RED PHOSPHORUS INFLUENCE ON RIGID PU/PIR FOAM FLAMMABILITY AND THERMAL STABILITY

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Polyurethane/polyisocyanurate (PU/PIR) foam is effective thermal insulation material which is broadly used in construction industry. PU/PIR foam must have good mechanical properties, low density, low thermal conductivity, high fire resistance and thermal stability.

Fire retardants are added to fulfil demanding fire resistance tests. Additive halogenated fire retardant agents are most commonly used in PU/PIR industry. Many of these chemicals are now recognized as global contaminants and are associated with adverse health effects in animals and humans, including endocrine and thyroid disruption, immunotoxicity, reproductive toxicity, cancer, and adverse effects on fetal and child development and neurologic function[1].

It is required to replace halogenated fire retardant agents for a less human and animal health hazardous and environment-friendly fire retardant chemicals. Red phosphorous dust could provide such alternative. The present study describes Latvian State Institute of Wood Chemistry (IWC) investigation into red phosphorus influence the rigid PU/PIR foam flammability and thermal stability.

PU/PIR foams were prepared by mixing industrial polyol with several components in sequence red phosphorus powder, cyclopentane and isocyanate. Red phosphorus powder was introduced in rigid PU/PIR foams in 1, 2, 5, 10 and 20 % contents by mass. After that, the mixed substance is poured into closed type mold. After 24 hours of curing apparent density (ISO 845), compression strength (ISO 844), thermal conductivity (ISO 8301), closed cell content (ISO 4590), reaction to fire (ISO 5560-3) and thermal stability (ISO 9772) was tested.

Reference:

1. *Shaw SD, Blum A, Weber R, Kannan K, Rich D, Lucas D, Koshland CP, Dobraca D, Hanson S, Birnbaum LS*. Halogenated flame retardants: do the fire safety benefits justify the risks? //Rev Environ Health-2010.- 25,4-P.261-305.

BALANCE BETWEEN ACOUSTIC AND THERMAL INSULATION PROPERTIES OF RIGID POLYURETHANE FOAMS OBTAINED FROM AROMATIC POLYESTER POLYOLS

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Rigid polyurethane (PUR) foams is one of the most important materials used as thermal insulators of buildings, refrigerators, cold stores, pipes, refrigerated transport, in chemical and food industries and also in space technologies[1]. Petrochemical polyols used in PUR production can be replaced by polyols from different natural oils or from by-products of chemical industry, also from recycling processes of municipal waste. Prospective municipal waste product, with potential high added value after recycling is polyethylene terephtalate (PET). Production of aromatic polyester polyols from PET residues is based on transesterification of them by diethylene glycol in the presence of functional additives[2]. PUR foam composition, with isocyanate index 120 were designed from PET polyol as main component, using water as environmentally friendly blowing agent. Up to now, PUR compositions were developed and tested, with main idea, as thermal insulation material, but also acoustic (sound absorption) properties is very important in modern construction industry[3].

In present research were obtained PUR foams with the same macromolecular architecture at densities from 30 to 210 kg/m^3, at the same time retaining all the important characteristics of thermal insulation materials, such as high closed cell content, sufficient compression strength, low flammability, low water absorption. All obtained PUR foams were tested according EN ISO 10534-2:2002 “Determination of sound absorption coefficient and impedance in impedances tubes”, at the same time cell structure were analysed. Sound absorption tests show, that higher sound transmission loses present foam materials with higher density, but optimum has been reached at density approx. 100 kg/m^3. Sound absorption (noise protection) at frequencies close to 500 Hz for PUR foams with density 100 kg/m^3 is 8 fold more effective as foam with density 30 kg/m^3, the further increase of density is not economically justified.

It is confirmed, that optimal density should be chosen to meet balance between thermal and acoustic insulation properties for each particular building element and structure, also economic considerations must be taken into account.

Acknowledgements. The study was financed by the Latvian State Institute of Wood Chemistry Bioeconomy grant “AtkritBiomasKM”.

References:

1. Chemistry and Technology for Polyurethane / Ed. By *Ionescu M*. - U.K: Rapra Technology Ltd, 2005. – 586 p.
2. *Vitkauskiene I, Makuška R.* Glycolysis of Industrial Polyethylene Terephthalate Waste Directed to Bis(hydroxyethylene) Terephthalate and Aromatic Polyester Polyols // Chemija – 2008. – Vol.19, No.2 – P. 29–34.
3. *Jaouen L., Renault A., Deverge M.* Elastic and damping characterizations of acoustic porous materials: available experimental methods and applications to melamine foams // Appl.Acoust. – 2008 – Vol.69 – P.1129-1140.

CHARACTERISATION OF UREAURETHANE ELASTOMERS WITH RAPESEED OIL-BASED POLYOL

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Renewable resource can replace partially or to some extent totally, petro-chemical based polymers through the design of bio-based polymers, that can compete or surpass the existing petro-chemical based materials on a cost-performance basis.

Polyurethane elastomers (EPUs) are the most distinguished group of polymers, because of their excellent properties such as good resistance to abrasion and to oils, grease and weather conditions [1]. They are used for many applications: from flexible to rigid foams, to thermoplastic polyurethane and elastomers [2]. Currently, polyurethanes industry is highly dependent on oil as its two main raw materials, polyols and isocyanates, are largely petroleum. Because of global warming and the oil crisis, began to look at alternative substrates, which are renewable and plant origin [3].

In this work, we examine bio-based ureaurethane elastomers (EPUUs) with a 40% wt. of rapeseed oil-based (RO) polyol with a different content of hard segments (HS).

Rapeseed oil is used for fuel production, as well as the production of polyols for the production of polyurethanes, especially for the production of polyurethane foams [4]. Rapeseed oil is also used as a supplement to two-component polyurethane sealant mass-bonding to the insulating glass production, because it gives good elastic properties of matter. Polyol from rapeseed oil has been used very successfully in the market polyurethanes.

Thermal analysis was performed using thermogravimetry (TGA) and differential scanning calorimetry (DSC). Infrared spectroscopy (FTIR) was done to describe chemical constitution of the studied materials. Mechanical properties were testing by dynamic mechanical thermal analysis (DMTA) and static tensile test. Density (ρ) was determined via hydrostatic weighing in conformity with the norm ISO 2781. Hardness (H) was determined using durometer Shore A in conformity with the norm ASTM D2240-75. Resilience (η) was tested by Schobe method in conformity with the norm PN-71/C-04255 and abrasion (ΔV) in conformity with the norm ISO 4649.

The addition of RO polyol to EPUUs changed and improved the structure of material properties of the resulting materials. Different content of hard segments (HS) make changes in the chemical and physical structure of testing materials.

References:

1. *Mizera M., Kirpluks M., Cabulis U., Leszczyńska M., Półka M. and Ryszkowska J.* Characterisation of ureaurethane elastomers containing tall oil based polyols // Ind. Crops Prod. – 2018. – Vol. 113 – P. 98–110.
2. *Chattopadhyay D. K. and Rayu K. V.* Structural engineering of polyurethane coatings for high performance applications // Prog. Polym. Sci. – 2007. – Vol. 23 – P. 352–418.
3. *Prasanth K. S. P., Mohanan A., Bouzidi L., Narine S. S.* Phase behavior of novel triacylglycerols derived from metathesis modified plant oils // Ind. Crops Prod. – 2016. – Vol. 94 – P. 431–444.
4. *Malewska E., Bąk Sz., Kurańska M., Prociak A.* The effect of various rapeseed oil-based polyols on selected properties of flexible polyurethane foams // Polimery. – 2016. – Vol. 61, No. 11-12 – P. 799–806.

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

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Microencapsulation allows to protect the active ingredient from the external environment, mask undesired flavours, a possible controlled release of compounds among others [1]. The potential utilizations of polyurethanes and polyurea polymers have been discussed for a variety of pharmaceutical, medical and cosmetic applications, such as drug or other bioactive materials encapsulation and controlled release [2].

The originality of our study resides on the use of interfacial polyaddition technique (IFP) for synthesis of poly(urethane-urea) microcapsules (PUUMC) in the proposed herein environment–friendly water/butyl acetate emulsion system (w/o) at low and high temperature. The influence of diisocyanate (1,6-hexamethylene diisocyanate (HMDI)), toluene-2,4-diisocyanate (TDI), 4,4’-methylene diphenyl diisocyanate (MDI) on the structure and properties of PVA-based PUUMC. The maltogenic α-amylase (MG) from *Bacillus stearothermophilus* was encapsulated in PUUMC and encapsulation efficiency has been studied in detail. The aqueous phase was PVA solution in water and the oil phase was surfactant Span 85® solution in butyl acetate. After emulsification, diisocyanate was 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 (14–177 m^2/g), pore size (8–21 nm) and volume (0.06–0.77 cm^3/g) of shell of microcapsules depended on reaction conditions and initial components reactivity and were determined by using BET and BJH methods, respectively. Size and morphology of the PUUMC were evaluated by optical and scanning electron microscopy. The mean diameters of PUUMC were 322 ± 16 μm, 334 ± 17 μm and 412 ± 20 μm when they were obtained from PVA and HMDI, TDI or MDI, respectively. Optical microscopy showed that the PUUMC were spherical, monocore when HMDI or TDI were used however multicore PUUMC were obtained in MDI case. The activity of native MG and encapsulated MG in PUUMC was estimated by Neocuproine method. The MG immobilization proceeded by covalent binding, entrapment and physical adsorption into PUUMC. EI of MG was increased when a more reactive diisocyanate was used for the synthesis of PUUMC and when MG was encapsulated during the PUUMC synthesis at lower temperature. Microcapsules with encapsulated MG were studied as enzyme delivery systems and release rate of MG from PUUMC was estimated. The controlled release profile of MG was in most cases when TDI was used for the PUUMC synthesis. Incomplete release of MG from capsules was obtained when HMDI was used for the synthesis of PUUMC.

References:

1. *F. Paulo, L. Santos*. Mater Sci Eng C.- 2017.-77-P. 1327-1340.
2. *E. P. Cipolatti, A. Valerio, G. Nicoletti, et al.* J. Mol. Catal. B: Enzym.- 2014.- 109- P. 116-121.

RIGID POLYURETHANE FOAMS AS EXTERNAL TANK CRYOGENIC INSULATION FOR SPACE LAUNCHERS

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So far, different methods of hydrogen storage for ground and aerospace vehicles have been proposed and investigated in different studies, and it has been shown that the most favourable type of tank system depends highly on the kind of vehicle and operation[1]. In the framework of the present activity, work is carried out on the development of rigid polyurethane (PUR) foam material for external cryogenic insulation of a LH2 tank for the next generation launcher with a cryogenic upper stage. The main advantage of PUR foams in comparison with other thermal insulation materials is possibility to cover this material on the complicated shape metal surfaces by spraying method. The spraying of PUR foams on metal constructions is chemical – technological process.

The properties of PUR foams and their adhesion to substrate materials depend not only on the chemical structure and macromolecule architecture of the polymeric matrix, but also on the technological factors of PUR foam production. The tasks of this research are to investigate some technological effects on the physical and mechanical characteristics of the selected foams and their modifications as well as development of necessary polyol component for production of spraying cryogenic insulation with optimal technological parameters. The used PU foam composition is calculated and optimised using previously described[2] approach for development of cryogenic insulation. Physical-mechanical, adhesion, flammability, UV-stability and cryo-pumping tests there were performed at room and cryogenic temperatures, also thermal expansion coefficient was determined.

As a result of work performed within research, PUR foam material has been developed for the use as external insulation material for fuel tank structures. Raw ingredients from suppliers within EU have been used exclusively. The material has been tested for its performance in normal (room) and relevant (cryogenic conditions) environment and found to be physical/mechanically durable and appropriate for use in space application. Accelerated ageing/decay test indicate the material to be long-lasting. Safety coefficient, which characterizes the capability of insulation to withstand cryo-shocks, for optimal compositions reaches 5.

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References:

1. *Westenberger A.* Liquid hydrogen fuelled aircraft-system analysis (CRYOPLANE), Final Technical Report (Publishable version). Airbus Deutschland GmbH, 2003.
2. *Stirna U., Beverte I., Yakushin V., Cabulis U.* Mechanical properties of rigid polyurethane foams at room and cryogenic temperatures // J. of Cell. Plast. – 2011. – Vol.47, No.4 – P.337-355.

SYNTHESIS OF VALUABLE POLYOLS FROM POST CONSUMED RAPESEED OIL USING ENZYMATIC EPOXIDATION PROCESS

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The global pursuit for the more sustainable world encourages research projects to focus on finding methods of production that are characterized by the use of renewable or recycled sources, low carbon footprint and restricted amounts of synthetic and toxic reagents involved. The aim of this research is to use a post-consumed rapeseed oil as a renewable feedstock in the epoxidation process. Vegetable oil is easily convertible intermediates and have a wide commercial use because of their varied chemical activity. Epoxides have been used as raw materials for products such as alcohols, glycols, plasticizers, high-temperature lubricants, polyols and polymers e.g., polyurethane, polyesters and epoxy resins

Developed enzymatic epoxidation process allowed to remove small molecular weight acids that are used as an oxygen carrier in the state of art methods. Instead, tall oil, which is a side stream of cellulose Kraft pulping process, was used to in-situ produce peroxy carboxylic acids that are essential for epoxidation process. The influence of tall oil fatty acid content on post-consumed rapeseed oil epoxidation process was investigated. An advanced bio-catalyst, immobilized Lipase enzyme (Novozym 435) was used in the epoxidation process, 3% of total oil mass. There is a prospect of regeneration and multiple use of this enzymatic catalyst which yet have to be studied. The kinetics of the epoxidation process was studied by collecting samples every hour and measuring iodic value, epoxy value, acidic value and performing FT-IR spectroscopy.

Obtained results showed that the amount of epoxy rings increased significantly while the amount of unsaturated bonds decreased. The yield of oxirane rings in epoxidized post-consumed rapeseed oil was similar to neat rapeseed oil. For neat rapeseed oil after 7h of the process there was 0,29 moles of epoxy groups in 100g of oil and for post-consumed rapeseed oil, there was around 0,25 moles of epoxy groups per 100g of oil. This results are promising for reuse of post consumed rapeseed oil to generate valuable epoxidized oil which has a large variety of applications including polyurethane foams.

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MECHANICAL PROPERTIES OF COMPOSITE MATERIAL BASED ON SCRAP TYRES AND POLYURETHANE BINDER WITH DIFFERENT REACTIVITY

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INTRODUCTION

Recycling and utilization of used vehicle tyres still must be considered as an important way to unload the environment from non-degradable waste [1]. Production of composite materials [2] is one of most perspective ways for the reuse of scrap tyres, and the produced composite material can be used in a wide range of applications [3]. In our previous investigations optimization of composition and technology of the composite material's production from mechanically grinded scrap tyres and polyurethane type binder were realized [4,5]. The special objective of this work is to investigate correlation between selected mechanical properties of the composite material and reactivity of the polymer binder.

EXPERIMENTAL METHODS

Grinded at room temperature, unfractioned rubber crumb from scrap tyres and polyurethane type polymer binder with different reactivity (C_{-CNO} 2.4, 5.5 and 7.4%) were used. Composite material samples were prepared by mechanical mixing of required components ($C_{pol.}$ 8,13,18,23 mass %), molding of samples in uniform molds and hardening of samples under definite conditions ($T = 18\text{-}23^0$ C; RH = 28-34%; P = 0.04 kg/cm^2). Shore C hardness (ISO 7619-1; ISO 868), compressive stress at 10% deformation σ_{10} at different loading modes (static and cyclic) and compression modulus of elasticity E (EN 826) in correlation with the composition of composite material and reactivity of polymer were investigated.

RESULTS AND DISCUSSION

Influence of polymer binder content and reactivity, on investigated parameters was observed. It was shown that values of Shore C hardness increases by the increase of polymer binder content in the composite material independently from isocyanate functional group content in polyurethane type binder. It was demonstrated also that higher content of isocyanate groups in the polyurethane binder provides higher degree of cross- linking of polymer and therefore provokes increase of tested in compressive mode mechanical properties as well as higher Shore C hardness of the composite material samples. Correlation between reactivity of the polymer binder and mechanical properties of the composite material in compressive mode of deformation stress at 10% deformation as well as in cyclic mode of deformation was demonstrated for composite material.

CONCLUSION

1. The obtained results show that variation of composition of the composite material and reactivity of the polymer binder have strong influence on the selected mechanical properties of the material.
2. Purposeful selection and mutual combination of composition of material and activity of polymer binder can ensure desirable and predictable mechanical properties of composite material.

References:

1. *Mark J.E., Erman B. and Erich R*. The Science and Technology of Rubber/3 d. Ed.by Elsvier Inc.- USA-2006.
2. *Hughes A.H. and Pennington S*. Precoated rubber crumb for composites// GB Patent 2364708.
3. *Shulman V.L.* Tyre Recycling – Ed by Smithers Rapra, Shrewsbury, GBR, 2004.
4. *Plesuma R.,Megne A, Mateusa-Krukle I. and Malers L.* Significance of technological parameters for selected mechanical properties of composite material based on scrap tires//Prog. Rubber Plast. Re. -2015- Vol.31- P.69-75.
5. *Plesuma R. and Malers L*. Polyurethane binder mechanical properties under different crosslinking conditions//Key Eng. Mater. - 2016 -Vol.721- P.3-7.

SYNTHESIS OF RIGID POLYURETHANE FOAMS WITH WASTE BASALT FILLER

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The aim of this work was to analyze the effect of waste basalt powder on selected properties of rigid polyurethane foams. The basalt powder is a waste produced during the extraction of basalt rocks. The basalt/polyurethane composition were obtained using the basalt powder as a filler in amounts 3, 6, 9, 20, 30, 40 wt% with respect to the mass of the polyurethane components. The influence of waste filler on the change of thermal and mechanical properties, thermal stability and flammability of rigid polyurethane foams was analyzed. The application of waste basalt powder caused an increase of the polyurethane system's reactivity. The increased reactivity has been confirmed by the changes of the dielectric polarization of reaction mixture during foaming process. Values of the thermal conductivity of obtained rigid polyurethane foams were in the range 22 – 25 mW/m·K, while the apparent densities were similar about 38 kg/m^3.

References:

1. *Matykiewicz D., Barczewski M., Knapski D., Skórczewska K.* Hybrid effects of basalt fibers and basalt powder on thermomechanical properties of epoxy composites // *Compos. Part B Eng.* – 2017. - Vol. 125 – P. 157–164.
2. *Prociak A., Kurańska M., Osiewicz M., Auguścik M., Ryszkowska J. Michałowski S., Bradło D., Żukowski W.* Rigid polyurethane foams filled with a waste alumosilicate // *Przem. Chem.* – 2016. - Vol. 1 - P. 188–193.

RHEOLOGICAL PROPERTIES OF HIGHLY FILLED BLENDS BASED ON POLYPROPYLENE MODIFIED BY ELASTOMERS

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Modern polymer composite materials are multicomponent systems. Addition of mineral fillers into polymers allows to create materials with the required performance characteristics and leads to costs reduction [1]. One of the directions in the creation of materials with increased impact resistance is modification of filled polymers with elastomers [2]. However, the addition of fillers and plasticizers affects not only the properties of the polymer material, but also the processing ability of the material. The study of rheological properties allows estimating the effect of the composition components on the properties of polymer melt [3].

The filled compositions based on polypropylene (PP) 21030 and blends of above mentioned polypropylene with «Vistamaxx 6202» are investigated. The calcite concentrate (CC) of 1TK mark (LLC «Tekhnokom») with particles size of 2.5 μm (max 20 μm - 1,5%) was used as a filler.The viscosity of the melts of the compositions was determined on a capillary viscosimeter MB-2 in the shear stress range $(0{,}1\div5{,}7)\cdot10^4$ Pa at the temperature of 230°C.

It was determined that all investigated compositions show the anomaly of viscosity. Rheological studies indicate that addition of calcite concentrate in polypropylene up to 50 % wt. results in decreasing of the viscosity of the melts throughout the range of concentrations and shear stresses compared to pure polypropylene. This can be ascribed to surface treatment of the filler with stearic acid at the stage of its preparation, such that non-polar "tails" are formed on its surface in the form of stearic acid chain.

Addition of 5% wt. propylene-octene block copolymer to the compositions filled with calcite concentrate in order to obtain polymer materials with increased impact strength shows a synergistic effect on reducing the viscosity of the compositions. There by the addition of plasticizer in an amount of 5% wt. and calcite concentrate in an amount up to 50% wt. into polypropylene allows to regulate the rheological characteristics for the creation of impact-resistant polymer materials, and also reduces the abrasive influence of the filler on the extrusion equipment and energy requirement for the processing of high-filled compositions.

References:

1. *Xanthos M.* Functional Fillers for Plastics//Second, updated and enlarged edition.Weinheim, Germany:Wiley-VCH. 2010-507 p.
2. *Drobny J. G.* Handbook of Thermoplastic Elastomers (Second Edition) A volume in Plastics Design Library/ ed SinaEbnesajjad- Oxford: Elsevier, 2014.-P. 209–218.
3. *Sengers W.G.F.* Rheological properties of olefinic thermoplastic elastomer blends//Doctoral thesis.Dutch Polymer Institute- 2005.- 172p.

TERMAL, MECHANICAL AND RHEOLOGICAL PROPERTIES OF WOOD PLASTIC COMPOSITES BASED ON POLYPROPYLENE AND BIRCH PLYWOOD SANDING DUST

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During the last 20-30 years numerous of researchers have paid attention to the studies of different properties of wood plastic composites (WPCs) [1]. The most useful from the wide selection of the thermoplastic polymers is polypropylene (PP), but as a reinforcements different waste products comprising wood lignocellulose fibres often are used. Such materials also are different residues that arise in plywood production industry [2, 3]. Our previous studies of the thermal, the mechanical, the aging and the rheological properties of the polypropylene (PP) with 40 wt. % content of the new type of plywood sanding dust (PSD) showed positive influence of the PSD on PP matrix exploitation properties. Due to this investigation results were chosen two composites with the best exploitation properties. The composition of these composites contained lubricant and stabilizers [2,3], therefore for increasing of the colour intensity of materials selected composites composition was supplemented with additions of 2.5 and 3.0 wt. % of the pigment concentrate based on the low density polyethylene (PIG). In our work two the new systems with the following compositions: **1-A(1)** PP+40 wt.% PSD+3 wt.% Struktol TWP+0.33 wt. % stab.108+0.33wt.% stab.1010+0.5 wt.% stab.770+ 2.5 wt.% PIG and **1-A(2)** PP+40 wt.% PSD+3 wt.% Struktol TWP+0.33 wt. % stab.108+0.33 wt.% stab.1010+1.0 wt.% stab.770+ 3.0 wt.% PIG were approbated. For composites tensile, flexural and impact strength as well as microhardness tests were done. Also thermal properties like softening temperature (by VIKA), melting and thermal oxidation temperatures were noted. The changes of the colour of materials were evaluated by lightness, common colour changes and whiteness degree measurements. To clarify the composites fracture mechanism SEM studies were used. The processing possibilities, rheology of the composite melts were noted by capillary viscosimetry tests. Our studies showed the following results: the tensile strength of the new composites increase about 25-30% and the modulus for 4.0-4.5 times to compare with the results of the similar systems given in [3]. The microhardness maintain at the same level and change in limits 92- 113 MPa. The melting temperatures are a bit smaller (1-2 ^{0} C). The degree of crystallinity of 1-A (1) and 1-A (2) is higher about 5-10 %, but the lightness, the whiteness degree and the common colour changes are smaller than in [3]. The next studies revealed that the investigated composites thermal stability is high: the softening temperatures by VIKA at load 1 kg are 154.4 and 158.6 ^{0} C, the beginning of the thermal oxidation temperatures are 250.5 and 253.5 ^{0} C, the thermal expansion of the samples at 90 ^{0} C is only 3%. The rheological experiments showed that the composite melts viscosity decreases with increase of the temperature and shear rate, the fluidity index is smaller than 1, that is typical for pseudoplastic polymer liquids. SEM pictures of the fractured surface showed that composites failure has mixed character: partially fracture both the polymer matrix and the border surface of the polymer matrix and wood fibre.

References:

1. Polyolefin Composites /Ed. by *D. Nwabunma and T.Kun* - John Wiley & Sons, Inc., 2007.- P. 3-82, 87-123, 150-201.
2. *Kajaks J., Kalnins K. and Matvejs J.* Rheological properties of wood plastic composites based on polypropylene and birch wood plywood production residues //Key Eng. Mater., 2017- Vol.762-P. 226-232.
3. *Kajaks J., Kalnins K. and Matvejs J.* Accelerated weathering of wood plastic composites based on polypropylene and birch plywood production residues *//Open Engineering, 2018 (in press).*

POLYPROPYLENE COMPOSITE CHARACTERIZATION AND GRAIN HUSKS PRE-PREPARATION

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Nowadays interest is focused on the use of natural fibre biomass for the production of polymer composites, which allows the production of materials with improved properties, particularly, mechanical properties. The use of natural fibres in polymer compositions also makes it possible to reduce the consumption of fossil resources and the costs of the material. These composites possess low density, anti-corrosion characteristics and durability. However, natural fibres are polar, but most of the thermoplastic polymers, including polypropylene, are non-polar. Using a maleic anhydride compatibilizer can increase compatibility between the polar fibre and the nonpolar matrix, leading to improved functional properties of the composite material.

Within the experimental part of the work, technologies were developed for 1) shredding of oat and spelt husks before introduction into the polypropylene matrix, 2) production of the grain husks containing polypropylene composites (PP 56,7 w.%, MAH-g-PP 3,3 w.% and husks 40 w.%) and 3) processing the above mentioned composites by injection moulding technology.

From the results of the experimental work, it was concluded that before the introduction of oat husks into the composite, they should be dried for at least 19 h in order to get rid of the absorbed moisture (commonly at about ≈ 6 w.%). The introduction of chopped oat husks into the polypropylene matrix composite improves its mechanical properties (increases the modulus of elasticity and flexural strength at break), particularly, in the presence of a maleic anhydride groups containing compatibilzer, that improves interaction between the polar natural fibres and nonpolar polypropylene matrix. The grain husks shredding mode (speeds within the range of 700-3000 rpm) does not significantly affect the thermal, mechanical and calorimetric properties of the composite. The effect of grain husks on the melting temperature and crystallinity degree of the polypropylene matrix is also relatively small. The degree of crystallinity of composite increases slightly with the use of the coupling agent.

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References:

1. *Bledzki A. K., Mamun A. A., Bonnia N. N., and Ahmad S.* Basic properties of grain by-products and their viability in polypropylene composites // Ind. Crops Prod. – 2012. – Vol. 37, No. 1 – P. 427–434.
2. *Bledzki A. K.* The utilization of biochemically modified microfibers from grain by-products as reinforcement for polypropylene biocomposite // Express Polym. Lett. – 2014. – Vol. 8, No. 10 – P., 767–778.
3. *Sobczak L., Lang R. W., and Haider A.* Polypropylene composites with natural fibers and wood - General mechanical property profiles // Compos. Sci. Technol., vol. 72, no. 5, pp. 550–557, 2012.

MECHANICAL PROPERTIES ANALYSIS OF POLYPROPYLENE BIOCOMPOSITES REINFORCED WITH CELLULOSE PARTICLE FILLERS

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During the last decade, biocomposite materials, such as Polypropylene biocomposites, are studied extensively for application in various fields. One of application cases are an innovative and eco-friendly polymer matrix composites reinforced by natural fibers. These materials can offer several advantages as cost-effectiveness, mechanical properties, low weight and recyclability of the material. Biocomposite has been widely used in several engineering fields as the construction material and automotive application in recent years. The use of biocomposites in the development of next generation materials with required properties is of great interest, because the materials created possess improved mechanical properties and offer new possibilities of their application.

The main purpose of this study is to investigate the influence of polypropylene matrix with man-made cellulose fibres on mechanical properties of the injection moulded composite. For this purpose injection moulding grade polypropylene HP400R was applied as a matrix polymer and man-made cellulose fibres Cordenka and cellulose microfibres HM400X were used as fibres and fillers, respectively.

The static mechanical properties of the manufactured test specimens were measured in a tensile test according to EN ISO 527. The impact strength was tested according to EN ISO 180/A. The result values represent the averaged results of the measurements performed on 10 samples for each type of manufactured composite. A parametrical function approximations has been employed to assess the performance of those materials in different loading conditions. This research helps to understand mechanical properties of the developed hybrids and gives understanding how to changing properties by showing the basic dependencies.

USE OF RECYCLED CELLULOSE FILLER FROM TETRA PAK® PACKAGING WASTE FOR MELT PROCESSING BY KINETIC MIXER OF POLYBUTYLENE SUCCINATE BASED COMPOSITES

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We report polybutylene succinate and recycled cellulose composites prepared by melt blending in kinetic internal mixer. The recycled cellulose was recovered from the Tetra Pak® packaging waste after industrial separation of polyethylene and aluminum components in centrifuge. Final recycled cellulose component was used without further purification and chemical treatment. Prior to melt blending the recycle cellulose was dried overnight at 80 ^{o}C in vacuum oven. The size of the cellulose particles was determined microscopically by the measurement of 100 particles. Consequently, the average length is 150 μm and width – 10 μm. Then sustainable polybutylene succinate – recycled cellulose composites with the filler content 10-50 weight percent were melt processed at 115 ^{o}C for 10 min by the use of Brabender kinetic mixer. The prepared composites were grinded to pellets and shaped as films by compression molding for further investigations. Processing properties of these composites were evaluated. In situ rheological characteristics of the composites during the melt processing are discussed. Cone plate rheological tests for prepared composites were performed as well. Finally, full rheological behavior for polybutylene succinate – recycled cellulose composites was measured considering the filler content. To determine the limits of linear viscoelastic properties of the melts, dynamic strain sweeps were performed. While, linear rheological measurements were performed by applying a time dependent strain. Steady-state shear measurements at a certain temperature were also conducted to investigate the non-linear rheology of the melts. All measurements were conducted at 130 °C. It was concluded that the recycled cellulose filler from Tetra Pak® packaging waste and polybutylene succinate can be melt processed to composites up to 50 weight percent of the recovered component without any significant complications.

USE OF WASTE FROM THE LEATHER INDUSTRY FOR THE PRODUCTION OF BIOTECHNOLOGICAL PRODUCTS BASED ON COLLAGEN

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Every year leather industry generates vast quantities of by-products which could be a cheap and available source of collagen and collagen peptides [1]. Collagen peptides (CPs) have been reported to have a variety of health benefits including anti-oxidant, anti-microbial, anti-inflammatory, antiulcer, lipid-lowering, wound healing and anti-skin-aging activities [2]. These peptides have been widely used in food, cosmetic, biomedical, and pharmaceutical industries [1-3].

The main objective of present study was to obtain a biotechnological product based on collagen and to study its properties.

Lime fleshings from hides was fragmented into small pieces with size ≤ 0.5 sm^2. For extraction of collagen 10 g samples of basic material were selected [3].

Collagen was extracted from trimming waste using 0.5 M acetic in the presence of 5mM EDTA. The purity of extracted collagen was checked by sodium dodecyl sulphate polyacrylamide gel electrophoresis (SDS-PAGE). Collagen peptides were prepared from the obtained collagen. Collagen was enzymatically hydrolyzed by pepsin (3000 U×g protein^{-1}) at 37 ºC and pH 2.0 for 8 h. To stop the reaction, the mixture was heated immediately at 100 ºC for 5 min and then centrifuged at 4000 g for 30 min. The supernatant was subsequently filtered through ceramic membrane (200 μm) for separation of collagen peptides fraction (26 ≤kDa). The generated CPs were analyzed by SDS–PAGE using 18 % resolving gel.

The influence of CPs on antioxidant enzymes and lipid peroxidation were further explored. We could assume that the observed antioxidant properties of collagen peptides might be due their special amino acid compositions.

CPs supplementation also lowered serum level of pro-inflammatory cytokines such as IL-1β, IL-12, while level of anti-inflammatory cytokine IL-4 was within the control value. This findings may provide a basis for further design of new therapy for obesity.

References:

1. *Langmaier F., Kolozmik K., Sukop S., Mladek M.* Products of enzymatic decomposition of chrome-tanned leather waste// J. Soc. Leather Technol. Chem.-1999.- 83-P. 187-195.
2. *Lee C.H., Singla A., Lee Y.* Biomedical applications of collagen// Int. J. Pharm.-2001.- 221-P.1-22.
3. *Savchuk O., Ostapchenko L., Mokrousova O., Andreyeva O., Raksha N.* Extraction and Characterization of Collagen Obtained from Collagen-Containing Wastes of the Leather Industry // Solid State Phenomena. - 2017. -Vol. 267. – P. 172-176.

PECULIARITIES OF TIRE TEXTILE WASTE REPROCESSING TO LIQUID HYDROCARBONS

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The rapid growth of the automotive industry is growing and the number of used tires. A part of these tires are recycled into rubber crumbs, which are used for rubber roofs, roads and playgrounds surfaces. However, during the separation of rubber from the scrap tire remains the textile wastes (~17 %), which are polluted with different size of rubber pieces. Incineration of waste is not acceptable, because the generated solid waste extremely clogs combustion equipment voids and chimneys. These wastes are deposited in landfills and pollute the environment therefore utilization of it is a major issue to maintain a cleaner and healthier environment.

One of the ways of tire textile reprocessing is their decomposition to lower molecular weight products that have energetic value or other potential application. In this case, a simpler chemical destruction method of tire textile would be a moderate temperature (up to 600 °C) thermolysis [1, 2].The process typically yields products of three states of aggregation: gaseous, liquid, and complex residue, char. The main interest is devoted to a liquid product because of its convenient handling, transportation, high energy density, and possible future value upgrading.

In this research separated textile waste from the passenger car tires were investigated. Textile waste obtained after separation is more or less contaminated with rubber crumbs. The feedstock for the thermolysis process has been distributed into three different fractions according to the level of contamination: raw textile waste from recycled tires, marginally polluted textile waste, highly polluted textile waste [3].

In thermolysis experiments a 3000 cm3 capacity semi-continuous vertical reactor was used. The hermetically closed reactor loaded with 400 g of feedstock was heated by electrical muffle furnace, raising a temperature from 20 to 550 °C at a heating rate of 2.5 °C/min [4]. Samples of the obtained liquid products were analyzed using an IKA KV600 digital calorimeter.

It was found that, higher quantity of rubber in the textile waste gave more liquid and solid products. However, comparing these results with the data, which was gotten in the thermolysis of shredded tires, we can see that the yield of liquid and gaseous product deceases by 5 − 7.2 % and 5 − 8.1 %, respectively, the amount of solid phase increases by 12.4 − 13.1 %. The properties analysis of oils showed that the increases of the contamination level of tire textile waste gives a lower density of liquid product but the calorific value of it is higher compared with oil derived from marginally polluted tire textile waste.

References:

1. *Molto J., Font R., Conesa J.* A. Study of the Organic Compounds Produced in the Pyrolysis and Combustion of Used Polyester Fabrics. // Energy and Fluels. – 2006. – Vol. 20. – P. 1951 – 1958.
2. *Aynanoglu A., Yumrutas R.* Rotary kiln and batch pyrolysis of waste tire to produce gazoline and diesel like fuels. // Energy Conversion and Management. – 2016. – Vol. 111. – P. 261 – 270.
3. *Jonušas A., Milašienė D., Belukhina O*. Reprocessing of textile waste from used tire to the liquid products // Magic world of textiles: 8th international textile clothing & design conference: book of proceedings. – 2016. – P. 458-461.
4. *Jonušas A., Miknius L.* Effect of Pressure and Feedstock State on the Yield and Properties of Waste Tires Thermolysis Products. // Energy and Fuels. – 2014. – Vol. 28. – P. 2465 – 2471

EFFECT OF HEMP WASTE SURFACE MODIFICATION ON THE MORPHOLOGICAL, TENSILE PROPERTIES AND WATER ABSORPTION OF LINEAR LOW DENSITY POLYETHYLENE (LLDPE) COMPOSITES

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Use of renewable materials such as plant fibers and manufacture waste has been popular for a long time and is being used more and more. Lignocellulose reinforcement components can significantly improve properties of the polyolefin composites depending on the pre-treatment chosen and the intended purpose [1-3].

Research is focused on improving properties of LLDPE composites reinforced with waste from hemp primary processing which consists of secondary fibers, shives particles and fragments of the primary fibers. Hemp particle surfaces cleanliness of dust applying alkali pre-treatment and sol-gel treatment to reduce hydrophilicity of natural component were performed. Cross-linking between the filler and the polymeric matrix is provided with silane treatment. The eight composites variants with different fibers component pre-treatments but fixed hemp waste content (40 wt.%) were produced on two rolls mill [4].

The effects of fibers pre-treatment method on mechanical, morphological properties and water absorption of obtained composites have been investigated. Scanning electron microscopy (SEM) has been used to examine the morphology of the fiber surface. The tensile tests were measured by standard ASTM D 638 M – 3. Water exposure experiments conforming to the standard ASTM D 570-98 were carried out at a room temperature.

The lowest water absorption shows composites with the reinforcing components subjected to the sol-gel technology treatment using tetraethyl orthosilicate (TEOS). In turn, higher mechanical properties show samples silanized with aminopropyltriethoxysilane (APTES). ZnO nanoparticles filling increase the amount of samples absorbed water, since the pores that are generated during the manufacturing process serves as a channels for water absorption. SEM micrographs show that the sol-gel treated waste particles surfaces are damaged, but the surfaces of alkali treated and silanized particles are smooth. Small cubic formations on the silanized surfaces are detected. The composite cross-section not exhibit significant bounces, resulting from the fiber/particle pull-out, which suggests good adhesion between the matrix and reinforcing components.

References:

1. *Chimeni D.J., Toupe J. L., Dubois C. & Rodrigue D.* Effect of hemp surface modification on the morphological and tensile properties of linear medium density polyethylene (LMDPE) composites // Comp. Interfaces – 2016. - P. 1568-5543.
2. *Merkel K., Rydarowski H., Kazimierczak J., Bloda A.*Processing and characterization of reinforced polyethylene composites made with lignocellulosic fibres isolated from waste plant biomass such as hemp // Composites: Part B. – 2014. – Vol. 67 – P. 138–144.
3. *Reinu E. Abraham 1, Cynthia S. Wong 2 and Munish Puri.* Enrichment of CellulosicWaste Hemp (Cannabis sativa) Hurd into Non-Toxic Microfibres // Materials – 2016.- Vol. 9, Nr. 562 – P. 1-13.
4. *Zelča, Z., Kukle, S., Kajaks, J., Ručevska, I., Vihodceva, S.* Properties of Composites Based on Linear Low Density Polyethylene (LLDPE) and by Sol-gel Method Modified Fibres // IOP Conference Series: Materials Science and Engineering. -2016. - Vol. 111, No. 012012, P. 1-5.

BIO-COMPONENTS FROM MUNICIPAL WASTE

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Municipal waste such as used cooking oil can be a source of raw materials for the production of bio-components. This study was carried out to determine the potential of used cooking oil from palm and rapeseed oils in preparation of bio-polyols. Bio-components were synthesized by two-step process including epoxidation and oxirane ring opening. Epoxidation of oils was performed by reacting double bonds in the oil with a peracetic acid generated *in situ* by the reaction of 30 wt.% hydrogen peroxide and glacial acetic acid. The following catalysts such as: sulfuric acid and ion exchange resin Amberlite IR-120 were used in epoxydation reactions. Epoxidized oils with epoxy values from 0,12 to 0,34 mol/100g ware obtained. In the next stage the bio-polyols from epoxidized oils were obtained using diethylene glycol. Samples taken during the epoxidation reaction and ring opening as well as the final products were characterized by an evaluation of iodine, epoxy, hydroxyl and acid values. Products were also characterized using Fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC).

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INVESTIGATION OF THE PERSPIRATION RESISTANCE AND ACCELERATED-AGEING OF PARCHMENT

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For this time parchment is one of the best materials for writing, restoration of historical manuscripts, book editions, and production of decorative arts and crafts [1] due to the strength and durability of collagen, the derivative of which it is. However, as the polymer material of biogenic origin, parchment aging over time under the influence of conditions of the environment (for example, under the influence of moisture, temperature, etc.) which negatively affects its structure, physical, chemical and mechanical properties [2]. The most important factors that determine the resistance of the parchment to various influences are its production method and type of materials used. That is why the stability investigating of parchment properties under certain conditions is an important for improving the technology of production this unique type of natural leather.

In view of the above, the process of artificial aging of samples of parchment, obtained from sheep skins by several modern and old technologies is investigated in a research [3]. As the determinative factors selected the effect of artificial perspiration and accelerated-ageing by high temperature which sufficiently reflect the influence that parchment can undergo during exploitation and storage. To obtain a clear view of changing the parchment depending on the given conditions the biochemical changes of collagen structure have been analyzed using the method of polyacrylamide gel electrophoresis (SDS-PAGE), and due to the application the methods of physical-mechanical analysis – its shrinkage temperature, strength and elastic-plastic properties.

It has been experimentally established that parchment produced by modern technology, which provides accelerated liming with alkaline reagents, was proved to be the most resistant to artificial perspiration and high temperature by indices of shrinkage temperature and extension at tensile strength, and according to the index of tensile strength for transparency-parchment, obtained by the old technology, which consists in the use of potassium alum in filling. The results obtained can be explained by certain changes in the collagen structure and the presence of components that can prevent the negative effects of external factors on its derivative.

References:

1. Parchment: The Physical and Chemical Characteristics of Parchment and the Materials Used in Its Conservation / Betty M. Haines. – Pennsylvania: Leather Conservation, Centre, 1999. – 33 p.
2. *G. Della Gatta, E. Badea, R. Ceccarelli, T. Usacheva, A. Mašic and S. Coluccia*. Assessment of damage in old parchments by DSC and SEM // Journal of Thermal Analysis and Calorimetry. – 2005. – V. 82. – pp. 637–649.
3. *N.I. Adakina, T.O. Kolesnyk, O.A. Andreyeva*. Technological features of different methods of manufacturing leather parchment // Herald of Khmelnytskyi national university. – 2018. – No1 (257). – pp. 187–192.

COMPARATIVE CHARACTERIZATION OF AGED BITUMEN PROPERTIES

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Nowadays, in many industries, including the road industry, solutions are searched for the resources re-use and recycling. Roads are being built or restored every day and asphalt pavement service life depends on several factors, including traffic load, climate and temperature. The main critical factor, determining asphalt service life, is binder, in most cases bitumen. Bitumen is viscoelastic material, ensuring the necessary adhesion with other asphalt pavement components and providing waterproofing and flexibility to the pavement. As organic material bitumen is susceptible to aging under environmental factors and processing temperatures, as well, bitumen properties depends on crude oil source and distillation conditions. The mechanisms of bitumen aging include oxidation, photo oxidation and evaporation of volatile components at elevated temperatures, consequently, adhesion between asphalt pavements components decreases because bitumen has new intermolecular structure [1,2]. In spite of this, according to statistics [3], uses of reclaimed asphalt increases globally, generally, because of contribution to cost reduction and sustainable development.

The aim of this study is to characterize properties of bitumen from reclaimed asphalt pavement in comparison to neat and artificially aged bitumen. By considering that one of the most important parameters for determination of bitumen performance is viscosity, rheological behavior (such as, viscosity, complex shear module, phase angle etc) of the analyzed bitumens has been investigated, using the dynamic shear rheometer. Rheological investigations allow to judge about the potential effects of reclaimed bitumen on the processing, flexibility and durability of the asphalt pavement. As viscosity strongly depends on intermolecular interactions, structural peculiarities of the reclaimed bitumen have been investigated using the Fourier Transform Infrared Spectroscopy (FTIR) and Modulated Differential Scanning Calorimetry.

Analysis of FTIR spectra show that reclaimed bitumen is characterized by increased absorbance in carbonyl and sulfoxide group regions, testifying that bitumen becomes more polar under the influence of aggressive environmental factors (such as UV irradiation, temperature, moisture/condensate). Consequently, viscosity and complex module are increased, but phase angle is reduced over the wide temperature range.

As a result of the study it can be concluded that bitumen aging can be evaluated by using specific alternative artificial aging procedure (such as UV irradiation and temperature). Future studies are envisaged for modification of aged bitumen by means of low molecular (bitumen rejuvenator) and/or high molecular (polymer) agents.

References:

1. *Lavin P.* Asphalt Pavements: A Practical Guide to Design, Production and Maintenance for Engineers and Architects//CRC Press-2003.- 462 p.
2. *Y. S. Kumbargeri, K. Prapoorna Biligiri* / Transportation Research Procedia-2016.- 17 – P. 282 – 290.
3. http://www.eapa.org/promo.php?c=174 (accessed on 17.05.2018.)

RHEOLOGY OF WATER-CONCRETE MIXTURES CONTAINING COPOLYMERS OF ACRYLIC ACID AND VINYLIC MONOMERS WITH POLY(ETHYLENE GLYCOLE) SUBSTITUENTS

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Water-reducing additives also called plasticizers or superplasticizers make it possible to achieve good workability of the fresh concrete with a low water-cement ratio. The strength of concrete is inversely proportional to the amount of water added (certainly if the mix is not "starved" of water). So they improve workability and at the same time lead to producing of stronger concrete. In this study copolymers of acrylic acid (AA) and vinyl monomers with poly(ethylene glycole) (PEG) substituents of different length – methoxy poly(ethylene glycol) methacrylates (MPEGMA), allyl alcohol polyoxyethylene ether (APEG) and isopentenyl alcohol polyoxyethylene ether (IPPEG), using electrostatic and steric mechanisms of stabilization of concrete suspensions were investigated as superplasticizers.

Water-concrete ratio 0.25-0.30 can be used in the presence of such admixtures. So we face a colloid problem concerning stability and rheology of the concentrated suspensions. Polymer adsorbs on the concrete particle surface with "anchor" acid units, and poly(ethylene glycole) radicals are stretched in solution, provides concrete suspension with steric stabilization. It seems electrostatic effect does not play a noticeable role in this case because of a big length of PEG radicals.

Rheology experiments can be carried out correctly only under certain conditions. The concentration of plastisizer was chosen in such a way to provide a suspension with a good stability and to *avoid coagulation in the primary minimum*. A high potential barrier is found only due to the enough concentration of the plastisizer. So determination of a minimal concentration of polymer always must be done before a rheological study. For a stable suspension there are two alternative rheological behaviours: Newtonian flow in the absence of any structure (or Bingham) and tixotropic flow when a structure is formed due to coagulation in the secondary minimum. The last may appear if the attraction forces affect at a big distance from the particles surface. The reason of such forces can be interactions between PEG radicals. Under the straitened conditions like in the case of concentrated suspensions the secondary minimum can be in the middle between two particles due to superposition of two potential curves of interaction; and if it is a large enough the movement of particles is possible.

To investigate all the above we have considered the following factors influencing on a character of flow:

– the length of PEG radical,
– monomers ratio in macromolecules of plasticizers,
– molecular mass of plasticizers,
– the presence of multivalent ions in suspension.

The study of flow behaviour (dependence of shear stress on shear rate) and oscillation experiments have been carried out. The second gives an additional information about a possible structure because of showing of a ratio between viscous and elastic properties.

It was found that in the presence of PEG containing admixtures water-concrete suspensions can behave like Bingham and Newtonian liquids or be tixotropic.

MODELLING OF MECHANICAL PROPERTIES OF NOVEL POLYMER COMPOSITES REINFORCED WITH 2D GRAPHENE AND MXENE NANOPARTICLES

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Two-dimensional (2D) nanomaterials such as graphene, metal oxides, metal hydroxides, transition metal oxides and others are currently among the most intensively studied classes of materials that hold great promise for future applications in many technological areas. It seems, graphene is the best known 2D nanomaterial. The main advantage of graphene is excellent conductivity. Graphene is used in a wide range of application including light weight, high strength polymer composite materials. Graphene was discovered in 2004 but the commercial use of graphene is still limited due to expensive suitable for industry methods and some disadvantages. Graphene has hydrophobic surface resulting in agglomeration, poor compatibility and dispersibility in polymers, weak interfaces and insufficient mechanical reinforcement effect [1]. This turns for searching of the next evolutionary step in materials development providing solutions for the “beyond graphene” era, needed to meet the challenges of global competition.

The new 2D nanomaterials MXenes were discovered in 2011. They were produced by the extraction of the A-group layers from the transition metal carbides and/or nitrides, known as the MAX phases [2]. Although ternary carbides and nitrides after mechanical deformation can be formed into lamellas, the thicknesses of them varies from tens to hundreds nanometres [3]. While MXenes can be exfoliated into few nanometres sheets similar to the graphene [2].

In this study the comparative analysis of finite element modelling methodologies in support of the mechanical properties optimization for polymer composite reinforced with two types of 2D nanoparticles MXene and graphene was carried out. Three-dimensional finite element models were used with randomly distributed two types 2D nanoparticles in polymer matrix. A different conception for modelling of different particles was selected. As a very important aspect of modelling, the MXene/polymer and graphene/polymer matrix interface was taken into account.

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References:

1. *Starkova O., Chandrasekaran S., Prado L. A. S. A., Tölle F., Mülhaupt R., and Schulte K.* Hydrothermally resistant thermally reduced graphene oxide and multi-wall carbon nanotube based epoxy nanocomposites // Polymer Degradation and Stability – 2013. – Vol. 98 – P. 519-526.
2. *Naguib M., Kurtoglu M., Presser V., Lu J., Niu J., Heon M., Hultman L., Gogotsi Y., and Barsoum M.W.* Two-Dimensional Nanocrystals Produced by Exfoliation of Ti3AlC2 // Advanced Materials – 2011. – Vol. 23 – P. 4248-4253.
3. Encyclopedia of Materials: Science and Technology / Ed by *Buschow K. H. J., et al*. – Oxford, Elsevier, 2004. – 388 p.

FINITE ELEMENT SIMULATION OF INDENTATION EXPERIMENT ON BRANCHED EPOXY NOVOLAC RESIN

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The indentation test widely used to measure the depth of penetration of an indenter into test specimens. The results of this test can be used not only to determine the hardness of the material but also to obtain mechanical properties and the deformation behaviour of surface. This test is not expensive, non-destructive and need a small volume of coated material.

The main purpose of this study is to investigate the indentation test method and validation of it's by finite element simulation. The indentation experiment was performed on branched epoxy novolac resin (ENR) by using Vicker indenter. Samples were prepared by solution casting and UV curing method. The Vicker microhardness was measured on a Vickers M-17 1021 device equipped with optical microscope with a 40-g load and a loading time of 20 s.

The numerical analysis is performed by a 3D dimensional finite element (FE) axis symmetry model and is carried out by using the finite element program ANSYS. The standard Vickers quadrangular pyramid diamond indenter was considered in this simulation. Mechanical properties for numerical simulation were taken according to the uniaxial tensile test.

The numerical results present's load–displacement curve obtained from the finite element simulation. Based on the load and displacement data, the material yielding stress was also calculated. The difference between the hardness values obtained from the finite element simulation and the indentation experiment are negligible.

Additionally, numerically-measured residual stress field around a Vickers indentation at the surface of ENR during loading and unloading was described. The FEM analysis shows that the load–displacement relation can provide much useful information on mechanical properties using the analysis developed here.

PREDICTION METHOD OF ELECTRICAL CONDUCTIVITY OF NANO-MODIFIED GLASS FIBRE REINFORCED PLASTICS

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Glass fibre reinforced plastics (GFRP) is non-conductive construction material, however with carbon nanotubes (CNT) modifying it can get additional functionality due to its gained electrical conductivity. That opens a prospective for its use in a wide range of high-performance applications in civil engineering, biomedical, aerospace, and automotive industries [1, 2].

Main aim of the study is to predict electrical conductivity of GFRP with nano-modified epoxy matrix using structural approach. GFRP composites under investigation were based on UD Glass fiber and two matrixes modified with carbon nanotubes: Araldite LY 1564 + Aradur 3486 epoxy resin from masterbatch EpoCyl™ 128-05 and Nano-Force E200 epoxy system + Nano-Force E hardener.

Electrical conductivity of epoxy resin modified by CNT (concentrations < 1 %) was modelled using structural approach. Electrical conductivity of unidirectional GFRP layer was measured experimentally and modelled based on conductivity of polymer matrix and assuming non-conductive fibres. It is supposed that epoxy matrix and composite on different structural levels follow the Ohm’s law. Two components of tensor of electrical conductivity for monotropic material in main axis of symmetry were calculated for composites by several different ways. Control experiment was performed on a sample of GFRP monolayer cut from the unidirectional plate under different angles.

Conductivity of composite lamina consisting of N layers was calculated for symmetrical layup with orientation of layers $\pm\theta$. Experimental verification was performed for several GFRP samples with layers’ layup of $[0/90]_4$ and $[\pm45]_4$. The calculated data are in a good agreement with the experimental values.

References:

1. *Bandaru P.R.*, Electrical Properties and Applications of Carbon Nanotube Structures// Journal of Nanoscience and Nanotechnology-2007.- 29- P. 3-21.
2. *Kulakov V., et al.* Effective electrical conductivity of carbon nanotube–epoxy nanocomposites// Journal of Composite Materials- 2017.-51-21-P. 2979-2988.

METHODOLOGY FOR THE BUILDING OF CURING KINETIC MODELS

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Thermoset resins (epoxy, polyester, vinyl ester) are widely used for production of constructive parts using different technological processes. Nowadays design, rationalisation and optimisation of any technological process is difficult without a simulation of it. This simulation is not possible without a curing kinetic model of the resin, developed separately.

Task of the resin kinetic study is to describe the rate of the resin reaction in time or temperature domain. In kinetic analysis, it is generally assumed that the rate of the resin reaction can be described by the Arrhenius relationship multiplied by a reaction function that depends on the resin properties and varies with the resin reaction model. The most commonly used are the first and *n*-th order models, Prout-Tompkins [1], Kamal-Sourour [2] and *n*-th order autocatalytic models.

The curing process of thermoset resin is an irreversible exothermic chemical reaction. This process can be characterised by a degree of cure. Physically this value is a relative amount of the reacted resin in conditional mixture of unreacted and reacted resin. According to this formulation, the rate of the resin reaction can be described by the rate of the change of the degree of cure. Since the chemical reaction is exothermic and the evolve of the heat is proportional to the reaction, the degree of cure can be described as the ratio of the amount of heat evolved during the reaction up to the present time to the total heat of reaction. This approach is used in the present methodology for the building of curing kinetic models of thermoset resins, then at the first step dynamic Differential Scanning Calorimetry (DSC) tests of the resin at at least 3 different heating rates are carried out. As a result of these tests normalised heat flows of resin samples in time and temperature domains are obtained. At the second step of the methodology, the total heat of reaction and the experimental degree of cure in time domain is calculated for each heating rate using DSC data. Then coefficients of the Arrhenius relationship, activation energy and frequency factor, are determined by the Kissenger method [3] or another approach [4] from the heating rates and peak temperatures, obtained by DSC tests. At the last step the coefficients of selected reaction function are determined by a fitting of the experimental degree of cure curves applying the least squares method.

The proposed methodology was successfully applied for a building of the curing kinetic model of polyester resin POLRES 305BV. Different reaction models were used and compared. The best precision was obtained with the Kamal-Sourour model but the *n*-th order model gave the worst result.

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References:

1. *Prout E. G., Tompkins F. C*. The thermal decomposition of potassium permanganate // T. Faraday Soc. – 1944. – Vol. 40 – P. 488-498.
2. *Kamal M. R., Sourour S.* Kinetics and thermal characterization of thermoset cure // Polym. Eng. Sci. - 1973. – Vol. 13, No. 1 – p. 59–64.
3. Kissinger H. E. Reaction kinetics in differential thermal analysis // Natl. Bureau Stand. - 1957. – Vol. 29, No. 11 – P. 1702–1706.
4. ASTM E 698. Standard test method for Arrhenius kinetic constants for thermally unstable materials.

INVESTIGATION OF THE RESIDUAL STRENGTH OF CFRP ALUMINIUM HONEYCOMB SANDWICH PANELS

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Ultra lightweight composite materials are increasingly used in the aerospace structures due to their high specific stiffness and strength, corrosion resistance, and fatigue performance. Nevertheless, the major drawback is the uncertain ty linked with accumulation of damage due to the accidental out-of-plane load during the manufacturing process and/or service life [1-3].

Present study examines sandwich panels, which are made of carbon fiber face sheets and aluminum honeycomb core and focuses on determining their residual strength after intentional damage. The literature reviewed suggests that damage tolerance is affected by a multitude of factors, from panel construction to boundary conditions [3]. The effects of varying factors, such as the skin thickness, layup, core density and diameter of hemispherical indenter, have been examined. The experimental set-up and testing were performed according to the ASTM standards. All the relevant mechanical test procedures have been developed internally and verified using dedicated prototype specimens.

Artificial damage in the middle of sandwich specimens was introduced using two quasi-static indentation and low velocity drop-weight impact. Hemispherical indenters of two diameters, namely, 20 mm and 150 mm, were applied. In quasi-static indentation tests, indenter penetration depth was used as criteria for the barely visible damage size. In drop-weight impact tests the degree of damage was measured in terms of impact energy. The C-scan for each specimen was carried out before and after the damage introduction. The depth of the residual damage was measured using a laser distance meter.

The residual strength was estimated through the edgewise compression test. The specimen edges were fixed by potting them into epoxy/sand mixture to prevent their undesirable and premature failure. A designated potting stand was designed and manufactured for such purposes.

The study has demonstrated, that increasement of the honeycomb density, leads to decrease in the safety margin in structure. While thicker skins may also leads to a catastrophic propagation of indent and decrease in residual strength.

References:

1. *Wei T., Falzon B. G., Chiu L. N. S., Price M.* Predicting low velocity impact damage and Compression-After-Impact (CAI) behavior of composite laminates // Compos. Part A-Appl. S. – 2015. – Vol. 71, P. 212–226.
2. *Petit S., Bouvet C., Bergerot A., Barrau J. J.* Impact and compression after impact experimental study of a composite laminate with a cork thermal shield // Compos. Sci. Technol. – 2007. – Vol. 67, No. 16-17 – P. 3286-3299.
3. Damage resistance and tolerance investigation of carbon / epoxy skinned honeycomb sandwich panels / Hill M. D. Leicestershire, United Kingdom, 2007. – 365 p.

DEVELOPMENT OF UV-CURED EPOXY RESIN BASED ON MARINELINE® FORMULATION FOR APPLICATIONS AS EFFICIENT REPAIR SYSTEM OF BOAT TANKS' PROTECTIVE COATING

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The purpose of this presentation is to clearly show the use of one component uv-cured epoxy resin coating formulation as a new coating repair service system for coated tanks and other ships. The developed repair procedure with the uv-curing of MarineLine® should be used when the protective coating has been misapplied, damaged, or contains holidays or pinholes. Thereto here we report that the developed photopolymerization technology of one component epoxy resin to be used as very efficient replacement of two-component MarineLine® epoxy resin to receive protective coatings for applications and maritime industries where thermal curing processes and two-component resin hardening are unacceptable. Dense cross-linked epoxy coatings with a thickness of 150 μm thickness was photoinitiated by metal organic salt. Epoxy crosslinking efficiency of UV-light polymerization accomplished by Hg-lamp with certain power continuous irradiation were investigated as a function of the photoinitiator content and curing time. It was found that higher hardness of the polymer resulted in an increased cross-linking density of the developed chain network. UV irradiation time longer than critical time (min) results in the photodegradation of the polymer. The obtained hardness and other properties of the rigid photocured coatings is equal to the thermally cured two component epoxy resin formulation.

Acknowledgement. The financial support of the RTU Scientific Platform for Science and Innovation Project ND:YAG laser induced photopolymerization of Novolac polymers is gratefully acknowledged.

RAFT POLYMERIZATION OF N-HETEROCYCLIC VINYL MONOMERS IN THE PRESENCE OF DIBENZYL TRITHIOCARBONATE

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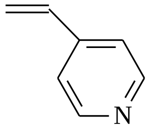
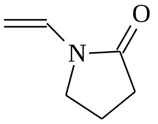
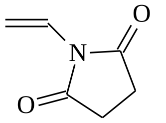
In the last two decades RAFT polymerization is the leader in popularity among researchers engaged in the synthesis of polymers with a certain macromolecular architecture. According to the accepted classification, 4-vinyl pyridine (4VP) and N-vinyl pyrrolidone (VP) refer to "less-activated" monomers in RAFT polymerization like vinyl acetate. Consequently, xanthates and dithiocarbamates are the effective RAFT agents for them, and dithioesters and trithiocarbonates are not effective. It would be logical to refer N-vinyl succinimide (VSI) and 5-vinyl tetrazole (5VT) to the same group of monomers. For the first two, the above is confirmed by experimental data and a low chain transfer constant (C_{tr}) to dibenzyl trithiocarbonate BTC (calculated only for 4VP). Unexpectedly, VSI and 5VT showed themselves as "more-activated" monomers in relation to BTC. Below the VSI constants of chain transfer to BTC and monosubstituted trithiocarbonate formed in the first stage of RAFT polymerization in the presence of symmetric trithiocarbonates poly(RAFT)$_1$ are shown.



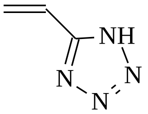
4VP(C_{tr}~1)



VP



VSI(C_{tr}~19 $C_{tr}\rightarrow$poly(RAFT)$_1>29$)



5VT

Homopolymerization of these monomers in the presence of BTC has been successfully investigated. The next steps are: (*1*) the study of the polymerization features under the same conditions (accordance with the adopted scheme, kinetics, chains microstructure of polymers obtained); (*2*) synthesis of new polymers interesting, first of all, for medical and biological applications. This is because three of the four monomers (VP, VSI and 5VT) form non-toxic polymers that can be used within a living organism.

Polymers based on these monomers form an interesting range on hydrophilicity: strongly hydrophilic and water-soluble poly(VSI) and poly(5VT), and less hydrophilic, insoluble in water poly(4VP) and poly(VP). Since block copolymers can be easily obtained in the RAFT polymerization, this is the way to the synthesis of copolymers capable of self-organization and the formation of micelles in aqueous solutions. For example, in the case of VP-VSI copolymers, micelles can be formed with a core of VSI blocks and an outer sphere of VP blocks. The same is possible if we replace VP with 5VT. In addition, VSI units are capable of alkaline hydrolysis leading to the opening of VSI cycle. In this case, the N-vinyl amidosuccinic acid (VSA) units are formed and the polymer becomes water-soluble. Interesting polymers can be obtained by polymerization of 4VP with VSI. After hydrolysis, the copolymers have basic and acid groups in their chains. The balance between them depends on pH of the solution. In alkaline media, carboxyl groups of VSA units are ionized and carry a negative charge; 4VP units are not ionized and relatively hydrophobic. With decreasing of pH dissociation of carboxyl groups is suppressed, the negative charge disappears; 4VP units are protonated, positively charged and become more hydrophilic. Naturally, the entire spectrum of states is realized during the transition from a strong alkaline to a strong acid medium and back. In this way stimuli (pH) responsive polymers can be obtained.

PHYSICO-CHEMICAL PROPERTIES OF AMPHIPHILIC STYRENE/ACRYLIC ACID COPOLYMERS IN POLAR SOLVENTS – FINE ADJUSTMENT VIA RAFT COPOLYMERIZATION

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Radical reversible addition-fragmentation chain transfer (RAFT) polymerization is a powerful tool for molecular design of compositionally uniform AB copolymers with a given chain microstructure [1]. Using this tool, we have synthesized a number of acrylic acid (AA)/styrene (S) copolymers using 90/10 (mol/mol) AA/S monomer mixture, polar or nonpolar solvent (N,N-dimethylformamide (DMF) or 1,4-dioxane), monomeric (dibenzyl trithiocarbonate (BTC)) or polymeric (polystyrene trithiocarbonate (PSTC) and poly(acrylic acid) trithiocarbonate (PAATC)) RAFT agents. In all cases living character of copolymerization was confirmed, the degree of monomer conversion exceeds 90%. The resultant copolymers have number average molecular masses ~ 10 000 – 27 000 and dispersity M_w/M_n ~ 1.3.

Though synthesis conditions (temperature, initiator, RAFT agent and monomer concentrations) were identical in all cases, physico-chemical properties of synthesized copolymers were quite different. Thus, copolymers BTC-(AA/S) and PAATC-(AA/S) synthesized in dioxane, were soluble in water but insoluble in DMF. In dilute aqueous solutions, their macromolecules adopt compact conformation of a shrunken coil (average hydrodynamic diameter ~ 2.4 nm). Such copolymers can be quantitatively precipitated by adding oppositely charged complexating agent – dodecyltrimethylammonium bromide.

On the other hand, the same copolymers (BTC-(AA/S) and PAATC-(AA/S)) synthesized in DMF, as well as PSTC-(AA/S) (synthesized in both DMF and dioxane) were insoluble in water. These copolymers were soluble in DMF, where their macromolecules adopt conformation of an unperturbed coil (average hydrodynamic diameter ~ 6 – 7 nm).

Noticeable differences in properties of synthesized copolymers can be attributed to differences in microstructure of AA/S chains. We assume predominately random distribution of AA and S units along copolymer backbone in BTC-(AA/S) and PAATC-(AA/S) copolymers synthesized in dioxane vs. predominately microblock distribution of AA and S units for these copolymers, synthesized in DMF, as well as for PSTC-(AA/S). Thus, varying the chemical nature of the RAFT agent and polarity of the solvent, fine adjustment of physico-chemical properties of AB copolymers with similar average composition can be successfully achieved.

This research was financially supported by Russian Foundation for Basic Researches (project 17-03-00131).

Reference:

1. *Chernikova E.V., Sivtsov E.V.* Reversible addition-fragmentation chain-transfer polymerization: fundamentals and use in practice // Polym. Sci. ser. B. – 2007. – Vol. 59, No. 2 – P. 93–123.

SYNTHESIS AND PROPERTIES OF *meta*-SUBSTITUTED ELECTROACTIVE BENZOPHENONE DERIVATIVES

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Organic luminescent materials have attracted increasing attention for their potential applications in the fields of displays and sensors [1]. To achieve better performance, it is of great importance to have a deep understanding of the inherent light-emitting process and internal mechanism. The employment of thermally activated delayed fluorescence (TADF) in the active layers of organic light emitting diodes has been stated to be very efficient [2]. TADF materials can achieve 100 % of use of excitons through reverse intersystem crossing because of their low energy gap between the lowest singlet excited state S_1 and triplet excited state T_1 [3]. The strategy to achieve such characteristics is to employ both donor and acceptor moieties in a single molecular structure.

In this work, we present benzophenone-based emitters bearing donor-acceptor-donor electronic structure. Benzophenone is known to be a stable acceptor [4]. A series of thermally activated delayed fluorescence (TADF) materials containing *para*-substituted benzophenone and dimethydihydroacridine moieties were used in non-doped green OLED with EQE of 4.3% [5]. The donor moieties such as tetrahydrocarbazole, phenoxazine and dimethydihydroacridine were chosen due to their favorable HOMO orbitals delocalization and electron donating ability [6].

We report on the synthesis and properties of electroactive compounds bearing benzophenone moiety as an acceptor and tetrahydrocarbazole, phenoxazine and 2,7-*ditert*-butyl-9,9-dimethylacridine species as donors attached in *meta*-position. The investigated compounds were found to be efficient materials exhibiting both thermally activated delayed fluorescence and aggregation induced emission enhancement characteristics.

Acknowledgement. This research is/was funded by the European Social Fund according to the activity 'Improvement of researchers' qualification by implementing world-class R&D projects' of Measure No. 09.3.3-LMT-K-712.

References:

1. *Sasabe H., and Kido J.* Multifunctional Materials in High-Performance OLEDs: Challenges for Solid-State Lighting // Chem. Mater. – 2011. – Vol. 23, No. 3 – P. 621–630.
2. *Lee S.Y, Yasuda T., Yang Y.S., Zhang Q., and Adachi C.* Luminous Butterflies: Efficient Exciton Harvesting by Benzophenone Derivatives for Full-Color Delayed Fluorescence OLEDs // Angew. Chem. –2014. – Vol.126, No. 25 – P. 6520–6524.
3. *Komino T., Nomura H., Koyanagi T. and Adachi C.* Suppression of Efficiency Roll-Off Characteristics in Thermally Activated Delayed Fluorescence Based Organic Light-Emitting Diodes Using Randomly Oriented Host Molecules // Chem. Mater. – 2013. – Vol. 25, No. 15 –P. 3038–3047.
4. *Jun C.-H., Pu Y.J., Igarashi M., Chiba T., Sasabe H., and Kido J.* A Donor–Acceptor-type Host Material for Solution-processed Phosphorescent Organic Light-emitting Devices Showing High Efficiency // Chem. Lett. – 2014. –Vol. 43, No. 12 – P. 1935–1936.
5. *Huang B, Ban X, Sun K, Ma Z, Mei Y, Jiang W, Lin B, Sun Y.* Thermally activated delayed fluorescence materials based on benzophenone derivative as emitter for efficient solution-processed non-doped green OLED // Dyes and Pigm. – 2016. – Vol. 133, No. 3 – P. 380–386.
6. *Komatsu R., Sasabe H., Seino Y., Nakao K., and Kido J.* Light-blue thermally activated delayed fluorescent emitters realizing a high external quantum efficiency of 25% and unprecedented low drive voltages in OLEDs // J. Mater. Chem. C. – 2016. – Vol.4, No. 12 – P. 2274–2278.

KINETIC FEATURES OF FORMATION OF SUPRAMOLECULAR HYDROGELS BASED ON L-CYSTEINE, SILVER NITRATE AND METAL HALIDES

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The study of gelling processes in supramolecular hydrogels based on low-molecular weight compounds (amino acids and their derivatives) is of scientific and practical interest. Low-concentration hydrogels based on L-cysteine (L-Cys), silver nitrate and halides of various metals exhibiting antimicrobial activity could find application in various fields of medicine and pharmacology. It was found that the hydrogels based on the amino acid L-Cys, silver nitrate and chloride or bromide anions can be obtained by direct mixing of all the initial components [1]. The aim of this work is to study the kinetics of gelation in three-component systems based on L-Cys and silver nitrate, in which metal halides (Cl^- or Br^-) are used as the gelation initiator.

The molar ratio of the initial components (Ag^+/L-Cys) varied from 1.33 to 2.00, the L-Cys concentration in the samples was 1.5 or 3.0 mM, the metal halides content was varied from 0.25 to 1.5 mM.

The strength of the hydrogels was estimated by a five-point scale [2] by the character of the deformation of the gel sample in the test tube, when it was turned over 180 degrees. This allowed us to determine the optimal composition of the gel systems with maximum strength and stability over time. In addition to strength, an important characteristic of the hydrogels is their stability over time. It is found out that the L-Cys-$AgNO_3$ based hydrogels with chloride or bromide anions keep their properties such as transparency, homogeneous state, thixotropic properties (the ability to repeatedly restore its structure after mechanical stress) for a long time - from 2 weeks till two months.

The kinetics of the formation of the spatial gel network in L-Cys-$AgNO_3$ based samples with different contents of Cl^- or Br^- and silver ions was studied by viscosity measurements. It should be noted that viscosity, gelation time, thixotropic behavior of the hydrogels with chloride and bromide anions are different. The kinetics of gelation in L-Cys-$AgNO_3$ samples was studied also by means of UV spectroscopy and dynamic light scattering (DLS) techniques.

The DLS results showed that the radius of the aggregates formed in the systems depends on time and mainly on the concentration of all components. It is established that particle size distributions for each of the studied systems are variable. In the electronic spectra of the samples with Cl^- or Br^-, there are significant differences that can be explained by the features of the supramolecular chains consisting of silver mercaptide molecules and halide anions. Scanning electron microscopy confirmed various of the structure of the samples containing chloride and bromide anions.

The work is performed under financial support of the Ministry of Education and Science of the Russian Federation in the frame of realizing of the State task in the field of the scientific activity (project N4.5508.2017/BP).
This work is performed by means of the Equipment Center for collective Use of Tver State University.

References:

1. *Ovchinnikov M.M., Laguseva V.S., Khizhnyak S.D., Pakhomov P.M.* One-stage gelation of L-cysteine-silver solutions // Vestnik of the Tver State University. Series: Chemistry. – 2017. – Vol. 4, No. 4 – P. 135–145.
2. *Khizhnyak S.D., Komarov P.V., Ovchinnikov M.M., Zherenkova L.V., Pakhomov P.M.* Mechanism of gelation in low-concentration aqueous solutions of silver nitrate with L-cysteine and its derivatives // Soft Matter. – 2017. – Vol. 30, No. 13 – P. 5168–5184.

SELF-ORGANIZATION PROCESSES IN THE MIXED AQUEOUS SOLUTIONS OF L-CYSTEINE, SILVER NITRATE AND POLYETHYLENE GLYCOL

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Supramolecular gel-forming system based on low-concentration aqueous solutions of L-cysteine and silver nitrate was discovered in 2003 [1]. Interest in these compositions arose in the 70s and has not faded in our days [2]. However, the vast majority of these studies were devoted to the chemical aspects of the interactions of cysteine with various silver salts [3-5]. At the same time, the introduction of various polymers into the system can give it a new yet unexplored properties. So, the goal of this work is to investigate the processes of self-organization and gel formation in a mixed system of cysteine-silver aqueous solution (CSS) and polyethylene glycol (PEG).

Using a set of methods (viscometry, UV - and IR-spectroscopy, pH-metry and dynamic light scattering), self-organization processes in aqueous solution of PEG, L-cysteine and silver nitrate under the action of sodium sulfate were studied.

The first results show, the introduction of PEG in CSS leads to gel formation. However, the obtained gels are quite weak and have the short period of life. The complex approach confirmed the visual observations: the viscosity of obtained gels poorly grew at polymer adding; the systems had no tixotropic properties; pH, sizes of aggregates, zetta potential and conductivity of systems became constant.

The investigation of the morphology of obtained hydrogels by scanning electron microscopy revealed the formation of a dense lamellar-chain like structure but only at low concentration of a polymer. At increase of the polymer concentration in the system there was no any morphology organization. Thus, getting the good results in this case demands the further investigations which can be related to the molecular weight changing of the polymer and finding of the concentration range for compatability of the gel precursors.

The work is performed under financial support of the Ministry of Education and Science of the Russian Federation in the frame of realizing of the State task in the field of the scientific activity (project N4.5508.2017/BP. This work is performed by means of the Equipment Center for collective Use of Tver State University.

References:

1. *P. M. Pakhomov., S. D. Khizhnyak, et. al. //* Colloid Journal, - 2004, - Vol. 66, No 1 - P. 65.
2. *L.O. Andersson //* J. of Polym. Sci., - 1972, - Vol. 10, - P. 1963.
3. *P. M. Pakhomov, S. S. Abramchuk, et. al.* // Nanotechnologies in Russia, - 2010, - Vol. 5, No 3–4 - P. 209.
4. *P. M. Pakhomov, M. M. Ovchinnikov, et. al. //* Polymer Science, Ser. A, - 2011, - Vol. 53, No 9 - P. 820.
5. *O. A. Baranova, N. I. Kuz’min, et. al.* // Fibre Chemistry, - 2011, - Vol. 43, No 1 - P. 90.

SYNTHESIS AND STUDY OF THERMORESPONSIVE AMPHIPHILIC COPOLYMERS

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Over the past few years, scientific impact of synthesis of thermoresponsive copolymers are grown significantly. Their unique ability to change the conformation due to minor change of temperature, allowed such materials to use them in biomedical field, such as drug delivery systems[1], biosensors[2], etc.

A series of different amphiphilic statistical p(St-*stat*-PEO_5MEMA) copolymers were synthesized via RAFT polymerization. The macromonomer PEO_5MEMA was used because of its hydrophilicity and temperature responsiveness, thus the hydrophobic part of copolymers were varied by change of styrene amount. Copolymers were investigated using ^1H NMR, FT-IR and Raman spectroscopy, molecular sieve chromatography (MSC). The properties of aqueous solutions of p(St-*stat*-PEO_5MEMA) copolymers at different temperatures were investigated using dynamic light scattering (DLS).

Such copolymers have unique properties, it is critical solution temperature (LCST), which could vary dependently of p(St-*stat*-PEO_5MEMA) composition. LCST values increasing linearly from 0 to 67 ^oC with the mol % PEO_5MEMA in composition. The p(St-*stat*-PEO_5MEMA) copolymer consisting of 73.1 mol % PEO_5MEMA has LCST (35 ^oC) which is close to the physiological temperature.

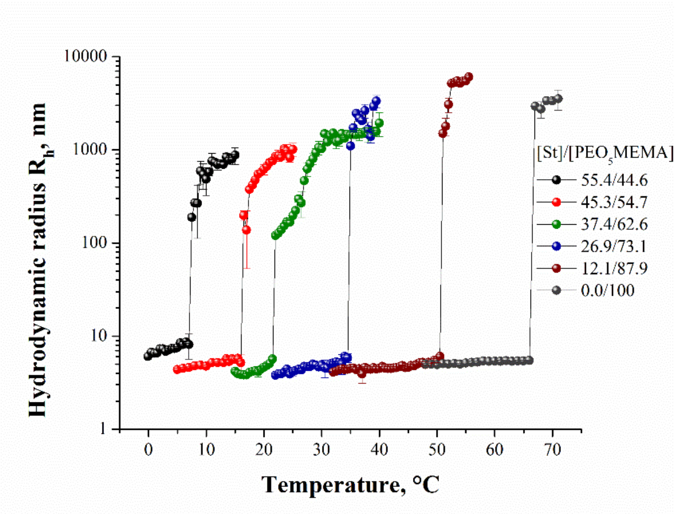

Fig. 1. Temperature dependence of the hydrodynamic radius of different composition p(St-*stat*-PEO_5MEMA) copolymers in aqueous solutions.

Acknowledgements. Financial support from the Research Council of Lithuania under the project MIP-054/2015 is gratefully acknowledged.

References:

1. Schmaljohann, D. Thermo- and pH-responsive polymers in drug delivery. *Adv. Drug Deliv. Rev.* **58,** 1655–1670 (2006).
2. Zhang, Q., Serpe, M. Responsive Polymers as Sensors, Muscles, and Self-Healing Materials. *Top. Curr. Chem.* **369,** 377–424 (2015).

VANILLIN-BASED PHOTOCROSS-LINKED POLYMERS

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Photopolymerization engendered high interest both in academia and in industry due to the considerable practical and economic benefits. Photopolymerization have the advantages of rapid cure, low energy consumption, high efficiency, low volatile organic compound emission, and the large number of applications in not only conventional areas such as coatings, inks, and adhesives, but also in high-tech domains, such as microelectronics, optoelectronics, laser imaging, stereolithography, and nanotechnology.1) The renewable feedstock use in materials production using photopolymerization processes reveals the great potential of renewable raw molecules and their ability to substitute petrochemical-based materials. Recently, vanillin and its derivatives have attracted much attention as renewable building blocks for high performance polymers mainly because of their rigid aromatic structures. Synthetic vanillin from lignin or guaiacol is more commonly available, however it can be extracted from natural sources as well. With its functionalities and large-scale availability, vanillin is an ideal scaffold for monomer synthesis.2)

In this study, the photocross-linking of vanillin derivatives bearing various functional groups was carried out using one of the most advanced thiol-ene click methods. The advantages of this method are following: high reaction rate, high monomer conversion, low inhibition of oxygen, the formation of a uniform polymer network, low shrinkage of polymer layer and homogeneous mechanical properties.3) The influence of different functional groups of vanillin derivatives, chemical structure of thiols, different radical photoinitiators and organic solvents on the reaction rate and quality of the obtained photocross-linked polymer layers was investigated.

It was determined that the highest reaction rate and the best quality of the obtained photocross-linked polymer layers was demonstrated by starting material mixtures composed of vanillin diacrylate or vanillin dimethacrylate and 1,3-benzenedithiol using ethyl (2,4,6-trimethylbenzoyl) phenyl phosphinate as photoinitiator. The photocross-linked polymers of these compositions were selected for further investigations of mechanical and thermal properties.

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References:

1. Yagci Y., Jockusch S., Turro N.J. Macromolecules 2010, 43(15), 6245–6260.
2. Zhang C., Madbouly S.A., Kessler M.R. Macromol. Chem. Phys. 2015, 216, 1816-1822.
3. Hoyle C.E., Bowman C.N. Angew. Chem. Int. Edit. 2010, 49, 1540-1573.

FORMATION OF COMLEXES BETWEEN PHENOLIC COMPOUNDS AND CHITOSAN

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Over the past years there has been increasing interest in phenolic acids like caffeic acid (CA) and rosmarinic acid (RA). The main reason is their role in preventing diseases associated with oxidative stress [1]. The presence of unsaturated bonds in the molecules of CA and RA makes them unstable and vulnerable to heat, oxygen, light and moisture. The stability of phenolic acids can be improved during formation of complexes with chitosan.

The aim of the present work was to investigate the formation of CA or RA and chitosan (CH) complexes (CA-CH, RA-CH) by evaluating kinetic and equilibrium adsorption of CA or RA onto CH powder.

In the kinetic studies CA or RA aqueous solution was poured over CH powder and shaken at a temperature of 30 ^{o}C. After certain time intervals the mixture was filtered and residual concentration of CA or RA in the filtrate was estimated. The pseudo-second kinetic model was used to describe the obtained kinetic data. Kinetic curves showed that adsorption of CA on CH powder is a one step process, whereas, during adsorption of RA the two steps of adsorption can be distinguished. In the first step, adsorption of RA proceeded quickly and reached equilibrium after 120 min. By continuing the adsorption process, further increase in the amount of adsorbed RA was observed. The adsorption of CA on CH as well as the adsorption of RR on CH in the first step proceeded due to electrostatic interaction between ionized carboxylic groups of acids and ionized amino groups of CH. Hydrophobic interaction was proposed as a main force in the second step of RR adsorption on CH.

Equilibrium adsorption of CH or RR on CH powder was studied at temperatures of 30 ^{o}C, 35 ^{o}C and 40 ^{o}C. Obtained adsorption isotherms showed that with an increase in the adsorption temperature the amount of CA adsorbed onto CH powder decreased, while the amount of RA adsorbed onto CH powder increased. Analysis of the Langmuir adsorption model parameters confirmed that adsorption of both CA and RR proceeded on the active sites of CH. The parameters of Freundlich and Dubinin-Radushkevich adsorption models also have been calculated. Analysis of thermodynamic parameters of adsorption showed that adsorption of both CA and RA on CH was spontaneous. The negative values of the changes of enthalpy and entropy implied that adsorption was exothermic process, and the order of systems during adsorption increased.

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

Reference:

1. *Scalbert A., Manach C., Morand C., Remesy C., and Jimenez L.* Dietary polyphenols and the prevention of diseases // Crit. Rev. Food Sci Nutr – 2005 – Vol. 45, No. 4 – P. 287–306.

AMPHOTERIC HYDROXYETHYL STARCH POLIELECTROLYTE COMPLEXES

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Amphoteric starch contains both cationic and anionic groups in the same molecule. Generally, cationic starch derivatives are starch ethers prepared by using tertiary amino or quaternary ammonium groups containing reagents. Meanwhile, anionic starches can be synthesized by introducing phosphate, phosphonate, sulfate, sulfonate or carboxyl groups into starch molecules. The introduction of positive and negative groups into starch may be realized by using several approaches: firstly anionization and thereafter cationization or firstly cationization and after that anionization.

The aim of the present work was to prepare amphoteric hydroxyethyl starches (CHES/AHES) of different composition and to investigate their polyelectrolyte complexes formation in water by using anionic and cationic compounds.

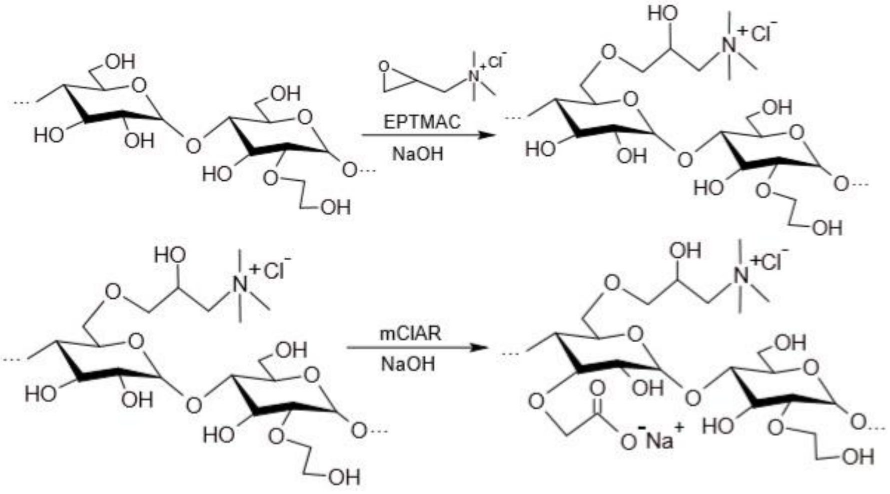

Fig. 1. Two – step amphoteric starch synthesis scheme

Preparation of CHES/AHES has been achieved by two - step reaction as demonstrated in the synthesis scheme in Fig. 1. Firstly, cationic hydroxyethyl starches (CHES) were prepared by the reaction of hydroxyethyl starch (HES) with (2,3-epoxypropyl)trimethylammonium chloride (EPTMAC) in the presence of sodium hydroxide at 45°C for 24 h [1]. Synthesized CHES then were reacted with monochloroacetic acid (mClAA) in alkaline solution at 55 °C for 48 h.

Several different types of polyelectrolyte complexes in water were formed by employing positively and negatively charged groups of CHES/AHES. The polyelectrolyte complexes were prepared by ionotropic gelation between cationic groups of amphoteric starches and anionic phosphate groups of sodium tripolyphosphate (NaTPP). The polyelectrolyte complexes of other kind were prepared by interacting anionic groups of amphoteric starches and cationic groups of poly(dialyldimethylammonium chloride) (PDADMACl). Polyelectrolyte complex particles were obtained and characterized by using various analysis methods.

Reference:

1. *Rutkaitė, R., Bendoraitienė, J., Klimavičiūtė, R., Lekniutė, E., Narmontaitė, I., Šinkūnaitė, V.* Charged starch nanoparticles prepared by polyelectrolyte complex formation // Chemija. – 2012. – Vol. 23. No. 4 – P. 328 – 335.

COMPOSITION AND PROPERTIES OF ROSMARINIC ACID – CHITOSAN COMPLEXES

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Rosmarinic acid (RA) is an ester of caffeic acid and 3,4-dihydroxyphenyllactic acid. Compared with other flavonoids, the higher antioxidant activity of RA is explained by the abstraction of hydrogen atoms of the *ortho*-position on the phenolic rings [1]. Chitosan (CH) is a naturally occurring polymer derived from chitin by deacetylation reaction. In acidic medium CH amino groups are protonated, and can form ionic complexes with negatively charged compounds [2].

The aim of the present investigation was to obtain RA and CH complexes (RA-CH) by adsorbing RA onto CH powder, to evaluate formed complexes by SEM and FT-IR spectroscopy, as well as, to assess the stability of RA-CH complexes in different media and the antioxidant activity of RA-CH by ABTS method.

To obtain RA-CH complexes, RA aqueous solution was poured over CH microgranules, stirred with a magnetic stirrer at room temperature (22±1 ^{o}C). After ionization of RA carboxylic groups the released hydrogen ions protonated amino groups CH, RA was simultaneously adsorbed on the surface of CH powder due to electrostatic interaction between ionized carboxylic groups of RA and ionized amino groups of CH, and prevented the dissolution of formed RA-CH complexes. The RA-CH with RA to CH molar ratio of 0.11, 0.22. 0.39, 0.6 and 0.8 were obtained. FT-IR spectra confirmed the composition of RA-CH complexes.

RR can be released from RR-CH complexes into solution of 0.1 M HCl or phosphate buffer (pH=6.8). However, RR-CH complexes are stable in distilled water ant ethanol.

The antioxidant activity of RA-CH complexes containing different amount of RA was estimated by ABTS assay. The rate of ABTS radical scavenging sharply decreased with an increasing amount of adsorbed RA, i.e. RA-CH complexes containing higher amount of adsorbed RA demonstrated prolonged antioxidant activity.

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References:

1. *Cao H., Cheng W.X., Li C. et al*. DFT study on the antioxidant activity of rosmarinic acid // Journal of Molecular Structure: THEOCHEM. – 2005. – Vol. 719, No. 1-3 – P. 177–183.
2. *Luo Y., Wang Q*. Recent development of chitosan-based polyelectrolyte complexes with natural polysaccharides for drug delivery // International Journal of Biological Macromolecules. – 2014. – Vol. 64. – P. 353–367.

THE EFFECT OF IONIC LIQUIDS ON THE PROPERTIES OF ELECTROSPUN MEMBRANES

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The present study was focused on analyzing the dependence of the additives used on the mechanical properties and conductivity of electrospun membranes. Ionic liquids (IL) 1-butyl-3-methylimidazolium chloride ([BMIm]Cl) and 1-ethyl-3-methylimidazolium bromide ([EMIm]Br) were used with concentration up to 10 wt%. Polyacrylonitrile was used as polymer matrix. Two different solvents dimethylformamide (DMF) and dimethylsuloxide (DMSO) were chosen to explore their influence on the conductivity and mechanical properties of membranes.

Higher specific stress values were achieved with IL [EMIm]Br. The highest specific stress value achieved was 87.93±5.15 N/tex for the membrane obtained from solution PAN in DMF with 1% added IL [EMIm]Br. Most stable values of specific stress were achieved with membranes obtained from solutions with DMF especially with added IL [BMIm]Cl. The membranes with higher conductivity showed lower specific stress values. Also the morphology plays major role in the values of specific stress. Membranes obtained from the solutions with solvent DMSO showed much higher values of median diameter than with solvent DMF. Fibre diameters in higher concentrations of IL were more dispersed which leaded to lower tensile stress values of the membranes. The optimum concentration to achieve adequate combination of different properties for the membrane depends on the solvent and IL used. The best value in this reasearh was achieved with IL [BMIm]Cl and solvent DMF at concentration 8 wt%.

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ELECTROSPUN FLEXIBLE ELECTRODE FOR APPLICATION IN SUPERCAPACITORS

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Supercapacitors are energy storage devices used for applications where high power density and good energy density are needed. Typically, for production of supercapacitor electrodes the casting method is used. However, those electrodes are rigid. On the other hand, electrodes with outstanding flexibility, good electrochemical performance and lightweight are crucial for implementing in wearable consumer electronics or portable electronics like roll-up displays and electronic paper. Flexibility of the electrode is rarely reported but highly desirable property of supercapacitors.

Inspired by the challenge, the electrospinning technology was applied to produce flexible electrodes. First, the styrene-co-acrylonitrile polymer (SAN) was dissolved in dispersion of carbon derived carbon (CDC) capacitive material. Then the ionic liquid (1-ethyl-3-methylimidazolium tetrafluoroborate) was added. Obtained 4-component dispersions were electrospun. The effect of dispersion preparation methodology and electrospinning parameters on final membrane (electrospun electrode) electrochemical performance and mechanical properties were evaluated.

Figure 1. Bending, folding and twisting operations performed on SAN membrane. The last photo was taken of the same sample after performing these operations, thickness of the membrane was 40 μm.

Electrospun membranes were highly flexible, bendable, foldable and twistable without inducing any visual damage (Figure 1). The tensile strength of obtained electrospun membranes (4,5 MPa) was ~20 times higher compared to roll casted electrodes, which is explained by the fibrous structure of the material. All the carbon-containing membranes had typical electrochemical double-layer capacitor cyclic voltammetry curves (Figure 2) and the highest specific capacitance was obtained is 72 F/g. In conclusion, a novel composite membrane of SAN+CDC with high specific capacitance, unique flexibility and twistability properties was developed.

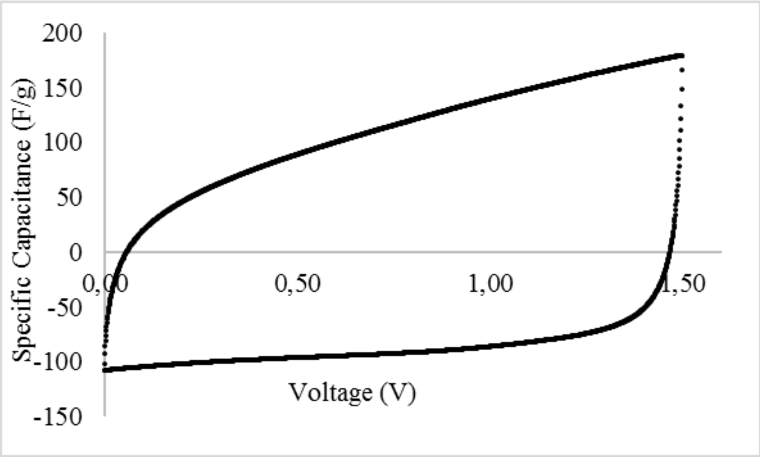

Figure 2. Differential specific capacitance [F·g-1] CV curves of most efficient membrane, measured at 10 mV·s-1 scan rate.

EFFECT OF PREPARATION METHOD ON MORPHOLOGY AND ELECTROCHEMICAL PROPERTIES OF ELECTROSPUN FIBROUS ACTIVATED CARBON BASED ELECTRODES FOR SUPERCAPACITOR APPLICATION

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Supercapacitors have drawn extensive attention during last years. Electrodes of EDLC-s are usually made of carbon allotropes that have high specific surface area. In recent years, the electrospinning process has found application in supercapacitor technology studies owing the high surface area of fibrous material, which is related to the performance of supercapacitors at high frequencies. This process involves formation of dry fibers from polymer solution using high voltage. Electrospun fibers have good mechanical properties, including resistance to cyclic loading and vibrations. Another advantage of electrospinning is the flexibility of making fibers which can be produced from a large assortment of different polymers and polymeric composites.

In this study porous coconut shell activated carbons (AC) have been mixed with polymer solution and electrospun into fibrous membranes. Polyacrylonitrile (PAN) has been chosen as the polymer matrix due to its good mechanical properties, electrospinnability and good ion permeability. ACs have been preliminarily grinded to the particles size below 500 nm in order to be smaller than expected diameter of the fibers obtained via electrospinning. The ACs have been dispersed within electrospinning polymer solution by various methods in presence of ionic liquid. To improve the conductivity, carbon black and conductive carbon nanotubes composite have been added to ACs.

Effect of preparation method on morphology, electrical and electrochemical properties of electrospun fibrous activated carbon based electrodes has been studied. For prepared electrode membranes their electrochemical parameters, like electrochemical stability window (V), internal resistance, cell and specific capacitance (F/g) have been evaluated. The specific capacitance of 83 F/g for fibrous electrode has been achieved which is identical to conventional AC-based EDLC electrodes having 80 F/g.

ELECTROSPUN NANOFIBROUS WEB POROSITY

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One of parameter which characterises the structure of nanofibrous web is porosity. A very important parameter for describing porosity is the maximum value of the pore diameter in the surface of electrospun web. Such evaluation is especially important for nanofibrous webs of barrier application, which are used, for example, for antimicrobial protection. Preliminary analysis of webs shows a very big inequality of pore diameters in different places of nanowebs. There are a few methods for measuring the porosity such as conventional methods using apparent density and bulk density, image analysis and mercury porometer. On the other hand, the analysis of webs show a very big inequality of pore diameters in different places of nanowebs, but this inequality has not been fully investigated yet. However, until date, an accurate estimation of porosity in these grades of materials (Nanofiber mat) is a difficult task. Porosity is also very important if the electrically spiked nano-formed cells are used for cell growth or barrier properties. In these cases, not only the maximum size of the pore, but also all the distribution of pores size are important. Many authors describe in their work the porosity of the structure of the nanoweb, but the papers do not provide porosity estimation methods. The investigations in describing nanofibrous web porosity have not yet been published. So, the evaluation of the structure, and especially the complexible evaluation of porosity is still an open question which needs to be solved in the future.

References:

1. *Malašauskiene J., Milašius R.* Mathematical Analysis of the Diameter Distribution of Electrospun Nanofibres//Fibres & Textiles in Eastern Europe- 2010.-Vol. 18, No. 6 (83)- P. 45-48.
2. *Doshi J., Reneker, D. H.* Electrospinning process and applications of electrospun fibers// Journal of Electrostatics-1995.-35(2-3)-P.151-160.
3. *Brochocka A.* Efficiency of electret polycarbonate nonwovens in respiratory protection against nanoparticles//Autex Reasearch Journal-2017.-Vol. 17. No 2.

ELECTRO-THERMAL PROPERTIES OF CARBON BLACK (CB) AND ETHYLENE-OCTENE COPOLYMER (EOC) COMPOSITE

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Self-regulating heating materials are desirable in fields where the installation and usage of electronics is troublesome or hard to accomplish. These are materials, with a positive temperature coefficient of resistivity – the resistivity of the material increases with the temperature [1]. By applying voltage to the material, the electrical resistance will keep increasing until it finds equilibrium at a particular temperature/voltage and does not heat further.

We investigated electro-thermal properties of carbon black – ethylene-octene copolymer (EOC-CB) composite for using the composite as self-regulating heating material. The materials electrical resistance vs temperature was measured as well as the temperature and the resistance change when voltage is applied to the material was investigated.

The samples were prepared by mixing ethylene-octene copolymer (EOC) granules with carbon black (CB) powder and dicumyl peroxide on a roll mixer. After that, the sample was vulcanized. A silver glue electrode was painted on the flat surface on opposite ends of the sample. Space between electrodes is 85 mm, the sample width 75 mm and thickness 0.7 mm.

Ethylene-octene copolymer and carbon black composites exhibit positive temperature coefficient of resistivity. Samples with ≥20 mass parts of CB when electrically heated exhibit a current drop in time in the beginning, but after a certain time/temperature there is a gradual increase in current strength. We explain this behavior by coexistence of two opposite effects – the decrease in conductivity because of thermal expansion of the matrix and the increase in conductivity due to increased mobility of carbon black particles which leads to agglomeration and subsequent formation of additional conductive channels.

Acknowledgements. The Latvian National Research Programme in Materials Science IMIS2 has supported this study.

Reference:

1. *Voet A.* Temperature effect of electrical resistivity of carbon black filled polymers // Rubber Chem. Technol. – 1981. – Vol. 54, No. 1 – P. 42–50.

ALIGNMENT OF MULTIWALLED CNT UNDER DIRECT CURRENT ELECTRICAL FIELD IN PVAc POLYMER

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It has been shown that alignment of carbon nanoparticles in viscous liquids (also polymer melts and solutions) can be realized by applying sufficiently high electrical field [1, 2]. Alignment of multiwalled carbon nanotubes (MWCNT) in polyvinyl acetate (PVAc) polymer solution was performed to create polymer films with tailored anisotropic nature of electrical resistance. This type of composite material offer unique properties – increased electrical conductivity in one direction and high resistance in other. Polyethylene glycol (PEG, Mw 300) was added to solution in various amounts to increase the plasticity of sample, because PVAc samples without PEG yield brittle films. Alignment of carbon nanotubes was done using DC electrical field with simultaneous electrical resistance measurement.

Anisotropy coefficient $A = \frac{\sigma_{\parallel}}{\sigma_{\perp}}$ has been calculated for prepared samples, where:

$\sigma_{\parallel}$ is the electrical conductivity parallel to direction of DC field used in alignment; $\sigma_{\perp}$ is the conductivity perpendicular to direction of DC field used in alignment.

Addition of PEG 300 offered more plasticity as evidenced by differential scanning colourimetry (DSC). However, the obtained samples do not possess uniform placement of aligned MWCNT areas – the anisotropic nature of material varies regarding the measurement position in sample.

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References:

1. *Knite M., Linarts A., Ozols K., Tupureina V., Stalte I., Lapčinskis L.* A study of electric field-induced conductive aligned network formation in high structure carbon black/silicone oil fluids// Colloids Surf. A – 2017. – Vol. 526 – P. 8-13.
2. *Oliva-Aviles A.I., Aviles F., Sosa V., Oliva I., Gamboa F.* Dynamics of carbon nanotube alignment by electric fields// Nanotechnology – 2012. – Vol. 23, No. 46 – P. 465710

PREPATATION OF CNT / GRAPHENE / IRON OXIDE – EVA HYBRID NANOCOMPOSITES FOR ESD APPLICATIONS

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This presentation discusses the preparation and characterization of filled polymer hybrid nanocomposites based on several combinations of CNT / Graphene / iron oxide nanoparticles and ethylene vinyl acetate copolymer (EVA). These complex hybrid composites were melt blended with nanoparticles concentration in the range 1-30 weight percent. The specimens (films, double bone specimens) for further tests were processed by compression molding and injection molding preparation methods.

The electrical conductivity, active and passive dielectric constant, dielectric loss factor, density, thermal and mechanical properties were evaluated for the present hybrid composites. It was concluded that the used conventional melt processing technology (extrusion, molding, injection) of these hybrid composites is essential advantage for industrial processing without significant modification of the present fabrication routes. The resulting hybrid composite materials have high performance properties; thus, these materials are intended to be used in applications for antistatic and ESD materials, and as well as, EMI and radar absorption materials.

PEDOT:PSS MODIFICATION WITH CNT/Bi_2Te_3 FILLER FOR THERMOELECTRIC PROPERTIES ENCHANCEMENT

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Research in thermoelectric materials nowadays have gained significant attention due to their ability to convert waste heat to electricity [1]. Compared to inorganic thermoelectric materials, conductive polymer poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) (PEDOT:PSS), has a great potential to be used as thermoelectric material presenting good electrical conductivity, flexibility and low density [2]. To further increase PEDOT:PSS thermoelectric performance, it was modified with bismuth telluride grown on multi walled carbon nanotubes (CNT/Bi_2Te_3).

CNT/Bi_2Te_3 filler was obtained by Bi_2Te_3 vapor synthesis on CNT surface. Then the PEDOT:PSS/CNT/Bi_2Te_3 composites were prepared by dispersing synthesized CNT/Bi_2Te_3 in PEDOT:PSS solution by ultrasonication and drop coated onto glass substrates. Seebeck coefficient was measured by in-house made device. It consisted from two separate Peltier plates with adjustable temperatures from -20 to +80 ^{o}C.

Pure CNTs dispersed in PEDOT:PSS showed only slight increase in Seebeck coefficient at 0.5 and 1 wt. % concentration. This might be due to the fact that at higher CNT concentrations CNTs starts to agglomerate and anymore does not provide sufficient dispersed conductive network throughout polymer matrix. However, CNT/Bi_2Te_3 addition raised the Seebeck coefficient values pointing to Bi_2Te_3 contribution to thermoelectric effect. It has been shown that overall thermoelectric properties of PEDOT:PSS can be adjusted simultaneously by the nature of each component like excellent electrical conductivity of CNTs and characteristic thermopower of Bi_2Te_3.

References:

1. *Toshima N.* Recent progress of organic and hybrid thermoelectric materials // Synth. Met. – 2017. – Vol. 225, P. 3–21.
2. *Wei Q., Mukaida M., Kirihara K., Naitoh Y. and Ishida T*. Recent Progress on PEDOT-Based Thermoelectric Materials // Materials – 2015. – Vol. 8, No. 2 – P. 732–750.

SAMPLE PREPARATION INFLUENCE ON POLYMER NANOSTRUCTURED CARBON COMPOSITE VOC SENSING ABILITIES

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Volatile organic compounds (VOC) can be dangerous to human health and even life. For example inhalation of high levels of toluene vapours for a short period may cause drowsiness, headache, nausea, visual changes, muscle spasm, dizziness, and loss of coordination. But long time exposure to toluene can result in nervous system effects such as reductions in thinking, memory, and muscular abilities, as well as some losses in hearing and colour vision [1].

In order to control VOC vapour concentration in air various devices has been developed, but there is a lack of small, mobile and precise device. In this work polymer and nanostructured carbon black composite was made with intent to use it in VOC vapour detection. As polymer material was used ethylene vinyl acetate copolymer (EVA) with 40% vinyl acetate content. As electroconductive filler was used carbon black (CB; PRINTEX XE-2) nanoparticles with average particle size 30 nm. Specific surface area of particles was 950 m^2/g and DBP (dibutyl phthalate) adsorption was 380 ml per 100 g.

In this work influence of composite sample preparation processes on VOC vapour sensing effect is going to be studied and the optimal preparation method (the method where sensing effect (relative electrical resistance change in VOC vapour) is the highest) will be chosen. In sample preparation process various substrates and composite solution application methods are going to be used.

Acknowledgements. This work was supported by the Latvian National Research Programme in Materials Science IMIS[2].

Reference:

1. “Toluene : Health Information Summary,” www.des.nh.gov, New Hampshire, USA, 2005.

RATIONALE USE OF NATURAL POLYMER MATERIALS FOR THE MANUFACTURE OF FOOTWEAR

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In the conditions of a sharp increase in requirements for quality shoes with certain, foreseeable properties, the possibilities of its certification and the rapid development of competition, a meaningful approach to the manufacture of this important product type becomes of particular importance.

Ensuring the ergonomics of the shoes is a complex task that is solved at all stages of the shoes production and begins with the making of pads or their selection, the choice of a package of materials on the details of the sole and upper of the footwear.

One of the best materials for footwear is traditionally considered to be made of animal hides, natural leather, the peculiarities of which structure and properties determine the high quality of the products obtained. Existing intermediate derma elements, so-called pores, cause high permeability for air and water vapor, good thermal and physical properties of the leather, which positively affects the hygienic properties of footwear. Due to its elastic-plastic properties, natural leather is well formed, which ensures good fitting of the material of the shoe pad without the formation of folds and wrinkles.

We consider modern natural materials, which have been used in the manufacture of footwear. Taking into account functional-consumer and production-economic requirements for special purpose footwear, a number of indices of leather properties for the upper of shoes are identified, which allow to objectively substantiate technological decisions aimed at reducing the risks of rejection of semi-finished products at all stages of the technological process, reducing resource and energy costs in the manufacture of products of the required quality: tensile strength, tensile strength of surface, extension at tensile strength, water resistance of flexible leather, hygroscopicity, thermal conductivity.

As a result of statistical processing of the most important and identical for different materials indices with the help of two independent methods – multicriteria compromise optimization in the form of generalized target function and complex evaluation in the form of a graphical-numerical method of the «polygon» – defined the expediency of using those polymeric materials of natural origin, which are the most capable to provide high quality and ergonomics of shoes.

THE USAGE OF MODIFIED MONTMORILLONITE TO ENHANCE THE QUALITY OF LEATHER VELOUR

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Semi-finished processes are final in the technological cycle of the leather velour manufacturing. When performing these processes a complex of specific properties is formed in velour. Uniform pile, density of the derma structure, surface color and its hydrophobicity are attributed to the velour qualitative characteristics. The most common defect of velour is discoloration of the pile surface during use of the velour products. The defect may appear due to a violation of the methodology of production and application of chemical materials used in the manufacture of grain leather. In order to obtain a high-quality velour, it is necessary to perform flushing after painting and technological application of sorbents for additional fixation of dyes. Montmorillonite is a silicate with an effective sorbent property. To increase the hydrophilicity of the surface, it is enough to use exchangeable sodium cations. As a result of the modification, the dispersion of montmorillonite acquires certain colloidal properties and allows forming the derma structure at its various levels [1]. Formation will contribute to the additional fixation of dyes in the structure and to obtaining a low and uniform pile.

The purpose is to study the dyeing quality of the velour previously treated with the montmorillonite dispersion. Samples of the chrome tanned velour are used for the study. The samples were treated with the modified dispersion of montmorillonite (2.5% of mineral), which was fixed with sodium formate (0.4%). The samples of the control group were not treated with the dispersion. The dyeing was carried out with of the black color anionic dye (4%), which was fixed with the formic acid (0.5%).

The studies have shown different stability of the velour surface color to mechanical impact. The differences are manifested in an increase of 20% of the color stability to dry friction of samples filled with the montmorillonite dispersion. Another big difference (37-39%) in the indicators is observed in determining the color stability to wet friction. Increase of these indicators testifies to formation of additional hydrogen bonds in the dyeing process. Duplication of the experimental samples stability to the action of organic solvents compared with the control group also indicates the formation of covalent bonds between the dye and the derma. Strength of the experimental leathers at the same time increased by 10-11%, and the lengthening decreased by 16-18% compared with the control group samples.

It is proved that the use of modified dispersions of montmorillonite in the semi-finished processes of velour production can increase stability of the colored surface to external influence and obtain the more advanced structure of the dermis. The latter will allow obtaining a smooth, low and elastic pile when grinding velour.

Reference:

1. *M. O. Marukhlenko, V. A. Palamar, O. R. Mokrousova*. Stabilizing derma collagen structure with modified dispersions of montmorillonite// IOP Conference Series: Materials Science and Engineering - 2016.-1 Vol. 111-P.1-8.

AFFECT OF RHEOLOGICAL PROPERTIES OF COMPOSITION BASED ON MODIFIED STARCH ON THE FILM FORMATION

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Recently in the field of medicinal preparations, became very popular obtaining additional therapeutic properties to the dressing materials by introducing into the polymeric material. Classic polymers that are widely used in the medicine has cellulose and other derivatives of polysaccharides as the main component of dressing [1]. At the same time, the greatest interest has protective coatings based on the natural hydrocolloids (agar-agar, pectin, carrageenan, starch, cellulose and alginates). Recently, among the new wound bandages, composite materials predominate and are used in the form of gels, films and applied by the method of "printing" on the textile basis of plaster. The advantage of such materials is the ability to change the composition and structure in a wide range, which allows regulate the properties of the polymer matrix and the level of biological activity.

In the present work, we studied the rheological properties at temperature 25 °C of aqueous solutions of corn starch, carboxymethylated starch, sodium alginate and mixtures of starch and sodium alginate. Important condition for the preparation of the optimal composition with the required viscosity is having respective data about the character of the dependence of the system viscosity on the concentration of a particular polymer.

Typically, for preparing the compositions, 10-15 % aqueous solutions of polysaccharides are used. Studies of the low concentration solutions (3-7 %) are needed for better understanding of the mechanism of changing the viscosity of starch by different shear stresses [2]. Significance of the flow index of the two-component system (starch-alginate sodium, modified starch-alginate sodium) are within the range of 0.303-0.445 by the Ostwald-de-Vila equation. As the concentration of polysaccharides increases (C, %), the viscosity of the solution increases respectively. For the polymer solutions, the change of their viscosity, depending on the concentration, is described by the following equation: $\eta_0 = KC^{\alpha}$. Based on preliminary calculations, the numerical values of the constants included in the given equation for polysaccharide solutions in water were equal: $K = 19.5 \cdot 10^{-4}$ and $\alpha = 3.35$. Most of the macromolecular compounds exhibit a significant deviation from the additivity in the compositions (thermodynamically incompatible) and therefore it is recommended to evaluate the compatibility of starch, modified starch with sodium alginate.

The compatibility of polymers in the solution was determined, used by the evaluation criterion the deviation of the components viscosity from its additive value. The compositions of polymers are compatible technologically.

References:

1. *Ищенко Е.В., Ирклей В.М., Вавринюк О.С., и др.* О некоторых свойствах крахмала и его карбоксиметилированных производных, применяемых в текстильной промышленности // *Проблемы лёгкой и текстильной промышленности Украины*. – 2004. – Vol. 1, No 8. – P.239-243.
2. *Іщенко О.В., Ресницький І.В.,Бессарабов В.І., Ляшок І.О., Плаван В.П.* Оптимізація складу і дослідження реологічних властивостей композицій на основі полісахаридів / Міжнародна наукова конференція «Сучасні технології одержання та переробки полімерних матеріалів» (ТРМ-2016), 21-23 вересня, 2016 р., Львів с.47

CHEMICAL MODIFICATION OF NANOCRYSTALLINE CELLULOSE WITH BIOCOMPATIBLE AND BIODEGRADABLE POLYMERS

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Bone generation by autogenous cell transplantation is one of the most promising techniques in orthopedic surgery and biomedical engineering. For a long time, biomaterials used for construction of such scaffolds were generally intended to remain inert, thus, unaffected by the reactions with surrounding tissues. However, it is currently appears that construction of biologically active materials in order to control cellular interactions and cell function is of great importance. Thus, numerous investigators have been currently addressing the means by which biological recognition might be imported[1,2)].

Among these strategies might be the incorporation of biofunctional particles in the material. Such particles could create the time–spatial distribution of biological ligands while scaffold would be degraded *in vivo*. One of the candidates for creating such particles is the nanocrystalline cellulose (NCC). It shows biocompatibility and the possibilities for additional modification with a wide variety of ligands. To equalize its distribution in polyether materials (e.g. PLA, PCL) NCC could be modified with polymer or peptide molecules [3,4)].

In this research we demonstrated the different ways to modificate NCC with biocompatible and biodegradable macromolecules that can improve the distribution of nanoparticles inside the polyester-based materails. As such polymers for NCC functionalization poly(D,L-lactic acid) (PDLLA) and poly(L-glutamic acid) (PGlu) were chosen. The modification of NCC with PDLLA was carried out *via* grafting of the polyester from the surface during polymerization of D,L-lactide *via* ring-opening induced by cellulose hydroxyles in presnece of $Sn(Oct)_2$. The modification of NCC with PGlu was performed using the grafting of preliminary synthesized and purified PGlu to the NCC surface. In the last case, the different chemical pathways were applied and compared to find the most effective approach. Grafting of the chosen polymers was proved by solid state ^{13}C NMR and ATR IR-spectroscopy. Additionally, the amount of bound PGlu was determined.

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References:

1. *Kim S. H., Oh S. A., Lee W. K., Shin U. S., Kim H. W.* // Materials Sci. and Engin. – 2011. – Vol. C31 – P. 612-619.
2. *Howard D., Partridge K., Yang X., Clarke N. M. P., Okubo Y., Bessho K., Howdle S. M., Shakesheff K. M., Oreffo R. O. C.* // Biochemical and Biophysical Research Communications – 2002. – Vol. 299, No. 2 – P. 208-215.
3. *Braun B.,Dorgan J. R., Hollingsworth L. O.* Supra-Molecular EcoBioNanocomposites Based on Polylactide and Cellulosic Nanowhiskers: Synthesis and Properties // Biomacromol. – 2012. – Vol. 13 – P. 2013-2019.
4. *Eyley S., Thielemans W.* Surface modification of cellulose nanocrystals // Nanoscale – 2014. – Vol. 6 – P. 7764-7779.

INFLUENCE OF SILVER SELENIDE TREATMENT CONDITIONS ON THE BEHAVIOUR OF DIFFERENT NATURAL FIBRE

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The functional materials which may reduce or eliminate negative environmental influence to human health are becoming even more important in this period of intensive technological development. 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 this presentation the part of results of the research on formation of the silver selenide layer on different nature polymeric materials (as different textile materials, polymeric films, soft polymeric composites and etc.) is presented. Silver selenide exhibits many interesting and useful properties therefore are used in various fields. Silver selenide has applications such as photo chargeable secondary batteries, ion-selective electrodes, switching memory cells etc. Interest in silver selenide has increased since the recent discovery of large magnetoresistance (MR) in silver chalcogenides [1]. The sorption–diffusion method for the preparation thin layers of metal chalcogenides in the surface of polymer was used. Using this method the layers of CuxS, CuxSe and AgxSe on the surface of polyamide PA 6 films and PA 6 cloth in two stages were formed [2-4].

The aim of the present work is to investigate the peculiarities of silver selenide layer formation on the different nature fibre surface. By changing the conditions of chemical treatment process the fiber surface can be covered with a sparse, thin or dense layer of silver selenide. 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 and the highest – on flax fibre. Influence on the elongation of fibre is visibly lower.

References:

1. *Gates B, Wu Y, Yin Y, Yang P, Xia Y.* Single-Crystalline Nanowires of Ag_2Se Can Be Synthesized by Templating against Nanowires of Trigonal Se. // J of the American Chemical Society – 2001. – No. 123– P. 11500-11501.
2. *Ivanauskas R., Ancutiene I., Janickis V., Stokiene R.* Comparison of Sulfurization Agents for Obtaining Layers of Copper Sulfide on Polyethylene and Polyamide // Cent. Eur. J. Chem. – 2009. – Vol. 17, No. 4 – P. 864–869.
3. *Ivanauskas R., Baltrusaitis J.* Synthesis and characterization of polyamide-Cu_xSe composite thin films // Applied Surface Science – 2013. – Vol. 283, No. 15 – P. 360–366.
4. *Milasiene D., Ivanauskas R.* Modification the Polyamide Fabric with Silver Selenide // Cent. Eur. J. Chem. – 2013. – Vol. 12, No. 11 – P. 1976-1980.

EFFECT OF pH ON THE ABILITY OF DIFFERENT LIGNINS TO STABILIZE THE OIL-IN-WATER EMULSIONS

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The goal of the study was to compare the ability of various technical lignins to stabilize O/W emulsions depending on pH as well as on their chemical structure, molecular mass, sizes of the particles and thier concentration in the emulsion. It was found that the O/W emulsions stabilized with the alkaline lignin solutions demonstrate the highest stability. At the same time, with increasing content of lignin in the alkaline solution, the stability of the emulsion slightly decreases. At the same time, the O/W emulsions prepared with the help of the lignin solutions with pH 8.0 and 5.0, respectively, are characterized by a lower stability, which improves with the growing lignin content in the O/W emulsion. Different mechanisms of the stabilization of emulsions with the lignins at the liquid-liquid interface are suggested, and the main of them are electrostatic and steric ones. The findings indicate that the stabilization of the “rapeseed oil-in-water” emulsion with alkaline lignin solutions proceeds via the electrostatic stabilization mechanism, while in neutral and acidic medium, with increasing lignin concentration, the stabilization mechanism is more complicated with the growing role of the steric factors. The quality of the O/W emulsion stabilization is reflected by the size and zeta-potential value of the formed oil droplets. It was shown that, with increasing the lignin concentration in alkaline medium from 0.006% to 0.1%, the size of the emulsion droplets grows from 398 nm to 1260 nm, but the separation volume of the emulsion essentially increases. Compared with the lowest applied lignin concentration, the droplets’ size increased from 1.8 to 3.2 times for the emulsion stabilized with a 0.1% lignin alkaline solution. It is obvious that the higher the formed emulsion particle size, the faster the separation and the loss of the stability of the O/W emulsion. It was established that the emulsion droplets stabilized with the lignin solution with the lowest concentration have an enhanced stability and are characterized by the highest average charge of – 91 mv, which testifies the electrostatic mechanism of the stabilization of the O/W emulsion.

FUNCTIONALIZATION OF HARDWOOD BARK BY MECHANOCHEMICAL TREATMENT FOR OBTAINING WOOD-POLYMER COMPOSITES

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It is well known that mechanochemistry offers several benefits over traditional solvent-based methods like simplicity, short reaction conditions, ease of scale-up. Performing reactions without the need of solvents is advantageous, as it is eco-friendly and low-cost process. The mechanochemically treated substances, being used as a filler, have a large specific surface area and are characterised by the enhanced reactivity that is beneficial for their interaction with a polymer matrix in composites. Commonly, mechanochemical reactions are conducted by milling, grinding or extrusion. In chemistry, the use of ball mills has enabled the initiation of numerous metal-catalyzed transformations, organocatalytic and enzymatic processes, multicomponent reactions. In the pulp and paper industry, mechanical treatments of wood and wood-originated products are often used before their further processing.

The aim was to study the effect of mechanochemical treatment of grey alder bark as a lignocellulosic filler for obtaining bark-recycled polymer composites. In the work, we have functionalised the grey alder bark that was hardwood residue of wood mechanical processing, using the high energy ball milling with different rotation speed and mechanoactivation durability. During the mechanical activation in a planetary mill "Retsch", the lignocellulosic fibers were underwent to the action of a reaction mixture of ammonium hydroxide with persulphate ammonium with their different mass ratio. The performed physicochemical analysis of the functionalized bark samples shown that they essentially differed in the content of extractives, lignin, hemicelluloses and cellulose as well as in the amount of the introduced nitrogen. Depending on the mechanical treatment parameters, the functionalized bark yield ranged from 58% to 97%. The mechanism of the functionalization of bark included a plenty of consecutive and competitive radical reactions led to both oxidative destruction and polymerization/ polycondensation. The dominating of the lignocellulosic matrix destructure or its polymerization/ polycondensation depended on the values of the speed and the durability of the mechanical activation, as well as on the mass ratio of the reagents in the reaction mixture.

For making the wood-polymer composite samples, recycled polypropylene was used as a thermoplastic polymer matrix. The polymer content in the samples was 30 mass %. The raw blend consisting of the polymer and the functionalized bark was mixed in a high-speed mechanical mixer before its processing. The samples for tensile and bending tests were prepared by the extrusion and moulding method using HAAKE MiniLab II and MiniJet II. A comparison of the mechanical properties (tensile, bending) of the composites filled with the initial bark and the functionalized bark microparticles showed remarkable improvement in the mechanical properties of the functionalized bark filled composites.

EFFECT OF EXTRACTION ON THE COATINGS PRODUCED FROM NANOPARTICLE GELS OBTAINED FROM HARDWOOD AND SOFTWOOD BARK

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In this work, the effect of the coatings made from nanoparticle gels obtained from non-extracted and extracted in biorefinery hardwood (birch) and softwood (pine) bark on the barrier and mechanical properties of paper sheets was investigated. The bark was partially destructed by the thermocatalytic destruction method developed at the Laboratory of Cellulose of the Latvian State Institute of Wood Chemistry and then dispersed in a water medium in a ball mill at a concentration of 8-10%. As a result, gel-like dispersions were obtained, which contained nanoparticles. The obtained gels were coated on both sides of paper sheets produced by the Ligatne Paper Mill (Latvia). Gel concentration was 4-10%, and the coating thickness in the suspension form was 24, 40, 60 and 100%. After drying, thickness decreased.

Air resistance and mechanical properties of paper sheets without and with coatings were investigated.

It has been established that, in the case of non-extracted bark, air resistance increases slightly with coating thickness. However, in the case of extracted bark, especially birch bark, Gurley air resistance considerably increases with increasing coating thickness. Thus, the coatings made from 6% extracted birch and pine bark nanoparticle gels, at a coating thickness of 30 μm, increase the Gurley air resistance by 177 and 28%, respectively, in comparison with uncoated paper sheets. The greater effect of the coatings made from extracted bark nanoparticle gels is because the extractive substances hinder the bond formation between the cellulose fibres and nanoparticles. Gurley air resistance increases with the gel concentration.

The coatings made from extracted bark nanoparticle gels affect also the mechanical properties of paper sheets to a greater extent in comparison with those made from non-extracted bark nanoparticle gels. Thus, the tensile strength in the dry state of paper sheets with coatings made from gels obtained from non-extracted bark nanoparticle gels practically does not change with coating thickness. The coatings made from extracted birch and pine bark 6% nanoparticle gels at their thickness of 30 μm increase the tensile strength by 9.5 and 5.0%, respectively. Burst strength at a coating thickness of 30 μm increases by 21.4 and 11.5% in the case of non-extracted bark and by 46.2 and 22.8% in the case of extracted bark, respectively. The stretch of paper sheets at a coating thickness of 30 μm increases by 31.6 and 25.8% for non-extracted birch and pine bark nanoparticle gels and by 79.2 and 37.5% in the case of extracted bark. The mechanical properties of paper sheets with coatings depend on the nanoparticle gel concentration. The coatings decrease the tensile strength in a wet state.

Therefore, for reinforcing of paper sheets, coatings from extracted bark nanoparticle gels can be used.

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INVESTIGATION OF INFLUENCE OF FLAX/SILK WOVEN FABRICS PILLING RESISTANCE USING SPECIAL FINISHING MEANS

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Pilling is an important problem not only for textile and clothes manufacturers but also for users. The effect of the pilling process results in a significant decrease in fabric quality and a negative influence of the users comfort [1].

Pilling on fabrics is a well-known phenomenon, which is defined as the entangling of fibers during washing, dry cleaning, testing or wears to form balls or pills that stand proud of the surface of a fabric. During pilling, fibers become entangled and the different fibers around them join this structure, causing a more significant default on the fabric surface [2].

Pilling resistance of flax/silk woven fabrics was investigated in this case. Grey, usually finished, treated with pilling resistant material Aristan and treated with Aristan after washing fabrics were analyzed. It was established that appearance of fabrics changes during abrasion, i.e. pile appears on the fabric surface, after that pills start to form, which gradually cover the fabric surface. Finishing influences pilling resistance, i.e. after pilling resistant finishing this fabric property become better. Fabric‘s pilling resistance become better just till the first washing using pilling resistant material Aristan.

References:

1. *Jasinska J.* Assessment of a fabric surface after the pilling process based on image analysis // FIBRES & TEXTILES in Eastern Europe 2(73). Lodz: Institute of Biopolymers and Chemical Fibres.- 2009. -P. 55-58.
2. *Doustaneh A. H., Mahmoudian Sh., Mahmoudian M., Janagir A*. The effects of weave structure and yarn fiber specification on pilling of woven fabrics // World Applied Sciences Journal 24(4). Dubai: International Digital Organization for Scietific Information-2012.- P. 503-506.

PROPERTIES OF PRE-MODIFIED LINEN CLOTH DYED WITH REACTIVE DYE

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Cellulosic fibres are dyed with more types of dye, than for any other fibre. They are water- soluble dyes applied by one bath process [1]. Reactive dyes having been developed in the 1950s and in market from 1956 are very popular for dyeing and printing of cellulosic fibre [2]. Reactive dyes are extensively used in the textile industry, due to their wide variety of colour shades, high wet fastness, simplicity of application and minimal energy consumption [3].

With the development of society, the clothing industry has entered the period of material priority. With the increasingly view on health, "green" and environmentally friendly clothing, the linen textiles return in the fashion industry thanks to freshness, comfort, innovative technologies providing the elegance and demanding of linen clothing [4].

The aim of presented study is to examine the influence of linen cloth modification on colour properties of fabric dyed with reactive dyes. For notice of influence of alkali and enzyme treatment modification method on colour characteristics and fastness to rubbing, as well as tensile properties of cloths is used.

The raw 100% linen plaine weave fabric (surface density 162.8 g/m^2; producer "Larelini" Ltd, Latvia) for modification and for dyeing of RYB (Red, Yellow, Blue) subtractive primary colors the reactive dyes Cibacron (Ciba-Geigy, Switzerland) Yellow F-4G, Red FN- R and Blue FN-R, according the recommendation of dye producer exhaustion procedure were used.

The colour characteristics of fabric samples before and after test of light fastness determined L*, a* and b* values were measured in CIELab - 76 colour space using RGB system with Easy Colour QA device (Pocket spec Technologies Inc., USA on bought sides of textile). Lightness difference (ΔL*), common colour differences (ΔE), chroma (C) and hue (H) was calculated.

The colour fastness of dyed samples in light camber (Q- SUN, Xenon Test Chamber, model Xe-1-B, Q-LAB), the colour fastness to rubbing under wet and dry conditions with testing device AATCC Croc meter M238AA (SDL Atlas, USA) according the normative documents were tested.

The best rubbing fastness was observed for modified cloth. The influence of modifier depends on use of dye, but not significal after 72 h lightness testing. Decrease of lightness and increase of lightness diference was observed with alkali treating. Tensile strength on warp direction was higher than on weft direction and the elongation varied of pre-treating method of linen cloth.

References:

1. Koh J. Dyeing of cellulosic fibres// Handbook of textile and industrial dyeing Vol 2: Application of dyes/ Ed. By M. Clark, Woodhead Publishing Limited, 2011-P. 129-146.
2. Chattopadhyay D.P. Chemistry of dyeing// Handbook of textile and industrial dyeing Vol 1: Application of dyes /Ed. By M. Clark, Woodhead Publishing Limited, 2011.-P.150- 183.
3. *Farouk R., Gaffer H.E.* Simultaneous dyeing and antibacterial finishing for cotton cellulose using a new reactive dye// Carbohydrate Polymers- 2013.-P. 138-142.
4. Tang X., Zhong W., Zhuang D., Li C. and Liu Y. Application of New Environmentally Friendly Materials in Clothing// Applied Mechanics and Materials-2013.-2.-P. 295-298, 389-392.

THE MANUFACTURE AND PROPERTIES OF NONWOVEN COMPOSITES OF MIXED FIBRES

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The application of nonwoven composites (NWC) expands each year. The heat-bonded nonwovens (NW) are used for geotextiles due to the simple production cycle and low processing cost [1]. Geotextile are generally made from a limited number of polymers (polypropylene, polyethylene and polyester). The three main properties which are required and specified for geotextile are its mechanical responses, filtration ability and chemical rezistence [2]. To create the geotextile with desirable properties the mixes of fibres are used. The potential of natural fibres as reinforcement in composite materials is well recognized due to their attractive mechanical properties which enhance the possibility of producing eco-friendly materials [1]. In the previous studies the optimal composition of fibres mix and the production condition of nonwoven's composites was identified [3, 4].

The aim of this research is to investigate the properties and the factors affecting reinforced and non-reinforced composites of mixed fibres nonwoven's. The NWC series of the mixes of the local hemp fibres variety "Bialobrzeskie" of Kraslava district pre-treated with sodium hydroxide, recycled polyethylene terephthalate fibres and polypropylene fibres as well as series of composites with one or two side thermoplastic mesh reinforcing were produced by compressing method. For NW webs production the laboratory carding machine 337A MESDAN was used. The NWC,s were produced on laboratory press (LP-S-50/S ASTM) with pressure 26±2 kN at 160 ± 2 ºC temperature.

Mass per unit area and thickness of NWCs were calculated according ISO 9864:2005 and ISO 9863-1:2016. For testing of NWC mechanical properties universal testing machine Zwick/Roell BDO-FB020TN, according LVS EN ISO 13934-1-2001 was used. For determination of NWC resistance to water penetration hydrostatic pressure test according LVS EN ISO 9073-16:2009 and air permeability EN ISO 9237:1998 was applied.

The mass per unit area of NWC was 103, 2 g/m^2- 176, 0 g/m^2, thickness within 0, 31-0, 40 mm. The best water penatration results were obtained for NWC without reinforcing; the best air permeability, tensile strength, elongation at break and elastic modulus showed reinforced composites.

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References:

1. *Poundeyhini B.*, Nonwovens, Text.// World Com-2016.- 3, 4-P.32-35.
2. Handbook of technical textiles/ Ed. By Horrock A.R. and Anand S.C Woodhead publishing limited, 2004.- 358-372p.
3. *Bernava A., Reihmane S., Bitenieks J., Maniņš M.* Nonwovens Properties Made from Hybrid Fibres// Key Engineering Materials- 2017.-721-P. 53-57.
4. *Bernava A., Reihmane S., Bitenieks J., Merijs-Meri R.* The Properties of Mesh Reinforced Nonwoven Composites// Solid State Phenomena-2017.- 267-P. 63-67.

COMPRESSION PROPERTIES OF KNITTED SUPPORTS WITH SILICONE ELEMENTS FOR SCARS TREATMENT AND NEW APPROACH TO COMPRESSION EVALUATION

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The use of compression textile products for medical purposes has increased significantly since 1970. Originally, these products were used to exert pressure along the human body for the treatment of scars resulting from burns, and treatment of post-surgical condition. Nowadays innovative products for scars treatment fulfil various functions and contains extra elements for different purposes. Compression apparel for treatment after burns (usually 3th grade burns) has to generate not less than 24 mmHg compression and has to be worn at least 12 months, 23 hours per day [1, 2]. The average pressure level applied to the treated tissues is about 25 mmHg [3]. Compression apparel is often designed from knitted fabric with additional details for different purposes. Compression supports often have added silicone elements such as modified biocompatible silicon components or other parts for functional application and may also comprise other components, such as straps, fasteners and etc. for engaging the support with the body [4]. All rigid elements, inserted into support, can change elasticity of entire product. It is already known that in the area of low extensions, there is a strong linear dependence between the rigid element relative area and compression generated by the knitted orthopaedic support – compression linearly increases by increasing the area of the rigid element [5, 6].

The aim of this research was to investigate the mechanical behaviour of different knitted compression apparel products with silicon elements for scars treatment.

The unique complex mean of bandages for compression treatment was created in cooperation with JSC „Ortopedijos klinika“ and JSC „Plėtra“. Products were manufactured from knitted material with an elastic structure and layer of biocompatible silicon with medical plants substract which creats antihypertrophic effect for scars treatment. Knitted compression fabrics were made by knitting two types of elastomeric yarns together (4,4 tex PU core double covered with 2,2 tex PA6.6; 33 tex PU core double covered with 2,2 tex PA6.6). Samples were stretched till the selected tensile force and hold in this position for 120s in case to measure elongation in more accurate way. According to results, recommended elongation for selected products was found.

References:

1. *Varan, N.Y., Gursoy, N.C.* Textiles for Burn Treatments: an Overview // 5th Magic World of Textiles Conference Proceeding, 2010, Dubrovnik, Croatia, p. 171-175.
2. *Anzarut, A., et al.* The effectiveness of pressure garment therapy for prevention of abnormal scarring after burn injury: A meta–analysis // Journal of Plastic, Reconstructive & Aesthetic Surgery, 2009, Vol. 62, No. 1, p. 77-84.
3. *Legner M.* Medical Textile with Specific Characteristics Produced on Flat Knitting Maschines // Proceedings of the 2nd International Conference, August 24-25 1999, Bolton Institute, UK, p. 44-51.
4. *Kowalski K., et al*. Modelling and Designing Compression Garments with Unit Pressure Assumed for Body Circumferences of a Variable Curvature Radius // Fibres & Textile in Eastern Europe, 2012, Vol.20, No. 6A, p.98-102.
5. *Mikučioniene D., Ališauskiene D.* Prediction of Compression of Knitted Orthopaedic Supports by Inlay-Yarn Properties // Material Science, 2014, Vol. 20, No. 3, p.311-314.
6. *Mikučioniene D., Milašiūte L.* Influence of Knitted Orthopaedic Support Construction on Compression Generated by the Support // Journal of Industrial Textile, 2017, Vol. 47, No.4, p.551-566.

A PRELIMINARY STUDY ON SODIUM HYALURONATE LOADED POLYVINYL ALCOHOL NANOFIBER WEBS OBTAINED VIA ROLLER ELECTROSPINNING

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The aim of this study was to investigate whether it is possible to integrate cosmetic grade sodium hyaluronate or hyaluronic acid (HA) into polyvinyl alcohol (PVA) nanofiber matrix, as well as to analyze how different concentrations of HA effects the viscosity and conductivity of the spinning solution, fiber diameters, morphology and mechanical properties of the nanowebs. Cosmetic grade low molecular weight (50 kDa) HA was bought in a local biocosmetic store, while PVA (Mowiol® 18-88) was ordered in Sigma-Aldrich.

Both HA and PVA were dissolved in distilled water in different temperatures- HA in +20oC and PVA in 120-135°C, respectively. While the applied stirring speed was the same for both ingredients (1000 rpm), stirring time differed- 2 hours for PVA, 30 minutes for HA as HA dissolves relatively fast in water due to its well-known hydrophilic properties.

Five concentrations of HA were prepared and mixed into 10 wt% PVA solution to prepare 0,04 wt%, 0,06 wt%, 0,07 wt%, 0,08 wt% and 0,1 wt% spinning solutions. To ensure stability of the bioactive ingredients of HA, PVA was cooled down to +20oC after dissolving process. When both solutions had the same temperature, they were mixed together using magnetic stirrer. Stirring time- 1 hour, speed- 1000 rpm, no heating was applied.

Electroconductivity and viscosity were measured before electrospinning to prognose the success of nanofiber acquisition. It is known that viscosity values should be in the range 100-2000 mPa·s for solution to be spinnable. Prepared PVA and HA solution values varied from 581 to 1137 mPa·s. Measured electroconductivity values were 408-470 µS/cm depending on HA concentration.

Roller or needleless electrospinning was performed on Nanospider™ LAB 200 (Elmarco, Czech Republic) with following parameters- distance between electrodes 14 cm, roller speed- 2 rpm, applied voltage 65 kV, temperature- +20oC.

Fiber diameters were measured and morphology of the nanoweb was evaluated on atomic force microscope (AFM) Dimension Edge Veeco (Bruker, USA) using silicone cantilever OTESPA-R3, f0=300kHz, k=26N/m in tapping mode. 100 measurements of each sample were taken for nanofiber diameter analysis.

Fourier Transform Infra-Red (FTIR) spectroscopy was used to determinate HA in obtained nanofiber mats.

Mechanical properties were tested on Instron Universal Tester Model 2519-107 (deformation speed- 1 mm/min., applied load- 1 N) and the results were collected through program Instron Bluehill. PVA and HA nanomats were compared to pure PVA samples and the results show that HA does not enhance mechanical properties of PVA matrix therefore in further studies a complementary component should be added to improve tensile strength and elongation at break.

Nanowebs with 0,1 wt% and additional 0,52 wt% HA concentrations were tested on two cell lines- 3T3 mouse fibroblasts and HaCaT human keratinocytes. Applied method- Neutral Red Uptake (NRU) assay. The results showed increased cell activity when the highest concentration of HA was used to compare with the control group.

PREPARATION OF BIOCOMPATIBLE UV CURED FILMS FROM AA-HEMA-PDMS COPOLYMERS

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Tissue engineering remains a flourishing area of research with potential new treatments for many more disease states [1]. The developing field of tissue engineering aims to regenerate damaged tissues by combining cells from the body with scaffold biomaterials, which act as templates for tissue regeneration, to guide the growth of new tissue [2]. In biomedical applications, the criteria for selecting the materials as biomaterials are based on their material chemistry, molecular weight, solubility, shape and structure, hydrophilicity/ hydrophobicity, lubricity, surface energy, water absorption, degradation, and erosion mechanism. Scaffold materials can be synthetic or biological, degradable or nondegradable, depending on the intended use [3]. Synthetic polymers are highly useful in biomedical field since their properties can be tailored for specific applications. One of the major challenges in producing engineered tissue is the lack of ability to create large highly perfused scaffolds in which cells can grow at a high cell density and viability. Poly (dimethyl siloxane) (PDMS) has long been used as a flexible, biocompatible substrate for cell culture with tunable mechanical characteristics. However, its fragility and hydrophobicity are still a challenge.

The aim of this work was to obtain UV curable biocompatible films from acrylate-PDMS based copolymers. Copolymers from acrylic acid, divinyl-PDMS, hydroxyethyl methacrylate and glicidyl methacrylate (AAc-PDMS-HEMA-GMA) were obtained. Firstly, AAc-PDMS-HEMA copolymers were obtained by radical polymerization and after that reaction of HEMA hydroxyl groups with epoxy groups of GMA was carried out. UV-curing technique with photoinitiator IRG651 was used for obtaining films from AAc-PDMS-HEMA-GMA copolymers. Modified copolymers were characterized by FTIR, H^1 NMR spectroscopy and elemental analysis. Mechanical properties of films such as Young's modulus and relative elongation were examined. Increasing reaction time from 2 to 20 hours resulted in improving of mechanical properties of AAc-PDMS-HEMA-GMA copolymer films. However, in this case longer curing time for film formation was needed and higher swelling of films was observed. Increasing of copolymer concentration and amount of photoinitiator resulted in reducing of curing time for film formation, better mechanical properties and low swelling. Films with smoother structure, reduced swelling properties and insignificantly higher curing time were obtained by using ethylene glycol and glycerol as plasticizers. AAc-PDMS-HEMA-GMA copolymer films were hydrophilic. Obtained films exhibit good wettability in comparison to commercial PDMS film (Sylgard 184), their water contact angle was lower (64-71,7 °) than obtained in the PDMS (Sylgard 184) case (101°). Good biocompatibility to myogenic rat cells was determined. Mechanical properties of AAc-PDMS-HEMA-GMA copolymer films were similar to blood vessels of living organisms.

References:

1. *Dhandayuthapani B., Yoshida Y., Maekawa T., and Kumar D. S*. Polymeric Scaffolds in Tissue Engineering Application: A Review // Int. J. Polym. Sci. – 2011. – Vol. 2011, ID 290602, 19 pages.
2. *O'Brien F.J.* Biomaterials & scaffolds for tissue engineering // Materials Today. – 2011 – Vol. 14, Iss. 3 – P. 88-95.
3. *Ramakrishna S., Mayer J., Wintermantel E., and Leong K.W.* // Biomedical applications of polymer-composite materials: a review. // Compos. Sci. Technol. – 2001. – Vol. 61, No. 9, P.1189–1224.

REMOVAL OF GREASE FROM BONE TISSUE

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Museum funds contain zoological kits. From a zoological point of view, bones are very informative. When preparing them for long-term exposure, it is important that they are properly treated by removing the yellow bone marrow to prevent spoilage and undesirable oxidation processes.

There are described few methods for bones preparation removing grease form bone tissue. The simplest and most effective way of dealing with them is to use a bleach solution for boiling and cleaning [1].

The next one is the degresing with a xyol solution (60% industrial grade alcohol + 40% xylenes) [1]. The use of enzymes also is mentioned: trypsin has been utilized in enzymatic maceration methods for processing bone samples in anthropological laboratories [2].

The aim of the research is to carry out the degreasing of the bone tissue and prepare the bones for further museum storage with maximum preservation of the deoxyribonucleic acid (DNA) chain.

During the study, the activity of the enzyme preparation *"Vilzim LP CONC"* was performed under different conditions: the enzyme concentration, temperature, pH of the medium and the reaction time. Optimal conditions for the enzyme function have been determined, a method for degreasing bone tissue using the lipase *"Vilzim LP CONC"* and the nonionic surfactant *"Syntanol DS10"* has been tested.

Two types of bone degreasing methods are presented in the final project: the first one is using the enzyme preparation *"Vilzim LP CONC"* and the surfactant *"Syntanol DS10"*, the second using a mixture of organic solvents: ethanol and xylene.

Assessing the effectiveness of different treatments, determined the amount of removed fats from the bone tissue. Changes in the colour of the bone were detected: the difference in colour brightness and the overall colour difference (Fig.). Bone tissue DNA tests have shown that deoxyribonucleic acid can be isolated after different methods of degreasing of bone tissue, and bones are suitable for further genetic testing.

Fig. Untreated (right) and treated by mixture of enzyme preparation and surfactant (left) bones.

References:

1. *Nawrocki S. P.* Cleaning bones, Information leaflet of University of Indianapolis Archeology & Forensics Laboratory, http://archlab.uindy.edu/documents/CleaningBones.pdf.
2. *Li, R. and Liriano, L.* A bone sample cleaning method using trypsin for the isolation of DNA // Legal Medicine, – 2011. – Vol.13, No 6 – P. 304-30.