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Effect of high energy β-radiation and addition of triallyl isocyanurate on the selected properties of polylactide

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ABSTRACT

Comparison of some changes occurring in polylactide (PLA) due to high energy β-radiation and addition of triallyl isocyanurate (TAIC) was the main objective of the present study. It was found that irradiation of PLA by high energy β-radiation causes essential changes in its properties, that undergoes mainly degradation, to form a porous structure. The PLA degradation can be diminished by introduction into the polymer matrix of a low-molecular mass multifunctional compound like TAIC. Upon the electron radiation, effective crosslinking of PLA by TAIC occurs. Application of TAIC favorably influences hindering of the PLA degradation or, when the doses are very large, diminishes worsening of the PLA functional qualities. It was also found that the optimum crosslinking of PLA is obtained when the electron radiation doses of the range of 40–200 kGy are applied and the amount of TAIC equal 3–5 wt% is used.

1. Introduction

Biodegradable polymers constitute a new group of materials that in recent years have attracted great interest not only in medicine and tissue engineering [1–3] but also in mass application in, e.g., packaging industry [4–6]. Higher and higher availability, lower and lower prices as well as stimulating properties of these polymers, the most of which can be processed with the use of known machines, equipment, and technology (including extrusion, injection moulding, thermoforming, and blow moulding) [7], initiated numerous studies on production of new biodegradable materials, being carried out in research institutions.

Polylactide (PLA) is one of important biodegradable polymers, which may become a significant polymer in the 21st century [7–9]. Its physico-chemical properties are beneficial and the material may play a key role in many branches of economy (both in specialised and mass applications). However, this material is not easy to be processed because it has to be dried and can partially undergo mechanical-thermal degradation. It is also brittle and thus, it requires various additives. Moreover, in the packaging trade, PLA films exhibit unfavorable permeability towards several gases.

The above-mentioned disadvantages of the PLA and also other biodegradable polymers induced researchers to undertake actions aimed at improvement of the properties or restriction of the disadvantages. The mechanical, thermal, and processing properties may be modified by various methods. The predominant techniques include the production of composites or nanocomposites containing additives, like fillers, nucleants, nanocompounds, stabilizers, fibres etc. [10–14]. Blends of two or more polymers may exhibit properties beneficial with respect to the properties of single components [15–17]. The material properties may also be improved by grafting or copolymerisation [18–20]. Moreover, different chemical and physical processes are being used to modify the surface layer of the materials made of PLA [21–23].

The problems connected with improvement of physico-chemical, processing, and functional properties of PLA, performed by crosslinking of this material, are rather new. Known publications on the PLA modification by the ionisation radiation concern so far the neat PLA only while the authors have used mostly gamma (γ) and electron (β) radiation [24–29]. The radiation of these two kinds essentially affects on the PLA. The radiation alone does not crosslink PLA but leads to worsening of its properties by reducing the average molecular weight.

The crosslinking of PLA may be successfully carried out by using low-molecular weight multifunctional compounds, mainly allyl and peroxide ones. They include triallyl isocyanurate (TAIC), trimethylopropane triacrylate (TMPTA), 1,6-hexanediol diacrylate (HDDA), dicumyl peroxide (DCP), and dibenzoyl peroxide (DBP). The first three compounds crosslink PLA upon ionisation radiation only, but without the radiation, they are merely plasticisers towards this polymer. The crosslinking of PLA by the ionisation radiation with the use of the low-molecular weight multifunctional compounds is advantageous mainly because of improvement of

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resistance to strain at elevated temperatures. Moreover, PLA subjected to the ionisation radiation with the participation of TAIC may form a two-phase structure (crosslinked and degraded). This may result from creation of different radical structures that can undergo various radiation reactions, e.g., recombination, dissociation, disproportionation, etc. [30–31]. Besides, the material partially crosslinked this way may maintain its susceptibility to biodegradation [32].

Peroxides are chemicals that crosslink PLA upon elevated temperatures. The crosslinking performed in such a manner results in improvement of physico-chemical properties of PLA, but the product is not susceptible to biodegradation. Thus, this method leads to obtaining a material without one of the basic, necessary properties [33–35].

The analysis of the literature also revealed that, there are no known study on the effect of high energy β-radiation influencing the PLA properties. Getting to know the new effects of high energy β-radiation and of triallyl isocyanurate on the some properties of PLA, is interesting from both cognitive and utilisation aspects. This had inspired the author of the present article to undertake investigations aimed at comparison of changes in (i) melt flow rate, (ii) average molecular weight, (iii) gel fraction and degree of swelling, (iv) mechanical properties, (v) thermal properties, (vi) optical properties, and (vii) density, and irradiated PLA and irradiated PLA containing TAIC. The results are presented in the present paper.

2. Experimental

2.1. Materials

The following materials were used in this work:

Polylactide (PLA), type 2003D (NatureWorks®, USA), characterised by the melt flow rate (MFR) equal to 2.7 g/10 min (2.16 kg, 190 °C), average molecular weight of ca. 155,500 Da. The polymer contained 3.5% of D monomer units. Its structural formula is shown in Fig. 1.

Triallyl isocyanurate (TAIC) (Sigma–Aldrich GmbH, Germany), utilised in a liquid state, characterised by the density equal to 1.16 g/cm^3, melting temperature of ca. 23–27 °C. Its structural formula is shown in Fig. 2.

2.2. Sample preparation

Granulated samples were obtained using a single-screw extruder, type Plasti-Corder Lab Station (Brabender, Germany), with a screw diameter of 19.5 mm, the length/diameter ratio of 25, and the volume of a plasticizing channel reduced in proportion of 3:1. The device was also equipped with a two-opening die, belt conveyor together with a system of eight cooling fans, granulator, volumetric feeder, and dropper. The zone beneath the hopper was cooled by air blowing. The temperatures of barrel heating zones I, II, and III and of the die of the extruder were set to 180, 190, 190, and 190 °C, respectively. The screw rotational speed was constant (150 rpm). The crosslinking agent was dropped into zone I with a rate resulting in the concentrations of 5% with respect to PLA. Were obtained the reference sample (P0) and the PLA sample containing TAIC (T0).

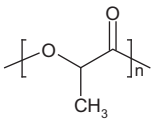

Fig. 1. Structural formula of PLA.

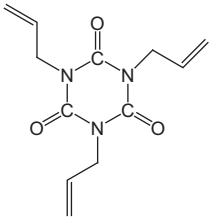

Fig. 2. Structural formula of TAIC.

Using a laboratory injection moulding press type Battenfeld Plus 35/75 (Battenfeld GmbH, Germany) and the prepared granulated materials (P0 and T0), normalised samples were produced in the forms of dumbbells and bars, according to a proper standard [PN-EN ISO 527-2:1998]. The moulded pieces were designated with the same symbols as those for the granulated materials.

Sample irradiation was carried out with the use of a linear accelerator type LAE 13/9, located at the Institute of Nuclear Chemistry and Technology in Warsaw, Poland. The samples (the granulated samples and moulded pieces) were irradiated with the high doses of 200, 400, 600, 800 or 1000 kGy. The maximum individual dose was 20 kGy. It was limited by an increase in temperature of the irradiated material, equal to ca. 4–7 °C for an individual dose of 10 kGy. Large individual doses cause intensive heating of the material, thus, some additional structural changes may occur. Therefore, samples were irradiated many times, as specified in Table 1.

During the irradiation procedure, all the granulated samples and moulded pieces were placed in aluminium containers in single layers of the thickness of up to 2 mm. The containers were put on the belt conveyor moving at the speed of 0.3–1.2 m/min. The actual speed was related to the radiation dose absorbed by a polymer material being modified.

Symbols of all the prepared samples are summarised in Table 2.

2.3. Methodology of research

Determination of the melt flow rate (MFR) was carried out according to a relevant standard [PN EN ISO 1133:2005] with a capillary plastometer type LMI 4003 (Dynisco, Germany). The measurements were made at 190 °C under the piston loading of 2.16 kg.

The influence of the β-radiation on the number-average molecular weight (M_n) and weight-average molecular weight (M_w) of P samples was examined by gel permeation chromatography (GPC) conducted in $CHCl_3$ at room temperature with an eluent flow rate of 0.8 mL/min, using a set of two PLgel 5 μm MIXED-C columns. Results were calculated using ASTRA 4.90.07 software.

The gel fraction (X_g) was calculated by measuring the amount of insoluble material part after dissolving the material in chloroform at room temperature for 24 h, using the following equation:

$$X_g = (W_g/W_o) \times 100\%$$

where W_o is the initial weight of the dried sample and W_g is the weight of the dried insoluble part of the sample after extraction.

Degree of swelling (X_s) was calculated using the following equation:

$$X_s = [(W_s - W_g)/W_g] \times (\rho_p/\rho_r)$$

where W_s is the weight of the solvent-swollen gel of the sample after keeping it in chloroform at room temperature for 24 h, whereas ρ_p and ρ_r are densities of PLA and chloroform, respectively.