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DURABILITY OF ADVANCED POLYMER COMPOSITES

Book of Abstracts

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PROGRAM

Chairperson: *Dr.sc.ing. Tatjana Glaskova-Kuzmina*		
10.00–10.15	**O. Starkova, S. Gaidukovs, and O. Platnieks** *University of Latvia, Riga Technical University (Latvia)*	**Hydrothermal ageing effects on mechanical properties of bio-based poly(butylene succinate)/nanofibrillated cellulose-based polymer composites**
10.15–10.30	**T. Glaskova-Kuzmina, A. Aniskevich, A. Zotti, A. Borriello, and M. Zarrelli** *University of Latvia (Latvia), Institute for Polymers, Composites and Biomaterials (Italy)*	**Hydrothermal ageing of the epoxy and basalt fibre/epoxy laminates filled with hybrid carbon nanofiller**
10.30–10.45	**A. Zotti, S. Zuppolini, A. Borriello, D. Borrelli, A. Caraviello, V. Vinti, and M. Zarrelli** *Institute for Polymers, Composites and Biomaterials, Sòphia High Tech, Research Center Material Composites and Special and Innovative Processes (Italy)*	**Effect of GNPs dispersion on mechanical, fracture toughness and thermal conductivity properties of epoxy-based nanocomposites**
10.45–11.00	**O. Bulderberga and A. Aniskevich** *University of Latvia (Latvia)*	**Stability of polymer epoxy matrix loaded with thermochromic microcapsules under UV light**
11.00–11.15	**G. Monastyreckis and D. Zeleniakiene** *Kaunas University of Technology (Lithuania)*	**Multifunctional polymer composites coated with MXenes**
11.15–11.30	**S. Gaidukovs and S. Beļuns** *Riga Technical University (Latvia)*	**Advanced materials from nanocellulosic networks**
11.30–11.45	**P. Shimpi and D. Zeleniakiene** *Kaunas University of Technology (Lithuania)*	**Structural health monitoring of 3D woven composites by carbon nanotube strain gauges**

11.45–12.00	**S. Stankevich, A. Aniskevich, and O. Bulderberga** *University of Latvia (Latvia)*	**Damage indication by electrical conductivity evaluation of MWCNT modified glass fibre reinforced plastic**
12.00–12.15	**O. Platnieks, A. Sereda, and S. Gaidukovs** *Riga Technical University (Latvia)*	**Sustainable biocomposites from poly (butylene succinate) and nanofibrillated cellulose**
12.15–12.30	**A. Barkane, E. Kampe, M. Jurinovs, O. Platnieks, and S. Gaidukovs** *Riga Technical University (Latvia)*	**Replacing petroleum-based components in UV-curable polymer inks without sacrificing performance**

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HYDROTHERMAL AGEING EFFECTS ON MECHANICAL PROPERTIES OF BIO-BASED POLY (BUTYLENE SUCCINATE)/NANOFIBRILLATED CELLULOSE-BASED POLYMER COMPOSITES

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Biopolymer-based plastics have gained great attention during the last decades motivated mainly by their biodegradability and strong public concern about plastic pollution. Recent improvements in the quality and functionality of bio-based polymers and composites have led to the growth of these plastic markets and gradually shifted from biodegradable applications to general and engineering applications. Along with this, requirements imposed on materials' durability are increasing. Insufficient mechanical strength, durability and lack of long-term performance studies under environmental ageing impact restrict using this new class of sustainable materials from advanced applications.

The present study is focused on the investigation of the hydrothermal ageing performance of poly(butylene succinate) (PBS) filled with nanofibrillated cellulose (NFC). The choice of the materials is motivated by their "eco-friendly" origin combined with reasonable mechanical properties. Composites with different contents (5, 10, 20, 30 and 50 wt.%) of NFC were produced via solution casting. The effect of humid environment (RH = 98%, T = 22 °C) and hot water (T = 50 °C) on tensile properties was studied.

Water absorption characteristics, the diffusion coefficient D and equilibrium water content w_∞, of PBS, greatly increased with the addition of hydrophilic NFC. In a humid atmosphere, the maximally loaded PBS/NFC samples are characterized by 7.6 and 2.7 times higher w_∞ and D compared to the neat PBS, respectively. These differences greatly increased for samples conditioned in hot water. The elastic modulus of PBS increased with the growing content of NFC reaching up to a 2.5-fold improvement. The strength and ultimate strain decreased significantly due to imperfect adhesion of NFC with PBS. Hydrothermal ageing resulted in properties' degradation, the higher after conditioning in hot water. The reinforcement efficiency of NFC on the stiffness of PBS is greatly diminished for aged samples. The elastic modulus of 50/50 PBS/NFC samples decreased down to 32% and 65% after conditioning in a humid atmosphere and hot water, respectively. PBS filled with 20 wt.% of NFC is identified as the most efficient composition, for which

a reasonable balance between the properties improvements and their susceptibility to hydrothermal degradation is found.

Acknowledgements

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HYDROTHERMAL AGEING OF THE EPOXY AND BASALT FIBRE/EPOXY LAMINATES FILLED WITH HYBRID CARBON NANOFILLER

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This work aimed to investigate the effect of hybrid carbon nanofiller (carbon nanotubes/carbon nanofibers in the ratio 1:1 by mass) over the electrical and flexural properties for an epoxy matrix and basalt fibre/epoxy laminates (BFRP) subjected to full-year seasonal water absorption. Hydrothermal ageing was performed by full immersion of the tested materials in distilled water according to the following four model seasons.

The mechanical properties were tested in three-point bending before environmental ageing and after each season. During flexural tests, the electrical resistance of the nanocomposites (NC) and BFRP/NC samples were evaluated. For nano-modified BFRPs, the slightly higher effect of absorbed moisture on flexural characteristics was found which can be attributed to higher defectiveness (e.g. porosity, the formation of agglomerates etc.).

The electrical conductivity for UD BFRP/NC before and after hydrothermal ageing was higher than for the NC revealing the orientation of electrically conductive nanoparticles and/or their agglomerates during lay-up manufacturing which was evaluated by the rules of the mixture.

Based on all results obtained it can be concluded that the most potentially applicable for damage indication was UD BFRP/NC along fibres since full-year hydrothermal ageing improved its electrical conductivity and, consequently, the ability to monitor damages was also enhanced.

Acknowledgements

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EFFECT OF GNPS DISPERSION ON MECHANICAL, FRACTURE TOUGHNESS AND THERMAL CONDUCTIVITY PROPERTIES OF EPOXY-BASED NANOCOMPOSITES

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Thanks to their high tensile and adhesive strength along with excellent chemical and solvent resistance, epoxy resins are widely employed in different applicative fields. Despite their remarkable properties, epoxy resins are brittle with low fracture resistance because of their structure: to overcome that flaw, generally, epoxy systems are modified with suitable fillers. With the addition of graphene to the carbon nano-filler family, a new category of nanocomposites has been developed, characterized by mechanical properties comparable to that of carbon nanotube-based composites[1] and high level of thermal conductivity[2]. An appropriate dispersion technique and quantitative analysis of Graphene Nano-Platelets (GNPs) degree of dispersion has been one of the main issues at the research level to achieve improved fractural and thermal property GNP-loaded nanocomposites. At the same time, the use of a solvent or complex functionalization has limited severely the scaling up of many dispersion techniques to attain industrial manufacturing.

In this work, we have investigated and analysed the effect of different dispersion technique on mechanical, fracture toughness and thermal conductivity properties of GNP based nanocomposites. The hosting matrix, one formulation of a patented space epoxy resin family, The resin system is characterized by a high value of fracture toughness, while graphene-based filler has a large aspect ratio (>1000). Three different dispersion techniques have been implemented: 1) an high shear rate mixing assisted by a solvent; 2) an industrial pre-stage mixing of solid-solid able to break the filler clusters followed by a high shear rate mixing without solvent; 3) a solvent assistant sonication. Preliminary results have demonstrated the effectiveness of premixing stage increasing the fracture toughness, in term of stress intensity factor and critical energy of the final nano-reinforced matrix with the addition of 0.5wt% of GNPs of about 7.5% and 24.5%, respectively.

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STABILITY OF POLYMER EPOXY MATRIX LOADED WITH THERMOCHROMIC MICROCAPSULES UNDER UV LIGHT

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By incorporation of stimuli-responsive microcapsules into a composite structure, its application possibilities could be extended. Such a smart structure is not only a part of the construction but also implements an integrated function of sensors. Encapsulated thermochromic dyes could be relatively simply mixed into a polymer structure and they can perform the function of detecting ambient temperature where it is important for the structure. On the other hand, atmospheric ultraviolet (UV) light can destroy the sensor.

The study aimed to evaluate the effect of UV light on the service-life of thermochromic microcapsules integrated into the polymer matrix and on mechanics of such structure. To achieve the aim several tasks were outlined: 1. Define the method of colour change control and quantitative evaluation. 2. Experimentally define colour changes and the critical time under UV exposure of thermochromic microcapsules integrated into the polymer structure. 3. Evaluate UV light effect on mechanical properties of polymer epoxy matrix loaded with thermochromic microcapsules. Dog-bone shape samples of an epoxy matrix with different concentrations of microcapsules (0, 0.5, 1, 2, 3, 5, 10 wt.%) were prepared and tested by tensile test. The visual reaction of colourless phase (at room temperature) and of colour phase at elevated temperature (over 60 °C) was compared. The colour change of samples was evaluated by images made in the photo lightbox (thus excluding the influence of ambient lighting in the room) and treated in Adobe® Photoshop® software. The Mean and Red, Green, and Blue (R, G, B) channels values from the Histogram of each image were compared.

Comparing elastic modulus values and the visual reaction of samples with different concentrations of microcapsules, it was defined that filled with microcapsules till 2 wt.% did not affect the value of elastic modulus. The intensive visual reaction was observed for samples filled with 3 wt.% and more. Based on this, samples with 3 wt.% were selected for further work and neat samples were used as a reference. It was defined that due to the samples' blue colour in the coloured phase, the most important change in the value is observed for the B channel. The intensity value change on 50% was achieved in the first 24 h of irradiation comparing with the reference sample. While the same 50% change in values was observed in the next 300 h of irradiation. Thus, the most critical degradation of microcapsules colour was observed in the first hours of irradiation. Tensile tests showed that the value of the elastic modulus did not change after the UV irradiation for 300 h, while

ultimate stress decreased by 20 and 10% respectively for neat epoxy and filled samples. It could be concluded that microcapsules located in epoxy are not protected from the influence of UV. Such polymer epoxy matrix loaded with thermochromic microcapsules could stay working only under a short UV irradiation time.

Acknowledgements

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MULTIFUNCTIONAL POLYMER COMPOSITES COATED WITH MXENES

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In recent years, the automotive and aeronautic industries focused on green technology, durability, and maximum performance. Therefore, the demand for lightweight, strong and multifunctional materials has grown significantly. The most studied and widely used in the 21st century is fibre-reinforced polymer composite, which already took place over aluminium in many applications. Such composites can be further modified with carbon nanotubes or 2D nanoparticles called MXenes, providing even more advanced characteristics. One of such is composite's real-time strain monitoring and local damage detection. It can help avoid unexpected structure failure and shorten maintenance procedures. Another feature can be an ultrathin layer for de-icing or electromagnetic interference shielding.

MXenes have shown great mechanical, electrical and thermal properties. Despite the wide use of 2D nanoparticles for wearable and flexible electronics[1], MXenes have not been tested with fibre-reinforced polymer composites before. This study aimed to investigate MXene adhesion to polymer, strain sensing under tensile and heating properties[2].

Acknowledgements

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[2] Monastyreckis G., Stepura A., Soyka Y., Maltanava H., Poznyak S.K., Omastova M., Aniskevich and Zeleniakiene D. MXene spray-coated composites with strain sensing capabilities, 2021, submitted.

ADVANCED MATERIALS FROM NANOCELLULOSIC NETWORKS

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Cellulose combines some of the most important aspects of the modern functional materials - abundance, non-toxicity and relatively cheap production costs. While often regarded as a waste product of many industries or by a product of some it can be recovered from diverse sources. Yet what makes is most appealing for researchers around the world is highly tuneable morphology combined with adaptable surface properties achievable by chemical and physical modifications.

Nanocellulosic networks of two types - aerogel/foam and nano paper will be discussed. Their structure and properties have been investigated and reported herein. Nanofibrilated cellulose has been prepared form waste sources of wood flour from plywood processing industry and hemp industry sector side stream waste. These advanced nano cellulosic network materials can be used as efficient insulation, filter, sorbent materials and also for structural composite materials.

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STRUCTURAL HEALTH MONITORING OF 3D WOVEN COMPOSITES BY CARBON NANOTUBE STRAIN GAUGES

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Structural health monitoring (SHM) in composite structures has been an area of interest for integrating novel materials which can impart functional properties such as high electrical and thermal conductivity to the composite materials. Nanoparticles like carbon nanotubes (CNT) and graphene are often used for SHM of polymer matrix composites The nanoparticles can be either applied on the surface of the composite substrate[1] or dispersed in the matrix of composite for SHM[2]. Such sensor elements can be integrated into the 3D fabric structure while weaving and thus smart composites can be manufactured which can monitor stress-strain inside the composite[3]. However, the use of conventional methods to infuse CNT in 3D woven fabric are unsuccessful due to the filtering of nanoparticles by fibres.

This study aims to develop smart nanocomposite by vacuum infusion process, which eliminates filtering of CNT and the final composite can sense damage and applied external strain. CNT were initially deposited on an absorbent knitted fabric material which was later placed on the surface of 3D woven fibre reinforcement and the vacuum was applied to the layup thus transferring the nanoparticles to the fibres. The resultant composites were subjected to flexural loading to study the sensitivity of CNT to the applied strain. Microscope studies were carried out to observe the percolation of CNT.

It was observed that the CNT network is sensitive to bending and tensile deformation. Microscopic studies showed that CNT can percolate through the thickness of the fabric without getting filtered. It can be concluded from the study that CNT smart strain gauge manufactured from this method can be used for in-situ SHM of the composites while being cost-effective and easy to manufacture.

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DAMAGE INDICATION BY ELECTRICAL CONDUCTIVITY EVALUATION OF MWCNT MODIFIED GLASS FIBRE REINFORCED PLASTIC

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Glass fibre reinforced plastic (GFRP) is electrically non-conductive construction composite. However, through the implementation of conductive nanoparticles, such as multi-wall carbon nanotubes (MWCNT), graphene nanoplatelets, 2D carbides MXene, etc., it can get electrical conductivity. For successful application of such advanced composite with specific electrical conductivity, sometimes it needs to be evaluated prior manufacturing process.

The main aim of this study was to check the capability of using a structural approach to predict the electrical conductivity of nanomodified multi-layered GFRP. The secondary task was to evaluate the possibility of the composite to detect the damage via electrical conductivity monitoring.

Samples of MWCNT modified epoxy resin and unidirectional (UD) GFRP with various reinforcement lay-up angles were produced. The electrical conductivity of MWCNT modified lamina and multi-layered GFRP was investigated on several structural levels. The electrical conductivity of the composite laminate was measured experimentally and calculated at various reinforcement angles.

Noticeable electrical anisotropy was observed for UD GFRP samples due to the orientation of non-conductive fibres. Electrical conductivity values for composite along the fibres were found to be three times higher than for transverse direction. Calculated and experimental electrical conductivity data for various fibre orientation angles were in a good agreement.

By applying conductive paint the electrode network of 8 x 8 contacts was formed on the surface of the MWCNT modified GFRP laminate with dimensions of 250 x 250 mm and lay-up configuration of $[0;90]_4$. Via measuring of the voltage distribution throughout the laminate, it was possible to detect the damage in the volume of the laminate. The obtained results showed that the electrode network located on the laminate surface is capable of determining location and quantification of the damage.

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SUSTAINABLE BIOCOMPOSITES FROM POLY (BUTYLENE SUCCINATE) AND NANOFIBRILLATED CELLULOSE

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Introduction of bio-based and biodegradable packaging has seen rapid growth in the last decade. The call for sustainable production and reduced pollution has resonated with lawmakers and citizens alike. Plastics meet many of requirements including being light, durable, and compatible with food and drugs safety protocols during storage. As an alternative to widely used polyethylene (PE) new polyester known as poly (butylene succinate) (PBS) has emerged and meets many of requirements. PBS is bio-based, biodegradable and is compatible with conventional polymer processing technologies. Nanofibrillated cellulose (NFC) has gained popularity due to renewability and existing preparation methods, that yield material with high mechanical strength, large specific surface area, barrier properties and non-toxicity. Thus, the combination of these components has a high potential for the preparation of functional biocomposite.

Herein, we report the comparison of preparation methods for PBS/NFC nanocomposites using conventional direct solvent casting and casting of a highly loaded masterbatch system that is processed with a secondary melt blending step. Tensile test, dynamical mechanical analysis, differential scanning calorimetry and thermogravimetric analysis were performed while biodegradation was studied under composting conditions. Introduction of the melt blending increased elastic modulus, storage and loss modulus but reduced maximum elongation, both methods yielded improved disintegration in the soil with a total time of around 2 months. Nanocellulose accelerated the decomposition process in the soil.

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REPLACING PETROLEUM-BASED COMPONENTS IN UV-CURABLE POLYMER INKS WITHOUT SACRIFICING PERFORMANCE

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Bio-based polymers have been researched in the last two decades in the purpose of reducing environmental issues caused by producing petroleum-based polymers and their after use waste. Unfortunately, even though some polymers, such as polybutylene succinate (PBS), polylactic acid (PLA), some vegetable oil-based polymers, like soybean oil etc., have already reached researched stage where they are implemented by industries, they usually are improved by petroleum-based additives. There aren't many, if any, fully bio-based polymer products that society can come across in everyday use.

This absence of fully bio-based polymer products alongside growing photocurable polymer industry has pushed us to replace commonly used petroleum-based monomers, such as 1,6-hexanediol diacrylate (HDDA) and trimethylolpropane triacrylate (TMPTA), that have been added extensively in bio-based polymer matrix research for UV-assisted photopolymerizations applications.

This report contains results of photopolymerization kinetics, thermal and thermo-mechanical properties investigations of fully bio-based polymer matrix with a photoinitiator, where TMPTA and HDDA have been replaced by two other bio-based monomers.

Replacing petroleum with bio-based monomers allowed increase bio-content in photocurable resin up to 97 wt%. Discussion on replaced bio-content resins photocuring kinetic investigation performed by FTIR, thermal stability evaluated by thermogravimetric analysis and thermo-mechanical performance analyzed by dynamic mechanical analysis if offered.

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