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Flax fibres reinforced polylactide modified by ionizing radiation

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ABSTRACT

Polylactide (PLA) composites containing flax fibre strands (20 wt%) and various content of triallyl isocyanurate (TAIC) as crosslinking agent were prepared by extrusion and injection moulding processes. The composites were modified by electron beam (EB) irradiation at dose values of 0, 10, 20, 30 and 40 kGy. The effects of EB and TAIC on the mechanical and structural properties of the composites were studied using tensile and impact tests, dynamic mechanical analysis (DMA), gel fraction measurement, differential scanning calorimetriy (DSC) and thermogravimetry (TG). However, the main attention was paid to biodegradation effects. Composites were biodegraded by means of enzymatic treatment and industrial composting. The composites were examined using mass loss analysis, DSC and photoelectron spectroscopy (XPS) in order to determine structural changes induced by biodegradation. Application of TAIC and EB at dose of 40 kGy led to the increase of tensile strength of about 20%. Besides crosslinking branching of PLA macromolecules was of significant importance. EB irradiation intensified enzymatic and composting degradation, however, when TAIC was applied, the composite was much more resistant to these processes.

1. Introduction

It is predicted that due the new synthesis techniques enabling cost effective production of high molecular mass polylactide (PLA) this polymer can replace some of petroleum based polymers. As being derived from plant resources and biodegradable at industrial composting conditions, PLA has many advantages over conventional thermoplastics. It shows good optical, mechanical and barrier properties even in comparison to petroleum based polymers. Despite many PLA advantages, high brittleness, low thermal stability and impact resistance limit some of its applications (Auras et al., 2010; Rasal et al., 2010).

Various modification methods were used to improve selected properties of this polymer. It was realized mainly by incorporation of non-organic fillers such as glass, carbon or aramid fibres, as well as nanofillers, especially montmorillonite (Żenkiewicz et al., 2010, 2011; Rytlewski et al., 2011; Malinowski et al., 2015).

On the other hand, many scientific and industrial projects focus on the use of plant-based fillers to produce completely biodegradable biocomposites. The most widely applied organic fillers were starch, wood flour, plant fibres such as hemp, flax, kenaf, bamboo, sisal, silk, coir or ramie (Luzi et al., 2016; Regazzi et al., 2016; Yusoff et al., 2016; Pickering et al., 2016). However, hydrophilic plant filler and relatively hydrophobic polymer matrix are not thermodynamically compatible, which results in poor interfacial adhesion. This interfacial adhesion significantly influences the final mechanical properties of the composites because the stress transfer between the matrix and fibres determines the reinforcement efficiency. Natural fibres are frequently treated chemically by mercerization, silanes, maleic acid or acetylation for cleaning and/or modification of surface energy in order to enhance the interfacial adhesion with polymer matrix (Liu et al., 2017; Rytlewski et al., 2014). However, this treatments are time and cost consuming processes imposing also some ecological risk. An sustainable alternative for chemical treatment offers a plasma or corona surface treatment and/or the use of ionizing radiation like electron beam (EB) or gamma irradiation (Moigne et al., 2017).

It was reported that EB irradiation of natural fibres can lead to dehydrogenation, destruction of anhydroglucose and crosslinking of cellulose depending on the applied doses (Han et al., 2006, 2007). This treatment can result in enhanced interfacial adhesion of natural fibres and polymer matrix as compared with untreated fibres (Choi et al., 2009; Pang et al., 2005). The advantages of EB irradiation are no use of chemicals and it offers a dry process at room temperature.

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Consequently, it saves energy, reduces the processing time and is environmentally friendly.

EB irradiation affects not only chemical structure of fibres, but can also modify the properties of polymer matrix, mainly by graftlinking/crosslinking and/or degradation/functionalization of polymer chains (Żenkiewicz et al., 2012; Malinowski et al., 2011). The crosslinking reaction can be controlled by the amount of suitable crosslinking agents. It was proved that triallyl isocyanurate (TAIC) is a suitable crosslinking agent for PLA (Jin et al., 2002; Quynh et al., 2007, 2008).

Consequently, in this work the effect of EB irradiation and TAIC on the chemical structure of flax fibres, PLA and their interphase was studied. Up to date, there is no report on the effect of EB on the properties, especially biodegradability of flax fibres reinforced PLA modified by EB in the presence of TAIC. Hence, this research study provides very important results complementing the state of the art in flax fibres reinforced biocomposites.

2. Material and methods

2.1. Materials

The following materials were used to prepare composites:

- Polylactide (PLA) 2003 D (D-repeat units: 3.5%, L-repeat units: 96.5%) provided by Cargill Down LLC with a melt flow index of 4.2 g/10 min. (2.16 kg, 190 °C) and density $\rho = 1.24\ g/cm^3$.
- Flax fibres, originated from the harvest in the year 2014, Belgium (Kortrijk region). The fibres were obtained by natural dew-retting and standard mechanical dressing. They were cut to a length of (5 ± 1) mm and their diameter was ranging from 15 to 25 µm as determined by SEM analysis. The flax fibres comprise cellulose (85–87%), hemicellulose (7–9%), lignin (2.5–4 %) and pectin (1.5–2.5 %) (Kozłowski, 2012).
- Triallyl isocyanurate (TAIC, Sigma–Aldrich GmbH, Germany) used as crosslinking agent.
- Proteinase K from Tritirachium album (Blirt, Poland) was the enzyme used for biodegradation, whereas the buffer consisted of 0.1 M Tris HCl and sodium azide (NaN_3).

2.2. Processing

Flax fibres were dried for 24 h at 60 °C before extrusion. All composites were prepared using a co-rotating twin screw extruder type BTSK 20/40D (Bűhler, Germany). The temperature profile of the extruder was 180, 182, 184, 186, and 185 °C, respectively. Flax fibres (20 wt%), TIAC (0, 1, 3 wt%) and PLA were dried, mixed and added to the extruder feeding zone. Dumbbell- and bar-shaped samples for mechanical testing were prepared using an injection moulding machine type Tederic TRX 80 ECO 60 (Tederic Machinery Manufacture, Taiwan). The temperatures of barrel heating zones of injection moulding machine were set to 175, 165, 165, 165 and 35 °C of the mould.

All EB irradiations were done with an electron energy of 1.5 MeV using an ELV-2 electron accelerator (Budker Institute of Nuclear Physics, Novosibirsk, Russia) (Dorschner et al., 1998). The samples were placed on the conveyor system of the electron accelerator. The speed of conveyor system during EB-treatment amounted to 1.2 m/min in order to apply a dose of 10 kGy per pass. The dose values amounted to 0, 10, 20, 30 and 40 kGy.

2.3. Examination

Determination of tensile strength and Young modulus were performed using a tensile testing machine, type Instron 3367 (Instron, USA), according to the PN-EN ISO 527-1 standard. Impact strength tests were performed using a Charpy apparatus (ATS-FAAR, Italy), according to the PN-EN ISO 179-1 standard.

Dynamic mechanical analysis (DMA) was performed using DMA analyser Q 800 (TA Instruments, USA). The bar-shaped injection moulded samples were examined in a dual cantilever mode at a constant frequency of 1 Hz and controlled amplitude of 15 µm as a function of temperature ranging from 25 to 160 °C.

The gel fraction (X_g) of samples in the form of granules were calculated using the following equations:

$$X_g = \frac{W_g}{W_0} 100\% - 20\% \quad (1)$$

where: W_o is the initial mass of the sample, W_g is the mass of the dried insoluble fraction of the sample after extraction from methylene chloride where samples were stored at room temperature for 24 h. Insoluble fraction contained also 20% of fibres. Consequently, it had to be included in Eq. (1).

Thermal stability of samples was evaluated using thermogravimeter Q500 (TA Instruments, USA). The samples were heated from 25 to 700 °C at the rate of 10 K/min under nitrogen atmosphere.

Differential scanning calorimetry (DSC) measurements were performed using calorimeter Q200 (TA Instruments, USA) under nitrogen flow. About 4 mg was cut off from polymer granules and placed on an aluminium pan for measurement. The samples were successively quenched to 20 °C, heated to 200 °C at a rate of 5 K/min, annealed at 200 °C for 3 min, cooled to 20 °C at a rate of 5 K/min and reheated to 200 °C at a rate of 5 K/min.

Dumbbell-shaped samples were put into an industrial compost pile composed of leaves (40 wt%), wood chips (30 wt%) and grass (30 wt%). The samples were placed in stainless-steel baskets that were put into the compost pile at a depth of 1 m from top. The temperature inside the pile varied from 50 to 69 °C, the pH was in the range from 7.0 to 8.7 and the relative humidity amounted up to 80%. The composting lasted for 8 weeks.

Composite granules were placed in a special compressing holder, attached to the DMA instrument to form thin films for enzymatic biodegradation experiments. The samples were compressed at 160 °C and 15 N then cut into strips of films weighing from 15 to 17 mg. Afterwards, the strips were placed in test tubes with the reaction mixtures containing 2 mg of the respective enzyme, 10 ml of 0.1 M Tris-HCl buffer and 2 mg of sodium azide. Finally, the test tubes were placed in an incubator. Enzymatic degradation took place at a constant temperature of 37 °C.

Surface chemical analysis was performed by XPS apparatus equipped with R3000 analyzer (Scienta Company) and X-ray lamp with the Al Kα anode (Prevac Company). The analysis of recorded spectra was performed in the CasaXPS program. Peaks in the O1s, N1s and C1s bands were modelled using and a linear background cut-off.

3. Results and discussion

3.1. Mechanical properties

EB irradiation has been used as one of the alternatives to modify the mechanical properties of polymers by inducing a crosslinking network in the polymer matrix. However, this modification did not provide significant effect to the structural-mechanical properties of neat PLA, as reported elsewhere (Ng et al., 2014). In this study, an increase in tensile strength (σ_M) with increasing dose was proved (Fig. 1), probably due to the use of TAIC. The highest increase in σ_M from about 63–76 MPa was observed for composite with 3 wt% of TAIC irradiated at 40 kGy. Since the tensile strength of short fibres reinforced composites with randomly distribution is very sensitive to the interfacial adhesion, we can conclude that EB treatment in the presence of TAIC enhanced the interfacial adhesion. In addition, it was also noticed that with increasing TAIC content standard deviation of σ_M for irradiated samples decreased. Therefore, we might conclude that EB irradiation in the presence of