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A study on the mechanical properties and the influence of water uptake and temperature on biocomposites based on polyethylene from renewable sources

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ABSTRACT

This work is aimed to evaluate the properties in terms of structural applications of the fully biobased composites obtained at reasonable price, without additional and costly chemical modifications. The bio-polyethylene obtained from sugarcane ethanol (Braskem, Brazil) was filled with four different fillers (25 wt.%): wood flour, ultrafine cellulose powder, kenaf chopped fibres and microparticles of mineral tuff filler. Physical, mechanical and thermal properties of the biocomposites were tested, as well as the influence of soaking in water and temperature on tensile properties. The fracture surfaces were studied using scanning electron microscope. Low density, increase in stiffness, improved resistance to deformation on heat and thermal properties stabilization within the temperatures of usage were the main advantages of the biocomposites comparing to the neat biopolyethylene.

1. Introduction

For several years now biocomposites are gaining more and more interest among scientists and manufacturers and during that time a great number of papers have been published concerning processing, mechanical, thermal and other physical properties of such materials and the changes of the properties under various conditions. Great majority of such previous and present research focused on the composites with the matrix of biobased biodegradable polymers or traditional petrochemical plastics filled with natural fibres. Natural fibres have a lot of advantages which make them suitable for the use as a substitute of glass fibres, such as high specific strength and modulus and low environmental impact determined by using LCA (Life Cycle Assessment) methodology [1,2]. The choice of non-biodegradable polymers from renewable resources as matrices of biocomposites is a further step in producing new, light, eco-friendly materials. At preset such non-biodegradable biopolymers comprise over 56% of biopolymer market (European Bioplastics data, 2012). With the advance of knowledge and technology leading to a development of the industry of green polymer synthesis (e.g. in Braskem, Evonik, BASF, DSM, EMS, Toray), we can now design fully biobased structural composites, competitive for traditional plastics. One example of such materials are composites with biopolyamide matrix obtained from castor oil [3]. However, for structural Natural Fibre Composites (NFC) and Wood Plastic Composites (WPC) an obvious choice of the 'green' matrix seem to be a biobased polyolefin. Polyolefins basing on bioethanol are already present on the market (biopolyethylene) or will be launched shortly. Although there is limited number of these grades present today, their properties are similar to those of the counterparts [4].

Until now only few papers regarding biobased polyethylene composites or blends were published [4,5]. Castro et al. tested composites of HDPE from sugarcane ethanol and lignocellulosic curaua fibres in flexural, impact, DMTA, TG and DSC tests. There hydroxyl-terminated polybutadiene (LHPB) usually added as an impact modifier was also used as a compatibilizer agent. The presence of the curaua fibres enhanced some of the polyethylene properties, such as its flexural strength and storage modulus and LHPB addition was found to improve impact strength of the composites [5].

A large number of publications on WPC or NFC concern virgin or recycled petrochemical polyolefin matrix in regard to mechanical properties and the influence of different factors on the properties [6–13]. Usually, for the low filler content and for the fillers in the shape of particles rather than fibres (e.g. wood flour) the authors observed an increase in elastic modulus with no or minor improvement in strength and sudden decrease in deformability and impact

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strength [6,7,12,13]. Thermal and thermomechanical properties of such composites were also discussed in the literature – TG and DSC and DMTA test results were presented by different authors [14–17]. Thermogravimetric test results of WPC or NFC generally show that the composites have lower thermal stability than neat polymer, mainly due to the presence of hemicelluloses and lignin in the chemical composition of the fillers [16]. That hinders processing but within the operating temperature range the influence of such fillers on resistance to deformation on heat and on stabilization of mechanical properties with changing temperature may be positive.

A well-known disadvantage of natural fibres as polymer fillers for structural application is their high water absorption which in case of PE-based WPC or NFC makes non-hygroscopic material hygroscopic [9,17,19–21]. That leads to dimensional changes, accelerated ageing and it immediately affects mechanical properties [8,10,21–24]. Panthapulakkal et al. who measured flexural modulus and strength of HDPE/rice husk (65 wt.%) composite found that both of those parameters decreased significantly after about 67 days of soaking in water [23]. The authors explained that the decrease may be due to internal stress developed inside the composite because of the water-swollen filler, degradation in the interfacial adhesion formed between the filler and the matrix, and degradation of the filler as a result of long-term water absorption. The conclusions were similar in many other research, e.g. in Espert et al. work where injection moulded polypropylene with 10–30 wt.%. lignocellulosic fillers were tested [24]. It is expected that the strength properties of NFC in general would decrease with increased water uptake because of the reasons mentioned, however the modulus of elasticity may also change in another direction (see: Results and discussion Section 3.2).

Most of the studies on petrochemical poliolefine-based biocomposites conducted during the last two decades, including those already cited in the text, were focused on the hydrophilic fibre – hydrophobic matrix interactions and the strategies to improve interfacial adhesion in this system [11,14,16–18,24–27]. However, thinking of potential industrial applications, those methods that lead to an enhancement of the composites properties (e.g. silanes, maleated polyolefins, mercerization) have serious drawbacks, as they require additional and costly operations and may not always be ecologically acceptable [28]. In practice, the producers are likely to order ready-to use filler modified for the use with polyolefins but, depending on the application of a composite part, availability and price of the filler, it can be more economic to use unmodified one.

In the present work mechanical properties and the influence of water absorption and temperature on different biocomposites on biobased polyethylene matrix filled with lignocellulosic or mineral fillers are presented. The aim of the research was to evaluate the properties in terms of structural applications for the fully biobased composites obtained at reasonable price with ready-to-use lignocellulosic fillers for thermoplastics or with fibres supplied without additional and costly chemical modifications. As an addition to lignocellulosic fillers, natural inorganic filler in the form of crushed and milled tuff rock was also used in the study and presented as a potential interesting filler of a polyolefin matrix.

2. Materials and methods

2.1. Materials

The materials presented in this study are the composites with biobased and non-biodegradable matrix. Green PE SHC7260 a high density biopolyethylene produced from sugarcane-based ethanol was supplied by Braskem, Brazil. Green polyethylene (HDPE, LDPE and LLDPE) from Braskem is produced from December 2010 and in 2012 it comprised of 14.3% of the whole biopolymers market (European Bioplastics data). Presently it is used mainly in packaging applications.

There were four different fillers (25 wt.%) used to modify the properties of biopolyethylene matrix: wood flour, kenaf fibres, cellulose powder and tuff particles. Wood flour Lignocel BK 40/90 from soft wood (spruce) with particle size 300–500 μm and ultrafine cellulose ARBOCEL UFC 100 in a form of powder (approx. 8 μm diameter) were supplied by J. Rettenmaier & Söhne (JRS) company, Germany. The fillers were prepared for processing with thermoplastic materials by JRS. Chopped kenaf fibres were prepared in the Institute of Natural Fibres, Poznan, Poland and they were not chemically modified. Tuff particles of particles size 15–50 μm were prepared in the Institute of Materials Engineering of Cracow University of Technology [29]. Filipowice tuff was mined in Poland and then crushed, milled and calcined at 800 °C for 2 h.

Standard dumbbell type specimens ($10 \times 4 \times 150$ mm) were produced in Grupa Azoty in Tarnow, Poland, in a two step process. First, composite pellets were obtained by compounding extrusion using two-screw extruder MARIS TM 30VI with a gravimetric twin screw feeder (cylinder temperature: 100 °C – zone 1, 130 °C – zones 2–10, screw rotation: 60 rpm) and then injection moulded using Engel ES 200/40 HSL. The parameters of the injection moulding process are shown in Table 1. All tested materials are characterized in Table 1 with their acronyms used further in the text.

2.2. Methods

Mechanical properties were estimated by a tensile test (EN ISO 527) and a three-point flexural test (EN ISO 178), with an universal testing machine Insight 50 MTS with MTS axial extensometer with a constant crosshead speed of 10 mm/min. Modulus of elasticity (E_t), tensile strength (σ_M), strain at break (ε_B) as well as flexural modulus (E_f) and stress at 3.5% strain (σ_f) were determined. Tensile tests were carried out under standard conditions and at −23 °C and 80 °C using Instron thermal chamber. These values of lowered and elevated temperatures were taken from low and high limits of standard temperatures at which HDPE and its composites work in structural applications (e.g.: plastic pallets, car panels).

SEM images were acquired on the gold-sputtered tensile-test fracture surfaces of specimens using JEOL JSN5510LV.

Charpy impact strength of notched specimens (a_{cN}) was measured using Zwick HIT5.5P under standard conditions.

Materials density (ρ) was measured by hydrostatic method. Vicat softening temperature (VST) was measured according to ISO 306 under 50 N loading and with 50 °C/h heating rate using CEAST machine. Absorption of water (20 °C) was calculated after 1, 7, 30, 240 days of soaking, according to PN-EN ISO 62:2000. To determinate the influence of water uptake on mechanical properties and on the surface quality, tensile test was performed again after the 7, 30 and 240 days of incubation and the surface roughness average (R_a) was measured using profilometer Mitutoyo SJ-301.

DSC tests were performed at Poznan University of Technology, Faculty of Chemical Technology, Poland using NETZSCH model DSC-200 with computer software for test analysis. The measurements were made on the samples of 7–7.5 mg obtained from a central part of the injection moulded standard dumbbell-shape specimens in the temperature range between 40 and 190 °C under argon atmosphere. All measurements were taken according to the following program: heating between 40 and 190 °C at a scanning rate of 10 °C/min and cooling between 190 and 40 °C at a scanning rate of 5 °C/min. The whole process was carried out twice to analyse processing memory/history of the materials (the first heating–cooling cycle) and the thermal properties of the composites (the second heating–cooling cycle). An empty pan was used as a reference.