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Effect of compatibilizig agent on the properties of polylactide and polylactide based composite during ozone exposure

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ABSTRACT

Compatibilizers belong to the most important internal factors which influence the degradation process of polymer matrix. For this reason in the current study, polylactide (L), polylactide with 5% of poly(ε-caprolactone) (LK) as compatibilizing agent and samples with 5%wt. of montmorillonite (MMT) (LS5 and LS5K respectively) before and after various time of ozone exposure have been analyzed. The results from infrared spectroscopy, gel permeation chromatography, atomic force microscopy, differential scanning calorimetry and thermogravimetric analysis have been presented. It has been established that microstructural changes during ozone exposure of the samples with the presence of compatibilizer increase in relation to the samples comprising PLA and PLA filled with montmorillonite. Moreover it has been determined that the introduction of poly(ε-caprolactone) into pure polymer as well as into PLA-montmorillonite material accelerates ozone-induced degradation, although it does not change the mechanism of the degradation process.

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1. Introduction

Many biodegradable polymers are available nowadays for various applications and constitute substitutes for non-biodegradable plastics, and even metallic components. One of them is polylactide (PLA), which is the most frequently used linear aliphatic polyester. Due to its many favorable characteristics PLA is used in biomedical applications such as controlled release of pharmaceutics, prosthetic devices, bone screws or scaffolding for tissue engineering. For the same reason polylactide is viewed as a promising material for production of grocery bags, sacks, in compostable garbage and food packaging [1–4]. It seems that PLA could be a technical and economic solution to the problem of eventual disposal of very large amount of plastic packaging [5]. Moreover, PLA is considered as biodegradable polymer commonly derived from lactic acid. It should be noted that lactic acid is generally produced by bacterial fermentation of carbohydrates contained in corn or sugar cane [1,3]. Among biodegradable polymers, polylactide has recently gained an increasing commercial and industrial interest because of its good mechanical properties, thermal plasticity and biocompatibility [6–8]. However polylactide has got certain disadvantages: polylactide is characterized by low hydrophilicity, low elongation at break and it does not contain reactive side-chain groups. Apart from that PLA is a very brittle material what can limited its use in the applications that involve plastic deformation at higher stress levels [9]. For this reason in aim to enhance thermal stability, mechanical and barrier properties of polymeric materials, such as polylactide, polymers are often mixed with various types of fillers such as montmorillonite or carbon nanotubes [2,10,11]. Recently the most popular fillers were layered silicates, which introduced even at low filler content (1–5 wt.%) are able to improve mechanical, thermal, barrier and flame retardancy properties of polymers [1,12]. However in the case of polymer-based composites improvement of properties depends strongly on the nanofiller dispersion in the polymer matrix. It is well known that the layered silicate particles are usually hydrophilic and their interactions with non-polar polymers are unfavorable [13]. In order to improve the miscibility between polymer matrix and nanofiller two solutions have been found: modification of the nanofiller or an addition compound called a compatibilizing agent. Most researches indicate that the majority of commercial polymers are immiscible and compatibilization is needed to achieve properties required for specific applications [12,14]. It is well known that functional compatibilizers are required to reduce the interfacial energy and to

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homogenize polymers with nanofillers [13,15]. Most popular compatibilizing agents include: maleic anhydride as well as a random terpolymer of ethylene, acrylic ester and maleic anhydride or a random copolymer of ethylene and glycidyl methacrylate which are widely used to connect olefin polymers and inorganic nanofiller [13,14,16–18]. Also citric acid can act as a compatibilizer in starch/poly(butylene adipate-co-terephthalate) blends [14,15,19]. Some recent investigations have also been carried out with oxidized polyethylene or wax as compatibilizer. In both of these cases, significant improvements in mechanical, rheological and gas barrier properties have been observed [16,17]. Other materials used as compatibilizing agents are natural materials in the form of different carboxyl acids such as: myristic acid (C14), palmitic acid (C16) and stearic acid (C18), which were used in the case of polypropylene-based blends [15].

Compatibilizing agents effect not only the dispersion of the nanofiller in the polymer matrix, they belong to the most important internal factors which influences different degradation processes. One of these degradation processes is caused by ozone. Ozone is a gas responsible for oxidative degradation of different materials. In some cases this is desired process. For example ozone induces degradation of anthocyanins or ascorbic acid in fruit juice. A number of commercial fruit juice manufacturers in the US and Europe started to employ ozone for pasteurization. The FDA's approval of ozone as a direct additive to food in 2001 triggered interest in the application of ozone processing within the food industry [20]. In addition, researchers have proven that ozone can detoxify mycotoxins and kill bacteria [21,22]. For this reason ozonation is a very important technique that can be applied for instance in hospitals during disinfection and sterilization. Recent years have shown that ozone and hydrogen peroxide gas can be used for sterilizing rooms in hospitals. Results obtained so far indicate that the process mentioned above is more effective in terms of killing bacteria than sweeping a room with detergents. Although ozone is mainly used for disinfection, it can also be used in surface modification. In the case of polymer, ozone improves surface layer adhesive properties as well as allows introduction of specific functionalities into polymer [23–27]. However at the same time the presence of ozone influences the degradation process of polymers such as chitosan or poly(vinyl alcohol) [28,29]. Recently influence of ozone was discussed in relation to different types of composite materials such as polypropylene fiber composites and carbon/carbon composites [30,31].

The aim of this research was to explore the influence of the poly(ε-caprolactone) as compatibilizer on the ozone-induced degradation of pure polylactide and polylactide-based composites. In order to observe the morphology and structural changes, atomic force microscopy and FTIR spectroscopy were used. Thermal properties of samples during the degradation process were determined by means of differential scanning calorimetry and thermogravimetry technique. Molecular mass of the samples was calculated by using ^{1}H NMR technique. The changes in the properties of investigated materials were measured after 1, 2, 3 and 4 months of ozone exposure.

2. Experimental

2.1. Materials

Polylactide (PLA), type 2002D (NatureWorks®, USA), with melt flow rate of 5–7 g/10min (2.16 kg; 190 °C) and density of 1,24 g/cm^3 was used as the polymer matrix. Montmorillonite K10 (Acros Organics, Belgium) and Nanofil2 (Southern Clay Products, USA). were used as nanofillers. Poly(ε-caprolactone) (PCL) CAPA 6506 (Solvay Caprolactones, UK), was used as the plasticizing agent. Investigated composites were obtained in the same way as described in our previous work [12]. Designations and compositions of investigated materials are depicted in Table 1.

2.2. Conditions of ozone induced degradation

Pure polylactide (L), polylactide with addiction of 5% of poly(ε-caprolactone) (LK) in form of films as well as samples L and LK filled with 5% of MMT (LS5 and LS5K respectively) were subjected to ozone-induced degradation. The effect of compatibilizing agent on the ozonolysis of polylactide and polylactide composite was studied. The samples were placed in the presence of ozone and shielded from light. The stream of air was ozonized using an electric discharge ozone generator. The degradation process was performed with an increased quantity of ozone compared to tropospheric conditions, under atmospheric pressure and at room temperature. Materials were taken for analysis at different time intervals: after 1, 2, 3 and 4 months of ozonolysis.

Concentration of ozone during degradation process was controlled and calculated based on the FTIR analysis. For this reason the spectrometer Nicolet iS10 (Thermal Scientific) equipped with gas cell was used. The concentration of ozone obtained by FTIR technique equaled 2.57*10-5 mol/dm^3.

2.3. Material characterization

2.3.1. FTIR

Infrared spectra were recorded using Nicolet iS10 (Thermal Scientific) spectrometer in range of 800–3600 cm$^{-1.}$ All spectra of the investigated materials, in the form of a film, were recorded at the resolution of 4 cm^{-1} and 64 scan passes.

2.3.2. ^{1}H NMR

^{1}H NMR spectra were recorded at 700 MHz using a Bruker 700 spectrometer. $CDCl_3$ was used as solvent. The $CHCl_3$ resonance at 7.26 ppm was used as chemical shift reference. All experiments were carried out at 27 °C.

2.3.3. AFM measurements

In aim to visualize the topological morphology during degradation and to gather information on the surface roughness, the AFM technique has been chosen. The photographs of the surface of analyzed materials were taken by means of a microscope with a scanning SPM probe of the NanoScope MultiMode type (Veeco Metrology, Inc., Santa Barbara, USA) operating in the tapping mode, in air, at room temperature. Based on the 2D pictures the roughness parameter such as the root mean square (R_q) was calculated for scanned area (5 μm × 5 μm) using Nanoscope software. Samples were investigated before and after 1,2,3 and 4 months of degradation.

2.3.4. DSC method

DSC was carried out on a Polymer Laboratories, Epson, UK

Table 1
Compositions of investigated materials (L – polylactide; S-Montmorillonite, K-poly(ε-caprolactone)) [36].

Sample symbol	Sample composition (mass parts)		
	PLA	S	K
L	100	–	–
LK	100	–	5
LS5	100	5	–
LSK5	100	5	5

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