Ivane Javakhishvili Tbilisi State University

ივანე ჯავახიშვილის სახელობის თბილისის

სახელმწიფო უნივერსიტეტი

PolyChar 26

World Forum on Advanced Materials

მსოფლიო ფორუმი მოწინავე მასალებში

10-13 September

10-13 სექტემბერი

Tbilisi, 2018 თბილისი

WELCOME

Dear participants of the 26th Annual PolyChar World Forum on Advanced Materials in Tbilisi:

We are meeting for the 26-th time. The previous conferences had been held in Denton, Texas, (where our Forum has been founded in 1992), Guimaraes, Portugal (2004), Singapore (2005), Nara, Japan (2006), Buzios, Brazil (2007), Lucknow, India (2008), Rouen, France (2009), Siegen, Germany (2010), Kathmandu, Nepal (2011), Dubrovnik, Croatia (2012), Gwangju, South Korea (2013), Stellenbosch, South Africa (2014), Lincoln, Nebraska, USA (2015), Poznan, Poland (2016) and Kuala Lumpur, Malaysia (2017). When in 1992 Michael Hess and the undersigned organized a Conference on Polymer Characterization, we were planning a one-time event. Only with so many participants asking us "please do it again", we started a series.

This might be a good time to define some special characteristics of our Forum:

* we know that students have original ideas, constitute the future of our profession - and deserve 'equal rights' with established scientists and engineers. For this reason, students have equal opportunities to present their work orally and also are candidates for Young Investigator and Student Prizes. In fact, except for two prizes (Paul J. Flory Polymers Research Prize for which I have obtained a permission from Paul's family and International Materials Research Prize), all other Polychar prizes are precisely for students and young investigators.

* we do NOT publish conference proceedings. It is well known that such proceedings are hardly read by conference participants - and are inaccessible to anybody else. Instead, there is an opportunity - not an obligation - to bring to the Forum manuscript(s) which after at least two reviews are published in a respected journal - now in *Pure & Applied Chemistry*.

* after the initial growth time period in Denton, we now go each time to a different location, preferably in a new country. We preserve our continuity by meeting each year.

* there are three ways of doing research - experiments, theory, and computer simulations and modeling. We are striving to have all three represented.

* as discussed in W. Brostow & H.E. Hagg Lobland, *Materials: Introduction and Applications*, John Wiley & Sons 2017, Materials Science and Engineering (MSE) is a discipline created only in mid-20th century. MSE 'borrows' for its purposes elements of Mechanical Engineering, Chemistry, Physics, Biology, Civil Engineering - and has its applications in many fields including Medicine. We are striving to have a variety of science and engineering professions represented at our conferences.

Witold Brostow and Kevin P. Menard
Denton, Texas

WELCOME

Dear Colleagues, On behalf of the Organizing Committee of POLYCHAR 26, Annual World Forum on Advanced Materials I wish to extend cordial welcome to all participants of the PolyChar 26 and. 26 years ago, in 1992, this Forum took place in Denton, USA. We are delighted to host you in this year in very beautiful country Georgia. This year is significant for the university, because this year the Ivane Javakhishvili Tbilisi State University celebrates the 100 th anniversary.

For us it is very significant that just this memorable year the honorary doctor of the Tbilisi State University, the founder of the forum PolyChar Professor Witold Brostow conducts the PolyChar 26 Annual World Forum on Advanced Polymers and stay with us. The main idea of PolyChar is to take place at different parts of the world each year to give students and young scientists an opportunity to present their scientific work to a larger international audience, to meet prominent scientists, and to attend tutorials held by international well-known scientists.

Conference presentations of POLYCHAR 26 will be ranged broadly over topic: Predictive Methods and Simulations, Structure-Property Relationships, Surfaces, Interfaces, Adhesion and Tribology, Material Synthesis and its Molecular Characterization, Rheology and Processing, Mechanical Properties and Performance, Electrical and Dielectric Properties, Nanomaterials and Smart Materials, Biomaterials, Green Materials and Composites, Materials for Energy and Recycling.

According to the PolyChar tradition, on the first day of the PolyChar 26 meeting on 10 September, eight prestigious researchers for young participants of the forum will conduct short lecture courses on the following current topics:

Polymers, biopolymers and advanced nanocomposites for additive manufacturing: challenges and opportunities; Tribology: friction, scratch resistance and wear; Viscoelastic behavior of polymers; Understandable approach about electric and dielectric properties of conductive filler- polymer composites in terms of elementary quantum mechanics; Application of polymeric materials in energetic sector; Flexibility and related properties of polymers; Macromolecular orientation in polymers; Polymer liquid chromatography.

We hope that this year meeting, gathering almost 120 participants, shall provide a good platform for academic and industrial scientists to discuss and acquaint recent advances in the area of polymers and advanced materials recent advances in the area of polymers and advanced materials.

Chair of PolyChar 26
Professor, DSc. Omar Mukbaniani
Georgian members of organizing committee

PolyChar 26
Schedule

10 September Ivane Javakhishvili Hall		
9.00 -11.00	**Registration**	
11.00-11.30	**Opening Ceremony**	
11.30-11.50	***Coffee Break***	
	Course of Polymer Characterization	
	Co-chairmen:	***Prof. D. Berek, Prof. T. Sterzynski***
11.50-12.25	***Victor M. Castaño***	Polymers, biopolymers and advanced nanocomposites for additive manufacturing: challenges and opportunities
12.25-13.00	***Tomasz W. Liskiewicz***	Tribology: friction, scratch resistance and wear
13.00-14.00	***Lunch Break***	
14.00-14.35	***Witold Brostow***	Viscoelastic behavior of polymers
	Co-chairmen:	***Prof. V.M. Castaño, Dr. T. Liskiewicz***
14.35- 15.10	***Masaru Matsuo***	Understandable approach about electric and dielectric properties of conductive filler- polymer composites in terms of elementary quantum mechanics
15.10-15.45	***Rimantas Levinskas***	Application of polymeric materials in energetics sector
15.45-16.05	***Coffee Break***	
	Co-chairmen:	***Prof. Masaru Matsuo, Prof. Rimantas Levinskas***
16.05-16.40	***Allison T. Osmanson***	Flexibility and related properties of polymers
16.45-17.20	***Tomasz Sterzynski***	Macromolecular orientation in polymers
17.20-17.55	***Dusan Berek***	Polymer liquid chromatography
20.00		***Welcome Reception***

11 September **Ivane Javakhishvili Hall**	
Invited speakers	
Co-chairmen: ***Prof. Lola Olantunji, Prof. Regina Jeziorska***	
10.00-10.20	***Ondrej Kylian*** - Plasma polymers – from thin films to nanoparticles and nanocomposites *Department of Molecular Physics, Charles University, Prague*
10.20-10.40	***Marino Lavorgna*** - Multifunctional polymer nanocomposites based on graphene and its derivatives: the key role of filler distribution *Institute of Polymers, Composites and Biomaterials, Portici*

10.40-11.00	***Rimantas Levinskas*** - National open access scientific centre for future energy technologies: opportunities for research and testing of polymeric materials *Lithuanian Energy Institute, Kaunas*
11.00-11.20	***Coffee Break***
	Co-chairmen: *Prof. Nodar Lekishvili, Prof. Ondrej Kylian*
11.20-11.40	***Victor M. Castaño*** - Viscoelastic behavior of polymers *Centro de Fisica Aplicada y Tecnologia Avanzada and Secretaria de Desarrollo Institucional, Universidad Nacional Autonoma de Mexico, Mexico*
11.40-12.00	***Jean-Marie Raquez*** - Spontaneous self-healing polyurethanes *Centre d'Innovation et de Recherche en Matériaux Polymères (CIRMAP), Service des Matériaux Polymères et Composites, University of Mons, Mons, Belgium*
12.00-12.20	***Sujitra Wongkasemjit,*** Development of mesoporous catalysts for preferential oxidation of carbon monoxide *Petroleum and Petrochemical College, Chulalongkorn University, Bangkok*
12.20-12.40	***Tomasz Sterzynski*** – The visualization of the flow of molten polymers; theoretical approach and measurements possibilities. *Poznan University of Technology, Polymer Division, Poznan/Poland*
12.40-13.00	***Ramaz Katsarava*** - Pseudo-proteins – a new family of biodegradable polymers for sophisticated biomedical applications. *Institute of Chemistry and Molecular Engineering, Agricultural University of Georgia, Georgia*
13.00-14.00	***Lunch Break***
	Co-chairmen: *Prof. Miroslava Trchová, Prof. Liuba Myasnikova*
14.00-14.20	***Regina Jeziorska*** - Polyolefin composites with increased resistance to microorganisms: structure–property relationships. *Industrial Chemistry Research Institute, Warsaw, Poland*
	Oral Presentations
14.20-14.35	***Witold Brostow*** **–** Thermophysical properties of polymers *Laboratory of Advanced Polymers & Optimized Materials (LAPOM), Department of Materials Science and Engineering and Department of Physics, University of North Texas ,Denton, USA*
14.35-14.50	***Karsten Leucker*** **-** Revealing correlations of bonding area and pilling behaviour of polypropylene nonwovens using a novel objective test method. *Institute of Polymer Materials, Friedrich-Alexander University Erlangen-Nürnberg (FAU),*
14.50-15.20	***Coffee break***
	Co-chairmen: Dr. Daniel Tobola, Prof. Jimsher Aneli
15.20-15.35	***Laurent Lebrun -*** Polymer membranes containing ionic liquids carriers for metal ions extraction. *CNRS, UM R 6270, PBS Laboratory, Normandy University*
15.35-15.50	***Hiran Mayook Lal*** - Flexural creep study of glass-carbon hybrid fibre reinforced polymer composite rods *Harbin Institute of Technology (HIT), Faculty of Engineering, Laboratory*

	of FRP composites and structures(LFCS), School of Civil Engineering, 150090 Harbin, China
15.50-16.05	***Karol Bula*** - Platelet particle's as a flow markers in polymer-metal hybrid joints. *Institute of Materials Technology, College of Construction Engineering and Management, Poznan University of Technology*
16.05-16.20	***Luciana S. Spinelli*** - Chemical modification of poly(ethylene-co-vinyl acetate) and its influence on the crude oil flow *Federal University of Rio de Janeiro, IMA/LMCP, Rio de Janeiro, Brazil.*
16.20-16.35	***Andrzej Pawlak*** – The crystallization of polymers with reduced density of entanglements. *Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Poland.*
16.35-16.50	***Stanislav Patlazhan*** **-** Microhydrodynamics of shear thinning fluids past superhydrophobic walls. Numerical modeling**.** *Semenov Institute of Chemical Physics of Russian Academy of Sciences, Moscow. Russian*
16.50-17.50	**Poster Sesion I**
11 September lecture hall 115	
	Co-chairmen: Prof. Narine Durgaryan, Prof. Milos Netopilík
10.00-10.15	***Luciana S. Spinelli*** - Chemical modification of poly(ethylene-co-vinyl acetate) and its influence on the crude oil flow. *University of Rio de Janeiro, IMA/LMCP, Rio de Janeiro, Brazil;* ***Petrobras/CENPES, Av. Horácio Macedo, 950, Cidade Universitária, Rio de Janeiro, Brazil (on leave).***
10.15-10.30	***Daniel Tobola*** **-** Wear and friction of P/M Vanadis 6 tool steel after combined surface treatment processes. *Institute of Advanced Manufacturing Technology, Cracow, Poland*
10.30-10.45	***Miroslava Trchová*** **-** Vibration spectroscopy of polyaniline *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague*
10.45-11.00	***Gleb Vaganov*** -_Synthesis and characteristics of new polyimide powder for selective laser sintering *Institute of Macromolecular Compounds of the Russian Academy of Sciences, 199004 Saint-Petersburg, Russia*
11.00-11.20	***Coffee Break***
	Co-chairmen: Prof. Ramaz Katsarava, Prof. Jean-Marie Raquez
11.20-11.35	***Narine Durgaryan*** **-** Aromatic diamines as monomers for the synthesis of electroconductive polymers *Yerevan National University, Erevan, Armenia.*
11.35-11.50	***Liubov Myasnikova*** **-** In situ synchrotron study of heating of a single nascent Ultrahigh molecular weight polyethylene particle *Abram Ioffe Institute of Russian Academy of Sciences, St. Petersburg, Russia*
11.50-12.05	***Nune Martikyan*** **-**_Syntheses and investigation of polymers containing triazene group *Yerevan State University, Armenia*

12.05-12.20	***Milos Netopilik*** – Modeling size-exclusion chromatography performance. *Institute of Macromolecular Chemistry, Czech Academy of Sciences, Prague, Czech Republic*
12.20-12.35	***Huseyin Bekir Yildiz*** **-** Generating enhanced photocurrent using p(sns-nh_2)/cds np/calixarene structure modified gold electrode systems *Department of Materials Science and Nanotechnology Engineering, Faculty of Engineering, KTO Karatay University, TR42020 Konya, Turkey*
12.35-12.50	***Naghash Miraqyan-*** Reaction of 1,4-benzoquinone with aniline oligomers and some aromatic diamines: synthesis and investigation *Yerevan National University, Armenia*
12.50-13.50	***Lunch Break***
	Co-chairmen: Prof. Luciana S. Spinelli, Prof. Huseyin Bekir Yildiz
13.50-14.05	***Andrzej Galeski*** **-** Cavitation of polymers related to chain entanglements and nanofillers *Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, Poland*
14.05-14.20	***Jimsher Aneli*** - Effect of microstructure on the electric conductivity of oriented polymer composites Dvali *Institite of Machine Mechanics, Tbilisi, Georgia*
14.20-14.35	***Elena Ivan'kova*** **-** Effect of carbon nanoparticles on properties of polyetherimide fibers *Institute of Macromolecular Compounds of the Russian Academy of Sciences, St. Petersburg, Russia*
14.35-14.50	***Nino Zavradashvili*** **-** Synthesis and study of multifunctional cationic polymers**.** *Institute of Chemistry and Molecular Engineering, Agricultural University of Georgia, Kakha Bendukidze University*
14.50-15.05	***Tengiz Kantaria*** **-** New polymer synthsis via alkyne-azide step growth click polymerization *Institute of Chemistry and Molecular Engineering, Agricultural University of Georgia, Kakha Bendukidze University Campus, # 240 David Aghmashenebeli Alley, Tbilisi, Georgia*
15.05 – 15.35	***Coffee Break***
	Co-chairmen: Prof . Dirk W. Schubert, Prof. Stanislav Patlazhan
15.35-15.50	***Omar Mukbaniani*** – Brush-type fluorine containing polymer electrolyte membranes *Department of Chemistry, College of Exact and Natural Sciences, Ivane Javakhishvili University, Tbilisi, Georgia*
15.50-16.05	***Arya Uthaman*-** Development of epoxy/cnt adhesives with high glass transition temperature and mechanical properties *School of Civil Engineering, Harbin Institute of Technology, Harbin, China; IIUCNN, Mahatma Gandhi University, Kottayam, Kerala, India*
16.05-16.20	***Mariia Svyntkivska*** **-** Conductive and superhydrophobic cotton fabric through pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate) assisted thermal reduction of graphene oxide and modification with methyltrichlorosilane *Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, Poland*

16.20-16.35	***Achim Frick -*** Enhanced battery life through assembly injection molding of hybrid polymer-aluminum sealing structures *Aalen University, Institute of Polymer Science and Processing iPSP, Aalen*
16.50-17.50	***Poster Sesion I***

12 September

Ivane Javakhishvili Hall

	Co-chairmen: Prof. Ewa Piorkowska, Prof. Agnieszka Szadkowska
10.00-10.15	***Dirk W. Schubert -*** Novel theoretical self-consistent mean-field approach to describe the conductivity of carbon fiber filled thermoplastics *Department of Materials Science, Institute of Polymer Materials, College of Engineering, Friedrich-Alexander University Erlangen-Nürnberg (FAU), Erlangen, Germany*
10.15-10.30	***Agnieszka Szadkowska -*** Polylactide and thermoplastic starch nanocomposites *Industrial Chemistry Research Institute, Warsaw, Poland*
10.30-10.45	***Nandika D'Souza-*** Thermoset and thermoplastic foams for building applications *Mechanical and Energy Engineering Department, University of North Texas, Denton, TX 76203* *Materials Science and Engineering Department, University of North Texas, Denton, TX 76203*
10.45-11.00	*Ewa Piorkowska* **-** Crystallization and properties of star-shaped and linear poly(l-lactide)s *Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, Poland*
11.00-11.30	***Coffee Break***
	Co-chairmen: Prof. Tshwafo E. Motaung, Prof. Zhenjiang Li
11.30-11.45	***Rachele Castaldo*** - A versatile synthetic approach towards hyper-crosslinked resins and nanocomposites with tailored adsorption properties *Institute for Polymers, Composites and Biomaterials, National Research Council of Italy, 34, 80078 Pozzuoli, Italy*
11.45-12.00	***Akaki Peikrishvili -*** Liquid phase shock wave consolidation and syntheses of nanostructured mgb$_2$ based superconductivity composites *Ferdinand Tavadze Institute of Metallurgy and Materials Science, T'bilisi*
12.00-12.15	***Marina Gahutishvili -*** Silver -arsenic, gold-arsenic nanoparticles in polymeric matrices *Ivane Javakhishvili University, Ilia Chavchavadze Ave. 3, Tbilisi 0179, Georgia*
12.15-12.30	***Sophio Kobauri -*** Synthesis and study of bis-azlactone based new biodegradable polymers for potential biomedical applications *Institute of Chemistry and Molecular Engineering, Agricultural University of Georgia, Kakha Bendukidze University Campus, Tbilisi 0159, Georgia*
12.30-12.45	***Zhenjiang Li*** - Hydrogen-bonding organocatalysis in ring-opening polymerizations. State Key Laboratory of Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University

12.45-13.00	***Khatuna Barbakadze* -** Development and properties of antimicrobial hybrid composite films to control biocorrosion processes *Institute of Inorganic-Organic Hybrid Compounds and Non-traditional Materials, Department of Chemistry, College of Exact and Natural Sciences, Ivane Javakhishvili University*
13.00-14.00	***Lunch Break***
	Co-chairmen: Prof. Ololade Olantunji, Dr. Akaki Peikrishvili
14.00-14.15	***Tshwafo E. Motaung* -** Characterization and comparison of maize stalk and sugar cane bagasse residues *Department of Chemistry, University of Unizulu (KwaDlangezwa Campus), 3886, South Africa*
14.15-14.30	***Aleksandra Nesic* -** Development of pla films loaded with grape vine cane extract for food packaging application ***University of Concepcion, Technological Development Unit, Cordillera 2634, Parque Industriale, Coronel, Chile***
14.30-14.45	***Ketevan Chubinidze* -** calmodulin functionalized with the fluorescent dye and gold nanoparticle for the targeting of calmodulin mediated processes in eukaryotic cells *Iv. Javakhishvili Tbilisi State University, Faculty of Exact and Natural Sciences, 0179 Tbilisi*
14.45-15.00	***Olatunji Ololade*** - Fish scale biopolymers: extraction, processing and application in novel transdermal delivery systems *Department of Chemical and Petroleum Engineering, University of Lagos, Akoka-Yaba, Lagos, Nigeria*
15.00-15.30	***Coffee Break***
	Co-chairmen: Prof. Mariia Svyntkivska, Prof. Andrzej Galeski
15.30-15.45	***Susmitha Sayana* -** Sustainability of Portland concrete containing polymeric fillers and fly ash *School of Engineering and Applied Sciences, Columbia University, New York, NY 10027, USA*
15.45-16.00	***Nathalie Hnatchuk*** - Preventing thermal degradation of PVC insulation by mixtures of cross-linking agents and antioxidants ***Laboratory of Advanced Polymers & Optimized Materials (LAPOM), Department of Materials Science and Engineering and Department of Physics, University of North Texas, Denton, TX 76207, USAF***
16.00-16.15	***Hee Jae Hong* -** Effects of UV stabilizers on polypropylene outdoors *Laboratory of Advanced Polymers & Optimized Materials (LAPOM), Department of Materials Science and Engineering and Department of Physics, University of North Texas, Denton, TX 76207, USA*
16.15-16.30	**SciCom meeting**
16.30-16.45	**Announcement of the Prize Winners – Liubov Myasnikova** **Invitation to Polychar 27 in 2019 – Gennaro Gentile**
16.45-17.45	**Poster Session II**
19.00	***Gala Diner***

Poster Presentations Session I
11 September

12 September

Poster presentation Session II

13 September Excursion 10.00

Abstract

Professor Victor Manuel Castaño Meneses

Victor-Manuel Castano-Meneses holds BSc, MSc and PhD in Physics from the Universidad Nacional Autonoma de Mexico, where he is a Full-Professor at the Centro de Fisica Aplicada y Tecnologia Avanzada. He spent 2 years as a Postdoctoral Fellow at IBM´s Yorktown Heights Research Center and has authored and co-authored over 700 peer-reviewed papers in international journals. Prof. Castano is one of the most cited latinamerican scientists in his field and has advised over 70 PhD thesis and numerous BSc and MSc dissertations. He also holds more than 20 patents and has been able to effectively transfer nanotechnology knowledge from the lab to the industry.

POLYMERS, BIOPOLYMERS AND ADVANCED NANOCOMPOSITES FOR ADDITIVE MANUFACTURING: CHALLENGES AND OPPORTUNITIES

***Victor M. Castaño*, Jesus Quezada, Ana Karla de la Borbolla**
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A review of the main challenges that additive manufacturing, in particular in the biomedical area pose, will be presented. In particular, the polymers that are currently under use of have been proposed are analyzed in terms of their capabilities and limitations. A detailed discussion of the challenges that should be surpassed if a working 3D technology for reconstructive medicine is to be available in the near future is offered.

References

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Abstract

Dr. Tomasz Liskiewicz

Dr Tomasz Liskiewicz is an Associate Professor in School of Mechanical Engineering at the University of Leeds. He has 15 years of international academic and industrial experience in surface engineering and tribology. Dr Liskiewicz has first-hand industry experience from his two-year industrial secondment in Alberta (Canada). His research interests are focused on tribology, surface engineering and biomimetics. He is actively using a wide range of surface analysis techniques. Dr Liskiewicz acts a member of Editorial Boards, and he is an Editorial Assistant and referee for a number of international journals in the field of materials science. He is a Honorary Secretary of Tribology Group Committee at the Institute of Physics in London.

TRIBOLOGY: FRICTION, SCRATCH RESISTANCE AND WEAR

Tomasz Liskiewicz

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Tribology is a relatively new word in the vocabulary of the scientific world, having being defined in the United Kingdom in 1966. However, it may be thought of as a bringing together of the far better known subjects of friction, wear and lubrication. Tribology is derived from the Greek word TRIBOS meaning rubbing. So one interpretation might be that it is the science of rubbing. In fact, the formal definition, which is interestingly still absent from many modern technical dictionaries, is “the science and technology of interacting surfaces in relative motion and of related subjects and practices”. Interacting Surfaces implies that there must be at least two bodies involved and that they must be capable of transmitting normal or tangential force between them. This may occur directly by contact or through an interposed solid, liquid or gas medium. In either instance, the surfaces are going to be separated by a very small distance, typically of the order of micrometres. The need for Relative Motion between the surfaces in the definition of tribology clearly defines tribology as being concerned with friction, wear and lubrication. This motion can take many forms such as sliding, rolling, spinning, bouncing or combinations of one or more of these motions.

After attending this introductory lecture, you should be able to:

- Understand the fundamental concepts that constitute tribology;
- Appreciate the importance of tribology to mechanisms;
- Recognise the complex nature of contact between real rough surfaces;
- Describe the laws and simple theories of dry friction;
- Understand the basic mechanisms and phenomena of wear;
- Appreciate the very complex nature of friction and wear in reality.

Professor Masaru Matsuo

Masaru Matsuo has completed his PhD at Kyoto University in Japan and he was a professor of Nara Women's University. After his retirement, he became a full time professor of Dalian University of Technology in China. Since September 1st 2014, he is a visiting professor of Dalian University of Technology.

UNDERSTANDABLE APPROACH ABOUT ELECTRIC AND DIELECTRIC PROPERTIES OF CONDUCTIVE FILLER- POLYMER COMPOSITES IN TERMS OF ELEMENTARY QUANTUM MECHANICS

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Most of natural science students have taken "Materials Science" as one of their undergraduate courses. Certainly, they have acquired knowledge about physical and chemical properties of materials and have been learned about the Schrödinger equation, the probability density of electrons in a hydrogen-like atom and the eigenvalue of energy. However, most of the scientists who have majored in polymer physics in their graduate courses show little interest in the Schrödinger equation – while this equation allows to investigate electric properties of conductive polymers and conductive filler-polymer composites. Polymer scientists thus operate nearly qualitatively by using the simplified final equations proposed by solid physicists and electrical engineers. This way, one considers the conductivity of the filler-polymer composites by using the theoretical tunneling analyses established for conductive (or semi-conductive)–insulator–conductive systems.The present paper introduces more detailed treatments of electric and dielectric properties of filler-polymer composites in terms of elementary quantum mechanics.

Electric properties are dependent on temperature. The initial theory for tunneling current was constructed largely for a single temperature [1] but subsequently improved as a function of temperature [2]. The improved theory has been utilized in many papers, since the conductivity increases up to the glass transition temperature region of the polymers adopted as medium and the characteristics of the composites have attracted much attention in industry. The current vs. voltage diagrams for the composites show deviations from Ohm's law – not foreseen in the theory since that theory assumes voltage close to zero. An improvement has been provided by this presenter and his colleagues in terms of fluctuation-induced tunneling conduction [3].

The analysis can be also adopted for dielectric properties of the composites. The analysis has been performed on the basis of curve fitting of complex impedance between the experimental results and a theoretical curve calculated by equivalent circuit with a series arrangement of several units containing resistance and capacitance associated with possible electron transfer. Based on the good agreement between experimental and theoretical results, the theoretical AC conductivity as a function of frequency also agrees well with the experimental results. The DC component at the frequency $\longrightarrow 0$ provides detailed information of electric current behavior in the composites. As a result, the tunneling current is governed by average surface area of the fillers over which most of tunneling occurs - rather than by the gap distance between adjacent semi-conductive fillers [4]. The detailed treatments shall be presented in the Short Course.

References

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2. P. Sheng. *Phys. Rev. B.* ***21***, 2180, 1980.
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Abstract

Professor Rimantas Levinskas

APPLICATION OF POLYMERIC MATERIALS IN ENERGETICS SECTOR

Rimantas Levinskas

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One of the effective ways to protect steels against corrosion is its additional passivation by formation of protective films. Protection against corrosion inside boilers and heat exchangers is more effective by passivation the surface of high temperature resistant steels using amines. When steel is passivated by amines, the monomolecular or several molecules thick film builds up blocking out factors leading to corrosion. The film stability and passivation effectiveness depend on the amine molecular structure. For surface passivation were used solutions of monoethanolamine and polyamines. It was established that amines having branched structure are more stable thermally comparing with linear structure saturated amines. The best passivation of steels has been determined using emulsion of heat resistant amines (tert-alkylamines) produced by the Institute of Heavy Synthesis “Blachovnia” (Poland).

Also, the phosphate treatment case of ferrous metals with removable polyamide coatings was investigated. The phosphatization can be carried out by immersion of metal articles into phosphate solutions or by usual painting method. During it the continuous not soluble crystal or amorphous film forms on the surface of articles. The point of our work was to investigate phosphatizing of ferrous metals with chemical compounds introduced into polyamide coating and to regulate adhesion between the coating and the metal surface. Results of research for optimization the peeling force of the polyamide coatings became a groundwork for creation of easily removable films for the screening or reduction of alfa – and beta- particle streams, emitted from polluted surfaces. Polymeric films are formed on surfaces from solutions by the ordinary painting method. The usual film thickness was 100-200 micrometers, its drying time in normal conditions was no longer than 5 hours. Due to special anti-adhesives in the solution the adhesion strength of such films was 80-120 N/m. Thus, films were easily removed from different geometric surfaces of ferrous and non-ferrous metals, glasses, plastics, painted and other surfaces. The radioactive dust (diameter less than 0,5 mm) were removed together with the polymeric film, because film formed on the protected surfaces accumulates radioactive substances inside structure of polymer during polymerization of polyamide solution.

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Abstract

Professor Witold Brostow

Witold Brostow is Regents Professor of Materials Science and Engineering at the University of North Texas in Denton and Professor of Mechanics and Robotics at the AGH University of Science and Technology in Cracow. He is President of the Scientific Committee of the Polychar World Forum on Advanced Materials and President of the International Council on Materials Education. The textbook *W. Brostow & H.E. Hagg Lobland, Materials: Introduction and Applications, John Wiley & Sons, New York 2017* has worldwide enthusiastic reviews.

FLEXIBILITY IN RELATION TO OTHER PROPERTIES OF POLYMERS

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Certain mechanical properties of materials have been defined for a long time; tensile modulus which represents a measure of the material resistance to deformation when a tensile force is applied is an example. However, describing materials for specific applications one also has been using terms such as “brittleness” and “flexibility” without a definition. Therefore, the present author and two colleagues have defined brittleness B by an equation [1], namely

$$B = 1/(\varepsilon_b \cdot E') \qquad (1)$$

where ε_b = strain at break in tensile testing while E’ = storage modulus at 1.0 Hz determined in dynamic mechanical analysis (DMA). B has been connected to several properties, mechanical, tribological and thermodynamic ones [2].

We have now defined flexibility Y also by an equation [3]:

$$Y = V_{sp}/[\Sigma_i^n u_{bi}] \qquad (2)$$

Here V_{sp} is the specific volume in cm^3/g while $\Sigma_i^n u_{bi}$ is the sum of the strengths of bonds in the monomer of a given polymer. We have assumed that the larger is V_{sp}, the more there is space between the chains enabling their movements and reorientation. V_{sp} is related to the free volume V_f but there is no simple proportionality between these quantities. The summation in the denominator in Eq. (2) follows the ideas of Linus Pauling.

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Abstract

Professor Tomasz Sterzynski

Tomasz Sterzynski, professor at the Poznan University of Technology, head of the Polymer Division at the Faculty of Mechanical Technology and Management. A grant holder at the group of polymer rheology (Prof. Dr. Joachim Meissner) of the Federal Institute of Technology (ETH) in Zurich and Humboldt Foundation grant holder at the group of polymer physics (Prof. Dr. Wilhelm Ruland) at Philips University in Marburg (Germany). In 90th maître des conferences position at Ecole d'Application des Hauts Polymers, Louis Pasteur University in Strasbourg. He is an author and co-author of many papers and conferences at the domain of polymers structure and processing, co-author of several patents, member of European, German and Polish students mobility and grants selection board. Member of many conferences committees, chairman of the World Forum on Advanced Materials in 2016, editor of the special issue of Macromolecular Symposia, reviewer of international journals at the domain of polymer science, supervisor of 14 doctor thesis and over 150 diploma works in France and in Poland.

MACROMOLECULAR ORIENTATION IN POLYMERS

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Macromolecular orientation in polymers may be produced by both, a specific suitable post processing or /and as a hazardous effect accompanying the melt processing. The examples of orientation created at the flow of molten polymers by injection molding, extrusion of profiles and films, as well as by other processing technologies like compression molding etc. will be briefly presented.

The orientation plays a significant role by anisotropy/isotropy properties of polymeric products. Thus, its determination is substantial for the description of multidirectional mechanical properties, heat transportation, thermal stability etc. The creation of uniaxial or biaxial orientation state allows to achieve specific products like ultra-resistant fibers and bands, thermo- shrinkage films, direction related heat transfer etc.

The macromolecular orientation state may be detected by secondary effects observation of orientation dependent properties, like elastic modules, elongation, heat transportation, electrical properties and thermal stability. The direct determination of the Herman's function, representing average position of the macromolecular chains relative to the drawing/production direction is usually done by Wide Angle X-rays Diffraction (WAXS) in transition mode or by polarized Fourier Transformed Infrared Spectroscopy (FTIR). Particularly, the second method allows an access on the macromolecular orientation in both, amorphous and crystalline phases.

Abstract

Professor Dusan Berek

POLYMER LIQUID CHROMATOGRAHY

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Synthetic polymeric materials exhibit large variability of their end-use properties, which strongly depend on the molecular characteristics of macromolecules involved. These are - *molar mass*, *chemical structure* and *physical (molecular) architecture.* All molecular characteristics of man-made polymers exhibit a distribution, so that we deal with *averaged (mean) values* and with *distributions* of molecular characteristics. If more than one distribution is present in a polymer (molar mass distribution is always present!) one speaks about *a complex polymer*. A mixture of two or several polymers with distinct chemical composition or architecture is *a complex polymer system.* Liquid chromatography, polymer HPLC is a group of method commonly applied for determination of molecular characteristics of synthetic polymers. The most important is gel permeation/size exclusion chromatography, GPC/SEC, which is based on the entropic control of polymer retention within the column packed with porous particles. Its basic principles such as its retention mechanism, measurement procedures, principal applications, materials, as well as its hardware will be discussed. The limitations, drawbacks and pitfalls of GPC/SEC from the point of view of the method users will also be presented [1,2]. GPC/SEC separates macromolecules according to their size in solution, which depends on all molecular characteristics of macromolecules under study. Therefore, the method can hardly give exact results on molar mass averages and distributions for complex polymers and complex polymer systems. It is necessary to include enthalpy based retention mechanism to employ a coupled method of polymer liquid chromatography [3]. Following topics will be discussed: Enthalpic interactions in LC columns and their effect on polymer retention; liquid chromatography under critical conditions; eluent gradient polymer LC; temperature gradient polymer LC and the new approach, LC liquid chromatography under limiting conditions of enthalpic interactions. The most recent development in polymer HPLC is two-dimensional liquid chromatography, 2D-LC [4], which combines two independent chromatographic systems and can produce information on two different molecular characteristics of a polymer. We will present basic principles, strategies and applications of 2D-LC. Here again, limitations, drawbacks and queries of coupled methods and 2D-LC will be rendered.

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Abstract

VISCOELASTIC BEHAVIOR OF POLYMERS

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The fundamental concepts of viscoelasticity will be reviewed, along with a discussion on the different types of polymers, in terms of their dynamical mechanical behavior. The main techniques to obtain information of viscoelasticity will be analyzed. Finally, the scientific and technological implications of these concepts will be presented.

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Abstract

PLASTIC DEFORMATION OF GLASSY POLYMERS AND OLIGOMERS. EXPERIMENT AND MOLECULAR DYNAMICS

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The following peculiarities were found in experimental studies of deformation behavior of amorphous solid polymers. Upon annealing, the yield peak appears and grows. It disappears during the secondary deformation applied after the significant plastic flow. However, the yield peak occurs again after annealing. The creep and stress relaxation slow down during annealing while they accelerated significantly after the preliminary plastic deformation [1-2].

All the described features are confirmed by the molecular dynamic simulations [3-5]. The phenomenological model of plastic deformation was proposed. This model is based on the assumption of development of certain structural elements (alike the growing shear cracks), which are responsible for plastic deformation. It is suggested that decrease in shear resistance is caused by the decrease of local material density within the structural elements [6].

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Abstract

A DEFINITION OF FLEXIBILITY AND ITS CONNECTION TO DYNAMIC FRICTION OF POLYMERS

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We have defined flexibility of polymers by an equation. Flexibility Y is not an inverse of the brittleness B, the two equations are compared. The flexibility equation includes summation of the strengths of chemical bonds – the concept introduced by Linus Pauling. The flexibility is plotted as a function of dynamic friction; a single curve for polymers is obtained and represented by an equation. This work is a part of a larger program aimed at providing equations relating mechanical, thermodynamic and tribological properties of polymers and thus saving large amounts of experimentation time.

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Abstract

NOVEL THEORETICAL SELF-CONSISTENT MEAN-FIELD APPROACH TO DESCRIBE THE CONDUCTIVITY OF CARBON FIBER FILLED THERMOPLASTICS – PART II - VALIDATION BY COMPUTER SIMULATION

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The electrical conductivity of polymeric fiber composites is generally strongly dependent on the constituent conductivities, the fiber filler fraction, the fiber aspect ratio and of the orientation of the fibers. Even though electrically conductive polymer composites are emerging materials of high scientific and commercial interest, accurate mathematical models for describing such materials are rare. A very promising mathematical model for predicting the electrical conductivity below the electrical percolation threshold, for both isotropic and anisotropic composites, was however recently published by Schubert. The shortcomings of that study were that the model included so far only one predicted parameter and that it was not sufficiently validated. In this current study, finite element modelling (FEM) was used to successfully validate the model from Schubert for isotropic fiber composites and to accurately determine the predicted parameter. Our theoretical predictions were finally compared with experimental conductivity data for isotropic CF/PMMA composites with fiber filler fractions in the range 0-12 vol.% and fiber aspect ratios from 5 to 30. The model forecasts, without any adjustable parameters, were satisfactory close to the experimental data.

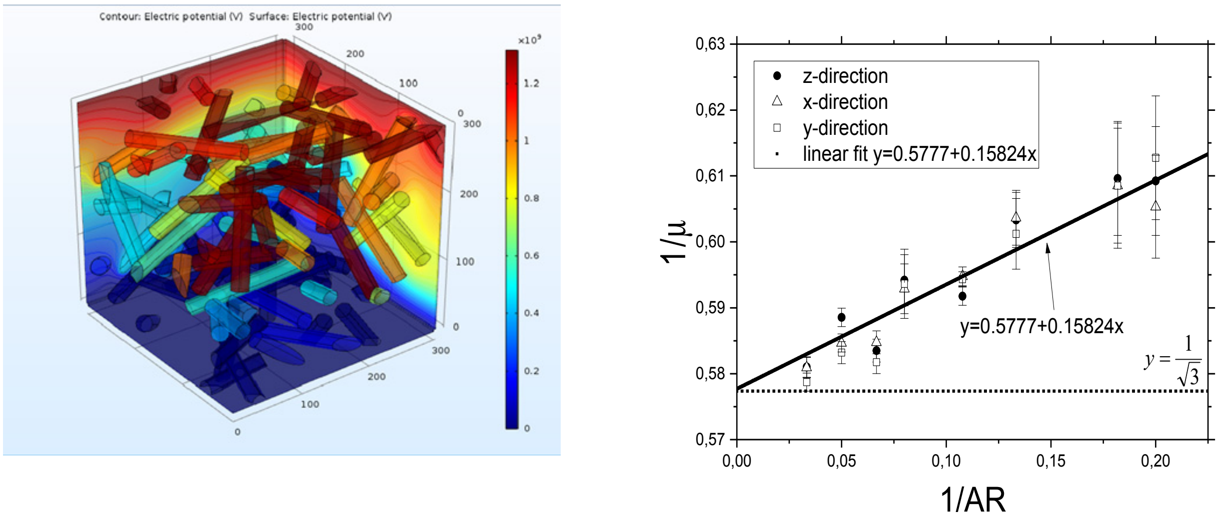

Figure 1. (a) Electric potential and current density when an electric potential difference is applied in the z-direction. Voltage decreases from top to bottom. **(b)** Correlation between the structural parameter μ and aspect ratio. 1/ μ as function of the inverse aspect ratio 1/AR. The solid line represents a linear fit. The 1/ μ value for infinitely long fibers (i.e. fibers with 1/AR=0) is highlighted with a solid circle positioned at 0.5777. The intercept deviation as compared to the prediction, i.e. 1/ μ=1/ √3, was only 0.061%.

Abstract

REVEALING CORRELATIONS OF BONDING AREA AND PILLING BEHAVIOUR OF POLYPROYPLENE NONWOVENS USING A NOVEL OBJECTIVE TEST METHOD

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Various test methods are available for assessing the abrasion resistance of fabrics and nonwovens as standardized tests [1-4]. Methods determining the pill formation are defined as well [5].
It has been demonstrated that none of the existing testing methods for abrasion resistance is suitable for the testing of low basis weight polypropylene nonwovens in the range of 15 g/m² to 25 g/m². Thus, a novel test method has been developed in which the samples are scanned after certain intervals of abrasion cycles on the Martindale abrasion tester using a standard flatbed scanner. From the greyscale images generated, the total pill area and the number of pills can be determined automatically as shown in Figure 1 using a simple image evaluation procedure that was optimized in this study.
It was possible to objectively determine the influence of the bonded area of thermally point bonded polypropylene nonwoven on the pilling behaviour. Therefore polypropylene fibres have been calendered using bonding patterns with 8, 16 and 32 % bonding area. These nonwovens were evaluated with the novel testing method and the influencing factors on the differing pilling behaviour were examined, showing a significant influence of the bonded area on the pilling behaviour.

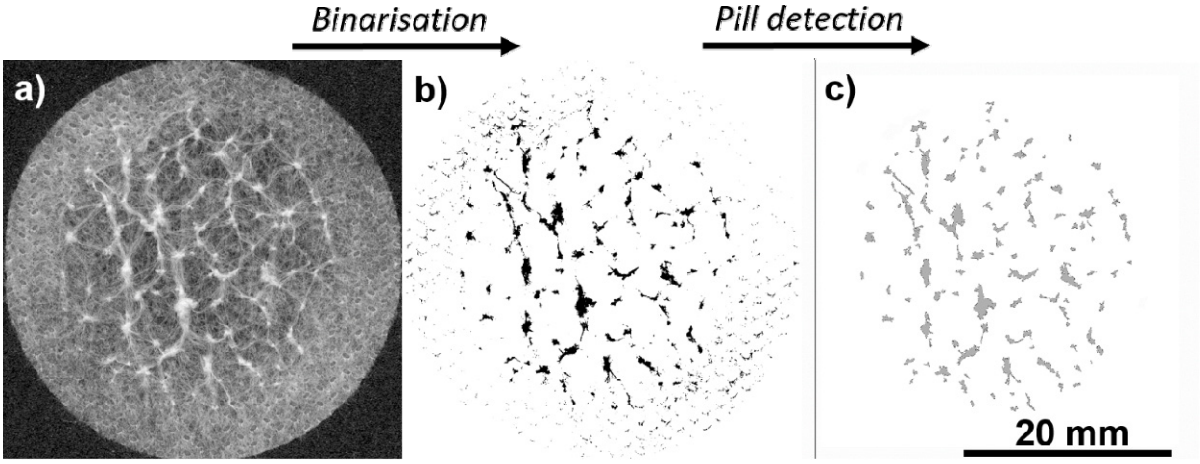

Figure 1. Greyscale image of the scanned nonwoven a), the binarised image b) and all detected pills c) where the bright patches in the neat nonwoven are removed for the pill area measurements.

Acknowledgement: Funding for the Martindale abrasion tester was provided by the Bavarian Polymer Institute.

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Abstract

POLYMER MEMBRANES CONTAINING IONIC LIQUIDS CARRIERS FOR METAL IONS EXTRACTION

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The presence of toxic heavy metals in wastewaters resulting from industrial activities represents an important environmental concern due to the toxic effects of metals ions, even at very low concentrations. Therefore, the removal of metal ions in wastewaters is a technological challenge. Rare earth elements find many applications particularly in high-tech industries and are now considered as strategic resources. However, almost of them are produced by only China. The stable supply of such metals is a concern for many countries. Consequently, recycling and recovery in wastes are now considered as valuable secondary resources.

The membrane processes have several advantages over conventional methods to recover metal ions. Among them, supported liquid membranes (SLM) have many attracted assignments but they suffer from a lack of stability. The use of high hydrophobic supporting polymer and carriers could improve the stability of the SLM during the process. In the present work, the approach was to use polyvinylidenefluoride (PVDF) support membrane and long fluorinated chains ionic liquids (ILs) as carriers. Moreover, ILs with phosphonated anions were used because they are known as efficient complexing molecules for metal ions extraction [1].

Novel ILs were first synthesized and purified: isooctylmethylimidazolium bis-2-ethylhexylphosphate ($iOMim^+$ $D2EHP^-$) and 1-butyl-3-decylimidazolium di-1-H,1-H,2-H,2-H-perfluorodecylphosphate ($C10BIm^+$ $PFC10^-$) [2]. The SLM was performed by impregnating a micro-porous PVDF supporting membrane with IL in dodecane. The membrane were characterized by transport experiments on heavy metal ions Hg(II), Cd(II), and Cr(III) and on rare earth ions Eu(III), Nd(III), Y(III) and Yb(III). The transport of the ions was modeled in studying the influence of the carrier, ions concentration, *p*H and temperature.

Extraction properties were highly influenced by *p*H and by the hardness of metal ions and carriers. Indeed, hard anions ($PFC10^-$) and ($D2EHP^-$) formed very stable complex with hard metal ions Yb(III) and Cr(III) that were less easily dissociated for diffusion. On the contrary, the SLMs were highly permeable for soft Hg(II) and Nd(III) ions that were weakly complexed by the anions. The diffusion of ions was faster with ($C10Bim^+$ $PFC10^-$) than with ($iOMIm^+$ $D2EHP^-$) carrier due to a difference in the mechanism of transport (explained by the thermodynamical data): by jumping from site to site for the first and by vehicular type mechanism for the second. The strategy for stabilizing the SLM by using fluorinated IL was effective, because the membrane containing ($C10BIm^+$ $PFC10^-$) carrier leached only 5 % of IL after four consecutive diffusion experiments.

SLMs containing high hydrophobic IL as carrier were successfully used for the extraction of soft metal ions. Such IL and PVDF polymer support respond to the lack of stability of SLMs. The extraction performances were correlated to the ions hardness and to the ion-carrier complexes stability.

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Abstract

FROM MECHANICS TO THERMODYNAMICS: A RELATION BETWEEN BRITTLENESS AND THERMAL EXPANSIVITY OF POLYMERS

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The isobaric thermal expansivity is an underestimated property. The entire composite structures disintegrate into pieces on heating without the use of any mechanical force when the constituents have significantly different expansivities. While one typically tries to relate mechanical properties among themselves and thermodynamic ones among themselves too, we provide an equation relating the linear isobaric expansivity to the brittleness B for a number of polymers with a large variety of chemical structures and consequently with a large variety of properties.

Abstract

FLEXURAL CREEP STUDY OF GLASS-CARBON HYBRID FIBRE REINFORCED POLYMER COMPOSITE RODS

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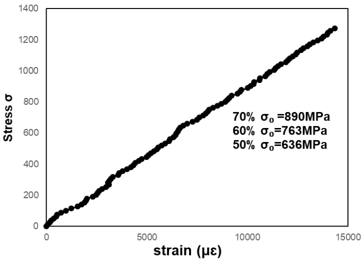
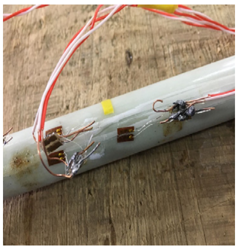
In this work deals with the short term and long term viscoelastic property (creep) study of GFRP/CFRP hybrid fibre reinforced polymers(HFRP). The main objective of this study is to optimise the property of HFRP rods in the application of oil extraction process. Regarding the time dependent viscoelastic property of the hybrid FRP has been not yet studied. The HFRP rod used in this study is 19mm diameter with an inner diameter 12mm of CFRP component and outer layer of GFRP component with 3.5mm thickness and span of the material is à1000mm.

In this study we kept the rod under constant load of 50%, 60% and 70% of the ultimate load for a duration of 5000 hours. The time dependent flexural modulus and the creep behaviour of HFRP rods were successfully modelled using Findley's power law. The time dependent viscoelastic responses, creep coefficient & reduction factor are predicted successfully. From the result it shows a close agreement with the experimental strain and the

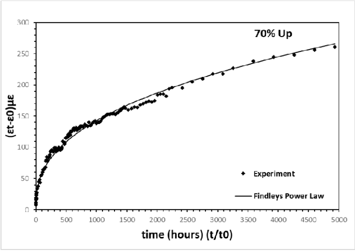
predicted strain, over 20 years it is noticed that there is a reduction of flexural modulus of 10.5% for the high modulus HFRP rods. The time dependent viscoelastic responses, creep coefficient & reduction factor are predicted successfully.

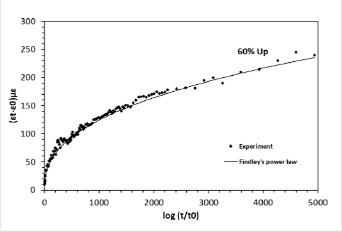


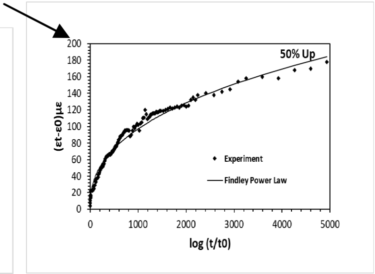


$$\varepsilon(t) = \varepsilon_0 + m(\frac{t}{t_0})^n \longrightarrow$$

$$\varepsilon_t = \varepsilon_0' \sinh(\frac{\sigma}{\sigma_\varepsilon}) + m'(\frac{t}{t_0})^n \sinh(\frac{\sigma}{\sigma_m})$$

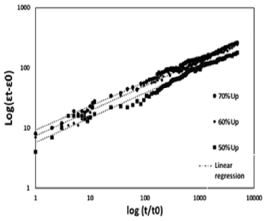


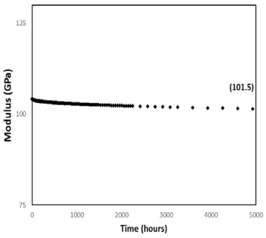


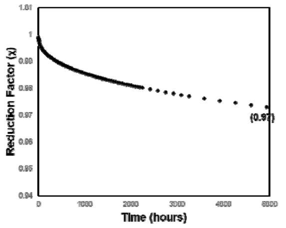


$$\log(\varepsilon_t - \varepsilon_0) = \log(m) + n\log(\frac{t}{t_0})$$

$$E_v = \frac{E_0 E_t}{E_t + E_0 t^n}$$







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PolyChar 26 World Forum on Advanced Materials

Abstract

POLYFUNCTIONAL POLYCONJUGATED COOLIGOMERS OF PHENYL ACETYLENE WITH 1,4-BENZOQUINONE

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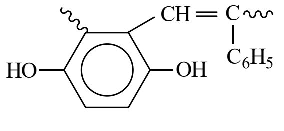
The copolymerization reaction of 1,4-benzoquinone (BQ) and phenyl acetylene (PhA) in the solution (benzene, toluene, dioxane) in the presence of the catalyst of cation type $BF_3{\cdot}O(C_2H_5)_2$ has been carried out. It has been established on the basis of IR-spectral and elemental analysis that the prepared products are the cooligomers with molecular weight $\overline{M}_n = 900 \div 1500$ and $\overline{M}_w = 1500 \div 3500$ and consist of hydroquinone and phenyl acetylene links:



The kinetic regularities of the copolymerization process have been investigated by dilatometric method in a medium of benzene in the presence of $BF_3{\cdot}O(C_2H_5)_2$. It is seen from kinetic curves that the copolymerization of BQ with PhA proceeds at 313÷333K with high rate.

It has been experimentally found that the copolymerization process is subjected to the kinetic equation:

$$W = k[BF_3{\cdot}O(C_2H_5)_2]{\cdot}[BQ+PhA]^2$$

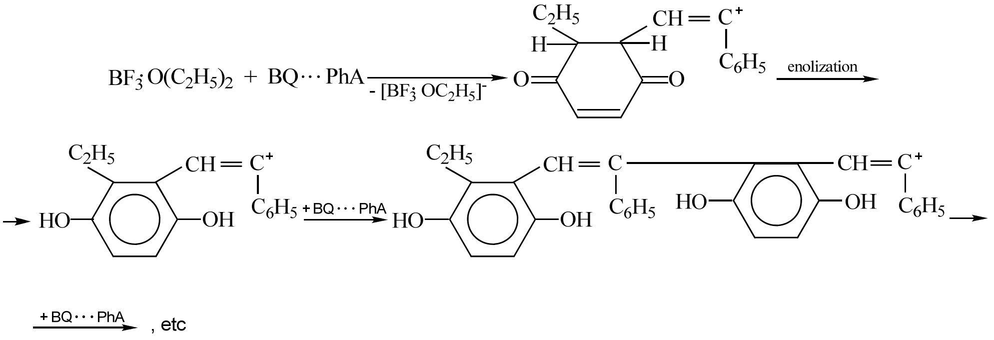
On above-mentioned equation the initial rate values ($(3.82 \div 11.0){\cdot}10^{-4}$ mol/l·s), reaction rate constants ($(1.12 \div 5.7){\cdot}10^{-3}$ $mol{\cdot}l^{-1}{\cdot}s^{-1}$) and activation energy (57.7 kJ/mol) (Table.) have been determined.

Table. Values of some kinetic parameters of the copolymerization of BQ and PhA in the presence of $BF_3{\cdot}O(C_2H_5)_2$ in benzene

№	$[BQ]_o$+ $[PhA]_o$, mol/l	$[BF_3{\cdot}O(C_2H_5)_2]_o$, mol/l	T, K	$W{\cdot}10^4$, $mol{\cdot}l^{-1}{\cdot}s^{-1}$	$k{\cdot}10^3$, $mol{\cdot}l^{-1}{\cdot}s^{-1}$
1	2	3	4	5	6
1	0.70	0.003	303	3.82	1.12
2	0.70	0.003	313	6.0	1.40
3	0.70	0.003	323	11.0	2.95
4	0.70	0.003	333	24.0	5.75
5	0.60	0.003	313	4.27	
6	0.50	0.003	313	2.83	
7	0.40	0.003	313	1.75	
8	0.70	0.002	313	3.69	
9	0.70	0.0015	313	2.61	
10	0.70	0.001	313	1.60	

E=57.7 kJ/mol

On the basis of results of study of the reaction products and kinetic data and also taking into account a nature of the catalyst there has been proposed the cation mechanism of the copolymerization of BQ with PhA:



A chain termination can occur either due to proton emission or due to chain transfer act to monomer basically to benzoquinone:

The synthesized cooligomers – powders of brown and dark-brown color, possess high reactivity in the electron-exchange processes and also in interaction with epoxide compounds. They show the paramagnetic, antioxidant, antistatic, antihypoxant and semi-conductor properties.

PLATELET PARTICLE’S AS A FLOW MARKERS IN POLYMER-METAL HYBRID JOINTS

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The isotactic polypropylene filled with talc and mica particles were used for prediction of polymer flow lines during filling cavity with metal insert. The talc orientation in polypropylene matrix was studied by scanning electron microscopy and polarized optical microscopy. For estimation of platelet particles orientation Hermans function was used. The evaluation of changes of Hermans factor in plastic part localized near metal insert was presented. We assumed that the sharp edges of talc particles visible in brittle fractured surfaces are the markers of the flow path of molten polymer during cavity filling (see fig. 1), so we paid a special attention on the plastic part region located near metal insert. Using Herman’s function, we have proposed four regions around metal insert that exhibit different talc orientation, which means individual morphology. We specified this region’s as a: randomly oriented region, completely oriented region (in case of flow direction), disorganized regionand typical fountain flow region.

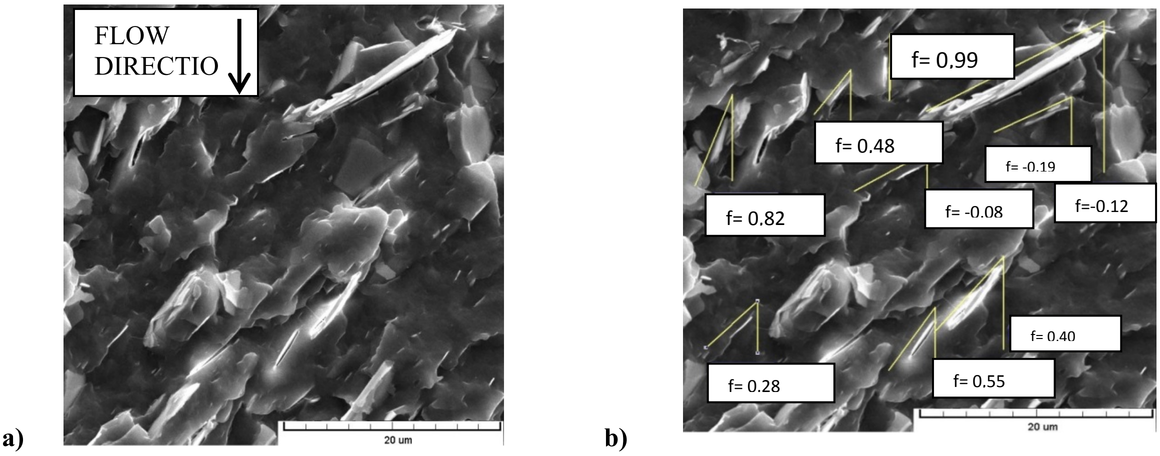

Figure 1. SEM images of a brittle fractured surface of PA6/10% by wt. of talc, a) illustration of talc particles orientation, b) Hermans factor values evaluated for visible particles

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Abstract

SYNTHESIS AND CHARACTERIZATION OF POLYMERS BASED ON CARDANOL AND THEIR INFLUENCE ON THE ADSORPTION OF ASPHALTENES IN KAOLINITE

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Oilsands have suspended fine solids in bitumen, in which asphaltenes become adsorbed. The main problems that the suspended fine solids can cause are the fouling of the catalysts and the reduction of the quality of the oil, generating high costs for oil industry [1-3]. The asphaltene's behavior in the crude oil is almost exclusively determined by the interactions between the molecules present in the oil and the aggregates of asphaltenes in an organic solvent medium. It is believed that polymers containing specific functional groups can be used as asphaltenes flocculants in a particular type of unconventional oil, assisting in further destabilization of the model system, and able to assist in the removal of suspended fine solids, such as kaolinite [1]. In this work, different polymers based on cardanol was synthesized, by bulk polymerization using a cationic initiator [1-4] and their influence was evaluated on the adsorption of asphaltenes in kaolinite [5]. The synthesized polymers were characterized by Fourier-transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (NMR ^{1}H), thermogravimetry analysis (TGA) and gel permeation chromatography (GPC). The adsorption of asphaltenes in kaolinite was first monitored by adsorption tests induced in the presence of toluene, without the synthesized polymers. Initially, an adsorption kinetics test was performed with the objective of determining the time of greater asphaltenes adsorption [1, 5]. Then, an adsorption isotherm was constructed in order to estimate the maximum amount of asphaltenes adsorbed in kaolinite, and hence to indicate if the adsorption process is favorable / spontaneous [1, 5]. In addition, the influence of synthesized polymers based on cardanol on the adsorption of asphaltenes in kaolinite was evaluated by reading the supernatant using an ultraviolet-visible (UV-Vis) spectrometer and the final concentration of asphaltenes in solution was determined, after adsorption tests [1]. The sulphur content present in asphaltenes adsorbed in kaolinite was determined by scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS). The wettability of asphaltenes and kaolinite, before and after the adsorption test, was also determined by contact angles measurements using a goniometer [1]. The results indicate that the adsorption process is spontaneous and favorable, at room temperature, and there is a time and a maximum concentration of asphaltenes for a complete adsorption occur. The presence of synthesized polymers based on cardanol contributed for a lower adsorption of asphaltenes in kaolinite, presenting better efficiency at higher concentrations. In addition, the contact angle measurements were useful for verifying the change in the wettability of the asphaltenes when they are adsorbed in kaolinite.

Acknowledgments. FAPERJ, CNPq, CETEM, Petrobras

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Abstract

VIBRATION SPECTROSCOPY OF POLYANILINE

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The contribution represents a set of selected studies that have been produced in last several years of active and intensive studies on conducting polymers, *viz.* polyaniline, by infrared and Raman spectroscopies. Its goal consists of the effort to guide the interested parties through the exciting pilgrimage of scientific research, which was undertaken in the last decade, during which we have concentrated on investigations of the molecular structure of polyaniline in its various forms and modifications.

In one series of experiments, we have studied the course of aniline oxidation and the molecular structure of the reaction intermediates [1]. The progress of the oxidative polymerization of aniline with ammonium peroxydisulfate in an aqueous medium has been monitored *in situ* by attenuated total-reflection Fourier-transform infrared spectroscopy. The growth of polyaniline film at the crystal surface, as well as the changes proceeding in the surrounding aqueous medium, were reflected in the spectra. In another study, we have followed the evolution of the molecular structure during carbonization of polyaniline [2]. Finally, we have observed the transformation of aniline oligomers into a material displaying two peaks in Raman spectra assigned to graphitic and disordered modes [3]. The evolution of new morphology and corresponding changes in molecular structure after heating were discussed on the basis of Fourier-transform infrared and Raman spectroscopies.

Within an IUPAC project, we identified the differences in molecular structure of polyaniline and aniline oligomers and related them to supramolecular morphology, viz. the nanotube formation [4].

Several studies concerned thin films produced by conducting polymers. We have illustrated the role of infrared and Raman spectroscopies in the studies of polyaniline film growth [5,6]. Spectroscopic methods are crucial in the evaluation of the performance of polyaniline films alone or in combination with nanoparticles of noble metals. The assessment of film ageing and stability was followed by these methods. The carbonization of polyaniline films to nitrogen-containing carbon analogues was also discussed. In the recent study, we have detected aniline oligomers on the polyaniline–gold interface using resonance Raman scattering on the final films deposited on gold [7].

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Abstract

CHEMICAL MODIFICATION OF POLY(ETHYLENE-CO-VINYL ACETATE) AND ITS INFLUENCE ON THE CRUDE OIL FLOW

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The deposition of the wax crystals on tube walls, followed by aggregation of these crystals, decreases the effective cross-sectional area of the pipe, reducing the flow and hampering production of petroleum. In extreme cases, the line can be totally blocked [1-2]. Among the preventive actions are those that modify the wax crystals and/or prevent their agglomeration and deposition. This line of actions includes coating pipes with anti-stick materials; the electromagnetic method, which modifies the crystals; and injection of chemical additives, called organic deposition inhibitors [3]. Various polymers have been used and/or proposed in the literature to inhibit the deposition of waxes. Among these are poly(ethylene-co-vinyl acetate) (EVA) and acrylate copolymers with long hydrocarbon chains [3-6]. These structures have in common relatively long hydrocarbon chains (the hydrophobic segment can interact better with the hydrocarbon chains of the paraffin) and polar groups (responsible for inhibiting the aggregation of the wax crystals formed). In this study, were realized chemical modification of EVA for insertion of hydroxyl groups and long pendant hydrocarbon chains (C6 to C18) and was evaluated the influence on the crude oil flow. The EVA samples, both after hydrolysis and after esterification, were analyzed by nuclear magnetic resonance of ^{1}H to determine the hydrolysis degree and esterification percentage. The solubility of the commercial and modified EVA samples was verified in toluene. The solubility test was performed in the temperature range of 25 ºC to 80 ºC, or until the sample was soluble. The solubility was confirmed after 24 hours under stirring. Analyses of pour point were conducted according to ASTM D97:2012 - Standard Test Method for Pour Point of Petroleum Products, with some adaptations. The results showed that the presence of the (CH_3COO-) group in the structure of the ethylene-co-vinyl acetate copolymers promoted the action of the polymer in lowering the pour point, supported by a low OH concentration and the presence of a long pendant hydrocarbon chain: the best results were obtained with intermediate chain lengths (C10 and C12) among those tested (from C6 to C18). With respect to the compositions of the additives, there appears to be an ideal balance between the hydrophobic segments and hydrophilic groups to attain the best performance in reducing the pour point of a determined type of crude oil.

Acknowledgements. CNPq, CAPES, FAPERJ, Petrobras, ANP

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Abstract

SYNTHESIS AND CHARACTERIZATION OF MODIFIED POLYCARDANOL AND ITS USE FOR THE DETERMINATION OF ASPHALTENES PRECIPITATION ONSET IN CRUDE OILS

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Asphaltenes can be defined, based on their structure, as molecules with relatively high molar mass composed of condensed aromatic rings, cyclic structures, and a small number of aliphatic hydrocarbon chains, as well as functional groups (such as carbonyl, amine and hydroxyl) and elements (such as sulfur, nickel and vanadium) [1-3]. Prediction of the asphaltene stability in crude oils from different production streams is very useful to the petroleum industry, because this knowledge can avoid serious problems from formation of solid deposits during oil flow in lines [4]. For oils whose precipitation onset is not well defined, a small quantity of another petroleum with easily detected onset can be added. The onset can be calculated by observing the asphaltene precipitation onset caused by titration with n-heptane [5]. Therefore, the purpose of this study was to synthesize and characterize modified polycardanol and evaluate the performance of these molecules, when dissolved in a solvent (toluene), in the determination of asphaltenes precipitation onset in crude oils. Polycardanol, called PCC0, PCC1, PCC2 and PCC3, were synthesized by polycondensation and polycardanol, called PCA, was synthesized by polyaddition via cationic initiation. Polycardanol (PCA) was modified utilizing nitric acid and dichloromethane as solvent. All synthesized molecules were characterized by Fourier-transform infrared spectrometry. Polycardanol samples were also characterized by gel permeation chromatography (GPC). The sample containing a nitro group (NO_2) in their structure (modified PCA) was quantified using elemental analysis (CHN/O). The precipitation onset was determined using near-infrared (NIR). The asphaltenes precipitation onset points of crude oil samples that do not have well-defined curves of absorption intensity in function of volume of titrated n-heptane can be ascertained by adding a solution of toluene containing an additive whose molecules have similar groups to those found in asphaltenes: aromatic ring, aliphatic chain and heteroatom. Polycardanol (PCA) and modified polycardanol presented this behavior when dissolved in toluene. However, the concentration of the additive in toluene should be adjusted in function of the characteristics of the crude oil, and for the same oil, the greater the solubility parameter range is of the model molecule, the lower the concentration necessary to identify the precipitation onset of the petroleum will be.

Acknowledgements: CNPq, CAPES, FAPERJ, Petrobras, ANP

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THE CRYSTALLIZATION OF POLYMERS WITH REDUCED DENSITY OF ENTANGLEMENTS

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The presence of macromolecular entanglements determines many properties of polymer and influences the crystallization from melt [1]. It is possible to reduce the equilibrium density of entanglements by dissolving of polymer followed by controlled solidification, stabilizing the disentangled state [2]. The purpose of this work was complex characterization of isothermal and non- isothermal crystallization processes of polypropylene (PP) and polylactide (PLA) having a reduced number of entanglements.

It was observed that the growth rate of PP spherulites in isothermal conditions increased with reduced concentration of entanglements. Reduction of entanglements shifted the temperature of transition between Regimes II and III, which means that more regular growth of crystals was possible at lower temperature. The range of temperatures at which polypropylene cavitated in regions of melt occluded by spherulites was limited to 137-139°C, with weak dependence on entanglements density. DSC studies showed that isothermal crystallization is faster in less entangled PP, however the crystallinity degree and long period of structure (by SAXS) were similar for studied materials. When the crystallization was completed during fast cooling, the differences between individual samples were more significant. The partial disentangling, overcoming some limitation for movements of macromolecules, made possible easier crystallization, even at low temperature of Regime III.

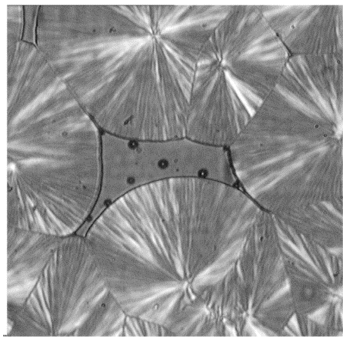

Figure 1. The isothermal crystallization of PP. Cavitation inside a weak spot is visible.

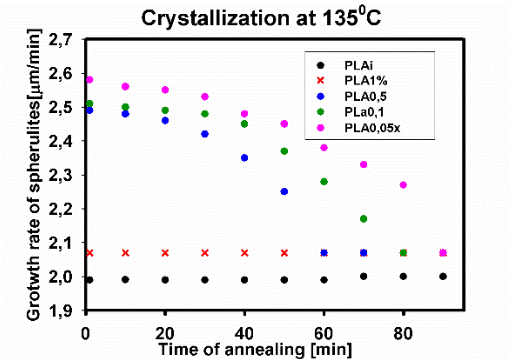

Figure 2. Growth rate of PLA spherulites crystallized at T=135°C after annealing in melt.

The studies of isothermal crystallization showed that growth of polylactide spherulites was faster when the polymer was prepared from a more dilute solution (0.5 wt% and less). The partially disentangled polylactide was used for studies of re-entangling process. The polymer was annealed in melt and changes of properties with time of annealing were analyzed. It was concluded that the re-entangling process is relatively slow and time of reaching the equilibrium density of entanglements is at least 60 min

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Abstract

SYNTHESIS AND CHARACTERISTICS OF NEW POLYIMIDE POWDER FOR SELECTIVE LASER SINTERING

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At the present time, additive processing technologies are rapidly developing along with traditional methods of processing thermoplastics, such as injection molding and extrusion in the manufacture of new products in the aircraft industry, engineering and instrument making. They allow providing a reduction of the time for technological production of complex products. One of the most advanced additive technologies for the processing of high-quality products from polymers is a technology of Selective Laser Sintering (SLS) [1].

To date, SLS processing is mainly limited to the use of standard thermoplastic polymers such as polyimide [2]. However, the aerospace, automotive and medical industries show an increased interest to SLS method for production of high-strength, heat-resistant polymer materials. Therefore, the aim of this work was to obtain a new thermally stable thermoplastic polymer powder for SLS technology based on a high performance semi-crystalline polyimides and to study its characteristics.

Thermoplastic semicrystalline polyimide R-BAPB was synthesized from R dianhydride (1,3-bis(3,3',4,4'-dicarboxyphenoxy) benzene) and BABP diamine (4,4'-bis (4 "-aminophenoxy) diphenyl). The effect of cyclization of polyamide acid on its structure and properties was studied. It was subjected to cyclization in polyimides using methods of thermal or chemical imidization.

The differential scanning calorimetry (DSC) was applied to determine the degree of crystallinity, the glass transition temperature and the melting point of the R-BAPB powder. The rotation viscosimeter was used for analysis the melt viscosity of the R-BAPB. The size, structure and morphology of the powder microparticles, as well as the fractional composition of the synthesized polyimide were studied by scanning electron microscopy (SEM). The specially designed laser sintering system was used for processing single layer film from powder particles by SLS. The mechanical properties of all the samples were tested and the values of tensile strength, modulus of elasticity and deformation before fracture were determined. Investigation of the technological properties of the powder showed that the chemical imidization method produces powders with a narrower particle size distribution and a higher bulk density compared to the thermally imidized powder

The SEM method established that a denser structure is formed for the samples obtained by the SLS method on the basis of a polyimide powder synthesized by chemical imidization. This leads to higher mechanical characteristics of the samples as compared to samples obtained from a thermally imidized powder.

The present study has been supported by the Russian Foundation for Basic Research (grant No. 17-03-00733A).

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MICROHYDRODYNAMICS OF SHEAR THINNING FLUIDS PAST SUPERHYDROPHOBIC WALLS. NUMERICAL MODELING

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The liquid flow through microchannels is characterized by a high hydrodynamic resistance. It requires a significant pressure drop to ensure a given flow rate. To solve this problem, the superhydrophobic coverings are used. These surfaces consist of a set of asperities and cavities. In the Cassie state, the liquid does not penetrate into the cavities leading to a slip flow at the liquid-gas contact areas while stick boundary conditions on the solid domains. These heterogeneous boundary conditions result in the effective sliding of fluids which reduces the hydrodynamic resistance. The intensity of the wall-slip is characterized by the slip length – the distance from the superhydrophobic wall of the channel to the point where velocity profile is extrapolated to zero.

In our talk we shall discuss flow peculiarities of non-Newtonian shear thinning fluids over the anisotropic superhydrophobic wall consisting of parallel solid stripes and gas-filled grooves under the simple shear flow. Two problems will be considered: (i) the physical mechanisms of the apparent slip of shear thinning fluids and (ii) mixing phenomena of Newtonian and non-Newtonian fluids in a microchannel.

By means of numerical modeling, it was found that perturbations of shear rate lead to the steady state heterogeneous distribution of viscosity of shear thinning fluid in a close vicinity of the superhydrophobic striped texture. The effective viscosity of this wall-layer was shown to be lower than viscosity of the upper layers. This results in the apparent wall-slip with the extrapolation length exceeding considerably the effective slip length of Newtonian fluids both along and across the stripes [1]. The apparent slip length of shear thinning fluid is a non-monotonous function of a basic shear rate. It attains its maximum at the shear rate corresponding to the inflection point of the viscosity curve of this non-Newtonian fluid.

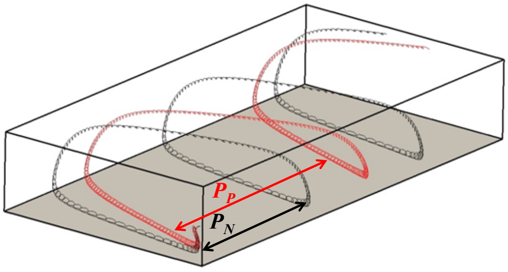

Figure 1. Helicoidal stream lines of Newtonian (P_N) and non-Newtonian shear thinning (P_P) fluids.

The oblique orientation of the superhydrophobic striped texture relative to the flow direction was shown to induce the secondary helicoidal flow both in Newtonian and non-Newtonian shear thinning fluids. This type of flow stimulates mixing of fluids in microchannels at low Reynolds numbers. It was found that period of the helicoidal stream lines of shear thinning fluids (P_P) is larger than that of Newtonian fluids (P_N). It was concluded that mixing efficiency of non-Newtonian media is lower than that of Newtonian liquids.

The numerical calculations were carried out on the computational resources of the Joint Supercomputer Center of Russian Academy of Sciences. The authors are grateful to Russian Foundation for Basic Research (grant 18-53-15013) for the financial support.

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Abstract

WEAR AND FRICTION OF P/M VANADIS 6 TOOL STEEL AFTER COMBINED SURFACE TREATMENT PROCESSES

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There are many ways to improve the quality of surfaces of tool steels for cold working such as mechanical treatments, chemical modification or else physical vapor deposition (PVD) coatings. The following combined processes of surface layer (SL) modification were performed: turning + burnishing (T+B), turning + burnishing + PVD coating (T+B+PVD), turning + burnishing + sulfonitriding (T+B+SN), turning + burnishing + nitriding + polishing (T+B+N+P) as well as turning (T) for comparison. Heat treatment was carried out in vacuum furnaces with gas quenching until the hardness of ≈ 62±1 HRC was achieved. 3D surface geometrical structure measurements, optical and scanning electron microscopy, X-ray diffraction, residual stress levels analysis and ball-on-disc tribological tests against Al_2O_3 balls as counterparts provided friction and wear values. Results will be presented at the Conference. The present paper represents a continuation of some earlier work on tool steels [1-4].

Acknowledgement: This report is a part of a project supported by the LIDER/13/0075/L-7/15/NCBR/2016 entitled "Development of an innovative technology of obtaining functional properties of cold working tools" funded by the National Center for Research and Development of Poland, Warsaw.

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AROMATIC DIAMINES AS MONOMERS FOR THE SYNTHESIS OF ELECTROCONDUCTIVE POLYMERS

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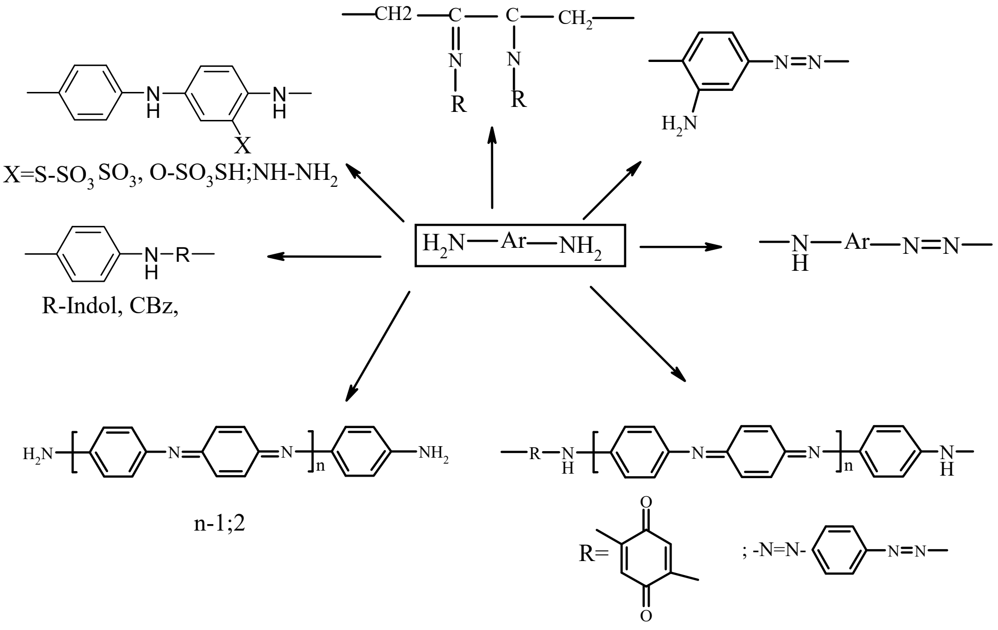
New possibilities of the synthesis of conjugated conductive polymers containing azo, triazene, phenyleneamine groups in the main polymer chain and the polymers with similar to polyaniline structures , as well , on the base of cheap and industrially available some aromatic diamines mainly m-phenylenediamine, p-phenylenediamine, benzidine have been discussed. The graphical overview of known [1-5]and newly established synthetic routs are presented on scheme



Polymers increase their conductivity up to 10^{-2} S/cm when doping with iodine and up to 10^{-5} S/cm when doping with hydrochloric acid.

Acknowledgement:The work have been done on financial support of the State Committee of the Ministry of Edication and Science of Armenia Republic (Research contract no SCS 15T-1D347).

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SYNTHESIS OF CARBAMIDE AND THIO-CARBAMIDE BASED POLYMERIZED FERTILIZERS

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Homo-polymers were synthesized on the base of carbamide and thiocarbamide, in water solution. Methanal was used as aldehyde component. Molar ratio of aldehyde component was varied form 0.8 to 3.0. Synthesis was carried out at 80^0C temperature.

When aldehyde component molar ratio is changed from 0.8 to 3.0, at the decrease of reaction medium pH from 7 to 3, the formed olygomers undergo structuring and are isolated from the reaction medium as structurized product gel. Optimal conditions are when amide and aldehyde components molar ratio is equivalent.

Succession of component addition to reaction medium makes impact on the structure of the obtained olygomers. When aldehyde component is added to the reaction medium step-wise, excess of amide components is preserved in the process of reaction, which impedes isolation of the product from the raction medium in the form of a gel. At these conditions oligomer structuring doesn't take place.

The process of carbamide-methanal interaction has been studied, Carbamide/methanal molar ratio was 1:0.8, correspondingly. At the initial stage temperature was 40^0C. In the process of reaction aldehyde concentration in the reaction medium decreased. After 0.5 hr its concentration fell to 2.5%. At this moment methylol groups were formed:

$$H_2N\text{-}C0\text{-}NH_2 + CH_20 \rightarrow H_2N\text{-}C0\text{-}NHCH_20H.$$

At the increase of temperature up to 80^0 and decrease of pH, methylol groups concentration decreases since they interact with carbamide $-NH_2$ group and form olygomer. Interaction of methylol groups with -NH- group hydrogen atom practically doesn't take place, since in the reaction medium, considering initial concentration, there still are $-NH_2$ groups not participating in the reaction, with which they interact, as a result of which oligomer is formed:

$$H_2N\text{-}C0\text{-}NH\text{-}CH_20H + H_2N\text{-}C0\text{-}NH\text{-}CH_20H \rightarrow H_2N\text{-}C0\text{-}NH\text{-}CH_2\text{-}HN\text{-}C0\text{-}NH\text{-}CH_20H$$

$$H_2N\text{-}C0\text{-}NH\text{-}CH_2\text{-}HN\text{-}C0\text{-}NH\text{-}CH_20H + H_2N\text{-}C0\text{-}NH\text{-}CH_20H \rightarrow$$

$$H_2N\text{-}C0\text{-}NH\text{-}CH_2\text{-}HN\text{-}C0\text{-}NH\text{-}CH_2HN\text{-}C0\text{-}NH\text{-}CH_20H \text{ and so on.}$$

IR spectroscopic studies showed that -NH- groups are preserved in the olygomer. The specter didn't show absorption zone characteristic for tertiary nitrogen. At these conditions spatial structure is not formed.

When carbamide and aldehyde molar ratio is 1:3, correspondingly, at the first stage of the reaction we observe creation of di- and tri-methylol derivatives:

$$H_2N\text{-}C0\text{-}NH_2 + CH_20 \rightarrow (HOCH_2)_2N\text{-}C0\text{-}NH\ CH_20H.$$

At this moment we observe also interaction of methylol groups, as a result of which methylene ether bonds are formed:

$$-CH_20H + -CH_20H \rightarrow -CH_2\text{-}0\text{-}CH_2\text{-}.$$

Besides, methylol groups interact with primary and secondary amine groups:

$$-NH_2 + -CH_20H \rightarrow -NHCH_2-$$

$$-NH- + -CH_20H \rightarrow -N=$$

as a result of which spatial structure polymers are formed.

Simplified scheme of reactions of homo- and copolymers formation is as follows:

$$nH_2N\text{-}CO\text{-}NH_2 + nCH_2O \rightarrow [-HN\text{-}CO\text{-}NH\text{-}CH_2\text{-}]_n$$

$$nH_2N\text{-}CS\text{-}NH_2 + nCH_2O \rightarrow [-HN\text{-}CS\text{-}NH\text{-}CH_2\text{-}]_n$$

$$n\text{-}xH_2N\text{-}CO\text{-}NH_2 + nCH_2O + n - yH_2N\text{-}CS\text{-}NH_2 \rightarrow [(-HN\text{-}CO\text{-}NH\text{-}CH_2\text{-})_{n-x} - (-HN\text{-}CS\text{-}NH\text{-}CH_2\text{-})_{n-y}]_n$$

$$n = x + y$$

Acknowledgements. The paper was prepared within the framework of the project # 2016-36 / STCU #6309 "Biodegradable polymers synthesis and application in environment protection from pollution" funded by the Shota Rustaveli National Science Foundation/Science & Technology Center in Ukraine.

SYNTHESIS AND INVESTIGATION OF PHOTOSENSITIVE COMPOUNDS ON THE BASIS OF ETHERS OF CYCLOPROPYLACRYLIC ACID

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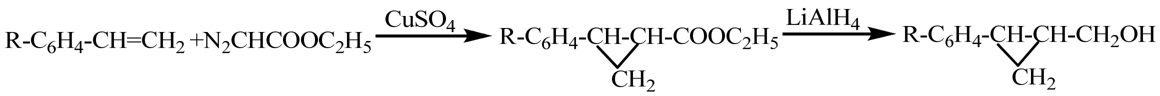
Now, the works on synthesis and application of the polymeric photosensitive negative compounds possessing high lithographic properties for reproduction of etched configurations in microelectronics, optics, precision engineering, etc are intensively carried out. The functionally substituted cyclopropane-containing monomers and polymers on their basis are the very perspective in terms of creation of new photosensitive materials. With this aim the new cyclopropylacrylates have been synthesized and their radical homopolymerization and photosensitivity have been studied.

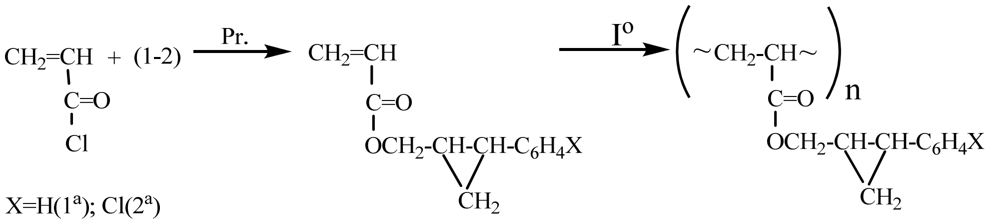
The necessity of the synthesis of a wide series of the compounds has been connected with change of their properties depending on polymer base, namely photosensitivity, thermal stability, film formation, adhesion to substrates, etc.

In this connection, it has been firstly studied the compounds forming in interaction of carboethoxycarbene with para-substituted styrenes in the conditions of thermocatalytic decomposition of ethyl diazoacetate in the presence of anhydrous $CuSO_4$ by the following reaction. Then by restoration the compounds 1-2 have been prepared. These compounds possess antimicrobial properties.



R=H(1); Cl(2)

The synthesis of phenylcyclopropyl methyl acrylate (1^a) and para-chlorophenylcyclopropyl methyl acrylate (2^a) has been carried out by interaction of chloranhydride of acrylic acid with para-substituted phenylcyclopropyl methyl acrylate in the presence of pyridine and polymerization on the following reaction:



The structure of the synthesized compounds and polymers has been established on the basis of spectral (IR- and PMR-) data, the purity of all compounds was controlled on GLC analysis and corresponded 99.6%. The obtained results were in accordance with IR-spectra, which were used to determine the availability of OH groups in the range 3300-3500 cm^{-1}. It has been revealed that the prepared polymers show the high photosensitive and bactericide properties.

The synthesized polymers are the photosensitive (50-52 cm^2/J) and under the influence by UV-irradiation are subjected to the photochemical conversions leading to structuring.

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Abstract

AMMONIA REMOVAL FROM WATER BY SULFONATED POLYMERIC RESINS

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Effluents generated during the petroleum refining process may contain a wide variety of compounds, such as: phenols, sulfides, polychromatic and aliphatic hydrocarbons, ammonia, nitrites and nitrates in different amounts [1,2]. An inappropriate discharge or a discharge containing high levels of ammonia compounds to the aquifers can start an eutrophication process. This consists of oxygen depletion in water due to the accumulation of nitrogenous nutrients, which increases the mortality rate of aquatic animals [3]. For this reason, the disposal of aqueous effluents containing an excess of ammonium ions is harmful and requires a prior treatment so that they can comply with the limits established by local regulatory agencies. In Brazil, the National Environmental Council (CONAMA) establishes that the limit of maximum concentration of ammoniacal nitrogen in effluents to be discarded is 20 mg/L [4]. Several processes are described to remove ammonia from effluents. However, the process must take in account the following issues to be used in effluent treatment: (i) the total ammonia content, since there are more suitable technologies to treat dilute solutions and others to treat concentrated solutions and (ii) the type of effluent to be treated. Thus, biological processes [5], solvent extraction [6] and electrolysis are used when the effluent presents high ammonium concentration. Ion exchange processes are used when the ammonium concentrations are low and a "refining" is required. For this, zeolites [7] and polymer resins [8] are used, both with acidic groups in their structure. In this work, spherical and porous ion exchange resins were synthesized and characterized, and their performance was evaluated in removing ammonia from water. Two distinct chemical structures were used: poly (styrene-co-divinylbenzene) (STY-DVB) and poly (glycidyl methacrylate-co-divinylbenzene) (GMA-DVB). These resins were sulfonated to incorporate the sulfonic groups to be used as ion exchange groups. The resins were characterized in terms of superficial area, porous volume and size, particle size, ion exchange capacity, morphology (by optical microscopy) and composition (by infrared spectroscopy and elemental analyses). In addition, two thermodynamic adsorption models (Langmuir and Freundlich) were evaluated considering the amount of ammonium cations adsorbed as a function of resin mass and temperature in batch studies. The quantification of ammonia was done using a selective ion electrode, coupled to a pH and ion meter, Methron. GMA structure did favour the sulfonation degree, since both resins presented very similar ion exchange capability (around 3.95 mmol/g). Sulfonated GMA-DVB resin showed slightly better performance than sulfonated STY-DVB resin, probably due to the differences in the surface area: 130.4 for STY-DVB and 154.9 for GMA DVB. The adsorption data were better represented by the Freudlich model, indicating physical adsorption of the contaminant on the resin. **Acknowledgements:** FAPERJ, CNPq, CAPES, Petrobras, ANP.

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SYNTHESES AND INVESTIGATION OF POLYMERS CONTAINING TRIAZENE GROUP

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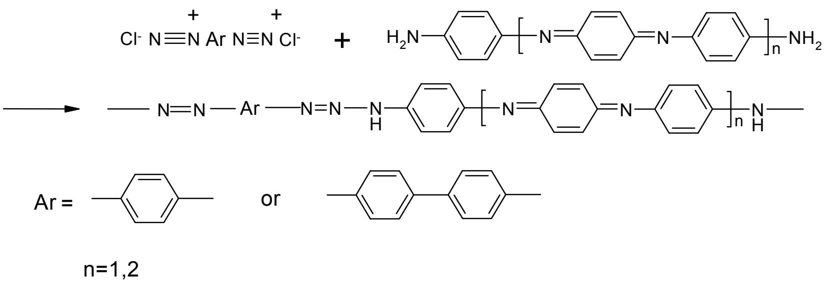
A range of polymer-supportedtriazenes and their metal-bound analogues were screened for use in catalysis and organic synthesis [1, 2]. UV laser ablation of triazene polymers is the objective ofintense experimental and theoretical research due to the potential applications in electronics [3-5]. Hence, the conjugated triazene-group-containing polymers may be of a big interest because of their applications possibility and as it has been shown previously they show good conductive and photoluminescence properties [6]. On the other hand among conducting polymers polyaniline is one of the most studied, because of its excellent electrical, magnetic and optical properties, and environmental stability [7,8]. Aiming to combine the properties oftriazenes and polyanilines, oligoaniline and 1,3-trazene group containing polymers have been synthesized and investigated. For this purpose NH2/NH2 capped aniline trimer*N*,*N*′-bis(4-aminophenyl)-1,4-benzoquinone diimineand pentamer1,4-di[N-4-aminophenyl-1,4-benzoquinonediimine-N`-yl]benzene were used [9] i.e. polymer in which trimer or pentamerunits are in the main polymer chain and connected with p-phenylenebistriazenyl groups. Obtained oligomers were used as a monomer for the synthesis of polymers with well defined structure. Polymers were obtained by the diazotation of p-phenylenediamine or benzidine (Scheme 1) and azo-coupling with corresponding oligomers.



Scheme 1

Comparative study of conductivities between obtained and some previously synthesized triazene-p-phenylene group containing polymers doped with iodine has been explored.

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Abstract

REACTION OF 1,4-BENZOQUINONE WITH ANILINE OLIGOMERS AND SOME AROMATIC DIAMINES: SYNTHESIS AND INVESTIGATION

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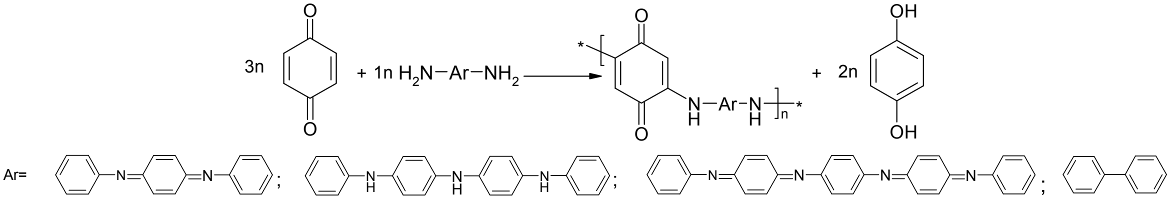
It is well known that benzoquinone groups containing polymers are in huge interest due to their electrical-magnetic and photo conducting properties. Some of them are used to understand some biological processes. These polymers also can be used as a surface drying for rusty steel [1].

We carried out the reactions of 1.4-benzoquinone with aniline oligomers in continuation of the work have been done with aromatic diamines in organic medium by known method [1]. In obtained polymers benzoquinone groups were linked with aniline oligomers. Polymers containing structural units of benzoquinone groups linked with one and two amino phenylene groups containing have been oxidized aiming to compare their electrical properties with starting materials. There are some difficulties in their studying because of poor solubility in organic solvents.



Scheme 1

Doping of obtained polymers by J_2 and HCl have been carried out. The study of doped polymers shows that the conductivity increases from $< 10^{-10}$ to $1.11x10^{-5}$ S/cm with doping level increase. Studies show that some undoped polymers have good photoluminescence property.

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BRUSH-TYPE FLUORINE CONTAINING POLYMER ELECTROLYTE MEMBRANES

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Efficient methods of energy storage and conversion are increasing in importance. Development of batteries and other energy storage devices with high energy density, low energy losses during operation, low cost and long lifetime is one of the most important challenges.

Among organosilicon compounds, the comb-type polymers with donor fragments at silicon atoms are very interesting in the present context. Changing the nature and structure of side donor groups enables to change the properties of the resulting polymers in a wide range.

We report synthesis of methylorganocyclotetrasiloxane $D_4^{RR'}$ with 2,2,3,3-tetrafluoropropyl propionate fluorine host donor side group and triethoxysilane groups (as cross-linking moieties) at silicon. A sol-gel reaction of the $D_4^{R,R'}$ allows creation of new solid polymer electrolyte membranes on the base of lithium salts (CF_3SO_3Li).

Preparation of new brush-type siloxane matrices with pendant propyl tetrafluopropylpropionate side groups was carried out via ring opening polymerization reaction of $D_4^{R,R'}$ in solution, in the presence of powder-like potassium hydroxide, at several temperatures.

So synthesized brush-type polymers were analyzed by FTIR, ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, DSC and GPC methods. Sol-gel reactions of polymers doped with lithium trifluoromethylsulfonate (triflate) have been studied and solid polymer electrolyte membranes obtained. The electric conductivity of the membranes was determined via electrical impedance spectroscopy.

Acknowledgments. The financial support of the Georgian National Science Foundation, Science and Technology Centre in Ukraine, Grant # STCU-2016-16 (6301) is gratefully acknowledged.

IN SITU SYNCHROTRON STUDY OF HEATING OF A SINGLE NASCENT UHMWPE PARTICLE

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Ultra-high molecular weight polyethylene is widely used for production of high performance fibers via gel technology, which is expensive and not user-friendly process because a large volume solvent recuperation needed. Nowadays, an alternative solvent-free route to high performance fibers is intensively developing [1-3]. It involves compaction/sintering of UHMWPE reactor powder at $T<T_m$ followed by orientation hardening of the sintered film. However, not any UHMWPE reactor powder could transform into high performance material. It is of great importance to find the key parameters controlling compactability and drawability of UHMWPE powders. Various parameters are considered as playing a decisive role in these processes (low number of entanglements, low green density, nascent particle size distributions…etc.). A number of authors suppose that the presence of monoclinic phase (MP) in the nascent polymer is indicative to its applicability to the dry processing [4, 5]. The estimates of MP content in powders differ, however, a lot (from 15 to 50%). Since the MP is only stable under stress, it allowed us to suppose that the observed MP is a result of a sample preparation (tableting for X-ray analysis) rather than intrinsic property of a nascent powder. So that the comparable X-ray analysis has been carried out for a compacted tablet (on D2 Phaser, Bruker) and for a single "virgin" particle (beam line "Belok" NRS Kurchatov) of one and the same UHMWPE reactor powder. Besides, the relaxation of MP in the tablet and in the single particle with heating was also investigated. It is found that the content of MP in the particle is ten times lower than that in a tablet. The origination of MP in the tablet and in the nascent polymer, as well as the difference in behavior of MP in both samples under heating are discussed.

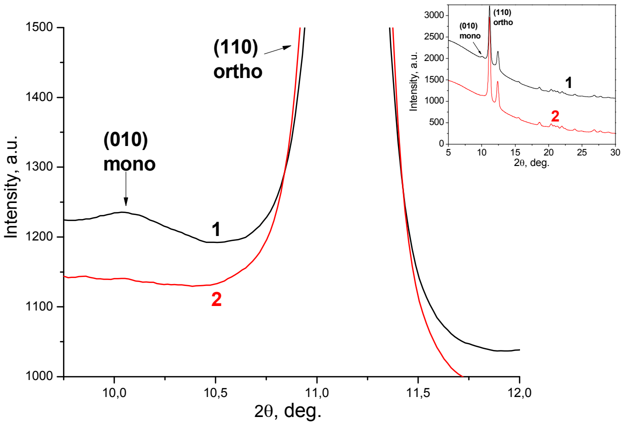

Figure 1. X-ray curves from a single nascent particle before (1) and after (2) heating to 80 °C

Acknowledgement: XRD characterization were performed using equipment owned by the Federal Joint Research Center "Material science and characterization in advanced technologies" with financial support by Ministry of Education and Science of the Russian Federation (id RFMEFI62117X0018).

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Abstract

MODELING SIZE-EXCLUSION CHROMATOGRAPHY PERFORMANCEM

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The performance of the size-exclusion chromatography (SEC) depends on a variety of operating variables as flow-rate, injected concentration and sample and mobile phase (MP) properties. Although the flow-rate of 1 ml per min is almost uniformly used, a detailed analysis showed that a reduction in flow-rate increases the performance of SEC greatly [1].

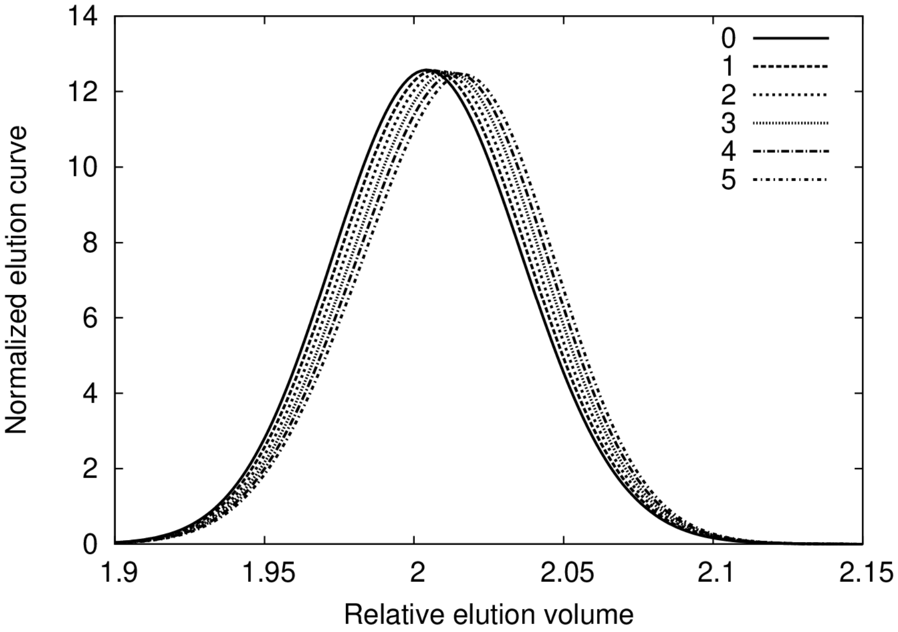

Figure 1. The SEC elution curves calculated for several values of $B \times m_{\mathrm{inj}} \times 10^4$ indicated with the curves.

It is also well known that the concentration effect in SEC is important if thermodynamically good solvents are used as MP. This effect can be simulated [2] for the band-broadening function (BBF), *i.e.*, the elution curve of a polymer with negligible dispersity in molecular weight, by the use of the plate theory, as shown for several values of the product of the slope B of concentration dependence of the partition coefficient K and the total injected mass m_{inj}, $B \times m_{\mathrm{inj}}$ in Figure 1. The shift of the peak-maxima is clearly seen. A comparison with an experiment can estimate the values of B.

Acknowledgement: The financial support of the Grant Agency of the Czech Republic (project 17-04258J) is gratefully acknowledged.

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SYNTHESIS OF SOME SYMMETRIC NON-CONDENSED BIS-INDOLE SYSTEMS AND POLYMERS ON THEIR BASIS

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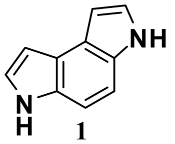
A lot of indole-containing heterocyclic systems have been synthesized at the Department of Organic Chemistry of TSU: isomeric pyrroloindoles (1), indolindoles (2), bis-indoles of various structures (3), etc.



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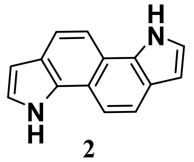

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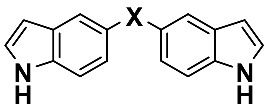

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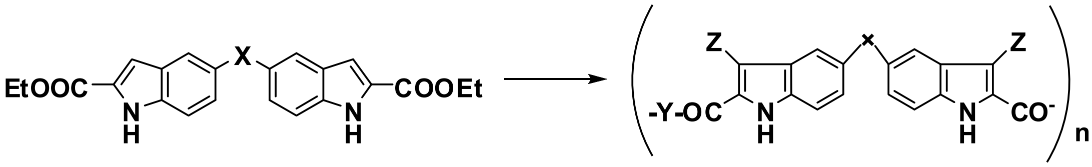

4 X= -,CH_2,O,S, SO_2,C_6H_4, CH_2-CH_2 ... **5** X= CH_2,O,SO_2;

Based on the $2,2^1$-diethoxy derivatives of symmetric uncondensed bis-indole systems (4), the corresponding sodium salts, dichloroanhydrides and some activated esters were synthesized. On the basis of dichloroanhydrides and activated esters, several polyethers and polyamides (5 Z = H) were obtained, as well as the products of their polymer-analogous transformation - polygamines (5 Z = CH_2-NMe_2). Polygamines are transferred to the corresponding polychetveric salts - potential pharmacologically active substances of prolonged action.

ADVANCED COPOLYMERS ON THE BASIS OF VINYLCYCLOPROPYL ETHERS

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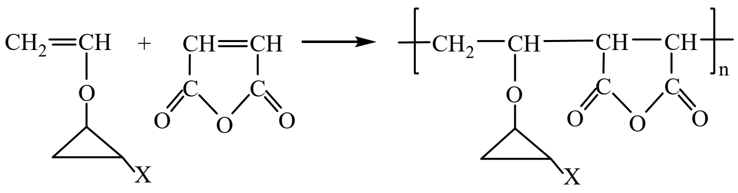
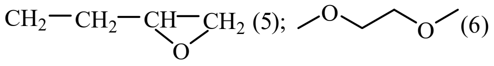
The polymers and copolymers on the basis of vinyl ethers possess unique complex of valuable exploitation properties, which enables to use them in various fields of science and technology, in particular – in microelectronics in preparation of UV-curing compositions and in production of protective coatings [1].

The vinyl ethers in the conditions of radical polymerization show low activity, which has been connected with high value of the chain transfer to the monomers. This has been stipulated by availability of the mobile hydrogen atoms of α-methylene group. The insufficient radical energy forming as a result of the radical addition on double bond for chain growth, and also the high value of the chain termination rate does not allow to prepare high-molecular products on the basis of these monomers. However, such compounds are well polymerized in the presence of the cation catalysts and under action of γ-irradiation. In a case of copolymerization with maleic anhydride the process is accompanied by appearance of the complexes of donor-acceptor type between comonomers and is completed by formation of the copolymers of equimolar composition.

In this work the results of joint polymerization of vinylcyclopropyl ether (1) and its ethoxycarbonyl- (2), carboxy- (3), methoxymethyl- (4), glycidyloxymethyl- (5) and acetal- (6) derivatives with electron-acceptor monomer – maleic anhydride are presented.



X = H (1); CO_2Et (2); CO_2H (3); CH_2OMe (4);



$CH_2-CH_2-CH-CH_2$ (5); (6)

The dependence of composition of the copolymer on composition of the initial mixture has been established and it has been shown by a method of NMR-spectroscopy that the copolymerization proceeds with formation of donor-acceptor complexes between comonomers

With the aim of force revealing of donor-acceptor interaction between comonomers, there have been calculated the equilibrium constants values, the temperature dependence of which allowed to evaluate also the thermodynamic parameters – enthalpy and entropy of the complex-formation process.

The photosensitivity of thin copolymer films obtained from synthesized substituted cyclopropyl vinyl ethers has been studied [2]. It has been established that in irradiation by full light of lamp DPT-1000 on air in the copolymers films synthesized by us, the cross-linked processes and formation of polymers of net structure insoluble in usual organic solvents – chloroform, acetone, alcohol, THF proceed. The unirradiated copolymer films containing along with anhydride and cyclopropane groups, epoxide, carboxyl and cyclic acetal groups in their macromolecules during storage in air for more than 2 days are partially cross-linked and lose solubility, while the films obtained from other copolymers remain unchanged.

It has been shown that an availability along with other reactive groups of cyclopropane ring as a side group in the macromolecule of the synthesized copolymers favors preparation of UV cured materials on their basis. The calculated values of photosensitivity of the prepared copolymers enable to make the photoresists of negative type on their basis.

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Abstract

ACRYLAMIDE COPOLYMERS FOR TREATMENT OF OILY WATERS

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In oil and gas industry, produced waters (oily waters) are a challenge in relation to their treatment. Offshore platforms often discharge this wastewater into the open ocean. However, there is a limit of concentration of oil and grease that it can be discharged, 29 mg / L as a monthly average, according to a Brazilian law. Different solutions for oil separation of produced water exist [1]. A conventional method in industrial wastewater treatment is the flocculation, mainly with using cationic polymers. They are responsible for neutralizing charges between the polymer and negative charged particles that were emulsified with the water production [2]. Studies have shown that hydrophobically modified polymers can act as cleansers of wastewater. Its hydrophobic parts can interact with the emulsified oil particles and subsequently combine into flakes [3]. In this work, the main objective was to evaluate the efficiency of modified polymers with different degrees of hydrophobicity in oil removal. Different types of grafting in copolymers were used as flocculant agents, including polypropylene oxide and methacrylate with long chains [4]. These new flocculants were characterized by gel permeation chromatography (GPC) equipped with triple molar mass detectors, zeta potential with nanosizer ZS, Malvern and NMR spectroscopy to discover molecules characteristics. The efficiency of the copolymers flocculation was evaluated by a 'jar test' procedure in an oily water at concentration of 265ppm. This test aimed to measure the oil removal in water and thus the flocculant efficiency. The polymers zeta potential was measured and the copolymer had no positive charge, as waiting, comparing in different pH conditions. Both this factor and its efficiency were attributed to the molar mass, the concentration and structure of the polymers used in each test.

Acknowledgements: CNPq, CAPES, FAPERJ, Petrobras, ANP

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Abstract

NEW FLUORINE CONTAINING SOLID POLYMER ELECTROLYTE MEMBRANES

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Solid polymer electrolyte membrane fuel cell is attracting much attention as a new power source for transportation, stationary, portable and consumer electronics power applications from the viewpoint of environmental and new energy issues.

The polysiloxanes are amorphous systems are characterized with very low glass temperature, extremely high free volume and high segmental mobility and present best matrix for Li-ion transportation. The high solubility of the corresponding salt in the polymer is another one factor for achievement of high ion-conductivity. This condition is created by introduction to the polymer-electrolyte main chain or side group of such „host" donor group, as ester oxygen imide group, halogen, especially fluorine groups. Formation of the grid like structures increases the mechanical properties of polymer-electrolytes [1-4]

The aim of our work is synthesis of $D_4^{R,R'}$ type methylorganocyclotetrasiloxane with 2,2,3,3,4,4,5,5-octafluoropentyl propionate side group and ethylsilyltriethoxy groups (as cross-linking moieties) at silicon, via hydrosilylation reaction of 2.4.6.8-tetrahydro-2.4.6.8-tetramethylcyclotetrasiloxane (D_4^H) with 2,2,3,3,4,4,5,5-octafluoropentyl acrylate and vinyltriethoxysilane at 1:3:1 ratio of initial compounds in the presence of platinum catalysts (platinum hydrochloric acid, Karstedt's catalysts and Pt/C) at various temperatures. The structure and composition of $D_4^{R,R'}$ compound have been determined by FTIR, ^1H, ^{13}C, ^{29}Si NMR spectroscopy methods. The sol-gel reaction of this compound has been carried out and solid polymer electrolyte membranes on the base of lithium salts (CF_3SO_3Li) have been obtained. The electro physical properties of solid polymer electrolyte membranes have been studied.

Acknowledgments. The financial support of the Georgian National Science Foundation STCU-2016-16, Science and Technology Centre in Ukraine, Grant # STCU 6301, is gratefully acknowledged.

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Abstract

SYNTHESIS AND STUDY OF MULTIFUNCTIONAL CATIONIC POLYMERS

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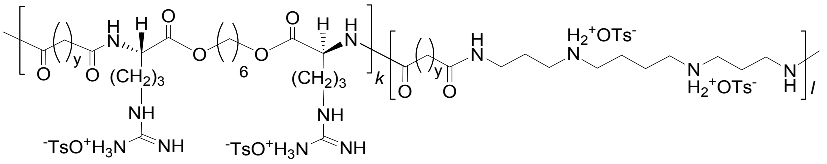
The importance of cationic polymers (**CPs**) is universally recognized since they exhibit unique biological properties. **CP**s can form electrostatic complexes with anionic biomolecules including nucleic acids and proteins and are of interest as active biological compound carriers to be used in both gene therapy and biotechnology. In addition, inherent bioactive properties such as antimicrobial, antioxidant, antitumor and anti-inflammatory stimuli responsiveness, make **CP**s more promising for enhanced therapeutic potential.[1-4] **CPs** that can be cleared from the body following executing their function, i.e. biodegradable, look especially valuable.

In this work we have created and studied new "hybrid" **CPs** - co-polymers of "parent" homo-polymers -amino acid L-arginine based **CPs (Arg-CPs)** and endogeneous tetraamine spermine based **CPs** (**Spm-CPs**), which we have previously reported [5-8] in order to combine valuable properties of the said parent polymers. In particular, a high compatibility with eukaryotic cells of the **Arg-CPs, and** a high and selective transfection activity of the **Spm-CPs** desirable for the application in gene therapy.

The goal hybrid **CPs** with general formula depicted below in Scheme 1, were synthesized as *p*-toluenesulfonic acid salts by solution active polycondensation[8].



y = 2,8

k/l = 0.00/1.00, 0.10/0.90, 0.25/0.75, 0.50/0.50,1.00/0.00

Scheme 1. Arg and/or **Spm** based **CPs** synthesized by SAP

The new **CPs** were characterized by standard chemical-physical methods such as UV, FTIR and ^{1}H NMR spectroscopy, size exclusion chromatography (SEC), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and circular dichroism (CD) spectroscopy.

The new **CPs** are expected to have a high compatibility with eucaryotic cells along with a high and selective transfection activity. Appropriate biological studies are in progress now.

Acknowledgement: This work was supported by the joint grant from the Science and Technology Center in Ukraine and Shota Rustaveli National Science Foundation of Georgia **#6298 "**New biodegradable cationic polymers composed of arginine and spermine - versatile biomaterials for various biomedical applications".

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PolyChar 26 World Forum on Advanced Materials

Abstract

PLASTICISING AND MIXING ZONE OF A CO-ROTATING TWIN-SCREW EXTRUDER

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Contemporary plastics processing industry calls for the development of novel manufacturing methods for materials of prime and consistent properties. This demand gives rise to new constructional solutions for plasticizing systems which would maximize efficiency and retain optimal properties of the material processed. Polymer composites and compositions are typically manufactured by means of twin-screw extruders equipped with screw segments. This proves to be beneficial as it is possible to adapt the geometrical properties of the segments to the material processed. This study was aimed to analyse the impact of the configuration of the plasticizing and mixing zone of a EHP-2x20 co-rotatingtwin-screw extruder on the properties of the talc-filled polipropylene extrusion. The analysed zone comprised 8 triple-lobe kneading discs, i.e. 10 mm long cam discs. The variableswere the inclination angle of the pseudohelix formed by the apices of neighbouring kneading elements (0°, 30°, 60°) as well as the distance between these elements (0.5 mm, 2.5 mm, 4.5 mm). In the research plan, 5 different zone configurations were considered, located invariably at the same distance from the feed end. Additional variables included the degree of filling with talc(10%, 13%, 16%) and the rotational speed of the screws (100 rpm, 250 rpm, 400 rpm).On the basis of the measurements taken, it was possible to determine the value of the following factors analysed: mass-flow rateof extrusion, head pressure, screw drive torque, extruder energy consumption per unit, ultimate tensile strength, and the melt mass-flow rate.

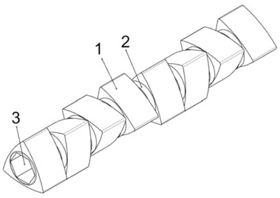

Figure 1. Example of plasticizing and mixing zone:
1- triple-lobe kneading element,
2- spacer,
3- hexagon drill for the screw core

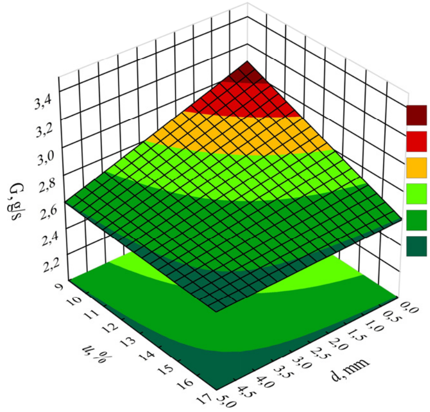

Figure 2. Response surface plots of mass flow rate of extrusion as a function of spacer width and talc content

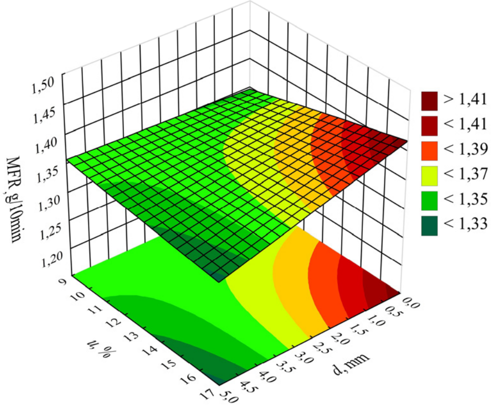

Figure 3. Response surface plots of melt mass-flow rate (MFR) as a function of spacer width and talc content

Abstract

THE ANALYSIS OF THE PRESENT AND NEW SOLUTIONS OF THE ADJUSTABLE GROOVED FEED SECTION OF THE EXTRUDER

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The paper will present the state of the art of the existent constructional solutions of the adjustable grooved feed section of a single screw extruder. This section is characterized by the fact that during the extrusion process it is possible to change the geometrical elements of the grooves without the need to stop the operation of the extruder and conduct the time-consuming exchange of the grooved sleeve. Next, different new conceptions will be presented. Selected solutions will be presented as 3D virtual models. For this reason, software Catia v5 will be used. The developed models are fully functional. They were tested for their regularity and collision occurrence. Also, virtual prototypes were created to determine the risk of any irregularities during movement. Selected models underwent numerical calculations. The range of the conducted numerical analyses included calculations concerning the estimation of the strength of construction elements exposed to the pressure caused by the transfer of polymer in the form of pellets as well as thermal calculations enabling to receive the temperature distribution as a result of friction of the material against the inner walls of the grooved section.
Also, calculations for particular models were made, in which a geometrical element was changed, e.g. the height of grooves. The results includedthe output, the average melt temperature at die exit, the pressure, the mechanical power consumption, the length required for melting, the mixing degree (quantified by *WATS*, a measure of the average strain suffered by all the particles inside the extruder) and the viscous dissipation (calculated as the ratio between the maximum and the barrel temperatures).Examples of the graphs showing the dependence of the polymer pressure along the plasticizing system and extruder head are shown in Figure 1.

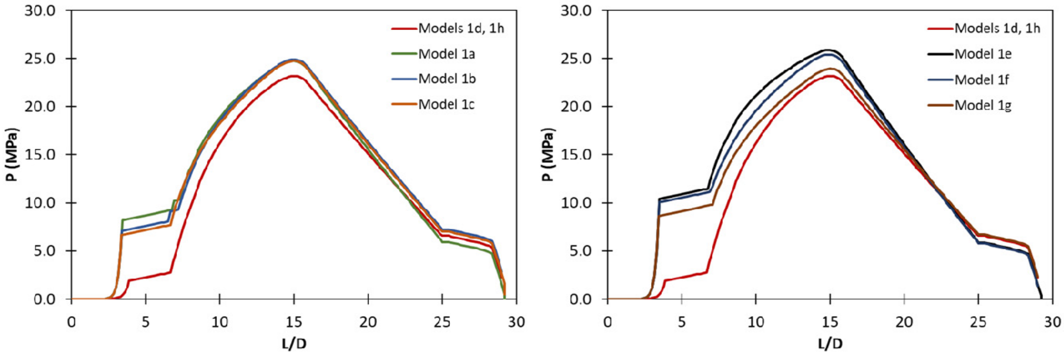

Figure 1. Pressure profiles for Solution Models 1at various heights of grooves, number of grooves 4, length of grooves 100 mm, diameter of the screw 25 mm

Acknowledgement: The project leading to these results has received funding from the European Union, Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 734205, project acronym

CAVITATION OF POLYMERS RELATED TO CHAIN ENTANGLEMENTS AND NANOFILLERS

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The presence of macromolecular entanglements determines many properties of polymer and influences cavitation. The mechanical properties of polypropylene samples with three different densities of macromolecular entanglements were examined in tensile test. The experiments were performed at temperatures from 20 to 100°C. SAXS, WAXS, DSC and SEM techniques were used to study the evolution of polypropylene internal structure with deformation. It was found that properties of polymer at yield were not changed by reduction of entanglements. However, the strain hardening phase of deformation depended on the density of molecular network formed by entanglements and the increase of stress was faster when polypropylene is more entangled. It was observed enhanced cavitation in disentangled polypropylene. The cavitation in disentangled polymer was possible not only at low temperatures, but even when the tensile deformation was performed at the temperature of 100°C.

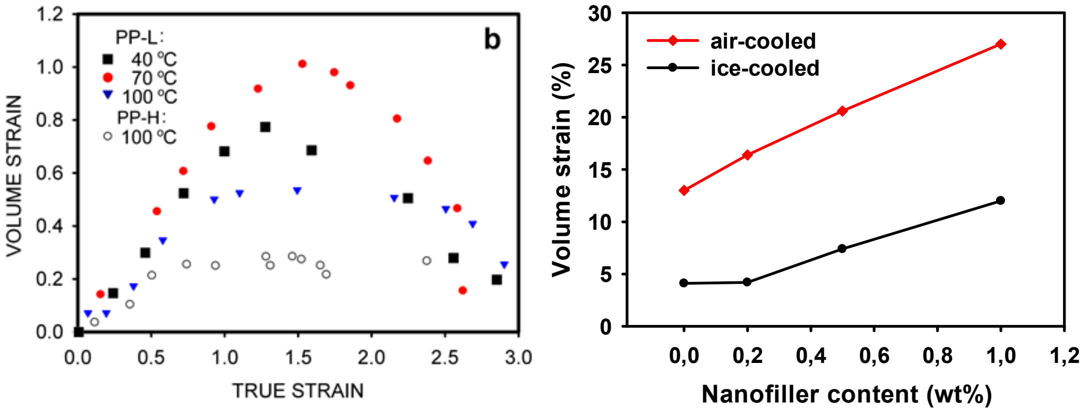
a) b)

Figure 1. a) The volume strain for disentangled PP samples tested at various temperatures and for comparison for entangled PP sample tested at 100 °C. The rate of deformation was 5%/min. b) Dependence between volume strain (at local strain of 100%) and nanofiller content in the HDPE/Al_2O_3 nanocomposites cooled in air and in iced water.

The impact of nanofiller on the cavitation process in nanocomposites was revealed, based on high density polyethylene (HDPE) and aluminum oxide (Al_2O_3) nanopowder with grains having 15 nm in diameter, as well as the influence of preparation conditions on the minimization of cavitation process.

The preparation conditions had a significant influence on the final materials properties and the rate of cavitation process. Nanomaterials with ≤ 1wt% of Al_2O_3 nanopowder prepared using ice-cooled method revealed much higher elongation at break, slightly lower yield point and significantly reduced cavitation process, compared to the air-cooled materials. More extensive cavitation appeared in the air-cooled system, composed of much thicker and more perfect crystals, causing a significant decrease in tensile strain at break of nanocomposites. SEM analysis led us to conclude that the minimum particle size able to cavitate HDPE was around 110 nm with no cavities around single nanograins. We propose their further use as nanofoams with various levels of cavitaties.

Acknowledgment: The projects were financed from the funds of the National Science Centre, Poland on the basis of the decision number UMO-2015/19/B/ST8/03870 and of the decision number 2016/23/B/ST8/03509 to make this research possible.

Abstract

GENERATING ENHANCED PHOTOCURRENT USING P(SNS-NH$_2$)/CdS NP/CALIXARENE STRUCTURE MODIFIED GOLD ELECTRODE SYSTEMS

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Two novel calix[n]arene-adorned gold electrodes producing high photocurrent intensities were successfully constructed by embedding gold electrode surfaces with both P(4-(2,5-di(thiophen-2 yl)-1H-pyrrol-1-yl)benzenamine), P(SNS-NH$_2$), conducting polymer and 4-mercaptoboronic acid-functionalized semiconductor CdS nanoparticles to facilitate the binding of calix[n]arene sulfonic acids with nanoparticles. This structure enabled an electron transfer cascade that both induced effective charge separation and efficiently generated photocurrent. The prepared electrodes were used to generate photocurrent by relying on the host–guest interactions of guests Br_3^- and I_3^-, which if positioned well in the system was able to fill electron–hole pairs of CdS nanoparticles. As a result, host calixarene derivatives crucially held Br_3^- and I_3^- ions at a substantial distance from CdS nanoparticles. Furthermore, the effects of various calixarenes on the photocurrent obtained indicate that the generation of photocurrent intensities by the system depends on the cavity sizes of calixarene derivatives, which provide an essential center for Br_3^- and I_3^- ions (Figure 1) [1].

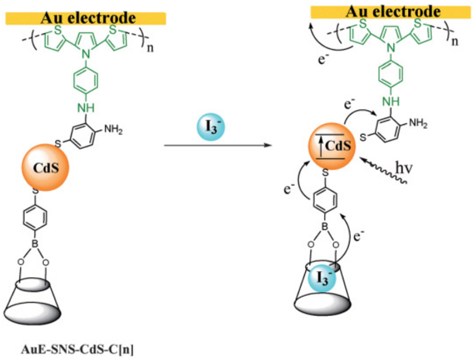

Figure 1. Generation of photocurrent by the P(SNS-NH2)-CdS NP-Calix[n]arene modified gold electrode in the presence of I_3^-.

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EFFECT OF ADDITION OF RECYCLED EPDM SIZE ON THE BENDING PROPERTIES OF POLYPROPYLENE

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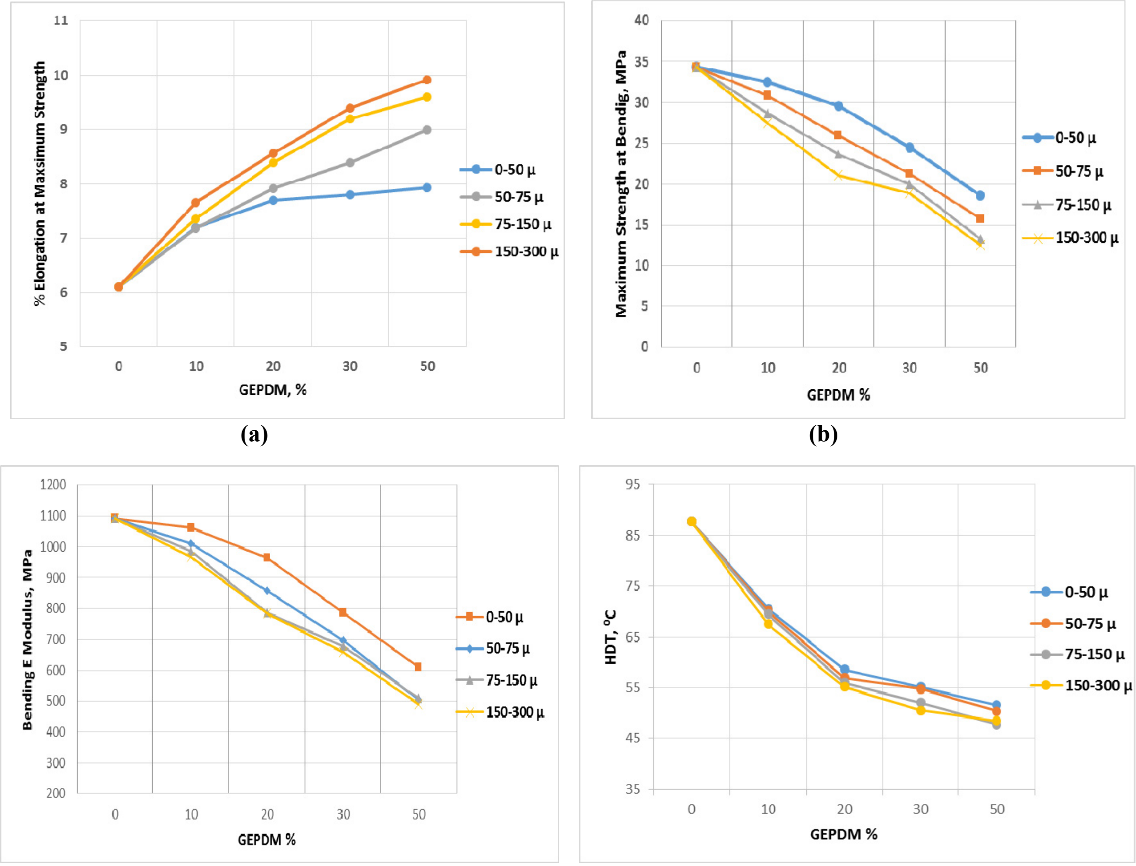
EPDM (ethylene propylene diene monomer) is an important synthetic rubber and is used in significant quantities in many different sectors. In parallel with the increase in the amount of usage, EPDM waste is emerging. Such materials do not have the possibility of being melted and processed again due to their cross-linking. EPDM waste is usually consumed in the form of fuel, which is already a significant loss for the import-based plastic industry. Another method of evaluation of EPDM residues is to add them to different polymers by bringing them into small dimensions [1-3]. The aim of this study is to investigate the effect of waste EPDM powders on the bending properties of polypropylene EPDM mixtures. Ground EPDM (GEPDM) with four different sizes (0-50, 50-75, 75-150 and 150-300µ) were added to polypropylene with four different weight ratios i.e. 0% 10%, 20%, 30% and 50% via extrusion method. Test samples were prepared out of those mixtures by injection molding.



(a) **(b)**

(c) **(d)**

Figure 1. Effect of ground EPDM size on the bending properties of polypropylene, (a) %Elongation at maximum strength, (b) Maximum strength at bending, (c) Bending E modulus, (d) HDT

The main conclusion out of this study was that the GEPDM can be used as filler in polypropylene. From the results it was found that elongation at maximum strength increased with the increasing GEPDM. Maximum strength at bending, bending E modulus and HDT values decreased. However, elongation at maximum strength increased, maximum strength at bending, bending E modulus and HDT values decreased with the increasing GEPDM size.

Acknowledgement: This work was supported by Marmara University, Commission of Scientific Research Projects under Project FEN XXX.

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EFFECT OF CARBON NANOPARTICLES ON PROPERTIES OF POLYETHERIMIDE FIBERS

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It is well knownthat aromatic polyimides possesshigh thermal stability, excellent mechanical and electrical properties, as well as chemical resistance. Nowadays, researchersare focusing on polyimide films, laminates, resins and coatings. However, the other application of polyimides gaining more attention is fibers. Oriented polyimide fibers, in contrast to films, allow one to enhance mechanical properties of the material by using nanoparticles with a high anisometry degree. Thus, the aim of the present work was to obtain thermally stable nanocomposite fibers based on polyimide matrix modified with carbon nanoparticles and to study their structure and properties.

The heat-resistant amorphous polyimide of the trademark ULTEM 1000 (SABIC Innovative Plastics) was studied in the present work. Vapor-grown carbon nanofibers (VGCF) with diameter ~ 150 nm, length ~ 10-20 um (Showa Denko) and single-wall carbon nanotubes (SWCNT) with diameter ~ 1.5 nm, length - 1.5 um (OOO «Carbon ChG») were usedto increase the mechanical characteristics of the polymer fibers.

Nanocomposite fibers based on polyimide were produced with the help of twin screwmicroextruder. In order to increase the, the polyimide fibers were subjected to an orientation thermal drawing at 230°C.

The SEM study mechanical properties revealed very good distribution of the carbon nanofillersthroughout the volume of the polyimide fiber. The mechanical testing of non-orientednanocomposite fibers showed that the introduction of VGCF led to an increase in tensile strength andmodulus, while deformation at break decreased. High-temperature drawing allows obtaining polyimide nanocomposite fibers with significantly increased mechanical properties. Similar effect was observed on the fibers with added SWCNT. However, in order to reach such level of mechanical properties, an amount of introduced SWCNT can be noticeably lower (10 times less).

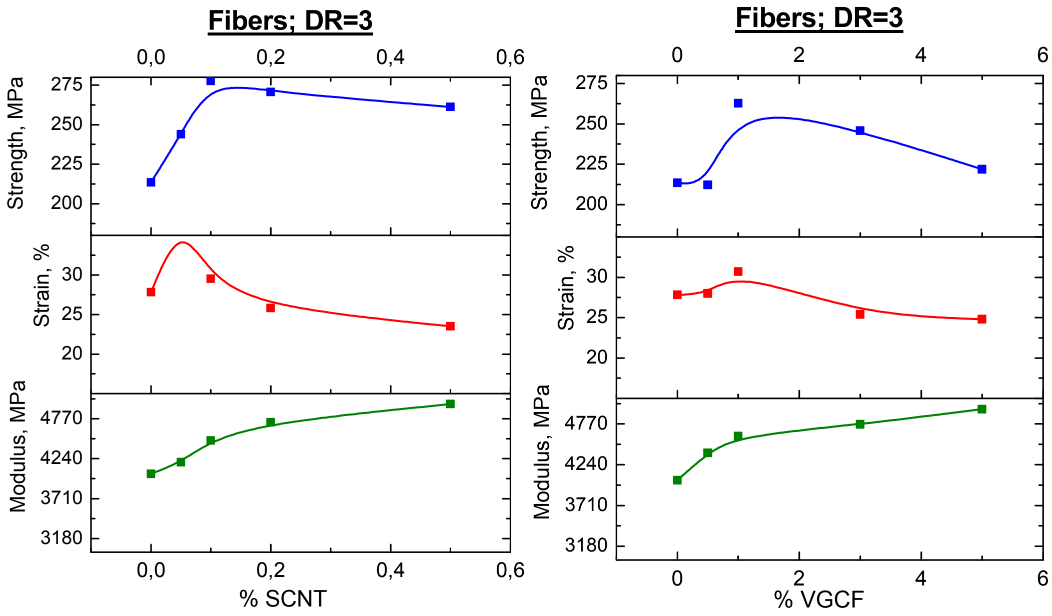

Figure 1. Influence of incorporated carbon nanofillers on mechanical characteristics of polyimide fibers.

Acknowledgement: The present study has been supported by the Russian Foundation for Basic Research (grant No. 18-03-00963 A).

POLYPROPYLENE COMPOSITES BASED ON OLIVE PITS (OPP): HOW THE FILLER RATIO AFFECTS THE COMPOSITE MECHANICAL PROPERTIES

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Wood plastic composites are made from wood and annual plant fiber or flours, mixing with plastics materials. Wood plastic composites provide better properties than resources that form it. This renewable material has many utilization areas because of outstanding properties such as enhanced strength, stiffness, creep, physical and mechanical properties and dimension stability. As replacements for conventional synthetic fibers like aramid and glass fibers, natural fibers are increasingly used for reinforcement in thermoplastics due to their low density, good thermal insulation and mechanical properties, reduced tool wear, unlimited availability, low price, and problem-free disposal. The purpose for the addition of cellulose-based fillers to thermoplastics is to reduce the cost per unit volume and to improve stiffness. An investigation was carried out on the effects of olive pits powder ratio on the mechanical and morphological properties of polypropylene polymer composites. Olive pits powder (OPP), in four different concentrations (5, 10, 15 and 20 wt %), was added to PP to produce composites. The properties, including elasticity modulus, tensile strength at break, yield strength, % elongation, hardness and Izod impact strength of the composites were investigated.

Table 1. Composition of the PP/OPP/MA-g-PP polymer composites formulations

Groups	PP (wt %)	OPP (wt %)	MA-g-PP (wt %)
1	100	-	-
2	90	5	5
3	85	10	5
4	80	15	5
5	75	20	5


olive pits granulation powder

Figure 1. Olive pits powder preparation

Acknowledgement: This work has been supported by the Scientific Research Project Program of Marmara University (project no: FEN-C-YLP-081117-0630).

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Abstract

SPONTANEOUS SELF-HEALING POLYURETHANES

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Polyurethanes (PU) are ranked 6th as the most produced polymer worldwide and represent high potential in various applications [1]. On use, PU-based materials are subjected to photo, thermal and mechanical aggressions, which limit their performance, lifetime and reliability. To address this problem, the self-healing concept is of great interest to design self-healing polyurethanes (SH-PUs). Indeed, based on the economic interests that represent the polyurethane market, developing SH-PUs with intrinsic ability to self-heal, like biological systems, shall represent a key-factor for more reliable, safe and durable polyurethanes [3-4]. In this work, the aim is to develop two self-healing approaches that proceed in an autonomous way. The first example is related to the possibility to heal local macroscopic damage by a confined temperature increase arising from the Joule effect [5]. The damage healing is promoted by the resistance to an electrical current at the crack tip. This new concept is demonstrated on thermo-reversible and electrically conductive poly(ester-urethane)/carbon nanotube nanocomposites derived from thermo-reversible Diels–Alder reactions between furfuryl- and maleimide-functionalized poly(ε-caprolactone) (PCL)-based precursors. Electrically conductive materials are then obtained after incorporating multi-walled carbon nanotubes into the thermo-reversible networks using reactive extrusion. Under mild electrical conditions, temperature in the range of the retro-Diels–Alder reaction can be obtained near the damaged site. The obtained results reveal the potential of this new approach for healing materials locally, while maintaining the overall material properties.

In view to achieve low-energy demanding healing, polyurethanes structures with appropriate urea that respond spontaneously to ambient humidity is demonstrated as a second example [6]. Self-healing process relies on the incorporation of hydrogen-bonded urea moieties along the polyurethane backbone. After a cut (named "free-urea" hereafter), a spontaneous formation of supramolecularly-driven water-urea clusters that bridge the crack was achieved, enabling to achieve the complete gap closure when water gets evaporated. This approach was illustrated with a non-hygroscopic urea and polypropylene glycol-based polyurethane by repetitive scratch-healing tests at different degrees of humidity and confirmed with a combination of macroscopic (tensile, quartz microbalance), theoretical and local probe spectroscopy technics (Internal Reflection Infrared Imaging). This model system shows the possibility of using moisture as trigger of healing.

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DEVELOPMENT OF EPOXY/CNT ADHESIVES WITH HIGH GLASS TRANSITION TEMPERATURE AND MECHANICAL PROPERTIES

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In this study, the epoxy/cnt adhesive having high Tg and mechanical properties have developed. The CNT/epoxy composites were prepared by mix CNT with PVP, as surfactant. The different composition of cnt was used from 0 to 2% at 0.5 interval. Of these, 1.5% epoxy/cnt sample Epoxy/CNT composite having high properties. The DMA result indicates 1.5% sample having high glass transition temperature. Strong interfacial adhesion facilitates efficient load transfer between epoxy and CNT resulting in improved mechanical property. Also after a higher concentration, the properties decreases due to agglomeration of CNT because of increase in resin viscosity. Evaluating the three point bending test and tensile test results, the 1.5% cnt concentration sample displays high mechanical properties. The scanning electron microscopy proves that in the 1.5% sample contain good dispersion of cnt in the epoxy matrix. In the contact angle measurement, the 1.5% cnt sample partake more hydrophobic nature From the water absorption test, the cnt added sample is having less hydrophilicity.

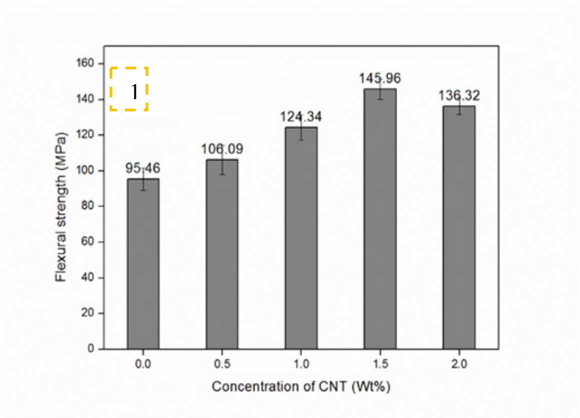

Figure 1. Flexural strength with wt (%) cnt concentration.

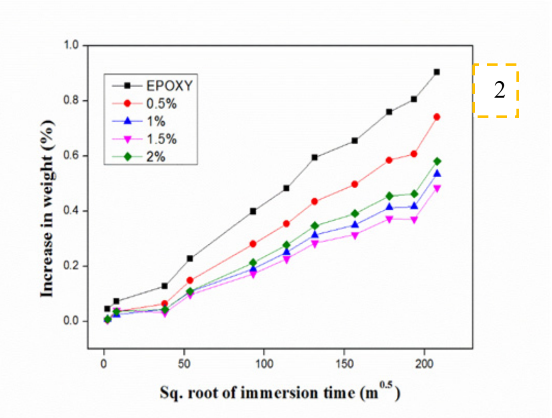

Figure 2. Water absorption for CNT/epox

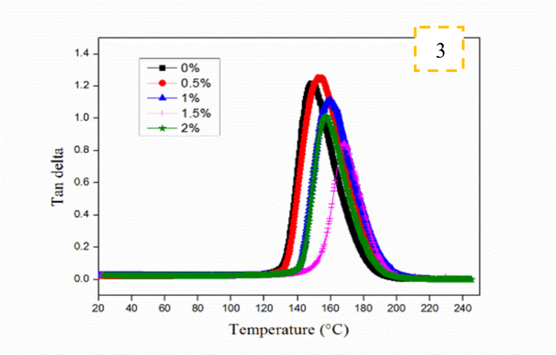

Figure 3. Tan delta versus temperature.

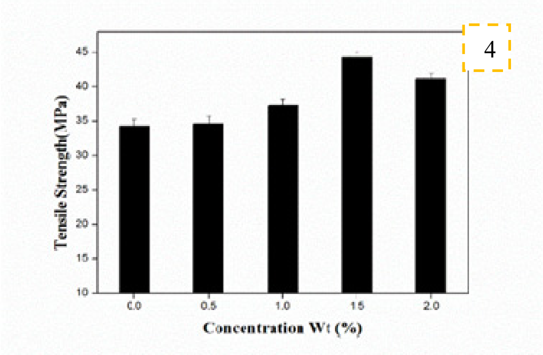

Figure 4. Tensile strength with wt (%) cnt concentration

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Abstract

EFFECT OF MICROSTRUCTURE ON THE ELECTRIC CONDUCTIVITY OF ORIENTED POLYMER COMPOSITES

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The well-known spine probe method based on electron paramagnetic resonance (EPR) is used for investigation of the micro-structure of the oriented polyvinyl alcohol and some composites based on it. After introduction of nitroxide stable radicals by diffusion in oriented with different degree thin polymer films the samples were tested by noted method via definition of the correlation times of stable radicals rotation around their axes. There were measured two parameters: electrical resistance and the stable radical concentrations in each elemental square of the central strip.

The electric conductivity of each elemental square of this strip was measured with use of impedance spectroscopy. It was determined the value of electrical resistance for each local square from one side up to second side in terms of unit volume of the squares with use two contact method [1]. The measuring of ESR spectra of the stable radicals localized in each elemental square of the strip was provided. With this aim the probes from each squares of the strip were cut and then the EPR spectra of stable nitroxide radicals were recorded by standard method on the EPR spectrometer at room temperature. Values of rotational diffusion coefficient of the radicals in the polymer matrix has been determined using formula $D_r = 1/6\tau$, where τ is a correlation time of radical rotation. With use of the spatial atlas of EPR spectra obtained via theoretical calculation of all experimentally permissible EPR spectra of the nitroxide radicals it is possibility of obtaining of numerical estimation of the corresponding correlation time and diffusion coefficient of the stable radicals in the polymer medium [2].

It is established that the free radicals concentration and their correlation time in local regions of the films is the lower the higher is the orientation (stretching) degree of the films. Noted processes correlate with analogical ones in the same polymer containing high dispersive electrical conducting filler (carbon black). In this case the diffusion of the free radicals to the polymer matrix is more difficult than in pure polymer - the significances of correlation time and diffusion coefficients of stable radicals decrease because of additive interactions of these radicals with filler particles. The dependence of electrical resistance on the local regions coordinates of the stretched film (in the stretching directions) has e bell like shape and correlates with change of the density of corresponded regions.

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+DIELECTRIC PROPERTIES OF THE POLYMERIC FUNCTIONAL COMPONENT USED IN THE ELECTROLUMINESCENT LAYER

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When creating electroluminescent layers it is necessary to use a functional element - a polymer binder with a special electrophysical property, which include a high dielectric constant ε and a small value of the dielectric loss tangent tanδ [1]. The main purpose of the binder, in the radiating layer, is to create barrier regions and the concentration of the electric field at the boundaries of the phosphor grains, the strength of which is proportional to the permittivity of the binder. The presence of a large value of this parameter allows, at a fixed level of brightness, to use a low operating voltage of the light source. Recently, it has been found that the most preferred binder dielectric for electroluminescent layers based on zinc sulfide is a cyanic ester of the polyvinyl alcohol (CEPA) [2], characterized by a high content of mobile cyanethyl groups - ((CH2) 2-CN) which provide high polarizability of binding material at a small value of dielectric losses. The practical application of electro-luminescent light sources is based on the stability of their main operating parameters during of explo-itation. A local increase in temperature can also occur when dissipative losses take place that cause a significant change in the mechanical and electrical properties. Investigations of temperature and frequency dependence can contribute to the determination of the mechanism of dielectric relaxation [3]. In the present work, an experimental study of the dielectric parameters of the CEPA layers formed on conductive transparent substrates was carried out by applying a controlled concentration from a solution of dimethylformamide. Measurements of the capacitance C and tgδ of the layers of the CEPA were carried out in a weak alternating field in the frequency range f = 1-20 kHz and at a temperature range T = 296-348 K using an immittance meter E7-20. Heating of the sample was carri-ed out in a muffle furnace Nabertherm B180 at a fixed frequency with an average temperature change rate of 1 grad/s. In Fig. 1 (a) shows the temperature dependence of the electrical capacity of the test sample for three values of the frequencies of the measuring field (1, 10, 20 kHz). It can be assumed that the observed increase in capacitance with increasing of frequency is associated with the displacement of mobile charge carriers within of inhomogeneity ragion and the formation of a sufficiently high concentration of relaxators. The hydroxyl groups -OH, which according to the IR spectroscopy data belong not only to the binder but also to the absorbed water and belong to the relaxing elements in the structure of the CEPA. It should be noted that the CN-groups with the content of the unpaired electron pair are characterized by a pronounced dipole structure, which contributes to the basic dielectric response. The effect of temperature (Fig. 1 (b)) on the behavior of the dielectric parameters is also revealed in an increase in the value of tgδ with an increase of temperature, especially pronounced in the low-frequency range, which leads to an increase in dispersion. An analysis of the observed relaxation process within the framework of the Cole-Cole model representation indicates the existence of a non-Debye relaxation mechanism with a wide distribution of relaxation times.

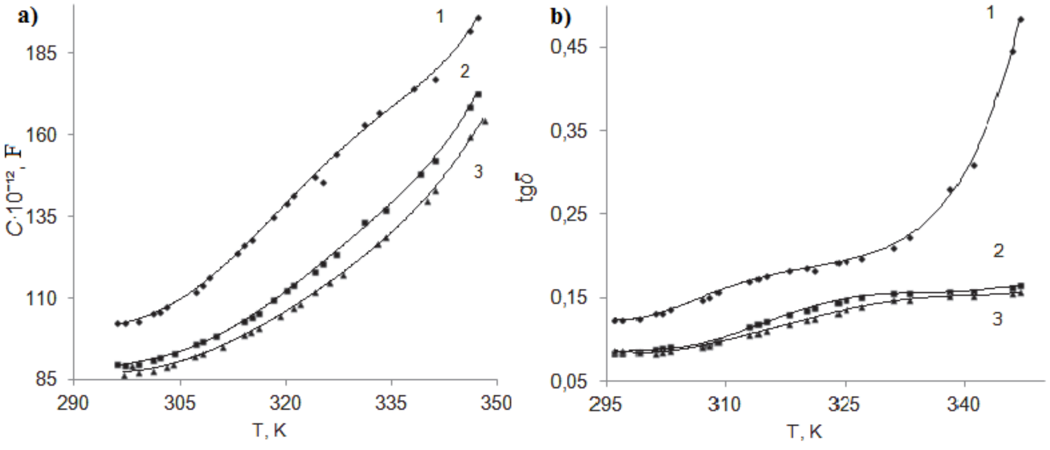

Figure 1. The temperature dependence of the capacitance (a) and dielectric losses (b) of the CEPA sample: 1 - 1, 2 - 10, 3 - 20 kHz.

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ENHANCED BATTERY LIFE THROUGH ASSEMBLY INJECTION MOLDING OF HYBRID POLYMER-ALUMINUM SEALING STRUCTURES

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Nowadays, the environmental impact of a globally increasing population and as a consequence thereof the rising demand for individual mobility is tremendous.Subsequently, if this demand is covered by cars with combustion engines, it would contribute evidently to increasingly unhealthy environmental conditions in capital cities like it has been observed over the past decades[1].

In order to maintain mobility, without a further increase of air pollution in exponentially growing cities, it is essential to e.g. consider electrically driven vehicles as a substitute for conventional fuel driven vehicles.

A crucial aspect, when it comes to electro mobility and thus to electrically driven cars and battery technology, is the durability of battery cells, which directly limits the eco-friendliness of the electrical concept when it comes toindividual mobility[2].

The battery capacity and by association the battery lifetime is significantlyreduced with the contamination of the battery electrolyte, especially when used in aharsh application environment e.g. electric car (Figure 1).

Therefore, a well designed and manufactured sealing of the battery poles, whichprovides seal tightness to prevent leakage and oxidation as well as water take-up of the electrolyte from the environment is the basis for the realization of efficient electrically powered vehicles with low environmental impactthrough enhanced battery life.

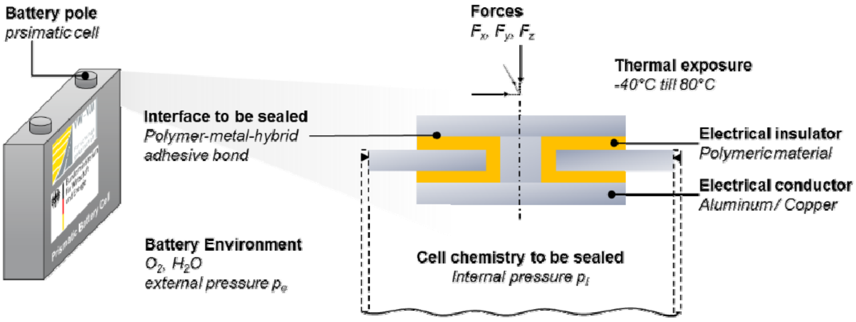

Figure 1. Stresses on the sealed poles of a sealed battery cell

In this paper, a conventional battery sealing technique is investigated and compared to an innovative and more efficient approach. A conventional battery sealing comprises of a complex assemblage and is based on a force fit between aluminum and polymer, that results in a reduction of the sealing potential over time due to stress relaxation in the polymeric component. The innovative approach of this study exhibits an adhesive bond in the polymer-aluminum interface, realized through assembly injection molding, and thus excels the short and long term sealing properties of a conventional sealed battery. The newly developed design and manufacturing principle resulted in an up to 230 times better sealing performance during helium leak test compared to a conventional battery sealing.

Compared to a force fit, the realization of an adhesion bond requires relatively complex knowledge of the aluminum surface characteristics and the polymer material composition as well as their interaction during assembly injection molding. Potential process influences on the adhesion strength and seal tightness of polymer-aluminum hybrids were investigated.Additionally the effect of pre-treatment methods on the aluminumand adhesion modification of the polymer material were taken into consideration. The aluminum surface was characterized using contact angle measurements, white light interferometry, scanning electron microscopy and X-ray photoelectron spectroscopy. The obtained adhesion strength was evaluated using double lap shear test specimens.It is shown that the nano scaled surface structure and chemical composition of an aluminum substrate and its physical interaction in combination with an adequately chosen polymeric material defines the achievable adhesive strength of an aluminum-polymer hybrid.

The results of the research provide a better understanding on the influence of the composition of aluminumalloy substrates on the achievable adhesive bond in polymer-aluminum hybrid structures produced by assembly injection molding. The elaborated findings enable for a highly efficient manufacturing of sealed battery cells.

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Abstract

NOVEL THEORETICAL SELF-CONSISTENT MEAN-FIELD APPROACH TO DESCRIBE THE CONDUCTIVITY OF CARBON FIBER FILLED THERMOPLASTICS

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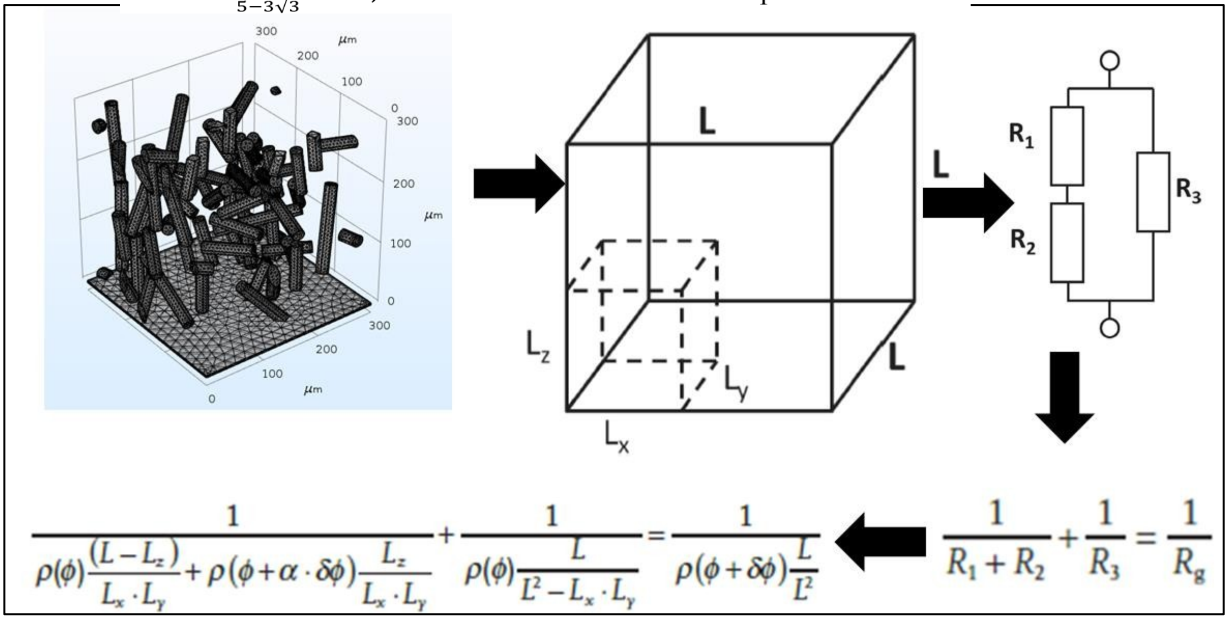
A novel theoretical approach is shown which yields a non-linear differential equation for the resistivity ρ of carbon fiber filled composites below the percolation threshold as a function of the volume fraction of the filler and the fiber orientation. The solution of the equation is given analytically and a particular value for the exponent predicted. The theoretical concept can be transferred to other composite properties.

$$\rho(\phi) = \rho_{Matrix}\left(1 + \left(\left(\frac{\rho_{Filler}}{\rho_{Matrix}}\right)^{\frac{1}{n}} - 1\right) \cdot \phi\right)^{n}$$

with $n = \frac{1-3\sqrt{3}}{5-3\sqrt{3}} \approx 21{,}39230444$ for isotropic oriented filler.



$$\frac{1}{\rho(\phi)\frac{(L-L_z)}{L_x \cdot L_y} + \rho(\phi+\alpha\cdot\delta\phi)\frac{L_z}{L_x \cdot L_y}} + \frac{1}{\rho(\phi)\frac{L}{L^2 - L_x \cdot L_y}} = \frac{1}{\rho(\phi+\delta\phi)\frac{L}{L^2}} \Leftarrow \frac{1}{R_1+R_2} + \frac{1}{R_3} = \frac{1}{R_g}$$

Figure 1. Scheme of the approach

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Abstract

DEVELOPMENT OF ACCELERATED METHODS FOR THE ISOLATION OF GRAPHENE OXIDE FROM REACTION MIXTURE

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We have studied some issues of isolation of graphene oxide (GO) from reaction mixture. By the oxidation of graphite powder (50 µm) at 45-50°C with potassium permanganate in sulfuric acid and by further decomposition of reaction mixture with water GO suspension is obtained, that contains potassium, manganese (II) ions and sulfuric acid, concentration of which reaches 55-58% (w/w). Isolation and purification of GO from an acidic solution is a long and time-consuming process. The main part of the above impurities can be removed by diluting the reaction mixture with water and decanting (4-5 times). Reducing GO losses as a result of decantation is important, and it reaches 12-17%. When the pH increases (pH 4-6), the GO sedimentation rate is significantly reduced, and it takes several days to complete. Vacuum filtration of such suspensions is a very slow process. To accelerate the sedimentation/flotation process, we tested many reagents, including surface-active substances (surfactants, cationic, anionic, nonionic), organic compounds, inorganic acid esters, complexones, etc. It has been found that the partial flotation of GO from the reaction mixture is possible with trihexyl phosphate, and tricresyl phosphate causes its sedimentation, which can be explained by the difference in densities between the two substances and water and the rinsing ability of GO. From strongly acidic solutions, GO is rapidly precipitated by low-molecular polyacrylic acids and their sodium salts (2-10 min). At the same time, the addition of LABSA in the reaction mixture results in the flocculation of GO and the obtaining of a stable colloidal solution. It is confirmed that the rate of flotation and sedimentation of GO from the reaction mixture depends on the methods of graphite oxidation, the particle size of the graphene oxide, the concentration of reagents and the composition of the suspension.

Abstract

PREVENTING THERMAL DEGRADATION OF PVC INSULATION BY MIXTURES OF CROSS-LINKING AGENTS AND ANTIOXIDANTS

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Poly(vinyl chloride) (PVC) wire and cable insulation has poor thermal stability, causing the plasticizer to separate from the PVC chain and produce an oily residue, lowering the tensile elongation at break and thus increasing brittleness. We have added 4 wt.% of three different types of cross-linking agents and antioxidants, as well as mixtures of both, to improve the thermal stability of the plasticizer and tensile properties of PVC after thermal exposure. We performed tensile tests, tribological tests, profilometry, scanning electron microscopy (SEM) and water absorption determination before and after thermal exposure at 136°C for 1 week. After adding the agents, elongation at break increased by 10 to 20 % while the wear rate and water absorption were lower than for the control sample. Less voids are seen in the SEM images after adding these two kinds of agents. The thermal resistance of the PVC cable insulation is best enhanced by combinations of cross-linking agents and antioxidants.

Abstract

CHEMICAL TRANSFORMATION OF CARBON NANOSTRUCTURES AND IT'S USING IN NANOCOMPOSITES

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Discovery of graphene as important materials carried out the coup in nanotechnologies. Great interest to graphene testifies lots of articles, which are published monthly in the scientific literature. It seems that less attention pay to chemical properties of carbon nanostructures. Carbon nanostructures have different functional groups that have ability to react with various organic and inorganic compounds [1]. That' why it is possible modification of carbon nanostructures by different compounds and then obtained organic and inorganic composites based on above mentioned modified nanoparticles. For example, chemically active metalorganic compounds of I, II and III groups' metals can react to all functional groups which contains carbon nanostructures. For purpose graphene suspension in DMF (obtained modified Hammers' method) has carried out by thermally at 170^0C (for removing of adsorbed water) then have added triisobutylaluminum solution in toluene. In a result isobutene has excreted at ambient temperature, It's mean that aluminum connected to carbon nanostructure by oxygen bridges. We have get $C_8O_2(OH)_2$ as estimated formula of graphene for quantitative calculation.

Modified graphene oxide suspension by alumoorganic compunds in DMF has mixed with alumina suspension in toluene then homogenization process carried out in nanomill. Concentration of graphene oxide suspension is 1.5%w in composite. Obtained mixture has dried and then consolidated in high temperature vacuum furnace at 14500C under pressure 478 kg/sm^2.

Microhardness is 15.88 GPa (loading - 200 g) of obtained ceramic materials. Microhardness is 12.025 GPa of ceramic materials obtained from pure alumina in same condition. Testing was carried out using the Oliver-Pharr method according to ISO-14577 standard. We are continuing works to determination optimal concentration of modified graphene oxide and researching other physical-mechanical properties [2].

Table 1. *Microhardness of ceramic materials*

№	P, gf	hmax, µm	DHV	DHV, GPa	Eit, GPa	HV	HV, GPa
Ceramic with modified graphene oxide (a)	200.726	2.47	1620	15.88	374.1	1845	18.08
Ceramic based on pure Alumina (b)	200.765	2.8485	1227	12.025	238.1	1777	17.41

Acknowledgement: The financial support of the Georgian National Science Foundation in Tbilisi, Grant №STCU 6212, is gratefully acknowledged.

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A VERSATILE SYNTHETIC APPROACH TOWARDS HYPER-CROSSLINKED RESINS AND NANOCOMPOSITES WITH TAILORED ADSORPTION PROPERTIES

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Hyper-crosslinked resins are high surface area polymers extensively studied for their excellent adsorption properties combined to high thermal and chemical stability. These resins are usually prepared by suspension polymerization followed by hyper-crosslinking.[1,2]

In this work, innovative microporous organic polymers (MOP) and nanocomposites (MOPN) were prepared through a new synthetic approach. High surface area MOP and MOPN were obtained by extensive hyper-crosslinking of a precursor polymer or nanocomposite prepared by bulk polymerization. This procedure permitted to obtain MOPN with good dispersion of high surface area functional nanofillers, such as graphene-based nanofillers, thus opening the way to a new class of hyper-crosslinked nanocomposites.[3]

In particular, MOPN based on styrene, vinylbenzyl chloride and divinylbenzene, containing graphene nanoplatelets (GNP) or surface modified graphene oxide (GO), were obtained. The use of GNP allowed modulating the pore size distribution and the adsorption properties of the HCL polymers. As concerning GO, it was preliminarily functionalized by surface grafting of poly(vinylbenzyl chloride), to improve the nanofiller dispersion in the polymer matrix and induce the participation of the nanostructured filler to the hyper-crosslinking reaction through the chloromethyl groups of the grafted polymer layer. With this approach, surface modification allowed creating new MOPN based on a peculiar microporosity, selectively localized at the polymer/filler interface.

MOP and MOPN were fully characterized by spectroscopic, morphologic, surface area and porosity analyses. The effects of the inclusion of functional nanofillers on gas adsorption and separation properties and on the adsorption of organic compounds from water solution were evaluated.

Finally, MOP and MOPN, after tailored size reduction, as schematized in Figure 1, were used as functional fillers in macroporous polymer systems, realizing a new class of composites with hierarchical porosity (macro/meso/microporosity) for environmental applications.[4]

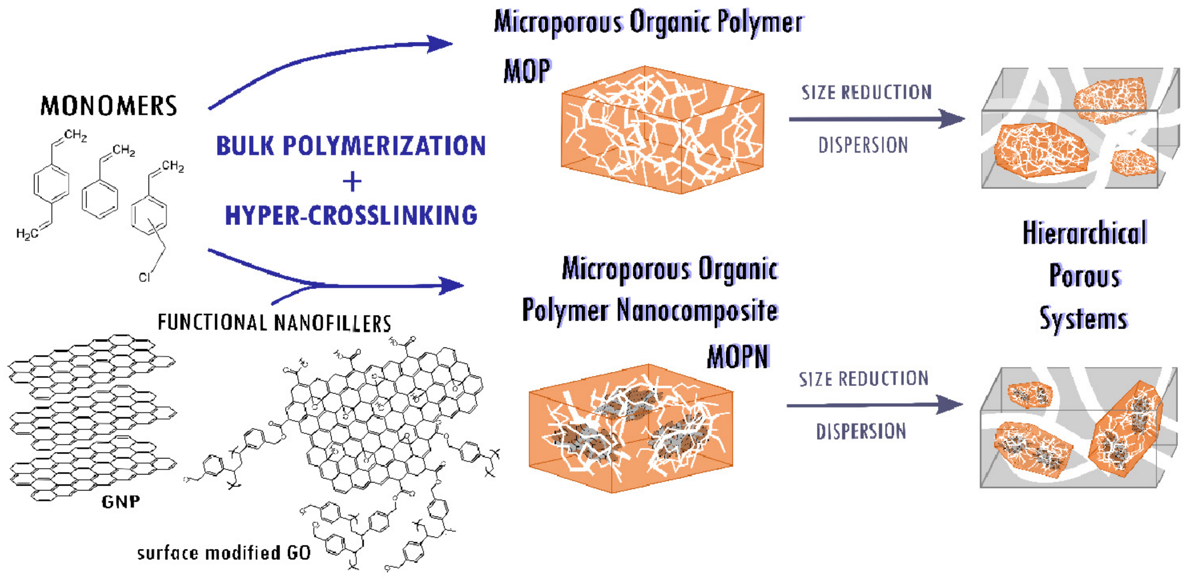

Figure 1. Innovative hierarchical systems based on macroporous polymers matrices and microporous resins and nanocomposites.

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PREPARATION AND CHARACTERIZATION OF CONDUCTING POLYANILINE CRYOGELS

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Miroslava Trchová

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One of the most important conducting polymers, polyaniline, is prepared by the oxidation of aniline with peroxydisulfate in acidic aqueous medium [1]. Among various application forms, especially conducting polyaniline hydrogels have recently attracted attention [2] When the preparation of polyaniline is carried out in the frozen aqueous solution of poly(vinyl alcohol), composite polyaniline/poly(vinyl alcohol) cryogels are obtained [3,4] (Fig. 1). In such case, the ice crystals serve as templates for the deposition of polyaniline at their interface, and they determine the porosity of future cryogel. Poly(vinyl alcohol) affords the mechanical properties. The conductivity can be controlled by the copolymerization of aniline with *p*-phenylenediamine over many orders of magnitude. The corresponding aerogels can be prepared by freeze-drying of cryogels. Their subsequent carbonization in inert atmosphere converts them to macroporous carbon enriched with nitrogen atoms.

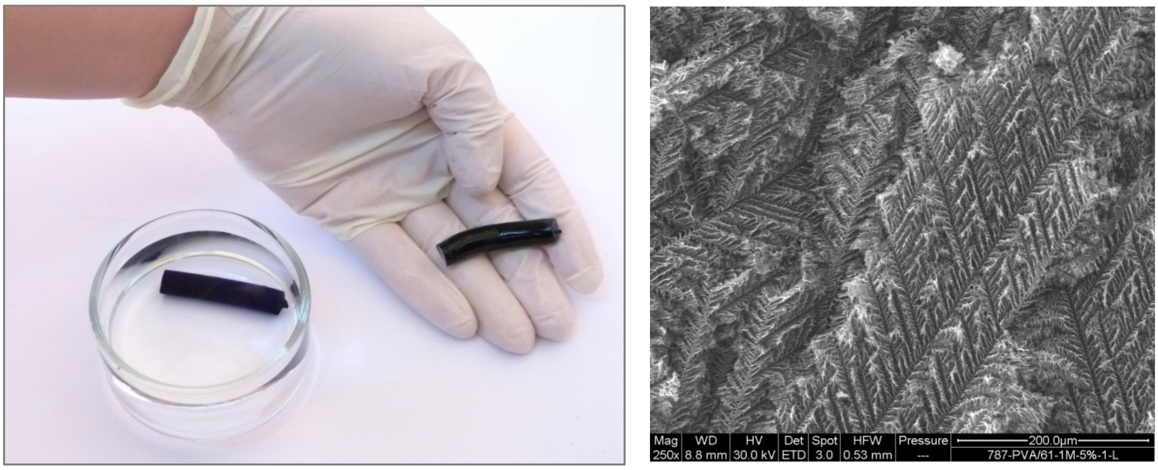

Figure 1. Polyaniline/poly(vinyl alcohol) cryogel (left) and its microporous structure (right).

Acknowledgment: The financial support of the Czech Science Foundation (17-04109S) is gratefully acknowledged.

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Abstract

POLYOLEFIN COMPOSITES WITH INCREASED RESISTANCE TO MICROORGANISMS: STRUCTURE–PROPERTY RELATIONSHIPS

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There are numerous ways by which bactericidal properties can be given to a polymer matrix: incorporation of volatile or nonvolatile bactericidal agents directly into polymers, coating or adsorbing agents onto polymer surfaces, immobilization of them to polymers by ion or covalent linkages, and the use of polymers that are inherently bactericidal. The antimicrobial activity of silver and copper is well established, especially when metals are applied in the form of nanoparticles (NPs). Silver and copper NPs have strong inhibiting and antimicrobial effects as well as broad spectrum of biocidal activities. However, the mechanism of antibacterial effect of silver or copper is still not fully understood. It is generally believed that interactions of silver or copper with thiol groups play the essential role in deterioration of bacteria. Nanoparticles of these metals are a new group of bactericidal materials due to the different physicochemical properties as compared to the bulk materials. The bactericidal efficiency of these metals increases with decreasing their particle size due to their larger specific area. The agglomeration of silver or copper NPs or colloids can result in the decrease in their bactericidal and fungicidal properties. The problem of NPs stability was solved by the development of spherical silica containing immobilized silver or copper NPs.

The influence of spherical silica containing immobilized silver (Ag-SiO_2) or copper (Cu-SiO_2) nanoparticles on the structure as well as thermal, mechanical and bactericidal properties of poliolefin composites will be discussed. All materials were compounded in a co-rotating twin-screw extruder and then injection molded. Maleated polyolefin were used to enhance the interaction between silica and polymer matrix, which faciletated the dispersion of silica. The composites were characterized with scanning and transmission electron microscopy (SEM, TEM). The crystallization behavior and thermal decomposition were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The mechanical properties were characterized by tensile, flexural, and impact tests as well as dynamic mechanical thermal analysis (DMTA). The ability of silica to give antimicrobial activity to polyolefin was also investigated and discussed. SEM and TEM results revealed that silica NPs aggregates were in general distributed homogenously. However, Ag-SiO_2 show lower degree of agglomeration than Cu-SiO_2 NPs. DSC results showed that the incorporation of silica NPs

could decrease the melting temperature but increase the crystallization temperature, and could lower the crystallinity degree. Moreover, the homogenous distribution of silica particles significantly affected the thermo-oxidative degradation of the composites. Cu-SiO_2 particles of 60 nm dimensions showed the best thermal stability, a maximum increment of 86 °C was obtained compared to pure polyolefin. DMTA results were in good agreement with the findings of the morphological and thermal studies. Improved stiffness indicating very good interfacial adhesion was observed. Excellent activity against different kinds of bacteria (*Escherichia coli*, *Staphylococcus aureus* and *Salmonella typhimurium*) has been proven.

Acknowledgement: This work has been financially supported by project no. UDAPOIG. 01.03.01-00-073/08-00 co-financed by EU (European Regional Development Fund).

Abstract

METAL-CONTAINING NANOPARTICLES IN MALEINIZED POLYETHYLENE MATRIX

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One of the perspective directions in a science of the polymers and material science of last years is the development of principles of preparation of the polymer nanocomposites, which are the newest type of functional materials and can be used in very various spheres of application [1,2].

Recently it is appeared a considerable interest to the composition materials on the basis of polymer matrices and nano-sized particles of metals, which has been stipulated by wide spectrum of their application – from catalysis to nanotechnology in information technique.

The development of nanotechnology opened the possibility of carrying out of the investigations in the field of composition nanomaterials and now allowed to move to the creation and use of advanced polymer materials for sensors, catalysis, nanoelectronics, etc [1].

A use of the metal nanoparticles of d-valency (zinc, cobalt, nickel, etc) in the polymers allows to prepare principally new materials, which find wide application in radio-, and optoelectronics as magnetic, electroconductive and optical media [2].

This work has been devoted to the mechano-chemical method of preparation of the metal-containing nanoparticles in maleinised polyethylene matrix without use of solvents by decomposition of salts of the organic acids in a medium of polymer in the conditions of the high shear deformations and investigation of properties of the prepared nanocomposite.

By a method of high-speed thermal decomposition of the metal-organic compounds in the conditions of the high shear deformations there have been prepared the metal nanoparticles in matrix of polyethylene of high pressure in two stages. At the first stage at temperature 130-140°C on laboratory rolls it was made the binary mixture of polymer and precursor. At the second stage the mixture was heated in microextruder "Brabender" in a medium of nitrogen at temperature 170-190°C for 10-12 min. The copper and zinc acetates were used as a precursor

The phase composition and structure of the prepared nanocomposites have been investigated by RPhA and IKS methods. It has been shown that in the investigated nanocomposites the reflections form planes of metal crystal lattice corresponding on card file ASTM in a series of d_{hkl} of copper oxide I (Cu_2O) and zinc oxide (ZnO) were observed.

The IR-spectra of the prepared nanocomposites show that in a case of copper-containing nanoparticles they do not interact with polymer matrix and are implemented in its interspherulitic fields. In a case of the zinc-containing nanoparticles it occurs a break of the bonds in maleic group of the polymer with conservation of C=O group and formation of COO^{-}group. Apparently, zinc-containing nanoparticles are partially kept az ZnO and partially added on COO^{-} group with formation of COO- Zn-OOC bond.

The prepared composites containing nanoparticles of the metal oxides can be used as the catalysts of the organic and petrochemical synthesis, adsorbents for water purification and also modifying agents of the industrial polymers with the aim of improvement of their operational properties.

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Abstract

PLASMA POLYMERS – FROM THIN FILMS TO NANOPARTICLES AND NANOCOMPOSITES

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Plasma polymers are macromolecular solids that are created as a result of the passage of organic vapors or precursors through a plasma. In contrast to conventional polymers, plasma polymers have random, highly branched and cross-linked structure. Despite the fact that their exact structure on the atomic level cannot be predicted, plasma polymers attract persisting attention. This is primarily due to the fact that their physico-chemical and bioadhesive properties may be easily tuned in a wide range by the proper selection of operational parameters (e.g. applied power, pressure, system geometry, precursor and working gas mixture). As it will be shown in this contribution on selected recent examples from our laboratory plasma polymers may be prepared in the form of thin, conformal films, nanocolumnar coatings or as nanoparticles with tailor-made size. Furthermore, by changing the deposition conditions, it is possible to produce these materials with different functionalities (e.g. hydrophilic or hydrophobic, bio-adhesive or bio-repellent, soft or hard) that makes them highly interesting for various fields. Finally, the deposition of plasma polymers may be easily combined with other plasma-based deposition techniques that makes it possible to fabricate advanced functional nanocomposites.

In this contribution the main attention will be devoted to the metal/plasma polymer nanocomposites that are prepared by the combination of plasma polymerization with gas aggregation sources of metallic nanoparticles. Different strategies will be overviewed that enable to produce nanocomposite materials with different architectures that span from nanocomposites, in which the metallic NPs are randomly distributed in the plasma polymer matrix, sandwiched and multi-layer nanocomposites with alternating layers of plasma polymer and metallic NPs, nanocomposites with gradients in the number of embedded NPs as well as core@shell or multi-core@shell metal/plasma polymer heterogeneous nanoparticles. Possible use of such materials as antibacterial coatings, optical films, platforms for ultrasensitive bio-sensing or wettability control will be discussed.

Acknowledgement: This work was supported by grant GACR 16-14024S from the Grant Agency of the Czech Republic.

Abstract

MULTIFUNCTIONAL POLYMER NANOCOMPOSITES BASED ON GRAPHENE AND ITS DERIVATIVES: THE KEY ROLE OF FILLER DISTRIBUTION

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Due to its promising properties, graphene and its derivatives have been widely proposed for the preparation of multifunctional polymer-based nanocomposites with enhanced electrical, thermal, barrier and mechanical properties. However, the ultimate properties of these materials mainly depend on the morphology of graphene nanosheets within the polymeric phase: homogeneous dispersion, 2D-layer seemly to a continuous graphene layer, or 3D-graphene network. This talk will review our activities focused on the design, preparation and characterization of advanced graphene-based nanocomposites, which may be used as potential solution for some of the most important societal challenges. The following topics will be presented. A) Layer-by-layer (LBL) assembly technique has been adopted for the realization of alternating multilayered coatings made of reduced graphene oxide (rGO) and high amorphous vinyl alcohol (HAVOH) deposited on PET substrate, which exhibit outstanding barrier properties to the oxygen permeation. B) An innovative approach, based on latex mixing and co-coagulation process, has been developed to prepare rubber/rGO nanocomposites with a 3D-segregated network of graphene nanosheets. The segregated morphology reduces significantly the gas permeability compared to pristine rubber matrix and enhances mechanical and electrical properties of rubber nanocomposites. C) A novel complex structure with high electrical conductivity based on open cell poly-urethane foams (PUF) and reduced graphene oxide (rGO)/chitosan (CS) aerogel has been produced by adopting a bi-directional freeze-casting approach. The final structure shows many unique features, such as good mechanical properties, excellent electrical conductivity and outstanding piezoresistive properties. D) Chitosan (CS)/graphene oxide (GO) nanocomposite aerogels have been prepared by freeze-drying. The obtained results on adsorption capacity and mechanical properties of the aerogels suggest that the fine tuning of the preparation procedure allows the easy production of highly performing CS/GO broad-spectrum dye adsorbents.

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Abstract

MICROSCOPIC EVALUATION OF THE HALLOYSITE NANOTUBES DISPERSION IN THE POLYETHYLENE MATRIX

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The rapid development in the field of material engineering makes it necessary to control material structure in the nanometric scale when modifying composite properties. In order to bring about the desired properties, the reinforcement phase must be dispersed properly in the matrix with the appropriate adhesion at the matrix-filler interface. To achieve that, various attempts to increase the specific surface of filler grains are made by activating the surface chemically or by covering with an intermediate, a compatibilizer. The aim of this study was to test the impact of a compatibilizer on the dispersion level of a nanofiller in the form of halloysite nanotubes (HNTs) in a low density polyethylene (LDPE) matrix. The content of halloysite nanotubes varied from 2 to 6 wt%. Compatibilizer used in this study is polyethylene grafted with maleic anhydride (PE-graft-MA). After sputtering samples with a thin layer of gold the homogenization analysis was carried out on the basis of photographs taken on a Scanning Electron Microscope (SEM), at a magnification of up to 3500 times. During the microscopic examination, the occurrence of agglomerates of halloysite nanotubes, which size reached several dozen micrometers, was observed (Figure 1). Despite the occurrence of agglomerates, the distribution of nanotubes can be described as good and even [1]. We may assume that the presence of agglomerates during the halloysite nanotubes manufacturing of nanocomposites is not unusual, according to the results presented in other papers [1-3].

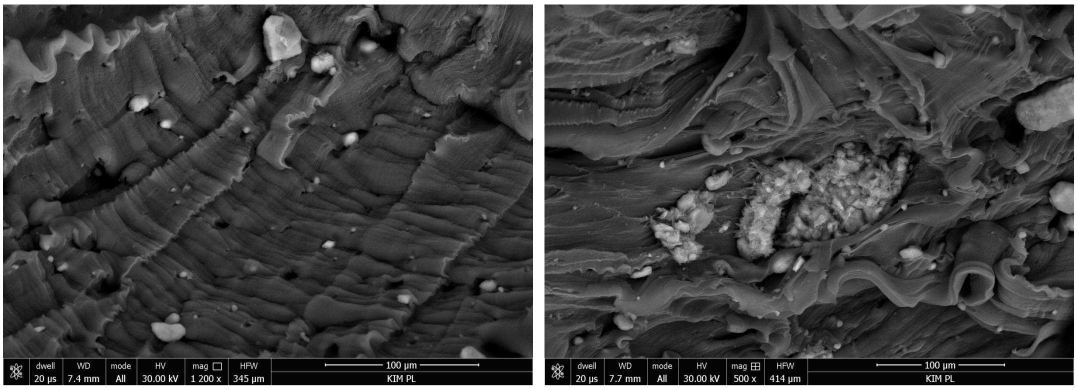

Figure 1. Distribution of HNTs in a LDPE matrix, content of 4 wt% (left) and 6 wt% (right)

Acknowledgement. The project leading to these results has received funding from the EuropeanUnion's Horizon 2020 research and innovation programme under the MarieSkłodowska-Curie grant agreement No 734205, project acronym NEWEX.

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Abstract

ZINC-CONTAINING NANOCOMPOSITES ON THE BASIS OF ISOTACTIC POLYPROPYLENE

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One of the most perspective directions of development of the modern science is the nanotechnology – preparation and use of materials having nanoparticles in the composition.

Recently it is appeared a considerable interest to the composition materials on the basis of polymer matrices and nano-sized particles of metals, which has been stipulated by wide spectrum of their application – from catalysis to nanotechnology in information technique.

The development of nanotechnology opened the possibility of carrying out of the investigations in the field of composition nanomaterials and now allowed to move to the creation and use of advanced polymer materials for sensors, catalysis, nanoelectronics, etc [1].

A modification of polypropylene by creation of various composition materials allows to expand considerably the fields of its application. The filled polypropylene takes one of the first places among filled thermoplasts. Now, more attention is paid to the development of composites with nano-sized fillers. Such composition materials possess higher indices than composition materials with micro- and macrofillers. An introduction of even small quantity of nanosized filler into polypropylene can essentially change the physical properties, improve the barrier qualities, increase the thermal stability, electro-conductivity, etc.

A use of the metal nanoparticles of d-valency (zinc, cobalt, nickel, etc) in the polymers allows to prepare principally new materials, which find wide application in radio-, and optoelectronics as magnetic, electro-conductive and optical media[2].

The purpose of work – investigation of influence of additions of the metal-containing nanofillers (NF) on peculiarities of physical-mechanical, rheological, heat-physical and thermal properties of composites on the basis of isotactic PP.

As NF it was used NPs of the zinc oxide, stabilized on polymer matrix of the industrial polyethylene of high pressure, prepared by mechano-chemical method in polymer melt. A content of nanoparticles – 5 mass %, size – 11÷17 nm, degree of crystallinity – 35 ÷ 45%. A ratio of components of the polymer mixtures (mass %): PP/ NF = 100/(0.5, 1.0, 3.0)

The nanocomposite polymer materials have been prepared by mixing of PP with zinc-containing NF on laboratory rollers at temperature 160 – 165°C. For carrying out of mechanical tests the prepared mixtures were pressed as the plates by thickness 1 mm at 190°C for 15 min and pressure 10 MPa.

The influence of NF on structure of the prepared nanocomposite PP has been investigated by X-ray phase method. RFA diffractograms confirm the availability of the zinc-containing nanoparticles in PP. The reflexes characteristic for zinc-containing nanoparticles correspond to a series of d_{hkl} zinc oxide (ZnO) on card file ASTM.

It has been shown that a small addition of NF in a quantity of 0.5÷3.0 mass p. leads to the increase of breaking strength and Vicat heat-resistance, in some decrease of specific elongation value. MFI value is increased from 9.5 for PP to 13(0.5); 17.7 (1.0) and 27 g/10 min. at NF equal to 3.0 mass p.

The carried out heat-physical and thermal analysis of the prepared nanocomposites showed the increase of melting temperature from 160 to 165°C. Decay activation energy of thermooxidative destruction increases from 122.49 to 175.5 kJ/mol which evidences about high thermal stability of the prepared nanocomposite.

The investigation of influence of additions of the metal-containing nanofillers, including zinc oxide nanoparticles, stabilized on polymer matrix of industrial polyethylene of high pressure on peculiarities of properties of nanocomposites on the basis of isotactic polypropylene revealed the improvement of strength and rheological indices and also thermooxidative stability of the prepared nanocomposites.

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Abstract

CONDUCTIVE AND SUPERHYDROPHOBIC COTTON FABRIC THROUGH PENTAERYTHRITOL TETRAKIS(3-(3,5-DI-TERT-BUTYL-4-HYDROXYPHENYL) PROPIONATE) ASSISTED THERMAL REDUCTION OF GRAPHENE OXIDE AND MODIFICATION WITH METHYLTRICHLOROSILANE

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Conductive composites based on environment-friendly substrates, including cotton fabrics, have attracted recently great interest. Being lightweight and flexible, such conductive textiles have a wide range of uses in various industries. Applications of graphene for modification of textiles are rare due to difficulties in its use in the form of aqueous dispersions. On the contrary, graphene oxide (GO) can be dispersed in liquids and deposited on textiles because of its structure and the presence of functional groups.

In the study, GO was deposited on a cotton fabric by the padding method. Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate), an antioxidant widely applied in the plastic industry, was used to assist thermal reduction of GO on the fabric in air. L-ascorbic acid was also applied for comparison. Reduction of GO at 180 and 220 °C imparted electrical conductivity. For all the materials the conductivity worsened during post-reduction cooling and during first few hours of storage at room conditions. The use of pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate), which assisted the reduction of GO at both 180 and 220 °C, allowed to obtain the cotton fabric with stable surface resistivity of 6.6 and 3.7 $M\Omega/cm^2$, respectively. Moreover, superhydrophobicity of the conductive fabric was achieved by modification with methyltrichlorosilane in an anhydrous environment [1].

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Abstract

THE VISUALIZATION OF THE FLOW OF MOLTEN POLYMERS; THEORETICAL APPROACH AND MEASUREMENTS POSSIBILITIES

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The characterization and total description of flow of molten polymers by processing present an important challenge, as well for the processing tools design as for the technology. This is particularly if the establishment of the manufacturing conditions for plastic products has to be done. The determination of local flow velocity, its direction and distribution within viscous-elastic flow, as it the case now-a-days by production of actually complex products, presents an object of interest by the processing tools designer, manufactures and the polymer processing teams.

The direct measurements are possible in a limited area if the stream temperature and/or pressure sensors should be placed directly in the flow. This measurement technique incites a number of technical difficulties like the necessity of heat and stream resistance of the sensor by required high receptiveness, but also the incorporation of a sensor into the flow may provoke creation of random flow instabilities.

The flow visualization technique brings new idea of touchless measurements of flow velocity and its distribution within the streaming media. The most important advantage is the possibility of flow movement registration without touching the fluid, *i.e.* without any distortion of the flow, as only the light beam should penetrate the liquid media in this case. Such technique is used sometimes by injection mold occupied with glass walls giving the possibility for a direct observation of the flow and its spatial circulation. The Laser Doppler Velocimetry (LDA), a touchless technique widely used by water and gases streaming measurements, may also be applied in the case of determination of velocity vectors in the case of investigations of molten polymers streams. In this case the laser beam focused in the flow allows to determine the velocity vector i.e. The technical problems by such measurements of molten polymers are the necessity to isolate the laser electronic from the heat of the melt and to use highly resistant optical glasses hard to shape. .

The various flow measurements techniques applied in the case of observation by molten polymer processing will be presented and discussed together with examples of simple numerical approaches of flow velocity distribution, depending on the geometry of the cross section of the channels and the type of visco – elastic fluid, like molten polymers.

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SYNTHESIS AND CHARACTERIZATION OF ORGANOSILICON POLYMERS WITH PHOTO SWITCHABLE FRAGMENT IN THE SIDE CHAIN

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Azobenzene, with two phenyl rings separated by an azo (–N=N–) bond, serves as the parent molecule for a broad class of aromatic azo compounds. The photochromic trans-cis isomerization of azobenzenes has been used extensively in molecular switches, often taking advantage of its shape change upon isomerization to produce a supramolecular result. In particular, azobenzenes incorporated into polymer backbone give switchable receptors and azobenzenes in monolayers can provide light-controlled changes in surface properties. These chromophores are versatile molecules, and have received much attention in research areas both fundamental and applied.

The aim of this work is the synthesis of new comb-type organosilicon polymers with azobenzene side groups in the chain. By the insertion of azobenzene chromophoric groups in the siloxane matrix the flexibility, hydrophobicity and thermal stability of obtained polymers as well as films will be increase compared with organic analogues [1-4].

For obtaining 1-(4-allyloxy)phenyl)-2-(4-fluorophenyl)diazene (I) on the first stage the diazotization (azo combination) reaction of 4-fluoroaniline with nitric acid have been carried out and corresponding 4-((4-fluorophenyl)diazenyl)phenol (II) have been obtained..

On the second stage the reaction of 4-((4-fluorophenyl)diazenyl)phenol with allyl bromide have been carried out and corresponding 1-(4-allyloxy)phenyl)-2-(4-fluorophenyl)diazene (III) have been obtained .

The structure and composition of the obtained compounds (I-III) have been determined via FTIR, ^{1}H, ^{13}C NMR spectra and molecular masses.

The hydrosilylation reaction of 2.4.6.8-tetrahydro-2.4.6.8-tetramethylcyclotetrasiloxane (D_4^H) with 4-((4-(allyloxy)phenyl)diazenyl)phenyl propionate at 1:4.2 ratio of initial compounds, have been performed in the presence of Platinum catalyst and corresponding adduct $D_4^{R'}$ (IV) have been obtained.

The polymerization reaction of compound IV has been carried out in the presence of dry nucleophilic potassium hydroxide, at 60-70^{0}C temperature and corresponding comb-type amorphous powder-like orange polymers with η_{sp}= 0.12 have been obtained, soluble in dioxane, chloroform.

The structure and composition of polymers have been determined via FTIR, ^{19}F, ^{1}H, ^{13}C, ^{29}Si NMR spectra data. GPC, DSC and TGA have been carried out. UV investigations of compound III and oligomer IV has been carried out. The *trans* form can be converted to the *cis* form using an appropriate wavelength (UV at 300-400 nm) of light. It was shown that A different wavelength (visible blue light >400 nm) can be used to convert the molecule back to the *trans* form. Alternately, the molecule will thermally relax to the stable *trans* form.

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DEVELOPMENT OF MESOPOROUS CATALYSTS FOR PREFERENTIAL OXIDATION OF CARBON MONOXIDE (CO-PROX)

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High-purity H_2 is necessary for proton exchange membrane (PEM) fuel cells, and preferential oxidation of carbon monoxide (CO-PROX) is widely used for this purpose because of its low cost and ability to reduce CO content to less than 10 ppm without excess H_2 consumption. In this work, high surface areas of mesoporous ceria-zirconia (CeO_2-ZrO_2) and mesoporous ceria-titania (CeO_2-TiO_2) were successfully prepared via nanocasting process using siliceous MCM-48 mesoporous material as a hard template. The synthesized mesoporous CeO_2-TiO_2 and CeO_2-ZrO_2 provided ordered structure with high specific surface area around 200 and 260 m^2g^{-1}, respectively. These two synthesized mesoporous materials were characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM) and N_2 adsorption-desorption. Copper (Cu) loaded onto the mesoporous CeO_2-TiO_2 and CeO_2-ZrO_2 supports by deposition-precipitation (DP) method exhibited high dispersion of Cu species, as confirmed by XRD. The structures and properties of the synthesized Cu- CeO_2-TiO_2 and Cu-CeO_2-ZrO_2 catalysts play a crucial role to interesting catalytic applications, such as preferential oxidation of CO (CO-PROX). The Cu- CeO_2-TiO_2 and Cu-CeO_2-ZrO_2 catalysts showed good potential for CO-PROX reaction with 100% CO conversion at 130 °C. Both catalysts also exhibited excellent stability after 48 h. It can be concluded that the prepared mesoporous CeO_2-TiO_2 and CeO_2-ZrO_2 by nanocasting pathway are promising candidates to be used as support for H_2 production application.

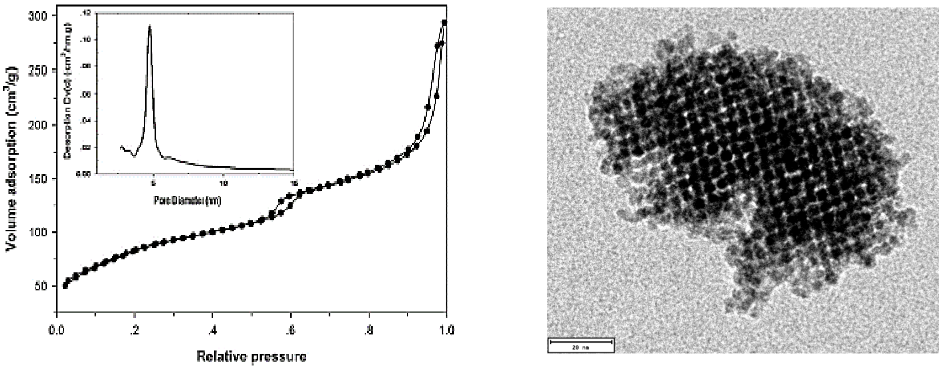

Figure 1. Mesoporous a) CeO_2 and b) Cu/CeO_2

Acknowledgement: Grant for International Research Integration: Chula Research Scholar, Ratchada Pisake Sompote Endowment Fund, Chulalongkorn University, Thailand; Royal Thai Government; Thailand Research Fund (Senior Research Scholar).

Abstract

DEVELOPMENT OF PLA FILMS LOADED WITH GRAPE VINE CANE EXTRACT FOR FOOD PACKAGING APPLICATION

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A novel active film material based on poly(lactic acid) (PLA) loaded with antioxidant grape vine cane extract was successfully developed by compression-molding technique. PLA is a biodegradable and renewable polymer, which represents a valuable alternative to plastic packaging films, often associated with environmental problems. The physico-chemical properties of the composite films were investigated and the release of wine extract was confirmed by migration studies in 50% v/v ethanol/water food simulant. In addition, in vitro antifungal activity against *Botrytis cinerea* was investigated. Among all tested concentrations, 15% of extract was the most suitable in terms of mechanical, water vapor barrier and antifungal stability of the PLA film. The obtained results suggest that the material could potentially be used for extending the shelf-life of food products with high fat content.

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Abstract

POLYMER COMPOSITES ON THE BASIS OF SECONDARY POLYPROPYLENE AND SOME MINERALS

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Environment ecological protection and utilization of the industrial wastes present today very important and actual problems. From the scientific- technical literature it is known that if the development of the composites based on secondary thermoplastic materials, in which the different dispersive or natural and artificial fiber fillers are used, about 40 % of the primary ores can be spared. In the secondary polymer composites the industrial technological wastes as trimming, injection molding heads technical tare, films, bottles and so on are used. In our case the secondary polypropylene industrial wastes as binder are used.

Polymer composites on the basis of secondary polypropylene and high dispersive powders of minerals wide spread in Georgia (andesite from Bakuriani, quartz sand from Sachkhere and slam from Okami) were obtained and investigated their some physical-mechanical, thermal and hydrophobic properties. It is shown that the ultimate strength and thermal stability of composites extremely depend on the filler concentration (20-60 wt %) and at definite significant of the concentration (near 40 wt %) have maximums. Among the fillers the andesite is one containing of which gives to composite maximum of strength higher than for other fillers. For the composites contained binary fillers (quartz sand/slam, quartz sand /andesite and slam/ andesite) there are fond the optimal concentrations, which ensure the obtaining of composites with improved properties (the synergistic effect at definite proportion of filler is appeared) - anomaly increasing of the ultimate strength at binding and compression. Thermal stability of these composites increases in the range 20-30^{o}C. Water absorption of all investigated by us composites is not more than 1.5%.

Abstract

NOVEL USAGE OF A POLYCARBONATE SOLAR ENERGY DRYER FOR THE PURPOSE OF HERBAGE AND DRUG PLANTS DRYING

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Polycarbonate is unusual because of a combination of high thermal stability, high resilience and transparency. Polycarbonate is one of the most successful glass substitutions in application to translucent structures. It combines high strength, low weight, wide (in comparison with other plastics) temperature range of use, flexibility, high thermal-insulating properties, low conductivity, fire-resistance, longevity. Polycarbonate has a high chemical resistance to many non-inert, which makes it possible to use it in corrosive environments for most non-inert substances, which makes it possible to use in aggressive environments.

Thanks to its physical and chemical properties, polycarbonate is widely used for the manufacture of greenhouses, awnings, coverings, various constructions.

Usage of solar energy dryer during drying of agricultural products can significantly increase the volume of dried fruit products. Usage of polymer materials, in particular, polycarbonates in the solar drying apparatus, produce good results. Polycarbonate solar energy dryer has been developed in the Georgian Technical University.

Experimental results for herbage and drug plants drying suggest that drug plants drying in a solar energy dryer took 4 hours, and the natural drying in the shade lasted more than 4 days. The process of drug plants drying in a solar energy dryer took almost 24 times less than natural drying in the shade.

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Abstract

EFFECTS OF UV STABILIZERS ON POLYPROPYLENE OUTDOORS

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Effects of harsh outdoor weather in Texas on polypropylene (PP) were simulated. Hindered amine light stabilizers (HALSs) and nano ZnO were used to stabilize PP film-based formulations exposed to ultraviolet (UV) light. 15 different compositions were studied. Tensile behavior, UV transmittance, thermal stability (by thermogravimetric analysis) and dynamic friction of so exposed PP films were determined. Scanning electron micrographs of fracture surfaces were obtained. The composition with 0.5 % ZnO + 0.5 % HALS 1 has the highest tensile modulus and also the highest elongation at break. After 6 weeks of UV exposure most compositions show the friction values lower than for neat PP.

Abstract

ANTIOXIDANT AND ANTIMICROBIAL EDIBLE FILMS BASED ON DEXTRAN CONTAINING POLYPHENOLS FROM YARROW EXTRACT

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Current trends in food biotechnology are focused on replacing synthetic polymers used for food packages by the natural ones. Biopolymers are made by sustainable processes in a cheap way. Moreover, they are nontoxic and can serve as a good alternative to traditional (petroleum) food packaging, due to great film-formation properties in a form of edible films and coatings for food products. Various polysaccharides, proteins, and lipids have been intensively investigated as edible materials that could improve the food quality, freshness, and provide food safety. However, natural polymers usually lack of antioxidative and/or antimicrobial properties. Therefore, many synthetic and natural additives can be incorporated into edible films. Among them, extracts of medicinal plants are giving more attention due to their safeness and proved health benefits.

The aim of this study was to obtain edible films based on dextran, with antioxidative and antimicrobial properties. Dextran obtained in our lab was used for preparing edible film with sorbitol as a plasticizer, while pulverized waste biomass obtained from the processing of medicinal herb yarrow (*Achillea millefolium*) was used as a source of polyphenols. It has previously been shown[1] that dextran-based films had excellent mechanical and water vapor barrier properties. In this work, spray dried ethanol extract of *Achillea millefolium* dust (AME) was incorporated into dextran films in concentrations 2, 3, and 4% (w/v). The composite films were analyzed regarding antioxidative, antimicrobial, and mechanical properties. All films showed high antioxidative activity (90% reduction of DPPH radical). However, to obtain high antimicrobial activity (higher than 50%), 4% of AME was required. Composite films showed antimicrobial activity against three Gram-positive bacteria (*Staphylococcus aureus*, *Listeria monocytogenes* and *Enterococcus faecalis* and one Gram-negative bacterium (*Pseudomonas aeruginosa*). Incorporation of AME into dextran film showed positive effect on tensile strength and negative effect on elongation. Composite film with the best mechanical properties (tensile strength 3.5 MPa and elongation at break 37%) was the film containing 4% AME.

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Abstract

THERMOSET AND THERMOPLASTIC FOAMS FOR BUILDING APPLICATIONS

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The concurrent improvement in thermal insulation and sound absorption is a critical need in a number of applications. In this presentation, we review thermoset PU foams, biobased PU foams and the use of supercritical CO_2 to foam PLLA. The structure-property-processing impacts are presented. The effects of reinforcement with kenaf core and micro cellulose fibrils is examined. The effect of the varied weight fractions of the cellular morphology of the foams was analyzed based on three main performance properties. Thermal Resistance, Sound Absorption and Mechanical Properties. In both thermoset and thermoplastic foams, new manufacturing approaches were developed to control cell nucleation, growth for final foam performance. Novel performances were obtained such as increased sound absorption, thermal insulation, mechanical performance.

Abstract

NEW WOODEN COMPOSITES INFLUENCE OF THE MORPHO-FUNCTIONAL ACTIVITY OF THE DIFFERENT TISSUES OF GROWING AND ADULT WHITE MICE

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Creation of wood polymer composites (WPC) presents very actual problem today. Obviously, it is due to very large perspectives of application of these products in the life. Today the composites particle board are very popular. This material is produced by hot pressing of thermosetting polymers and wood sawdust (Russian abbreviation DSP). This material is widely used in the industry of furniture. Wide spreading of this material is due to its low cost in comparison with poor wood material. However, particle board has many leaks among which are high water absorption and very bed environmental friendliness. This leak is due to phenol-formaldehyde contain formaldehyde, which is very toxic substance and stands out from noted material during long exploitation period.

The aim of this study is to investigate the influence of industrial particle board and new composite materials obtained on the basis of dry powder pine and inorganic binders of phenethyloxysiloxanes: PhES-50 and PhES-80 on the living organisms. Experimental objects were non-line growing and adult white mice.

Determining colchicine Mitotic index, immunohistochemical analysis (with proliferation marker protein- ki67) and common quantity of leukocytes in the peripheral blood of adult and old white mice.

It was determined that using of wooden sawdust tile as a construction material in animal cages, in which urea or phenol-formaldehyde resins are used as binding-adhesive substance, reduces the number of leukocytes by 50% of the peripheral blood in white mice also have a bad influence on hepatic binucleate liver cells and their mitotic index. Amount of leukocytes and others are not changed in case of using new composition materials, obtained on the basis of dry powder pine and inorganic binders of phenethyloxysiloxanes: PhES-50 and PhES-80.

Cellulose based new renewable composites, in which organic or silicon-organic polymers are used as a binding-adhesive substance, don't have negative influence on live system functionality compared with known phenol-formaldehyde resins.

FUNCTIONAL HYPER-CROSSLINKED RESINS WITH TAILORED ADSORPTION PROPERTIES FOR ENVIRONMENTAL APPLICATIONS

Rachele Castaldoa ***, Veronica Ambrogib , Roberto Avolioa , Mariacristina Coccaa , Gennaro Gentilea , Maria Emanuela Erricoa , Maurizio Avellaa***
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Porous materials characterized by high specific surface area (SSA) have attracted scientific attention for their various potential applications in catalysis, separation, gas storage, liquid and gas purification. Among other microporous materials, like zeolites, active carbons and metal-organic frameworks, hyper-crosslinked (HCL) resins stand out for their low density and for the possibility of tailoring their structure, porosity, and functionality. HCL resins are typically synthesized by extensive crosslinking through Friedel-Crafts alkylation of lightly crosslinked gel-type precursors. 1,2 The objective of this study was to prepare HCL resins based on vinylbenzyl chloride (VBC) and divinylbenzene (DVB) functionalized with amine and hydroxyl groups, in order to improve their properties for selective gas sorption and for water remediation applications. More in details, after a bulk prepolymerization step of VBC/DVB mixtures3 , precursors were modified with different amounts of ethanolamine. The modified precursor was then hyper-crosslinked by Friedel-Crafts alkylation. The functionalization degree of the resin was evaluated as a function of the relative amount of ethanolamine. Moreover, the effect of the functionalization on the SSA and the pore size and distribution of the HCL resins was investigated. The ethanolamine functionalization affected the bimodal pore size distribution of the unmodified resin, allowing obtaining an almost unimodal microporosity (see Figure 1). Gas adsorption measurements were used to evaluate the carbon dioxide selective capture properties of modified resins. Moreover, adsorption from solution tests were performed to evaluate the effect of the functionalization on the adsorption efficiency of the resins towards model pollutants (i.e. phenol) for water remediation applications.

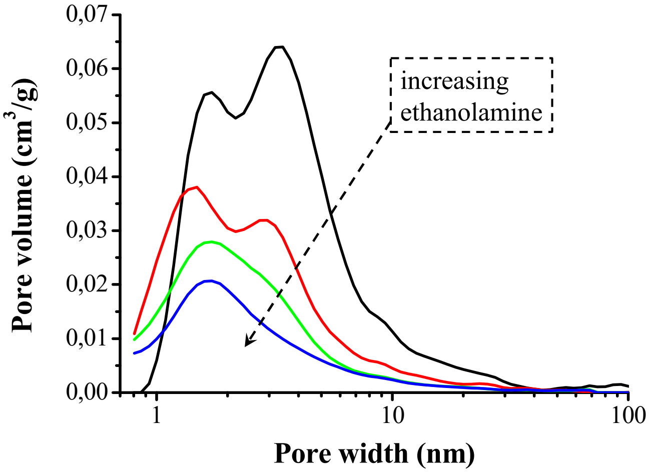

Figure 1. Pore size distribution of neat HCL resin (black curve) and ethanolamine modified HCL resins at increasing ethanolamine/precursor weight ratio.

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SILVER -ARSENIC, GOLD-ARSENIC NANOPARTICLES IN POLYMERIC MATRICES

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Arsenic was a well known and widely used medication for a variety of illnesses since more than 2400 years ago [1, 2]. Large amount of arsenic is available in Georgia: Reailgar(As_4S_4)-Orpiment(As_4S_6) and Arsenopyrite (FeAsS) ore of Georgia are of significant economic importance and they contain also some quantities of the precious metals Gold (Au) and Silver(Ag). The antimicrobial properties of Arsenic, Silver and Gold have been known to cultures all around the world for many centuries, but for combinations with Arsenic have not reported before. In [3] we have shown possibilities of removal of Arsenic from mineral resources and industrial waste in order to produce materials with antibacterial properties: Arsenic Antibacterial Polymer Composites Based on Poly(Vinyl Chloride) destroy bacteria [4].

We have used surfaces of gold (Au) and silver (Ag) nanoparticles with size of 31 nm modified by thioarsenic anions to form potentially promising novel Silver(Ag)-Arsenic(As), Gold(Au)-Arsenic(As) antibacterial agents. Modification of nanoparticles surface were confirmed by dynamic light scattering (DLS) measurements. In order to obtain antibacterial polymeric composites, Silver(Ag)-Arsenic(As)as well as Gold(Au)-Arsenic(As) nanoparticles systems were introduced into water-soluble polymeric matrices polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA). The nanocomposites so obtained were characterized by infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

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Abstract

DEVELOPMENT OF THE WASTELESS TECHNOLOGY OF CLEANING WATER OF PETROLEUM PRODUCTS

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Evident increase of enterprises and vehicles caused demand on oil products which to its part increases the probability of pollution of air and water with the mentioned products. The main source of water pollution with oil products is: oil producing and oil-treatment enterprises, pumps, pumping and transportation systems, large-scale highways for oil pipelines in the territory of Georgia, tankers, terminals and oil bases, oil product reservoirs, auto station complexes and stations.

Cleaning the sewage waters from oil is connected to some difficulties as oil products are in emulsified conditions and it - “oil in water” represents quiet fixed emulsion.

According to literary sources at present from oil products for water cleaning methods mechanic and physical-chemical methods are being used: coagulation, filtration, adsorption, micro and ultra-filtration [1-3]. It is noteworthy that biological and chemical methods [2] the majority of which are effective but these methods have their negative sides and it is non-ecological nature of their devices, problem of utilization of sorbent and filtering equipment adsorbent produced as a result of cleaning causes further pollution of waters and soil so second-hand pollution of environment is present.

The only solution is to create and introduce new effective technologies which will serve to cleaning of polluted waters with oil and oilproducts with minimal costs.

This work covers research of possibility of cleaning of oily waste water with use of sorption method, when the filtering material is presented with the secondary materials, namely porous polyurethane- wadding and a secondary product of wood processing – sawdust.

After filtration the sawdust loaded with petroleum products may be used as an additional source of heat. As for secondary polymeric material, we can easily expulse the low molecular mass fraction of petroleum product retained thereon. For example, we can receive petroleum product by pressing out and use polyurethane for new cycle of sorption. At the final stage of cleaning, we can use micro- and ultrafiltration for complete cleaning of water.

We have tested the secondary product of wood processing – sawdust and found that sawdust easily passes oily water. Maximum productivity of filter is 10 l/h per 1 kg sorbent in the whole period of filtering. After passing of 100 liters of 1% oil water solution productivity dropped by 75% due to fouling of sawdust.

We proceed with the works for matching of filtering material dimensions and combination of materials providing preservation of high speed filtration, also for solving of the problems of regeneration and utilization of filtering material.

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Abstract

STUDY OF DEGRADATION ABILITY OF MICROORGANISMS ISOLATED FROM SOME TYPE SOILS OF EAST GEORGIA TO POLYMERIZED NITROGENOUS FERTILIZERS

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From alluvial –carbonaceous type soils of Georgia the following microorganisms characterized by urease activity have been isolated: *Clostridium sp., Aspergillus sp. and Actinomyces sp.* Urease activity was checked up on Christiansen nutrient medium: urea 20 g/l, phenol red 0,012 g/l, KH_2PO_4 -2 g/ l, NaCL – 5 g/l, glucose 10 g|l , agar-agar 18g. Microorganisms isolated from soil and museum culture – urobacteria *Bacillus pasteuri* (control) were sown. Analysis of experimental results showed that on the Christiansen medium 6 strains of microorganisms were germinated, which were apt to destruct urea. 3 strains of these six, by their activity equaled to *Bacillus pasteurii.* Then, to isolate microorganisms capable to degrade polymer fertilizers, instead of urea we introduced into Christiansen nutrient medium the polymer fertilizers (1,5,10 and 15 g) for adaptation purposes. Analysis of results showed that from 6 strains isolated from soil two strains revealed ability to degrade polymer fertilizers (in the presence of 15 g polymer fertilizer in Christiansen medium). Morpho-physiological studies proved that these strains belong to *Costridium-* and *Actinomyces-* family.

Among the isolated microorganisms the strain *Actinomyces sp.* strain is distinguished by its urease activity. At cultivation of this strain over Kraselnikov's synthetic nutrient area, where instead of the nitrogen source – glycine, potassium nitrate, we used nitrogen-containing synthetic polymeras, significant growth-development (increase of bio-mass) was observed compared to the control (control: synthetic nutrient medium, source of nitrogen –potassium nitrate). Intense growth ability (destructive) of this culture is especially active, when in the cultivation medium definite combination of standard rate of nitrogen is used (nitrogen containing polymer+ potassium nitrate, at a ratio 9:1).

To determine optimal conditions for growth-development (intence accumulateion of biomass) of the culture under the study, *Actinomyces sp.*, we changed pH, carbon, as well as nitrogen sources in incubation medium. It was proved that from the carbon sources used in the study: starch, glucose, fructose, saccharose, starch is the optimal source (starting concentration of starch is one tenth of polymer concentration). Among nitrogen sources (potassium nitrate, hydrolyzed peptone, glycin), it was glycin (starting concentration 0.1 g + 0.9 g polymer) that revealed beneficial impact on the growth-development of the culture under the study. Cultures grown on these nutrient mediums were distinguished by high intensity of biomass accumulation and when grown on Christiansen medium – by maximum urease activity.

Acknowledgements: The paper was prepared within the framework of the project # 2016-36 / STCU #6309 "Biodegradable polymers synthesis and application in environment protection from pollution" funded by the Shota Rustaveli National Science Foundation/Science & Technology Center in Ukraine.

UV CURABLE PDMS FOR SLA PRINTER

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Three-dimensional (3D) printing is often considered synonymous with additive manufacturing. Several types 3D printer is known where usually use polymers are. Stereolithography (SLA) employs a single beam laser to polymerize or crosslink a photopolymer resin. By drawing on the liquid photopolymer resin with a light beam, thin layers of polymer are stacked layer by layer. Elastomer based on polydimethysiloxanes (PDMS) are important class of materials, because of properties such as chemical inertness, flexibility, optical transparence, also they have a very low surface tension (20.4 mN/m) and glass transition temperatures (146 K). it is possible to print a support material that holds the PDMS prepolymer in place until it can be cured by UV light using a photoactive cross-linking agent. It is possible to graft photoactive group on PDMS backbone and obtain new UV curable polymer [1,2].

For purpose obtaining UV curable PDMS at first we have used Aminopropyl terminated polydimethylsiloxane (Mw ~25 000) and reacted to 2-Isocyanatoethyl methacrylate at room temperature, then obtained viscous liquid. After addition of photo initiator into the viscous liquid, it placed into PTFE mold and cross-linked by UV. Colorless transparent elastomers were produced (Fig.1):

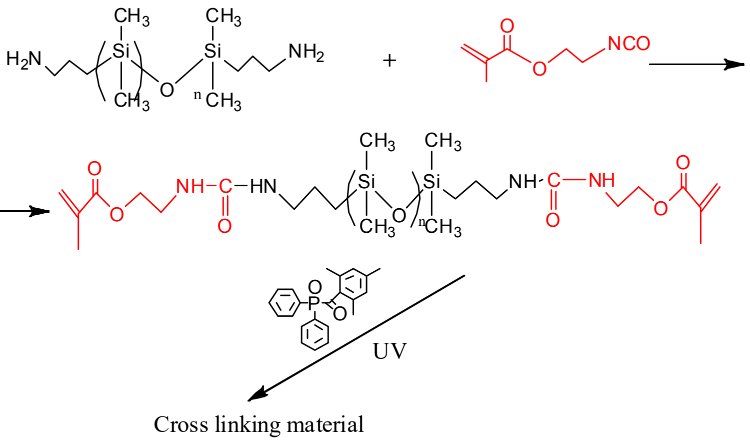

Fig. 1 Obtaining scheme of UV curable PDMS

The structure and composition of the obtained compounds were studied by FTIR, ^1H, ^{13}C NMR spectra data, SEM and optical microscopes, DSC, TGA, DMTA.

Measurement of the sample by DSC showed that, a peak was observed at 148.6°C, due probably to a thermal post-curing process.

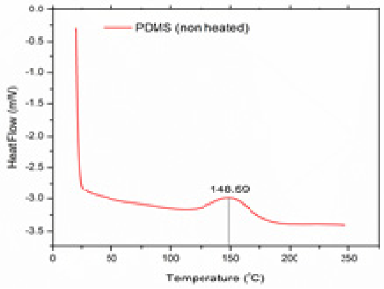

Fig. 2. DSC of UV curable PDMS

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Abstract

COMPOSITE CHITOSAN – SILICA CONTAINING SORBENTS

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The use of sorbents, obtained on the basis of natural materials and waste, has become relevant in recent times. Among natural materials, one of the promising materials for the production of sorbents is chitosan. It is well-known that chitin and chitosan containing systems are used in water treatment (purification) processes and sorption of heavy metals.

The use of chitosan as a sorbent without any modification of its structural characteristics becomes ineffective, since chitosan does not have a structured porous structure. This leads to the fact that not all functional groups participate in the sorption processes. Various porous materials (diatomite, bentonite, silica gel, etc.) can be used to structuring of the chitosan. However, such systems have already formed porous characteristics and it becomes impossible to obtain homogeneous systems[1,2].

The most promising among the structure-forming particulate materials is silica gel obtained during the simultaneous gelation of mixture of chitosan and silica sol. As the silica sol, an acidic alcosol was obtained, which was prepared according to the procedure described in [3]. Due to the fact that chitosan has a moderate solubility in neutral and alkaline conditions, it was necessary to obtain acidic silica sol in order to ensure homogeneous mixing chitosan with the silica sol.

Various composite porous materials have been prepared by the "sol-gel" method, which have been tested for the sorption of heavy metals from water. This method of obtaining composite sorbents allows to obtain sorbents with controlled porous characteristics. The mixture of alcosol-chitosan is also used to modify the structural characteristics of some other natural materials (peat, wood and paper wastes).The sorption capacities of the composites obtained were evaluated by the technique developed by us [4].

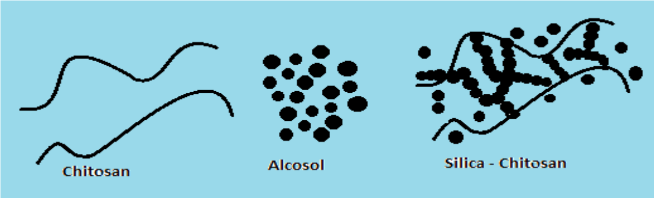

Figure 1. Silica-Chitosan composite.

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Abstract

A NEW GENERATION OF NANOPARTICLES MADE OF RESORBABLE POLY(ESTER AMIDE)S FOR OCULAR DRUD DELIVERY

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Most of the eye diseases are related to visual impairment and blindness. Treatment of these pathologies is one of the major challenges of modern ophthalmology. The eye is well protected by efficient mechanisms that rapidly remove drugs after instillation on the eye surface. Physical-biological barriers such as the cornea prevent drugs from intraocular penetration. Hence, eye drops are less effective for the treatment of various diseases, which necessitates a risk-containing procedure of intravitreal injection. One of the rational ways to overcome the problem is the application of drug-loaded polymeric nanoparticles (NPs) that are able to penetrate through the ocular barriers when administered topically. Amino acid-based biodegradable poly(ester amide)s (PEAs) are one of the most promising for the design of NPs.

We have elaborated biodegradable NPs of various types by nanoprecipitation of the PEA composed of L-leucine, 1,6-hexanediol and sebacic acid (8L6). The originally designed arginine-based cationic PEA and comb-like PEA containing lateral PEG-2000 chains along with 8L6 anchoring fragments in the backbones were used to construct positively charged and PEGylated NPs. The NPs were loaded with fluorescein diacetate (FDA) as a fluorescent probe to detect if the NP penetrated into the cells. A preliminary in vivo study on intraocular infiltration of the NPs has been done using wild-type C57BL/6 mice. After penetrating into the cellular lysosomes, FDA probes became visible due to the hydrolysis of the diacetate groups, thus allowing for the detection of the NPs as tiny fluorescent spots inside the tissues. One day after administration, fluorescent dots were found at various sites - always in the peripheral cornea and the sclera, and in different layers of the outer retina depending on the type of NPs used. Four days after administration, fluorescent dots were still visible in the peripheral cornea and the sclera with some of the NPs. These results show that the new type of NPs infiltrate the ocular tissues after topical administration and are taken up by the cells. This raises hope that the NPs may be useful for ocular delivery of therapeutic agents.

Acknowledgement: This work was supported by Shota Rustaveli National Science Foundation of Georgia (SRNSFG) [FR17_102, Elaboration of biodegradable nanocarriers for ocular drug delivery in ophthalmology].

PSEUDO-PROTEINS – A NEW FAMILY OF BIODEGRADABLE POLYMERS FOR SOPHISTICATED BIOMEDICAL APPLICATIONS

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Proteins are one of the most appropriate biomaterials for a variety of biomedical applications including resorbable surgical and pharmaceutical devices owing to their innate affinity to tissues, enzymatic biodegradability with releasing α-amino acids (α-AAs) which could be assimilated by the organism promoting in that way tissue regeneration. However, the proteins have some serious shortcomings among which the most important is *immunogenicity* that is attributed to their molecular architecture. We have developed a new generation of α-AA based biodegradable (AABB) polymers having a new macromolecular architecture less recognizable by the immune system of the living organism. The key monomers to build up the macromolecules of the new architecture are diamine-diester monomers made of α-AAs and diols. Several classes of AABB polymers – poly(ester amide)s (PEA), poly(ester urea)s (PEU) and poly(ester urethane)s (PEUR), both regular and functional ones, having the widest range of material properties have been designed. The AABB polymers, similar to proteins, show a high tissue affinity/compatibility and release α-AAs upon the biodegradation, therefore they can be considered as pseudo-proteins suitable for numerous sophisticated biomedical applications in regenerative medicine, pharmacy, etc. [1-7].

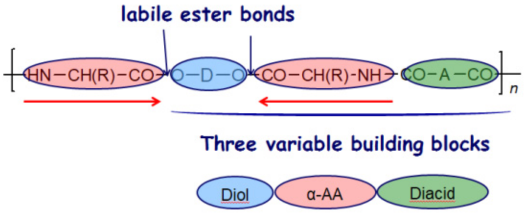

Figure 1. Representative structure of pseudo-protein of the PEA class

Acknowledgement: This study was funded in part by Shota Rustaveli NSF of Georgia, grant no. FR17-102.

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Abstract

SYNTHESIS AND STUDY OF BIS-AZLACTONE BASED NEW BIODEGRADABLE POLYMERS FOR POTENTIAL BIOMEDICAL APPLICATIONS

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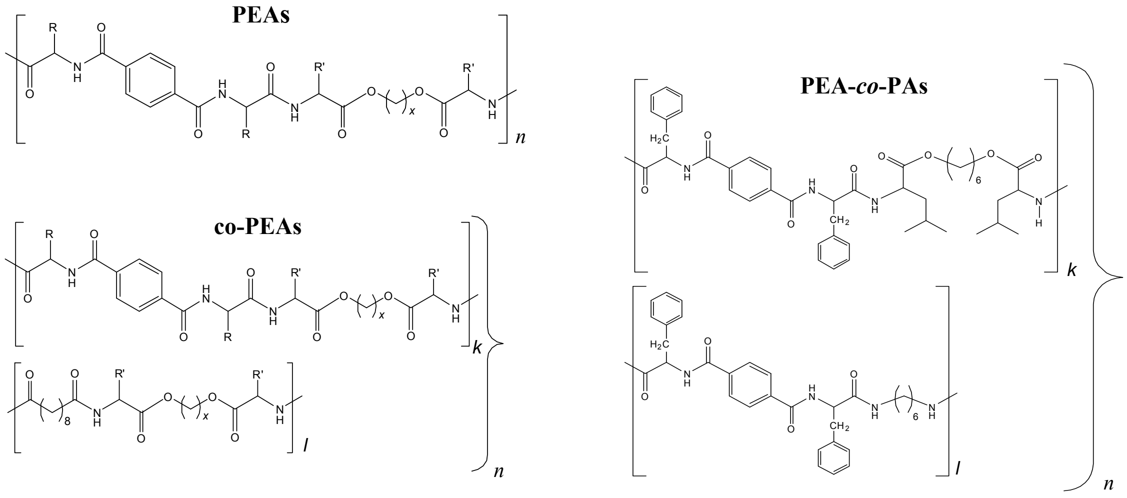
Three new classes of the amino acid based biodegradable (AABB) polymers were synthesized via step growth polymerization (SGP) of bis-azlactones and amino acid based diamine-diesters with activated fatty diester and alkylenediamine: a) poly(ester amide)s (**PEAs**) by SGP of bis-azlactones with diamine-diesters, b) hydrophobically modified co-poly(ester amide)s (***co*-PEAs**) by SGP of activated fatty diacid diester and bis-azlactones with diamine-diesters, and c) poly(ester amide-*co*-amide)s (**PEA-*co*-PAs**) by SGP of alkylene diamine and diamine-diesters with bis-azlactones (Scheme1).



R = $CH(CH_3)_2$ (**V**), $CH_2C_6H_5$ (**F**);
R' = $CH_2CH(CH_3)_2$ (**L**), $CH_2C_6H_5$ (**F**);
x = **6** or **12**

$k + l = 1$; k / l = 0.5/0.5, 0.3/0.7, 0.1/0.9

$k + l = 1$; k / l = 0.9/0.1, 0.5/0.5, 0.3/0.7, 0.1/0.9

Scheme 1. Synthesis of the Bis-azlactone based polymers

The obtained polymers were characterized in terms of yield, elemental analysis, solubility in organic solvents, FTIR and NMR spectra, GPC, hydrophobicity, thermal properties, and enzymes' catalyzed *in vitro* biodegradation.

The new PEAs showed relatively low-molecular-weights (M_w within 2,800-19,600 Da, GPC in DMF), whereas the new *co*-PEAs and PEA-*co*-PAs exhibited high-molecular-weights (M_w within 40-100 kDa) leading to good mechanical properties. Incorporation of the bis-azlactone fragments into the poly(ester amide)s backbone increased hydrophobicity and thermal stability, whereas incorporation of diamine-diester units into the backbone of the bis-azlactone based polyamides rendered them biodegradable [1].

Synthesized AABB polymers are potential candidates for constructing resorbable surgical and pharmaceutical devices.

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HYDROGEN-BONDING ORGANOCATALYSIS IN RING-OPENING POLYMERIZATIONS

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Ring-opening polymerization (ROP) of lactones catalyzed by (super)strong Brønsted acid offers valuable approach to important biodegradable aliphatic polyesters. However, the need of mild acidic catalyst in the ROPs is long sought but unmet. Here we describe a truly weak Brønsted acid, benzoic acid, in combination with a dual H-bond donor (dHBD), catalyzes ROP of δ-valerolactone (VL) in solution at room temperature. A unique preorganized sulfonyl guanidine type dHBD, 3-amino-1,2,4-benzothiadiazine-1,1-dioxide (ABTD), shows to be optimal to work with benzoic acid as cocatalyst, promotes benzoic acid active in ROPs of VL. Poly-δ-valerolactones of predictable molecular weights (from 2.13 to 9.33 kg mol–1) and narrow dispersities (Đ ≤ 1.16) are synthesized. The controlled/living characters of the ROPs are verified by NMR, SEC, and MALDI-ToF MS measurements. An enzyme-mimetic mechanism follows the machinery in active site of squalene hopene cyclase is suggested, in which carboxylic group behaves a "strong" acid in protonating a carbonyl. NMR titration experiments imply ABTD preferentially binding with benzoic acid and benzoic acid/ABTD pair protonates VL monomer. Weak benzoic acid is not weak for the first time in efficient cationic ROP of VL by protonation mechanism.

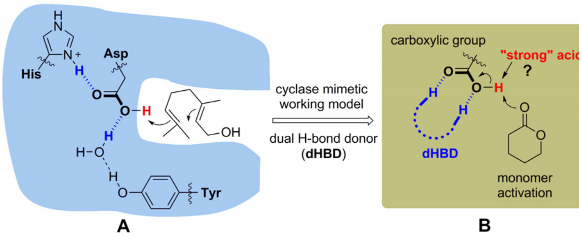

Figure. 1. Squalene hopene cyclases protonating alkenes [1] (**A**); Dual H-bond donor (dHBD) and carboxylic group as "strong acid" in protonating carbonyl of a monomer (**B**).

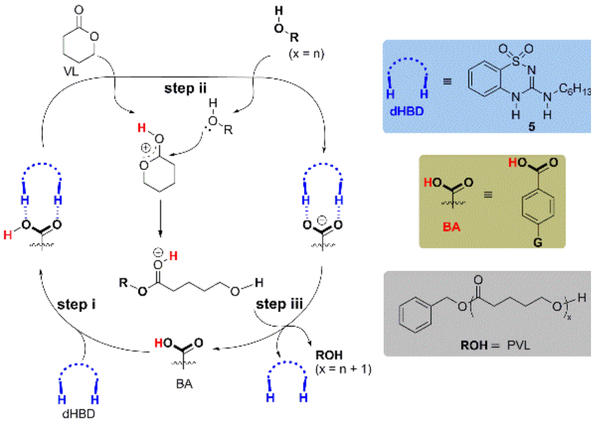

Figure 2. A plausible mechanism of cationic monomer activation of δ-valerolactone (VL) by cocatalysis of a benzoic acid (BA) and a dual H-bond donor (dHBD) in the ROP of VL.

Acknowledgement: Financial supports from the National Key Research and Development Program of China (2017YFC1104802), the National Natural Science Foundation of China (U1463201, 21522604), the Natural Science Foundation of Jiangsu Province, China (BK20150031), the Jiangsu Synergetic Innovation Center for Advanced Bio-Manufacture, the Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), the project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), the Top-Notch Academic Programs Project of Jiangsu Higher Education Institutions (TAPP).

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Abstract

DEVELOPMENT AND PROPERTIES OF ANTIMICROBIAL HYBRID COMPOSITE FILMS TO CONTROL BIOCORROSION PROCESSES

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Degradation of various art works (historic monuments, archeological patterns, museum exhibits, etc.) is the result of a delicate balance of aging, microbial pollutants, environmental conditions and wrong previous restoration treatments. Thus, development of novel efficient hybrid materials and further improvement of restoration performance formulations to control biocorrosion processes has significant interest of scientists aiming to rescue the cultural inheritance and environment as well.

Silicon- and fluorine-organic matrices with side epoxy groups and industrial polymers were used to create antimicrobial hybrid materials. As plasticizer modifiers polyorganosiloxanes with terminal functional groups at silicon atoms were used to improve elasticity, thermal stability, hydrophobicity, formation of homogeneous films and adhesion to the various substrates. As bioactive components we used nano and submicro biogenic metal oxides and hybrid heterometal coordination compounds containing organometallic and carbocyclic fragments as well.

The DSC measurements were performed with a differential scanning calorimeter from Netzsch, Selb, Germany, model DSC 200. All tests were conducted unter dry nitrogen in the temperature range from -100^{0}C up to +300^{0}C at a heating rate 5^{0}C/min. By differential scanning calorimetric analysis was shown the glass transition regions of the hybrid materials in the range between 125 and 230°C. The beta transition regions (T_β) of tested composites are in the temperature regions from -33°C to -43°C. The stability of the low temperature amorphous phase of the modified hybrids increases with respect to the pure polymeric matrices by modification with bioactive compounds.

Thermogravimetric analysis was carried out using Perkin Elmer TGA7 thermo gravimeter; temperature range 30-700^{0}C and a heating rate 10°C/min. Thermogravimetric study of all hybrids shows the resistance to thermal degradation with weight loss of 18-37% in the range of 420-440°C. Herewith resistance to thermal degradation is enhanced and weight loss is shifted to higher temperatures as the amount of polyorganosiloxanes increase and further is improved by addition of bioactive components.

Tribological characterization of materials deals with friction, wear, scratch resistance and design of interactive surfaces in relative motion. Tribological tests were performed for each material using a Micro Scratch tester (MST) [CSEM, Neufchatel, Switzerland] and Dynamic friction was measured using of a Nanovea pin-on-disk tribometer [Micro Photonics Inc.]. The modification mainly causes improvement of sliding wear resistance and viscoelastic recovery (75-90%) with respect to pure polymers, lowering of coefficient of dynamic friction and also increasing of hydrophobicity. Progressive scratch testing with linearly increased load (1.0 N - 30.0 N) results show that the modification does improve scratch resistance of hybrids with respect to pure polymers depending on the modifier type and its quantity. The study of surface morphology [Scanning electron microscope (SEM), Nicon Eclipse ME 600] and tribological properties after aging (70^{0}C, 10 days) show an improvement of characteristics of scratch resistance, wear and dynamic friction coefficient.

Thus, improved tribological and thermo-physical features of created inorganic-organic materials offer remarkable possibilities to the functional reliability and lifetime of material components and surfaces during exploitation and provide their long-term/short-term antimicrobial protection.

Acknowledgement: Financial support to one of us (Kh. Barbakadze) has been provided by the Fulbright Foundation, Washington, DC, in the form of a Senior Scholarship.

Abstract

INVESTIGATION OF COMPLEX FORMATION PROCESS OF ZINC WITH MACROMOLECULAR ORGANIC SUBSTANCES, ISOLATED FROM NATURAL WATERS IN HOMOGENEOS SYSTEM AT pH=5

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Natural macromolecular substances- fulvic acids have functional groups and they form stable complexes with heavy metals and radionuclides and stipulate migration forms of toxic metals in soils, natural waters and atmospheric precipitations.

In spite of researches, experimental datas on stability constants of complex compounds of fulvic acids are heterogeneous and they differ in several lines from each other. This condition is stipulated by the ionization degree and also by the changes of the value of pH in complex formation process, by the ignoring of average molecular weights of their associates, which finally causes the wrong result.

Our objective was to obtain pure samples of fulvic acids, to study complex formation process between zinc and fulvic acids at pH 5 in homogeneous system by the gel chromotographic method and calculation of the conditional stability constants.

For the isolation of fulvic acids from the Faravani lake was used the adsorption-chromatographic method. The charcoal was used as a sorbent.

Taking into consideration an average molecular weight of fulvic acids at pH= 5 (MwFA=2210) for the optimal determination we used sephadex G-25 (the limits of Fractionating100–5000)

Increasing quantity of standard solutions of fulvic acids and Certain concentrations of Zn(II) solutions,which were prepared from the standard solutions, made for determinations by the atomic absorption method were placed in fluoroplastic cylinders(capacity 15ml).

Constant ionic strength was achieved by adding KNO_3 solution. v=10ml. The concentration of hydrogen ions was regulated by the addition of 0.01 M KOH acid or 0.01 M HNO_3 in model solutions (pH meter pH 2006).

Aliquots of model solutions (2-2 ml) with different pH (2-2ml) which were placed in the top part of the gel chromatographic column. The elution process was done by 0.01 M KNO_3 solution. The quantity of metals connected with fulvic acids were determined in such fractions which releasing volume fits substances with molecular weight 300≤ Mw>5000 by the atomic-absorption method (Perkin Elmer 200).

Ligands number in the inner coordination sphere of complex equals to tangents of tilt angle of straight line built in coordinates lg ($[Zn\ (II)_{totsal}] - [Zn\ (II)_{free}]$) and lg $[FA_{tota}l]$.That value was 0.96.It means that in Zn(II)-FA system dominates complex with the structure 1:1. For calculation the exact value of tangents tilt angle of straight line, for this purpose was used the least square method.

For the calculation of stability constants was used Leden method, which is based on usage of Leden function F(L) $F(L)=F(FA)=[ZnFA]/([Zne(II)_{free}]x[FA_{free}])=([Zn\ (II)_{totsal}] - [Zn\ (II)_{free}])/\ /([Zn\ (II)_{free}]x[FA_{free}])= \beta 1+\beta_2 x[FA_{free}]$, where $[FA_{free}]$ free ligand.

Calculation of characteristics of Leden's during the study of fulvate complexes is easy.

The concentration of metals connected with fulvic acids quantitatively equals to the quantity of metals(mol/L) determined in gel chromatographic fractions $[FA_{free}]= [FA_{total}] - [ZnFA]$; $[Zn(II)_{free}]= [Zn(II)_{total}] - [ZnFA]$, where $[Zn(II)_{total}]$-the total quantity of zinc in solution(mol/L),which is constant value for concrete metal during the study of complex formation.

When the concentration of free ligand, aspires to zero, the stability constant can be found by the graphic method. The section which is cut on the ordinate by the straight line built in coordinates F(FA) ____ $[FA_{free}]$ equals to the stability constant. The value of stability constant was calculated by the least square method. $\beta= 4,47x10^3$

Abstract

EFFECT OF FILLER MODIFICATION ON SOME PROPERTIES OF COMPOSITES BASED ON EPOXY RESIN

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Polysiloxanes have chains constructed of alternately arranged silicon and oxygen atoms with organic groups attached to the silicon atoms. This structure give them a unique combination of properties that hold great interest for a host of practical application [1- 5].

The composites based on epoxy resin with some mineral fillers (diatomite, andesite) are used for demonstration of the effect of filler modification on the important exploitation properties of composites. Ultimate strength, softening temperature, and water absorption of the polymer composites based on epoxy resin with unmodified and/or modified by tetraethoxysilane (TEOS) minerals are described. Comparison of experimental results obtained for investigated composites shows that ones containing modified filler have an essentially better technical parameters mentioned above than composites with unmodified filler at corresponding loading. All functions of investigated parameters depending on the filler concentration have an extreme character – at definite signifycances of the filler concentrations the corresponding curves have the maximums. Obtained experimental results are explained in terms of composite structure peculiarities. Modifier molecules displaced on the mineral particle surfaces participate in chemical reactions between active groups of TEOS and homopolymer, in result of which modified mineral particles display more high compatibility of the ingredients than in case of same composites with unmodified fillers. The noted phenomenon is the main reason of improving of all technical parameters of composites. Experimentally is shown that the composites containing binary fillers diatomite and andesite at definite ratio of them possess the optimal characteristics – so called synergistic effect corresponding to maximal compatibility of the ingredients. Modifier in this case ensure to decreasing of the stress state in the composites structures.

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Abstract

DEXTRANSUCRASE ENTRAPMENT AS AN EFFICIENT ALTERNATIVE FOR INCREASED RECYCLING EFFICIENCY OF FREE ENZYME WITHIN AGAR-AGAR FILM MATRIX

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Dextransucrase (DS), the extracellular enzyme is of immense industrial importance, due to ability to produce dextran and oligosaccharides (OS). Worldwide interest in OS has been increasing, since they have been accorded the prebiotic status. However, the industrial application of DS for OS synthesis is limited, due to low yield of enzyme production and its low catalytic activity. Hence, there is a great interest for development of new technologies that can provide improved performance of biocatalyst. Enzyme immobilization technology is considered to be a crucial step for cheaper and more efficient usage of DS. Entrapment is one of the widely investigated immobilization methods, where enzymes are enclosed or confined within the polymer matrix without altering their native structure, developing bioreactors for commercial applications. Different matrices such as polyacryl-amide gel, alginate beads and agar–agar have been used for the entrapment of different enzymes and among them agar–agar is a biocompatible, non-toxic and strong solidifying agent for immobilization of various enzymes.

In this work, the entrapment of DS was initiated by different quantity (1:9, 1:4 and 1:1) of dialyzed enzyme into agar- agar solution. Agar solution was prepared in distilled water by vigorous shaking at 100°C, autoclaved and was allowed to cool to 40–45°C. Afterwards, enzyme was incorporated and mixed thoroughly. This mixture was immediately poured into a clean Petri plate and left to solidify at room temperature. Polymer films with and without immobilized DS were analyzed in terms of enzyme activity and reusability and mechanical properties (tensile strength, elongation at break and elastic modulus). In order to remove un-entrapped enzyme the films were washed with double deionized water and sodium acetate buffer (pH 5.4) three times prior to enzymatic assay. For quantitative analysis of samples for OS production a Dionex Ultimate 3000 HPLC system was used.

Results showed that maximum immobilization yield (74.11%) was achieved by use of 2 % agar and (1:9) enzyme: agar ratio. HPLC analysis confirmed the similar trend of OS formation in immobilized samples compared to free enzyme. The lowest tested fraction of enzyme immobilized into polymer matrix (1:9) improved tensile strength of films in comparison with control film, whereas higher concentration of enzyme led to decrease in mechanical resistance of films. Scanning electron microscopy of agar films before and after DS entrapment revealed significant morphological change on the matrix surface. Considering the economic feasibility, the entrapped DS indicated imperative recycling efficiency up to six reaction cycles. The results of this study revealed that an easily available and inexpensive matrix could be successfully employed for DS immobilization and OS production.

Acknowledgement: The authors gratefully acknowledge the financial support of Ministry of Science, Education and Technological Development of the Republic of Serbia under the project TR 31035.

CHARACTERIZATION AND COMPARISON OF MAIZE STALK AND SUGAR CANE BAGASSE RESIDUES

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The aim of this study was to investigate the properties pulverised cellulosic material from Maize stalks and sugar cane bagasse. Both biomasses were first subjected to a cutting mill for size reduction before boiling with water (Figure 1). The chemical compositions and mechanical properties of the maize stalk residues and sugar cane bagasse were performed using a TAPPI standard. Raman spectroscopy, Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and SEM were used to characterise the materials. The reduction in size resulted in improvement of both crystallinity and thermal stability of the materials. These dynamic properties will be tested in different polymeric metrics including PP, PET and HDPE.

Figure 1. Mechanical method used to cut biomasses.

Abstract

SAWDUST BASED COMPOSITE

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Several studies have shown interesting results in the use of wood waste to generate products with enhanced market value. Examples include building materials, composite materials, fertilizers and composting, absorbent media and biofuels.

A polymer composite on the basis of phenol-formaldehyde resin and sawdust with different dispersion known as particleboard is widely used, particularly in construction and furniture industries. Along with many positive characteristics there is a serious drawback: the presence of formaldehyde, a cancerogeneous material. World health safety organization experts have established that even very small concentrations of the formaldehyde in the human organism leads to such symptoms as headache, depression, and effect on the central nervous system. Long time action of the formaldehyde on the human organism leads to depression of human genetic activity, reproduction capabilities, skin and sight worsening.

We have developed new composites with improved properties containing dispersed sawdust (pine) particles (with length less than 50 μm). The binders were: polyethylene, PhES-50, PhES-80, liquid glass (LG), colophony and wood glue.

We have determined for our composites bending strength, impact viscosity, thermal stability by the Vicat method and water absorption. Structures were studied using an optical microscope, scanning electron microscopy and energy dispersion micro X-ray spectral analysis.

The composites containing PhES-80 with sawdust show improved thermal stability above a certain pressure level. This result is due to two reasons: a) the total volume of connected micropores distributed randomly in the composite body is reduced at relatively high pressures and, consequently, the rigidity and thermal stability of the material increases; b) PhES-80 creates intensive heterogeneous chemical bonds in composites. PhES-50 containing composites behave similarly but the total micropores volume is smaller than for the case of PhES-80. The latter seems characterized by high branching of molecules.

Acknowledgement: The financial support of the Georgian National Science Foundation in Tbilisi, Grant #STCU 5892, is gratefully acknowledged.

Abstract

FISH SCALE BIOPOLYMERS: EXTRACTION, PROCESSING AND APPLICATION IN NOVEL TRANSDERMAL DELIVERY SYSTEMS

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Fish scales are generally waste generated from fish processing. They are of particular economic and research interest as they are food waste discarded pre-meal and thus can be collected at point of sale or as food factory waste. They are an abundant source of biopolymers, fish scales have been reported to contain 30-40% protein (mainly collagen), 30 -50% Calcium and potassium carbonate and 20 – 30 % chitin (Knorr D, 1984), all of which are valuable when extracted and processed. Our previous studies have shown the potential for extraction of biopolymers from fish scales and their applicability in pharmaceutical applications (Olatunji et al, 2017; Olatunji & Denloye 2017; Mehdi et al, 2017). The present study investigates the transdermal transport profile of an active compound from a transdermal delivery system formulate using biopolymers extracted from fish scales.

The present study is aimed at extraction of hydrolysed collagen and chitin from fish scales, developing loaded formulations and transdermal drug delivery systems using these formulations and testing the developed transdermal systems for delivery of a specific therapeutic compound based on passive transport.

Biopolymers extracted from fish scales were loaded with active therapeutic compounds and the rate of release from the transdermal systems produced were studied using varying formulation parameters.

Results show that the biopolymers effectively degraded into skin tissue model and the active compound within the system is released into desired site. The formulations of the biopolymers had an effect on the transport profile within the skin tissue model, thus implying that the formulation can be varied to achieved desired release profile.

The significance of this work lies in the development of a novel transdermal delivery system using biodegradable polymers derived from aquatic waste with the ability to vary formulation parameters to achieve controlled transdermal delivery of therapeutic compound.

Acknowledgement: This research is funded by central research Council of the University of Lagos. Nigeria.

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Abstract

LIQUID PHASE SHOCK WAVE CONSOLIDATION AND SYNTHESES OF NANOSTRUCTURED MgB_2 BASED SUPERCONDUCTIVITY COMPOSITES

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The original hot shock wave consolidation method was developed to consolidate nanostructured MgB_2-Fe and MgB_2-C superconductive cylindrical billets near to theoretical density with good integrity of consolidated particles [1,2]. As investigation showed the application of high temperatures and liquid phase consolidation of Mg-B-Fe(C) blend powders above the 900°C provides initiation of chemical reaction between the Mg and B particles behind and on the shock wave front with formation of superconductive MgB_2 phase. As a result the high dense billets from MgB_2 composites with uniform distribution of nanocristalline particles of Fe and carbon in whole volume of consolidated billets are observed. It's seems that partial formation of FeB phases there takes place too. There were established too that the value of critical temperature and density of consolidated billets depends not only on value of temperature but as well on purity and type of precursors.

The figure presented below shows dependence of critical temperature and magnetic properties in consolidated MgB_2-Fe composites after fabrication at 940°C with intensity of loading 5GPa.

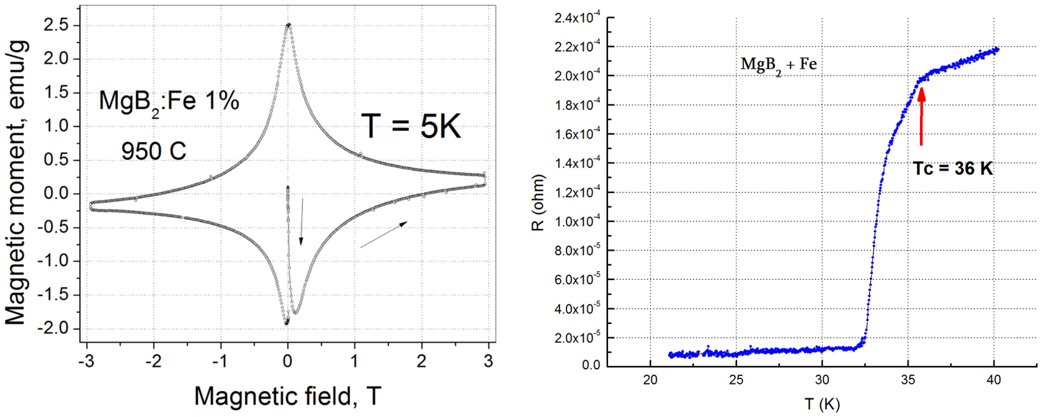

Figure 1. The characteristics of nanostructured MgB_2 -1%Fe composites after fabrication at 940°C with intensity of loading 5GPa.

The above mentioned and other features of structure/property relationship of fabricated MgB_2 - Fe and MgB_2-C nanostructured composites depending on consolidation conditions as well experimental set up and procedures will be described and presented.

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Abstract

CRYSTALLIZATION AND PROPERTIES OF STAR-SHAPED AND LINEAR POLY(L-LACTIDE)S

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Star-shaped poly(L-lactides) PLLAs were synthesized, 6-arm with M_w of 120 and 245 kg/mol and one 4-arm with M_w of 123 kg/mol. Linear PLLAs with M_w of 121-339 kg/mol were also prepared. Static crystallization of the PLLAs was studied in isothermal and nonisothermal conditions. The growth rate of spherulites was measured in a broad range of crystallization temperatures. Shear induced nonisothermal crystallization of the PLLAs occurring during post shearing cooling at 10 and 30 ^oC/min was also investigated.

At M_w close to 120 kg/mol the star architecture slowed down the spherulite growth above 120 ^oC, up to 145 ^oC. The spherulite growth in PLLAs with M_w > 200 kg/mol was slower than that in the other polymers and unaffected by the macromolecule architecture. The differences in the spherulite growth rate were reflected in overall crystallization kinetics in isothermal conditions and also in crystallization peak temperature and crystallinity developed during cooling [1]. Shear induced crystallization of the PLLAs was stronger than that of commercial polylactides containing D-lactide [2], and was influenced by M_w; the effect of shear was weaker at M_w close to 120 kg/mol, and much stronger for PLLAs with M_w > 200 kg/mol, although it was also dependent on the macromolecule architecture.

The rheological and tensile properties of the PLLAs were also examined, the latter in in the temperature range of 25-65 ^oC. The rheological properties and tensile properties at 65 ^oC depended primarily on M_w although the effect of the star architecture was also observed.

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Abstract

ACTIVE AGAR MINERALIZED COMPOSITE FILMS INTENDED FOR FOOD PACKAGING

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Polysaccharide-based materials represent an attractive alternative to plastics, due to their biodegradability, compatibility and great film forming properties[1]. As they are usually characterized by poor mechanical and barrier properties and lack of functionality, different components must be incorporated into these biopolymer materials in order to improve their properties. In this study, new mineralized, agar-based composite films with increasing Cu-phosphate mineral phase loadings (1, 2.5 and 5 mM) were prepared by *in situ* mineralization and solvent casting method. The presence of mineral significantly influenced the morphology, properties and functionality of the obtained composite films. Reinforcement with the Cu-phosphate phase improved in a concentration-dependent manner, optical, mechanical and water vapor barrier properties of the obtained mineralized films. In addition Cu-phosphate mineralized agar films exhibited antimicrobial activity against both, Gram positive and Gram negative bacteria, *Staphylococcus aureus* and *Escherichia coli*, respectively. The results of this study suggest that agar films mineralized with Cu-phosphate could be potentially used as affordable, eco-friendly and functional food packaging materials with tunable properties. Production procedure offers possibilities for increasing Cu-mineral phase content without compromising properties of the composite films.

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Abstract

MECHANICAL PROPERTIES, STRUCTURE AND BIODEGRADATION OF PLA BASED COMPOSITIONS WITH POLYSACCHARIDES

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The creation of the biodegradable polymer composites degraded under action of the environment on the harmless products is connected both with the necessity to utilize the polymer waste and with replace of synthetic polymers obtaining from oil. In this connection compositions of polylactic acid (PLA) produced from the natural raw with polysaccharides are very promising. PLA possesses good processability and high strength modulus, but it is expensive and it's biodegradability it low. Biodegradable polysaccharides have poor mechanical characteristic and processability, so the production of composites on their base promotes to eliminate these disadvantages. The compositions of PLA with starch, chitosan and ethylcellulose were obtained in the Brabender mixer. The mechanical tests showed that the addition of polysaccharides to PLA results in rise of modulus E, decrease of ε_b and slightly affected on the σ_b. To improve the composite plasticity the poly(ethylene glycol) (PEG) was used. It was established that addition of PEG leads to a decrease of the E and σ_b. At the same time abnormal dependence between the amount of introduced PEG and ε_b was found. So for the composition PLA–chitosan, containing 20 wt. % PEG ε_b increases up to 57,5 %, however the further rise in PEG leads to its fall to 29 %. The similar regularities were obtained for the compositions with other polysaccharides. The observed effect can be connected with the phase separation of the components with increasing of the PEG content. If the amount of the PEG is below 20%, the segmental mobility of PLA is improved and the increase of ε_b takes place; the further increase of PEG leads to the phase separation and decreasing of ε_b. The process of biodegradation was investigated by estimation of the samples resistance to the action of the mold fungi, measuring of samples mass loss after exposition in soil and by investigation of films structure by SEM. It is shown that the biodegradability depends on nature and ratio of the components. With using of SEM the appearance of defects in the structure of the composites after their exposure in soil, expressed in formation of holes and cracks leading to cracking and following fragmentation of the material was revealed.

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Abstract

POLYLACTIDE AND THERMOPLASTIC STARCH NANOCOMPOSITES

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In recent years the blends and nanocomposites of polylactide and thermoplastic starch arouse the interest of many research centers. The object of study is to develop a novel toughened polylactide/thermoplastic starch (PLA/TPS) nanocomposites. The effects of plasticizer (polydimethylsiloxanol) containing reactive silanol groups and neat (SiO_2) or modified, containing amino groups (A-SiO_2) nanosilica, on morphology as well as on thermal, mechanical and rheological properties of PLA/TPS blends, compatibilized by maleated PLA (MPLA), were investigated. Toughened PLA/MPLA/TPS (60/10/30) blend containing 3 wt. % of polydimethylsiloxanol and various contents (1, 3 or 5 wt. %) of silica was prepared in a co-rotating twin-screw extruder. The results indicated that polydimethylsiloxanol enhanced ductility and the initial thermal stability of plasticized blend. It can be supposed that using plasticizer can improve intermolecular interactions among the blend components through the reactive ≡SiOH groups. DSC and DMTA analysis showed that nucleation ability and reinforcing effect of A-SiO_2 on plasticized blend crystallization is much better than SiO_2. However, silica practically had no effect on the thermal degradation of composites. Moreover, silica remarkably improved elongation at break (Figure 1). Moreover, tensile strength and modulus increased compared to the blend without plasticizer. Silica further increased elongation at break of the material. However, the improvement strongly depends on silica content as well as its functionality. For neat silica, elongation increased whereas for the modified one decreased as silica content increased. Significantly higher value was observed for 1–3 wt.% of the chemically modified silica, indicating, most probably, intensive interfacial interactions among the hydrogen bonds of the anhydride groups of the MPLA, the hydroxyl groups of the starch and amine groups of the silica. Moreover, composites show lower tensile strength and modulus than that of plasticized PLA/MPLA/TPS blend, which increased with increasing silica content. This anomalous behavior may be resulting from preferential or virtually unpredictable distribution characteristics of silica around the micro-pores within toughened PLA/MPLA/TPS structure with respect to weight content and functionality. From the SEM images it is clear that the plasticized PLA/MPLA/TPS blend porous structure is highly related to the silica content and functionality. From DMTA, it was found that the modified silica is more efficient reinforcement than the neat one, due to the higher storage modulus of the composites.

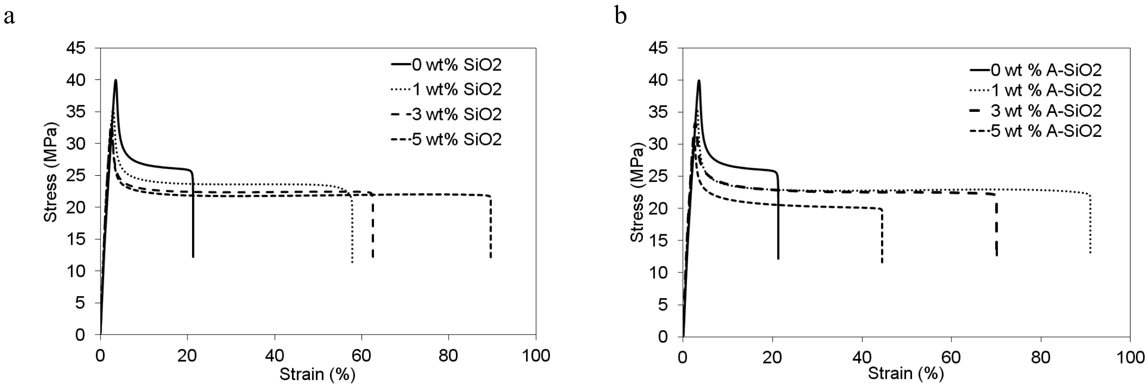

Figure 1. Stress-strain curves of PLA/MPLA/TPS/P composites with (a) SiO_2 and (b) A-SiO_2

Abstract

NATIONAL OPEN ACCESS SCIENTIFIC CENTRE FOR FUTURE ENERGY TECHNOLOGIES: OPPORTUNITIES FOR RESEARCH AND TESTING OF POLYMERIC MATERIALS

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National Open Access Scientific Centre for Future Energy Technologies (NOACFET) is a functional subdivision of the Lithuanian Energy Institute (LEI), which operates on the principles of open access for external as well as internal customers and provides scientific research and experimental services [1].

The NOACFET is a part of Open R&D Lithuania network, which consolidates facilities of 14 Lithuanian universities and 13 public research institutes as well as 7 science and technology parks. High-level R&D intellectual potential and infrastructure are concentrated to provide scientifically based solutions for business and society [2]. Agency for Science, Innovation and Technology (MITA) is responsible for the administration of Open Access Resources and Services register in Lithuania. „Open R&D Lithuania" network operates on a one-stop basis which means that customer does not need to go to research institutions and seek out who can do research, measurements, create technology, prototype or provide other scientific services. Customers just should write open@mita.lt and we will find a researcher or if it is needed scientists from different fields who can help business meet its needs, whether it is a small research or creation of difficult technology.

Activities related with polymeric materials research and testing mainly provided by the Laboratory of Materials Research and Testing of the NOACFET. This Laboratory developed the methodology of pipes set thermal conductivity determination by the guarded end method in accordance with the LST EN 253 and LST EN ISO 8497 standards, using its own designed equipment. This innovation was recognized as a Lithuanian product of the year 2013 and was awarded by a silver medal for the service "Determination of thermal conductivity of the thermally insulated pipe".

The NOACFET researchers constantly analyze demands of customers and expand the scope of services provided both in accredited and non- accredited field. They successfully participated in the comparative plastics testing's in Germany (Kunststoff-Institut Lüdenscheid and DRRR) in 2016. Finally, a high level of excellence was approved by special certificates. While cooperating with business representatives a decohesion testing of electrofusion-welded plastic joints was performed.

Acknowledgments. The author would like to thank Ministry of Education and Science, also, Agency for Science, Innovation and Technology for financial support under the project "Open access to science and research (MITAP II)".

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Abstract

NEW POLYMER SYNTHSIS via ALKYNE-AZIDE STEP GROWTH CLICK POLYMERIZATION

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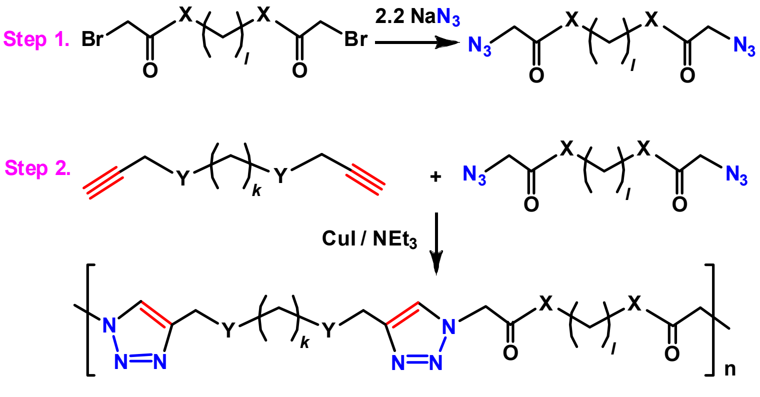
In the present work we have elaborated new synthetic strategy of step-growth polymerization (SGP) using copper(I) catalyzed azide-alkyne cycloaddition (CuAAC) "click" reaction for obtaining new 1,2,3-triazole containing heterochain "click" polymers. The new strategy is versatile and allows to synthesize different types (AB and AA-BB) and classes of click polymers - polyesters, poly(ester amide)s, poly(ester urea)s, etc. without using potentially explosive organic azides *via* safe one pot/two step/three component procedure (Figure 1). As a part of our systematic study, in the present work we are reporting on the first successful synthesis of click polyesters (PEs) *via* new synthetic strategy.

A systematic study of the new one pot/two step/three component CuAAC click synthesis of the PEs have been carried out and optimal parameters/ conditions of the reaction have been established [1]. The new 1,2,3-triazole-linked AA-BB-type click PEs have been synthesized under the optimal reaction conditions. The structure of the polymers was confirmed by FTIR and NMR spectrometry. The molecular weights and reduced viscosities of the click PEs were determined and their solubility and film-forming properties were tested. It was demonstrated that high-molecular-weight (Mw ≤ 73.7 kDa) click PEs with good elastic film-forming properties can be obtained *via* the new synthetic strategy. The DSC study of the click PEs showed that the incorporation of the rigid 1,2,3-triazole rings in the PEs' backbone substantially improved their thermal characteristics. Stable nanoparticles were obtained on the basis of the new PEs using the nanoprecipitation method. The obtained data opens an avenue to the synthesis of novel 1,4-disubtituted 1,2,3-triazoles containing heterochain polymers of various types and classes by applying the new synthetic strategy to both Cu(I)-catalyzed and copper-free click SGP.



X= O, NH, NR, etc. Y = CO-O, CO-NH, CO-NR, etc.

Figure 1. Synthesis of click polymers of various classes

Acknowledgement: This work was supported by the joint grant # 6298 from the Science and Technology Center in Ukraine (STCU) and Shota Rustaveli National Science Foundation of Georgia (SRNSF).

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Abstract

AZOCOMPOUNDS WITH EPOXY GROUPS AND OLIGOMERS ON THEIR BASIS

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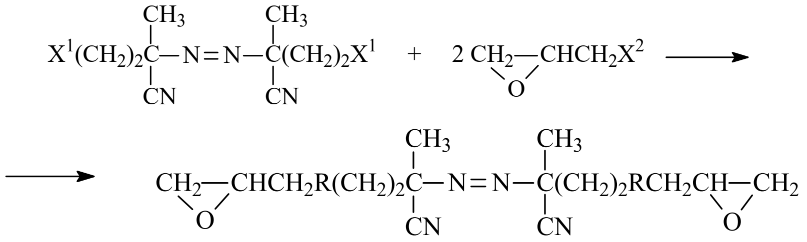
Functional azodinitrile compounds, along with the compounds containing peroxy groups in their structure, are used in different radical processes, in particular for obtaining monomer-based oligomers and polymers with carboxy, hydroxy, peroxy and other end-groups.

In this work we show the possibility of creating azodinitrile compounds with epoxy groups (ACEG), as well as obtaining oligomers and polymers with epoxy end-groups on their basis.

Generally the synthesis of ACEG is described by the following equation:



The initial compound for the synthesis was azocompound with carboxy and hydroxy groups. 2,3-epoxypropanol, epichlorohydrin and diepoxy derivatives of amines were used as epoxy components. The main kinetic regularities were determined for obtaining ACEG and methods of their synthesis were proposed.

Oligomers and polymers with epoxy groups were obtained via radical polymerization in the solution using the synthesized ACEG as an initiator. Divinyl, isoprene and styrene were the monomers. The structure of the synthesized oligodienes with epoxy groups was confirmed by the spectroscopy. The synthesized oligomers were found to be stereonon-regular compounds, 80% of which were chains of 1,4-addition.

By means of gel-permeation chromatography the oligodienes polydispersity was found to be 2.12. To decrease the polydispersity and increase the yield of multifunctional oligomers we propose to synthesize the mentioned oligomers by metered supply of ACEG.

The resulting oligomer has molecular weight of 4000 g/mol, functionality of 1.86 and polydispersity of 1.58.

Abstract

SUSTAINABILITY OF PORTLAND CONCRETE CONTAINING POLYMERIC FILLERS AND FLY ASH

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Portland concrete suffers in service brittle failure, extensive crack propagation, and wear rates increasing with time. In spite of all the effort expended, these problems persisted when we had started our project. We used several polymeric fillers and fly ash. Higher compressive moduli than the starting concrete are seen for some compositions, the highest for 5% of one of the polymers + 5% fly ash. The same composition has the lowest Taber abrasive wear loss. All composites show lower wear loss values than Portland concrete. After 25 days of acidic degradation in 4.0 molar aq. HCl, the starting Portland concrete suffers stronger degradation that our composites. Polymer swelling mitigates acidic degradation. Repetitive freeze-thaw cycles between 15°F and 85°F show disappearance of the deep voids present before the first cycle in our composites—but not in the Portland cement. While the use of fly ash mitigates contamination of the environment, it is the combination of fly ash with polymers which provides significantly improved properties - tribological, chemical and mechanical ones - of the Portland concrete.

Abstract

NEW INORGANIC POLYMERS : CONDENSED PHOSPHATES AND DIVERSE SPHERES OF THEIR APPLICATIONS

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Last time importance of the efficient and resource-saving technologies for synthesis and applications of new Inorganic Polymers - Condensed Compounds are out of any doubt which explains the relevance of our works thanks to our technological methods and experience that we have cultivated over many years. Multilateral spheres of utilisation of condensed phosphates are very diverse: ion-exchange materials, nanomaterials, efficient applying fertilizers, detergents, cement substances, catalytic agents, raw materials for phosphates glasses, thermo-resistant substances and also as food additive composites, besides, the phosphate's binding agents, phosphate-binders and laser materials are supplanted/ replaced by biomaterials, on the base of polyphosphates and hydroxyl apatite.

Presented work totalize information about synthesized by us many crystals and/or powder of Inorganic Polymeric Compounds, concretely diverse new groups of condensed phosphates, during investigations of the systems $M^{I}_2O - M^{III}_2O_3 - P_2O_5 - H_2O$ at 400K-850K (where M^{I} are various monovalent metals, including Ag and M^{III} – diverse trivalent metals). Numerous – specifically 72 - new formerly unknown double condensed phosphates so called inorganic polymers have been obtained. The possibilities of their application are investigated. For example cyclooctaphosphate $K_2Ga_2P_8O_{24}$ synthesized by us was studied for the catalytic activity in Moscow State University, the results showed that it has unique properties as an inorganic polymer and can be used as a best catalyst during organic synthesis reactions, specifically for the preparation of low molecular weight diene oléfines. Inorganic phosphates are used in engineering and the fields of constructions to such an extent that it would be quite justified to mention on the industry supplying the necessary phosphate materials. The basics component of these materials is the so-called phosphate adhesive used in the form of acid phosphates of various metals, phosphoric acid or condensed forms, all mixed with polyvalent metal oxides forming autonomous masses. At present, there are many metallophosphate acidic adhesives but on the outside among them, aluminum dihydrophosphate is widely used, aluminophosphate is more stable under storage conditions.

Abstract

CALMODULIN FUNCTIONALIZED WITH THE FLUORESCENT DYE AND GOLD NANOPARTICLE FOR THE TARGETING OF CALMODULIN MEDIATED PROCESSES IN EUKARYOTIC CELLS

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Calmodulin (CaM) is a multifunctional Ca^{2+} binding protein [1]. It functions as a central regulator of cellular metabolism in response to changes in cellular calcium levels by interacting with various targets. CaM has a potential therapeutic effect in cancer because of its suppressing action on cell proliferation and their capacity to revert the multi-drug resistance tendency of many tumor cells, including prostate cancer cells. Moreover, many effects of $Ca2^{+}$ in cells are mediated by the binding of $Ca2^{+}$ to CaM, which causes CaM to bind and activate target proteins. Consequently, the targeting and visualization of the regions in biological tissues, with over-expressed concentration of $Ca2^{+}$/CaM complex could be a valid therapeutic approach in the detection and curing of cancer. The acquisition of images of biological matter by using fluorescent labels and nanomaterials is generally referred to as bioimaging and forms a large field of its own [2]. Therefore, it could be of interest to use a nanocomposite consisting of CaM conjugated with fluorescent dye and Gold Nanoparticles (GNPs) as the potential optical indicator for the labeling of biological cells including cancer cells. In this study we investigate a CaM functionalized with fluorescent dye Nile blue (Nb) and GNPs, and show that a covalently linking CaM to the excited fluorescent dye and GNPs can stimulate a surface-plasmon-coupled emission, resulting a strong fluorescence enhancement. This effect successfully can be used for the targeting, labeling and visualization of CaM mediated processes, such as inflammation, metabolism, apoptosis, muscle contraction, intracellular movement, for the detection and treatment of cancer cells.

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