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Faculty of Chemical Engineering and Technology

Cracow University of Technology

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including

Special Session

“Polyhydroxyalkanoates: Synthesis, Modification and Applications”

Kraków, 17–19 May, 2023

BOOK OF ABSTRACTS



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WELCOME

Organizing Committee of the 8th INTERNATIONAL SEMINAR ON MODERN POLYMERIC MATERIALS FOR ENVIRONMENTAL APPLICATIONS, including Special Session “Recent Polyhydroxyalkanoates: Synthesis, Modification and Applications”, would like to cordially welcome you in Kraków.

During the conference new achievements in the synthesis, characterization and processing of polymeric materials for environmental applications will be presented and discussed. As the general aim of this seminars’ series is to present new knowledge on advanced environmentally-friendly macromolecular materials, contributions will cover the area of homopolymers, copolymers, blends, hybrids and (nano)composites that are either biodegradable (biocompatible) or may have a positive influence on the environment. Special attention will be devoted to polymer nanocomposites and hybrids as novel materials with promising properties that may can applied in e.g. biomedical sector.

We wish you a nice and productive stay in Kraków, called often the ‘magic’ city, and we hope that the 8th Seminar will be a useful platform to exchange scientific ideas and to meet with colleagues active in the field of polymers & the environment.

The Organizing Committee
MPM2023

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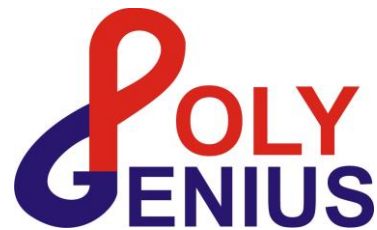
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ACKNOWLEDGEMENTS



ABSTRACTS

**PREPARATION AND CHARACTERIZATION OF PVC COMPOSITES
CONTAINING VARIOUS NANOFILLERS FOR WATER SERVICE PIPING
APPLICATIONS**

Dimitra Kourtidou¹, Evangelia Tarani*¹, Dimitrios Karfaridis¹, George Vourlias¹, Dimitrios N. Bikiaris², Konstantinos Chrissafis¹

¹*Laboratory of Advanced Materials and Devices, School of Physics, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece*

²*Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece*

Corresponding author: etarani@physics.auth.gr

Abstract

Polyvinyl Chloride (PVC) is a commonly used material in a variety of applications such as water pipes and cable insulation due to its lightweight, durable, and versatile characteristics. However, during its combustion of waste and/or house fires, hazardous are released [1]. Therefore, PVC's flame-retardancy and smoke-suppression have been a priority for many years. Various organic and inorganic additives have been used as fillers to achieve this goal. In this study, a fixed amount of additives such as UV stabilizers and inorganic nanofillers was incorporated into PVC, while at the same time varying contents of CuFe₂O₄ nanoparticles were added to the matrix to improve PVC's smoke-suppression properties. A preliminary study of the prepared materials' structural and thermal characteristics was conducted in this work. Scanning Electron Microscopy (SEM) images showed that the selected nanofillers were well-dispersed in the PVC matrix. The thermal stability of the materials was evaluated using Thermogravimetric analysis (TGA) while Differential Scanning Calorimetry (DSC) was employed to study the glass transition of PVC. Additionally, X-Ray Diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were used to conduct the structural analysis of the prepared materials. The addition of CuFe₂O₄ nanoparticles caused the partial immobilization of the polymer chains during the glass transition.

SYNTHESIS AND CHARACTERIZATION OF ECO-FRIENDLIER RESINS BASED ON PHENOL-FORMALDEHYDE AND SOY PROTEIN

Iouliana Chrysafi¹, Electra Papadopoulou², Kostantinos Chrissafis*¹

¹*Aristotle University of Thessaloniki, Physics Department, GR-541 24 Thessaloniki, Greece*

²*CHIMAR HELLAS S.A., 15 km National road Thessaloniki- Polygyros, P.O. Box 60666, GR 57001, Thessaloniki, Greece*

Corresponding author: hrisafis@physics.auth.gr

Abstract

Phenol formaldehyde (PF) [1] is a synthetic resin commonly used in a variety of industrial and commercial products, such as adhesives, insulation, and molded products. One of its main advantages is its high strength and durability, making it useful for a wide range of applications. However, due to its petrochemical origin, concerns about people's safety and the environment are raising [2]. When formaldehyde is released is a carcinogen and toxic to the environment, it can damage aquatic life, and contribute to the formation of ground-level ozone. In order to reduce these negative effects, it is important to use PF products in a responsible and sustainable manner, and to properly manage and dispose of any waste materials generated during production.

The scope of this research is to synthesize new PF-based resins, for wood adhesives, where a part of PF will be replaced by soy protein. PF was synthesized in three stages mainly due to polycondensation of hydroxymethyl-phenol. TGA and DSC were used to study the thermal properties including the thermal stability and thermal degradation of PF, soy protein, and the new PF-soy protein resins. FTIR analysis was also used to study the chemical properties of the samples.

Acknowledgements

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ALTERNATIVE AND ECO-FRIENDLY WOOD PLASTIC COMPOSITES BASED ON POLY(ETHYLENE SUCCINATE) AND HEMP FIBERS

Iouliana Chrysafi^{1*}, Eleftheria Xanthopoulou², Alexandra Zampoulis², Dimitrios N. Bikiaris²

¹*Aristotle University of Thessaloniki, Physics Department, GR-541 24 Thessaloniki, Greece*

²*Aristotle University of Thessaloniki, Chemistry Department, GR-541 24 Thessaloniki, Greece*

Corresponding author: iochrysa@physics.auth.gr

Abstract

The research aims to explore sustainable materials for the construction of Wood Plastic Composites (WPCs) in order to address the current triple planetary crises of climate change, biodiversity loss, and pollution. The ever-increasing plastic waste, particularly from polypropylene and high-density polyethylene, prompted the use of polyethylene succinate (PESu), a biodegradable polymer with good mechanical properties[1]. Additionally, deforestation, driven by the increasing demand for wood, has led the scientific community to seek substitute products that can replace natural wood. One promising alternative is the use of agricultural crop residues, such as hemp residues. Hemp is a lightweight material that has hydrophobic properties, long-term mechanical stability, and a low carbon footprint[2]. PESu was synthesized by a two-step melt polycondensation reaction, and composite materials containing hemp fibers at different concentrations were prepared by melt mixing in a twin-screw extruder. The chemical and structural properties of the materials were studied by FTIR and XRD techniques. The thermal stability and degradation of the composites were investigated by TGA analysis. Finally, the mechanical properties of the prepared materials were studied through tensile and impact strength tests.

Acknowledgements

This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH-CREATE-INNOVATE (project code: T2EAK – 00008).

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**“PROJECT TO REDUCE VOC/FOG EMISSIONS WITH A MAJOR REDUCTION
IN ODOUR LEVEL” – APPLICATION OF SOLUTION ELASTOMERS.**

Ewa Jagusiak

*Geyer&Hosaja Sp. z o.o. Partynia 12, 39-310 Radomyśl Wielki, Q-Tech Department
Technologist*

Abstract

Geyer&Hosaja is a leading manufacturer and direct supplier of all weather mats to many major automotive markets. In 2020-21, the company implemented an EU project – “Project of reducing the emission of volatile organic compounds with a major odour level reduction”. Reducing the emission of chemical substances inside the car is now a priority goal for car manufacturers, as the emitted substances not only cause discomfort but are harmful to the health of car users. The purchased laboratory equipment enabled research work focused on emissions and odour - gas chromatograph with flame-ionization detector (FID), inert selective mass detector (MS), thermodesorber, olfactometer. Additional equipment of the laboratory allowed to verify the other parameters of the products in accordance with the specifications of the automotive industry. Research work included analysis of raw materials used in the production of rubber products (new and current ingredients), testing the rubber compound (processability, designing the production process), testing of the finished product (acc. requirements). As a result of the research, we have eliminated raw materials that are a source of high levels of volatile organic substances, contain forbidden chemicals and emit an intense smell. Selected raw materials were used to compose rubber mixtures that meet all the required parameters. Products that fully meet the requirements were obtained. The impact of product storage on the reduction of emissions over time has been studied. On this basis, the minimum storage times for the products before the packaging process and the storage time before shipment to the customer were determined. The car mats we produce today are low odour, low emission products that meet international criteria for individual volatile substances emitted from the product. At the same time, this product meets the requirements for flammability, ozone resistance, heat resistance, xenon light resistance, etc.

Keywords: all weather mats, emission of volatile organic compounds, odour, reduction of emissions and odour level.

THERMAL STABILITY OF METHACRYLIC POLYMERS, ELIUM® RESIN AND ITS COMPOSITES

Emmanuel Richaud

Laboratoire PIMM, Arts et Metiers Institute of Technology, CNRS, Cnam, HESAM University, 151 boulevard de l'Hopital, 75013 Paris, France

Corresponding author: emmanuel.richaud@ensam.eu

Abstract

This paper deals with the thermal degradation of a methacrylic polymers, ELIUM® resin and its composites filled with aluminum trihydrate (ATH) used as flame retardant. ELIUM® is increasingly used as matrices for composites with the advantage of a low viscosity reactive mixture [1,2] which can be easily polymerized at moderate temperature [3].

Its thermal degradation was investigated by comparing PMMA, ELIUM® resin and ELIUM® filled with ATH fillers.

First, degradation was performed under inert atmosphere and studied by gravimetry. Basing on T_g and molar mass measurements, degradation was observed to be mainly driven by an unzipping mechanism. A kinetic model was proposed to predict mass loss whatever the temperature. Under air, an oxidation mechanism occurs due to the fast reaction of oxygen with alkyl radicals created by the unzipping mechanism. The kinetic model was hence completed [4].

In a second step, the degradation of thick composited blocks made of ATH and ELIUM® resin was by gravimetric and elemental analysis. It was discussed and explained from the above results together with a study of the stability of fillers. ATH seems to have minor effect on degradation mechanism but would increase oxygen diffusivity and the thickness of oxidized layer observed by microscopy.

Acknowledgements

Arkema is gratefully acknowledged for having supplied samples.

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ADVANCED MATERIALS MODIFIED WITH SILICON COMPOUNDS VIA CATALYTIC REACTIONS

Bogdan Marciniec

Faculty of Chemistry and Centre for Advanced Technologies, Adam Mickiewicz University in Poznan, Uniwersytetu Poznanskiego 8 and 10, Poznan, Poland

marcinb@amu.edu.pl

Abstract

Last year we published the review entitled “Inorganometallics and Catalysis” [1], which is focused on the synthesis, structure and reactivity of inorganometallic (metalloid-E) compounds containing a transition metal (TM) - E bond. Since that time a growing number of attempts have been made to propose complexes containing this bond, which could be later used as catalysts [2].

Per analogy to the role of organometallics in catalysis, which is also the basis for the synthesis of organometalloid derivatives, the compounds containing TM–E bonds, although distinctly different from organometallics, play a similar role of active intermediates in transformations of the p-block compounds whose best representative is silicon [3, 4]. Therefore, in the limited time of a lecture on special applications of silicon compounds (silicones, organosilanes and silsesquioxanes) in material science we concentrate on the catalysis by TM-complexes in (organo)silicon chemistry. In particular, a general strategy for heterogeneous catalysis by a single TM atom coming from such complexes will be presented [5].

The following processes for synthesis of silicon precursors of advanced materials will be discussed:

- hydrosilylation of unsaturated compounds by Si-H containing substituted silanes, (poly)siloxanes and silsesquioxanes as well as cross-linking of silicones;
- silylative coupling vs. cross-metathesis of olefins: compounds with vinyl-substituted silicon derivatives;
- metalation of compounds containing sp² and sp carbon–hydrogen and heteroatom-hydrogen bonds ;
- silylative coupling of alkynes with silicon iodides.

Finally, an extension of the above reactions of silicon compounds particularly to germanium and boron compounds can be valuable evidence of an exceptionally wide range of applications of inorganometallic catalysis for new materials of unique structures and specific properties to be used in new technologies [1].

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FROM THE INSIDE OF SILSESQUIOXANES TO THEIR MACROSCOPIC POTENTIAL

Beata Dudzic^{a,*}, Katarzyna Mituła^a, Monika Rzonsowska^a, Aleksandra Mrzygłód^a

a) Faculty of Chemistry and Centre for Advanced Technologies, Adam Mickiewicz University in Poznan, Uniwersytetu Poznanskiego 8 and 10, 61-614 Poznan, Poland

*beata.dudzic@gmail.com

Abstract

Silsesquioxanes (SQs) – a group of specific organosilicon representatives of diverse architectures. Their uniqueness results from the presence of inorganic siloxane Si-O-Si core and tuneable functional organic coronae which classify them as hybrid systems. Due to the nature of their defined construction that affects resulting physicochemical properties, they may be found in a wide range of applications.[1] The continuous interest in the chemistry of functionalized silsesquioxanes and their appliance is a derivative of not only a few types of cores of diverse structures but most of all the variety of reaction organic moieties that may be attached to it. The kind of organic functionalities at the Si-O-Si core affects the type of modification to which they may be subjected. Protocols based on TM-mediated catalytic reactions are of special importance because of their effectiveness and selectivities, e.g. hydrometallation, coupling or click processes, Friedel-Crafts, etc. Additionally, as the inorganic core is the scaffold for the different amounts of reactive moieties, it may result in the formation of various structures of resulting hybrid materials, i.a. grafted polymers, cross-linked systems, or 3D networks, and also coordination polymers. In addition, they may exhibit interesting physicochemical features.[2,3] Herein, we report on the studies on the formation of silsesquioxane-based systems – precursors of hybrid materials. Interestingly, in some aspects, the results of those modifications may be quite unexpected.

Acknowledgements:

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LOW COST CARBON FIBRES FROM LIGNIN / BIO-POLYAMIDE BLENDS

Baljinder K. Kandola*, Trishan Hewage, Muhammed Hajee and A. Richard Horrocks

*Institute for Materials Research and Innovation, University of Bolton
Deane Road, Bolton, BL3 5AB, UK*

Corresponding author: B.Kandola@bolton.ac.uk

Abstract

Lignin, a by-product from the paper and pulp industry, has a high carbon content (> 60%), excellent char-forming ability and a potential to be spun into fibres. These properties make lignin an ideal candidate to be used as a precursor for carbon fibres production. There are however multiple technical challenges, the main ones being compounding/spinning the lower molecular weight lignins and long thermal processing times required for carbonisation. In order to address the first challenge, the lignin can be blended with other thermoplastic polymers and the resulting blends melt spun into filaments. Another challenge is to increase the char yield of the lignin-based precursors for carbon fibre production, which can be addressed by adding crosslinkers and char promoters in the blends. In this work a hydroxypropyl modified organosolv lignin has been blended with a bio-based polyamide, PA 1010 and extruded into fibres. A number of crosslinkers have been added to the blends either as additives prior to melt spinning fibres or as surface treatments of the extruded fibres. The charring efficiency of the blends has been investigated by thermal analytical techniques (e.g. TGA, DSC, DMA). The mechanical properties of thermally stabilised fibres were improved from those of similarly thermally stabilised TcC/PA1010 fibres. It is envisaged that these could be successfully carbonised with higher carbon yield.

Acknowledgements

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ENVIRONMENTALLY FRIENDLY COPOLYMERS

Karol Tutek, Anna Masek

Lodz University of Technology, Street Stefanowskiego 16, 90-537 Lodz, Poland

Corresponding author: karol.tutek@dokt.p.lodz.pl; anna.masek@p.lodz.pl

Abstract

Science and industry are constantly searching for new materials to meet the needs of society. Polymers, with their wide range of mechanical, thermal and physicochemical properties, are one of the most developed groups of such functional materials. Their modifiability is also considerable, which is why polymeric materials have found applications in almost every area of life. As a result, they are very common and inexpensive, but most polymers are a problem for the environment because they are not bio-degradable in natural environments. Therefore, this line of research aims to use more environmentally friendly polymers, i.e. biodegradable biopolymers, in various areas of life and industry. However, to increase the possibility of their widespread use in functional materials, it is necessary to modify some properties to meet the specific needs of the consumer. To this end, biodegradable polymers acting as backbone chains have been modified by grafting the side chains of polylactide (PLA) and polycaprolactone (PCL)[1,2]. The starting polymers used were cellulose and its derivatives, starch or poly(vinyl alcohol) (PVA). This approach and the structural modifications carried out resulted in materials with unique physicochemical and thermal properties.

Acknowledgements

This work was completed while the second author was a doctoral candidate in the Interdisciplinary Doctoral School at the Lodz University of Technology, Poland.

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APPLICATION OF SILICON COMPOUNDS IN POLYMER MATERIALS FOR ADDITIVE FDM PRINT TECHNOLOGY

Bogna Sztorch

Centre for Advanced Technologies, Adam Mickiewicz University in Poznan,
ul. Uniwersytetu Poznanskiego 10, 61-614 Poznan, Poland; bogna.sztorch@amu.edu.pl

Abstract

Rapid development of manufacturing technology and prototyping based on additive techniques creates a significant gap in the area of materials which must meet their requirements and adapt to limitations of these methods. Intensive progress and increasing interest in additive techniques as well as in application possibilities puts stress on researchers to provide new solutions for increase in parameters such as tensile strength, abrasion resistance, processing viscosity, thermal stability and many others [1]. Organosilicon compounds of various structures are successfully used as efficient additives for the preparation or in processing of polymers and polymer composites [2]. As a part of the research, organosilicon functional compounds such as silsesquioxanes and polysiloxanes with various functional groups were used for the first time to obtain PLA composites for 3D printing. Functionalized octasubstituted organosilicon modifiers, both single type and mixed systems were obtained by hydrosilylation of olefins with octaspherosilicates in presence of Karstedt's catalyst [3].

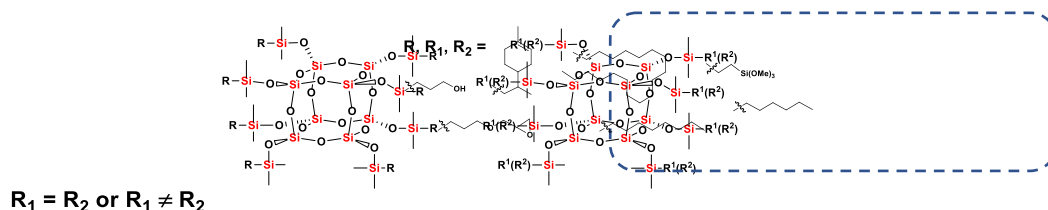


Figure 1. Octaspherosilicate derivatives used as PLA modifiers.

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SYNTHESIS AND FUNCTIONALIZATION OF BORASILSESQUIOXANES

Miłosz Frydrych¹, Bogna Sztorch², Bogdan Marciniak^{1,2}

¹ Faculty of Chemistry, Adam Mickiewicz University in Poznań, 8 Uniwersytetu Poznańskiego, 61-614 Poznań, Poland; frydrych@amu.edu.pl

^{1,2} Centre for Advanced Technologies, Adam Mickiewicz University in Poznań, 10 Uniwersytetu Poznańskiego, 61-614 Poznań, Poland; bogna.sztorch@amu.edu.pl (B.S.); bogdan.marciniak@amu.edu.pl (B.M.);

Abstract

In recent years there has been a growing interest in structures with heteroatom in the cage - heterosilsesquioxanes. They constitute a new class of silsesquioxanes, where the silicon atom in the structure or corner of the cage is replaced by another element. In this work borasilsesquioxanes with boron atom will be discussed [1].

The subject of these studies is the catalytic hydrosilylation reaction of silane, siloxane and caged-siloxanes with mono- and distyrylborasilsesquioxanes (obtained in accordance with [2-3]) in the presence of the Karstedt catalyst.

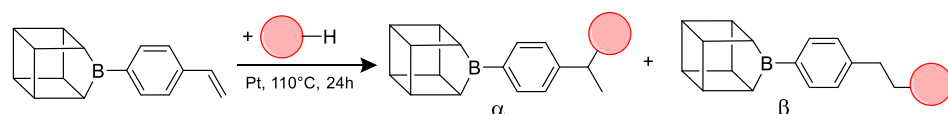


Figure 1. General scheme for hydrosilylation of vinylborasilsesquioxane with compounds bearing Si-H moiety.

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OCTA(3-THIOPROPYL)SILSESQUIOXANE AS A MODIFIER OF PLASTICS

Daria Pakuła¹, Robert E. Przekop², Bogdan Marciniak^{1,2}

¹ Faculty of Chemistry, Adam Mickiewicz University in Poznań, 8 Uniwersytetu Poznańskiego, 61-614 Poznań, Poland; darapak@amu.edu.pl

^{1,2} Centre for Advanced Technologies, Adam Mickiewicz University in Poznań, 10 Uniwersytetu Poznańskiego, 61-614 Poznań, Poland; rprzekop@amu.edu.pl (R.E.P.); bogdan.marciniak@amu.edu.pl (B.M.);

Abstract

The polymer market is characterized by continuous growth in response to the fast development of industry. Many literature reports indicate an improvement in the physicochemical properties (e.g. rheological, mechanical and hydrophobic properties, thermal stability) of plastics in which organosilicon compounds are introduced [1], but do not describe materials modified with octa(3-thiopropyl)silsesquioxane (SSQ-SH), which creates a significant gap of these materials development.

The aim of the work was to determine the influence of SSQ-SH on the functional properties of different plastics. Octa(3-thiopropyl)silsesquioxane was prepared by the hydrolytic condensation of (3-mercaptopropyl)trimethoxysilane according to literature [2-3] and our previous article [4] (Figure 1). The effect of the additives on the thermal, mechanical, hydrophilic-hydrophobic properties of the new materials was determined.

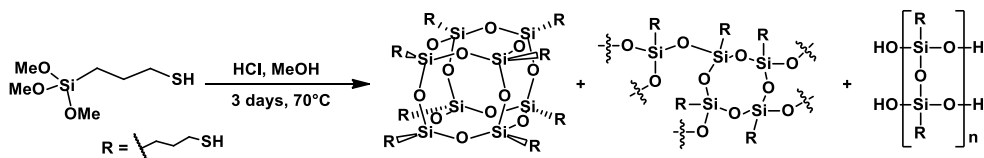


Figure 1. Hydrolytic condensation of (3-thiopropyl)trimethoxysilane.

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INTERMIXED GLASSY PHASE IN POLYMER/FULLERENE MIXTURES FOR PHOTOVOLTAICS

Daniele Cangialosi^{*1,2}, Sara Marina³, Jaime Martin^{4,5}

¹*Centro de Fisica de Materiales (CSIC-UPV/EHU) Paseo Manuel de Lardizabal 5, San Sebastián 20018, Spain*

²*Donostia International Physics Center (DIPC) Paseo Manuel de Lardizabal 4, San Sebastián 20018, Spain*

³*University of the Basque Country UPV/EHU*

⁴*Av. de Tolosa 72, San Sebastián 20018, Spain*

POLYMAT, University of the Basque Country UPV/EHU, Avenida Tolosa 72, 20018 Donostia-San Sebastian, Spain

⁵*Grupo de Polímeros, Centro de Investigaciones Tecnológicas (CIT), Universidade da Coruña, 15471 Ferrol, Spain*

*Corresponding author: daniele.cangialosi@ehu.eus

Abstract

Most organic solar cells (OSC) consist of a binary mixture of an electron-donating and an electron-accepting material, forming a so-called bulk heterojunction (BHJ). While mixing results in the formation of the crystalline phases of the two pure components, extraordinary importance from the viewpoint of performance is played by the intermixed amorphous phase, where the electron donor:acceptor interchange takes place. The characterization of the intermixed phase has hitherto remained elusive, in particular for what concerns its composition, a crucial parameter in photovoltaic performance. Our work goes at the very heart of this problem employing fast scanning calorimetry (FSC), which allows for the direct determination of the absolute composition of the intermixed domains in BHJ OSCs. Our method exploits the composition dependence of the glass transition temperature, T_g , of the amorphous intermixed phase. We apply this methodology to mixtures of a typical conjugated semi-conducting polymer, poly(3-hexylthiophene) (P3HT), with fullerene derivatives. Studying composition dependent T_g allows constructing a “master curve” subsequently employed to identify the weight fraction of the donor and acceptor in real device BHJ intermixed regions. Hence, our methodology, via the compositional characterizations of organic solar cells, paves the way to a rationale design of devices.

Acknowledgements

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**THE BIOCOMPATIBLE NANOCOMPOSITES BASED ON
POLY(3-HYDROXYBUTYRATE) AND HYPROMELLOSE. THERMAL AND
BIOLOGICAL PROPERTIES**

Anna Czerniecka-Kubicka^{1*}, Karolina Maternia-Dudzik¹, Weronika Gonciarz², Marek Pyda³

¹*Medical College of Rzeszow University, University of Rzeszow, Poland*

²*Department of Immunology and Infectious Biology, Institute of Microbiology, Biotechnology and Immunology, Faculty of Biology and Environmental Protection, University of Łódź, 90-237 Łódź, Poland*

³*Department of Chemistry, Rzeszow University of Technology, 35-959, Rzeszow, Poland*

*Corresponding Author: aczerniecka@ur.edu.pl

Abstract

The poly(3-hydroxybutyrate) (P3HB) was used to prepare biocompatible composites modified by the hypromellose. The aim of the study was to assess the biological properties and selected thermal parameters together with the phase contents of the obtained biocomposites. The phase transitions of nanocomposites and polymeric matrix were investigated using differential scanning calorimetry. Moreover, the non-equilibrium and equilibrium thermal parameters of composites and the unfilled nanocomposites were established based on thermal history. Based on equilibrium parameters (*i.e.* the heat of fusion for the fully crystalline materials and the change of heat capacity at glass transition temperature for the fully amorphous composites), the degree of crystallinity, mobile, and rigid amorphous fractions were estimated. The addition of hypromellose to the P3HB matrix caused a decrease in the degree of crystallinity in reference to the unfilled P3HB. Simultaneously, an increase of amorphous phase contents was noted. It was also noted that the rigid amorphous fraction exists only for nanocomposites containing 2% mass of nanofiller. Thermogravimetric analysis of nanocomposites was also carried out and showed that the thermal stability of all nanocomposites is higher than that of the unfilled P3HB. An additional 1% mass of nanofiller increases the degradation temperature of nanocomposites by about 37°C in reference to the unfilled P3HB. The immunosafety of the tested nanocomposites and the absence of, or very low, endotoxin contamination was confirmed by the Food and Drug Agency Guidance as well as the European Medicines Agency.

Keywords: poly(3-hydroxybutyrate), hypromellose, nanocomposites, biocompatible nanomaterials, thermal analysis, degree of crystallinity

NON-ISOCYANATE POLYURETHANE HYDROGELS MODIFIED WITH POSS: THERMAL AND HYDRATION PROPERTIES

Izabela Łukaszewska, Konstantinos N. Raftopoulos, Artur Bukowczan, Krzysztof Pielichowski¹

*Department of Chemistry and Technology of Polymers, Cracow University of Technology,
Warszawska 24, 31-155, Kraków, Poland*

Abstract

This study focuses on non-isocyanate polyurethane (NIPU) networks modified with POSS as a novel class of hydrogels. In this work, non-isocyanate polyurethane copolymeric hydrogels were synthesized using two hydrophilic monomers: poly(ethylene oxide)-based bis-cyclic carbonate (PEO-CC, $M_w \sim 650$ g/mol) and polyethyleneimine (PEI, $M_w \sim$ g/mol). A polymeric network was obtained through one-step aminolysis of PEO-CC at 55 °C, using 1,5,7-triazabicyklo(4.4.0)dek-5-en (TBD) as a catalyst and dimethylacetamide (DMAc) as a solvent. NIPU/POSS composites were synthesized with octaPOSS introduction alongside all other components. Hydrogel composites with POSS content: 1 wt%, 3 wt%, 5 wt%, 8 wt% and 10 wt% were synthesized. The reaction progress was monitored with Fourier-transform infrared spectroscopy (FTIR). The NIPUs were conditioned at different relative humidity (rh) levels until equilibrium. Materials conditioned over phosphorus pentoxide were regarded as dry materials and constituted a reference point for subsequent measurements of water uptake at each hydration level. Sorption isotherms were plotted. Water sorption isotherms follow a Brunauer type III form typical for soluble polymers and show high water absorption, up to 110 wt% at relative humidity 98%. Guggenheim-Anderson-de Boer model fits the data very well, in the whole humidity range, indicating a simple hydration mechanism. Materials at each hydration level were studied by FTIR (morphology, absorbed water influence on carbonyl region, mainly hydrogen bonding) and differential scanning calorimetry (glass transition temperatures). Upon water uptake an increased contribution of the component associated with strongly hydrogen-bonded carbonyls was observed in the carbonyl region. As expected, a strong plasticization was observed as a decrease in glass transition temperature values with increasing water uptake.. Interestingly, POSS addition, even in the amount of 10 wt%, did not hinder water absorption significantly. The differences in water uptake between composites became more pronounced only at very high rh levels (84% and 97%), but still remained moderate. The differences between composites glass transition temperatures (T_g) are most pronounced for dry materials. Upon POSS addition, decrease in T_g was observed for all composite materials, with the effect being more pronounced up to 5 wt% POSS content. Further increase in POSS content resulted in increase of T_g , however the values for high POSS-content composites remained lower in comparison to the matrix. Upon water absorption the differences fade up, as plasticizing effect of absorbed water takes over, and then reappear for high hydration levels (84% and 97%), where differences in water uptake also become more pronounced.

Acknowledgements

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SYNTHESIS OF NON-TOXIC AND ENVIRONMENTALLY FRIENDLY THERMOSETS

Said El Khezraji^{1,2}, Manal Chaib^{1,2}, Suman Thakur¹, Mohammed Lahcini², Raquel Verdejo¹

¹*Instituto de Ciencia y Tecnología de Polímeros CSIC, C/ Juan de la Cierva, 3 28006 Madrid, Spain*

²*IMED-Lab, Faculty of Sciences and Techniques, Cadi Ayyad University, Avenue Abdelkrim Elkhatabi, B.P 549, 40000, Marrakech, Morocco*

Corresponding author: r.verdejo@csic.es

Abstract

Increasing regulation of toxic or hazardous chemicals is driving the search for new synthetic routes to everyday materials. Among these, thermosets are of particular interest for their use as adhesives, coatings and foams. Here, we present several solutions to reduce the health and environmental impacts of these systems and, in particular, the production of PU foams (PUFs) and epoxy coatings.

First, we explore several approaches for non-toxic and environmentally friendly PUFs, presenting the use of a bismuth-based catalyst as a potential replacement for a traditional tin catalyst [1] and for bio-based, cross-linked, self-blowing non-isocyanate polyurethane foams via a simultaneous aminolysis and decarboxylation reaction [2,3].

Second, we develop a bio-based, self-healing thermoset with dynamic bonding and successfully create a new selenium-based curing agent for bio-based epoxy systems synthesized from gallic acid and vanillin derivatives with high bio-based content (~70%) [4].

Acknowledgements

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**LIQUID HEAT CAPACITY OF POLY(LACTIC ACID)
AND POLY(VINYL METHYL ETHER)**

Marek Pyda^{1,2}

¹ *Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600, USA;*

² *Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6197, USA (retired)*

Abstract

The experimental heat capacity of the liquid state above the glass transition of poly(lactic acid) (PLA) and poly(vinyl methyl ether) (PVME) was linked to the molecular motions and computed as the sum of vibrational, external (anharmonic), and conformational contributions. Most of the liquid heat capacity of PLA and PVME arises from the vibrational motion calculated as the group and skeletal vibrational heat capacity contributions. The external contribution to liquid C_p was computed as a function of temperature from experimental data of the thermal expansivity and compressibility of the liquid state. The conformational heat capacity contribution to total C_p of the amorphous PLA and PVME was established from a fit of the experimental, liquid heat capacity after subtracting the vibrational and external parts, to a one-dimensional Ising-type model with two discrete states characterized by parameters linked to stiffness, cooperativity, and degeneracy. The computed and experimental data of C_p at the liquid state showed good agreement, i.e., within a few percent, close to the experimental precision. The proposed approach can be used for the determination of heat capacities of more complex systems such as poly(lactic acid)-water and poly(vinyl methyl ether)-water which are widely used in environmental applications.

PREPARATION OF LIQUID CRYSTALLINE POLYURETHANE/POSS FIBERS VIA ELECTROSPINNING TECHNIQUE

Artur Bukowczan, Krzysztof Pielichowski

*Cracow University of Technology, Department of Chemistry and Technology of Polymers,
ul. Warszawska 24, 31-155 Kraków, Poland.*

artur.bukowczan@pk.edu.pl

Abstract

The aim of this work was to applied electrospinning technique to obtain liquid crystalline polyurethane/POSS fibers. Liquid crystalline polyurethanes modified by polyhedral oligomeric silsesquioxanes were prepared. Three concentrations of LCPU/POSS nanocomposites in hexafluroisopropanol were chosen. In order to investigate electrospinning parameters on morphology and size of the fibers: needle-collector distance, applied voltage, mixture dosing rate and different temperature of a process were tested. Obtained fibrous mats were then examined by scanning electron microscopy, differential scanning calorimetry and mechanical properties. Calorimetric study showed existence of liquid crystalline phase transition in obtained fibers. POSS was found to be well distributed on a fibers surface. Influence on mechanical properties of silsesquioxane particles was also observed.

WET SPUN BIODEGRADABLE AND BIOCOMPATIBLE 3D COMPOSITE MATERIALS FOR MEDICAL APPLICATIONS

Tomasz Witko

*Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences,
Krakow*

Abstract

Growing interest in novel materials and shrinking supplies of fossil fuels cause that materials of natural origin are attracting more and more attention of scientists and industry. The investigation of biopolymers has been reserved to biochemists and molecular biologists for over half of a century. Nevertheless, during the last decade, the soft matter physics, biophysics, chemists, and material scientists have been seized to this research field[1]. The current interest in developing novel materials has motivated an increasing need for biological and medical studies for a variety of clinical applications. Due to their features such as biointegrity and biocompatibility, they can not only displace traditional polymers, but also find completely new applications in biomedical sciences and industry. The growing demand for this type of polymers has resulted in intensive development of research and production companies dealing with novel materials. Thanks to the completely natural origin bacterially derived polyhydroxyalkanoates polymers are promising materials to suit the above purpose[2]. One of their characteristics is the biocompatibility with the mammalian cells. Therefore, the polymer can be used to manufacture scaffolds for tissue regeneration, starting from wound dressings constructions and ending with endo-prostheses or bone scaffolds coatings.

Multiple techniques such as double staining with fluorescent diacetate (FDA) and propidium iodide (PI) cytotoxicity assessment and long-term microscopic studies revealed high biocompatibility level of polymer and no toxic impact on Mouse Embryonic Fibroblast cells. Further research focused on cytoskeletal analysis of cells employing confocal microscopy. A cell's shape, internal organization, and functional polarity are provided by a three-dimensional filamentous protein network that consists of three distinct, yet interconnected, filament systems: intermediate filaments (IF), actin- containing microfilaments (MF) and microtubules (MT), called the cytoskeleton[3][4]. The cytoskeleton carries out three broad functions: it spatially organizes the contents of the cell; it connects the cell physically and biochemically to the external environment; and it generates coordinated forces that enable the cell to move and change shape[5]. The normal functioning of a cell requires constant interaction with its environment. Signals from neighboring cells or the extracellular matrix are continuously perceived by membrane bound receptors. There are also assumptions regarding that the cytoskeleton might act as an interconnected network of filamentous macromolecules, which extends over the entire cytoplasm[6]. This means that the role of the cytoskeleton is not limited only to the cell-shaped skeleton that is responsible for its contraction and migration, but also that filaments can serve as information and metabolite

routes. Cytoskeleton is involved in many cellular processes like endocytosis, cytokinesis. It plays an important role in such life necessary processes like cell division or intracellular transport[4,7][8].

Conducted research also includes an innovative method of creating three-dimensional polymer blends using the wet spinning method. A simple and efficient wet spinning technique of the production of a novel type of porous continuous fiber based on poly-3-(R)-hydroxybutyrate (PHB) and other composite materials was developed. The principle of this method lies in the process of slow precipitation of biopolymer dissolved in organic solvent into a high glass cylinder filled with cooled ethanol. Because the materials are intended to find applications in biomedical engineering (i.e bone or cartilage implants), author created PHB-ceramics composites. Author have selected calcium phosphate Ca-Pbio-materials, such as hydroxyapatite (HAp) , tricalcium and phosphate (α -TCP, β -TCP) because they have been widely used as bone substitutes before, because they have good biocompatibility and osteoconductivity. Fibrous materials produced out of different concentration of pure biopolymer and various ceramic fillers were broadly characterized to establish optimal production parameters. The influence of various PHB concentrations and precipitation rates on fibers and pore diameter was studied using SEM microscopy. The newly produced materials could be applicable in regenerative medicine as a replacement of currently used materials. Their scope of application can be also widened due to the known biodegradable properties of PHB, which will allow the use of materials in the form of elements absorbable inside the patient's body.

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ITACONIC ACID: A LITTLE KNOWN RENEWABLE MONOMER

Szczepan Bednarz¹, Kacper Mielczarek¹, Samuel Wierzbicki¹, Ewa Mierzwa¹

¹Cracow University of Technology, Warszawska 24, Krakow, 31-155 Poland, sbednarz@pk.edu.pl

Abstract

Itaconic acid (IA) is a natural unsaturated carboxylic acid produced on an industry scale by biotechnological processes. Recently, this monomer has attracted business interest as it is renewable and shares some chemical similarities with the petrochemical monomers acrylic and methacrylic acids. In addition, IA is a monomer that can be polymerized in several ways, providing a wide range of polymers with interesting properties. For this reason, in the last few years several large R&D projects have been carried out in the European Union, which focused on the technological development of IA in polymers and plastics production: Bio-Qued (budget €11 million), Biocore (€20 million), BioCon-SepT (€13 million). These projects have involved leading European universities as well as chemical industry giants such as Evonik, Arkema, Itaconix or Cargill. Unexpectedly, an obstacle to a greater industrial use of this acid is, among others, limited understanding of IA polymerization processes, including radical polymerization. Here we reporting our results on the radical polymerization of IA in both water and in deep eutectic mixtures [1-9] leading to low, medium and high molecular weight polymers with linear, branched or crosslinked architecture.

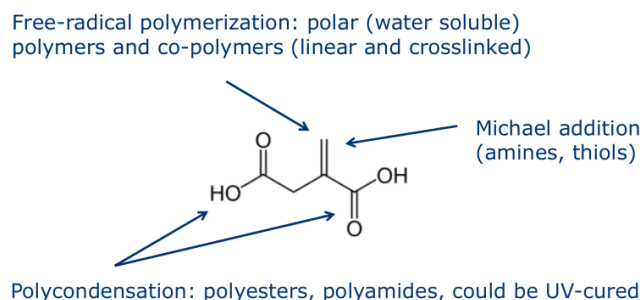


Fig. 1 Itaconic acid structure showing vinyl and carboxylic groups that allows polymerization of this monomer via polyaddition or polycondensation.

Acknowledgments

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NOVEL 3D-PRINTED CHITOSAN-BASED BIOACTIVE NANOCOMPOSITES

Marek Piątkowski^{1,*}, Wojciech Łabuś²

¹*Cracow University of Technology, Faculty of Chemical Engineering and Technology, Department of Biotechnology and Physical Chemistry, 24 Warszawska Street, 31-155 Cracow, Poland*

²*Tissue Bank, Dr Stanisław Sakiel Centre for Burn Treatment, Jana Pawła II 2 Street, 41-100, Siemianowice Slaskie, Poland*

*corresponding author: marek.piatkowski@pk.edu.pl

Abstract

Personalized medicine provides alternative solutions to traditional medicine in regard to the prevention, diagnosis and treatment of disease. For successful regeneration biomaterials prepared for patients special demands, are required. Three-dimensional bioactive nanocomposites can be applied for tissue regeneration, especially when are prepared from biopolymers with the use of Green Chemistry principles [1,2].

The aim of the study was the development of a new type of scaffolds based on chitosan and prepared with the use of 3D printing method. The research carried out confirmed preparation of custom-made scaffolds with very special microstructure. Cytotoxicity and genotoxicity studies confirmed biocompatibility of the obtained products.

Acknowledgements

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**CHARACTERIZATION OF BIOPOLYMERS:
WHAT'S DIFFERENT COMPARED TO CONVENTIONAL PLASTICS**

¹Catherine A. Kelly, ¹Mike J. Jenkins, ²Krzysztof Hodor, ³Shona H. Marsh

¹*School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham B15 2SE, UK*

²*Netzsch Instrumenty Sp. z o.o., Halicka 9, 31-036 Cracow*

³*Netzsch Instruments, Wolverhampton WV10 7FE, UK*

Abstract

Biopolymers have generated high interest from the packaging industry as a result of their sustainable and biodegradable properties. Polymers such as Poly(3-hydroxybutyrate) (PHB) and its copolymers can be processed into useable material with initial properties comparable to commercial polymers such as polypropylene (PP) and polyethylene terephthalate (PET). However, their high crystallinities > 50% result in poor ductility. Therefore, low molecular weight poly(ethylene glycol) (PEG) are added to PHB copolymers to affect the crystallization. It was shown that the rate of secondary crystallisation was reduced resulting in a more robust material.

Furthermore, the thermal stability of the copolymer is lower compared to conventional polymers used in packaging. Thus, the melt miscibility of PHB-co-HV and PEG was studied here to assess the effect of PEG on thermal stability. Typically, the glass transition temperature is analyzed with differential scanning calorimetry (DSC), but due to the high crystallinity it is not observable. Thus, a modified rotational test procedure is implemented to create Han plots and enable assessment of the miscibility. By studying various concentrations and molecular weights, it was found that PHB-co-HV and PEG can be blended effectively. This approach allows for fine-tuning the properties of PHB-co-HV, leading to the production of stable and suitable packaging materials. The addition of PEG also makes it possible to process the polymer at lower temperatures, which significantly reduces the degradation rate and broadens the narrow processing window typically observed with this type of polymer.

PRODUCTION OF FLEXIBLE POLYURETHANE FOAMS WITH COMPONENTS FROM RENEWABLE RAW MATERIALS WITH USE A PROTECTIVE FOIL

Szczepan Plewa*, Maciej Rembisz *

* *Cis Sp. z o.o., Pogwizdów 155, 37-126 Medynia Głogowska*

Corresponding author: technologia@cis.com.pl

Abstract

The purpose of the project was to replace some polyols of petrochemical origin with biopolyols and received blocks of flexible foams with using protective foil. For the modification of the polyurethane composition used biopolyols produced at least 70% from renewable raw materials such as vegetable oil. Unfavorable feature of commercial available biopolyols is the higher value of hydroxyl number (170-400 mg KOH/g) in relation to typical polyols of petrochemical origin used in the synthesis of flexible polyurethane foams.

Conclusions:

- Introduction of biopolyols (in tested amounts) do not have significant impact on the reactivity of the PUR system.
- Modification of the starting formulation by tested biopolyols had positive impact on the selected physical and mechanical properties (decreasing apparent density, increasing hysteresis and support factor, reducing compression set).
- Use of dark biopolyols caused nonhomogeneous discoloration in the whole block of foam.

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THE EFFECT OF MAGNETIC PARTICLES ON THE SELECTED PROPERTIES OF POLYURETHANE-BASED BIOMATERIALS

Katarzyna Nowicka, Aleksandra Gejdel, Kinga Pielichowska *

*AGH University of Science and Technology, Faculty of Materials Science and Ceramics,
Department of Biomaterials and Composites, al. A. Mickiewicza 30, 30-059 Cracow
kingapie@agh.edu.pl

Abstract

Bone is a complex tissue with hierarchical structure, and it is a challenging task to find a suitable replacement material. The most often investigated material for bone replacements are polymeric materials, and among them polyurethanes (PUs) are considered as one of the most promising materials. PUs consist of soft and hard segments and by changing the mutual ratio of both segments, selected polymer properties can be tailored. Another interesting modification can be an addition of fillers, such as magnetic particles for a possible cancer treatment via hyperthermia.

In this work, polyurethanes modified with magnetic particles (Fe_3O_4) were prepared in the one-step bulk polymerization. As a chain extender/crosslinker 1,4-butanediol and sodium alginate were used in order to improve bioactivity. As a soft segment PEG with average molar mass 1450, 2000 and 3000 was used. The effect of magnetic particles and PEG molar mass on the selected properties of the obtained polyurethane materials was investigated. Mechanical, thermal (DSC, TG), spectroscopic (FTIR), and microscopic (SEM) methods were applied. The obtained materials can be considered as potential candidates for biomedical applications, especially in bone repair.

Keywords: bone tissue replacement, polyurethanes, magnetite

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