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Material Behaviour

Effect of ozone exposure on thermal and structural properties of polylactide based composites

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ABSTRACT

One of the factors that influence the properties of polymers and polymer-based composites in ambient conditions is ozone. The aim of this work was to determine the effect of ozone on polylactide and its composites consisting of polylactide (L) as polymer matrix and Montmorillonite K10 (S). The variation of the materials structural and thermal properties after exposure to ozone, ranging from 1 to 4 months, have been studied using infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), atomic force microscopy (AFM) differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). The results indicate that the addition of the filler accelerates ozone-induced degradation. The incorporation of montmorillonite however does not change the mechanism of the degradation process. The AFM images of the microstructure of polylactide and polylactide-based composites after ozone treatment indicate that the introduction of an unmodified nanofiller into the system decreases the changes in the surface morphology. Present study reveals that ozone significantly influence the structure and properties of polylactide-based composites.

1. Introduction

In order to reduce the environmental pollution caused by polymer waste since 1970s new kinds of biodegradable materials have extensively been studied [1]. Because of their advantageous optical, chemical and mechanical properties, biodegradable polymers are largely utilized in biomedical applications [2,3]. One of promising materials is poly(L-lactide) (PLA), which is a linear thermoplastic polyester produced from renewable resources. In order to improve mechanical properties or decrease permeability to gases, different types of nanofillers are introduced into polymer matrix [4–7]. It is well known that the presence of nanofillers in the polymer matrix can influence the degradation processes. The photodegradation and the hydrolytic degradation of polylactide-based composites was previously discussed [8–12] but there is no publication devoted to changes in properties of polylactide composites induced by ozone.

Ozone is an allotrope of oxygen in which the molecule is composed of three oxygen atoms. This gaseous substance is known as one of the most powerful oxidizing agents with a redox potential of +2.07 V [13]. It should be noted that ozone can be beneficial or harmful depending on where it is found in the atmosphere. Ozone gas in the stratosphere forms an important and very effective protective barrier against harmful radiation from the sun by absorbing ultraviolet radiation. However ozone in the troposphere, the lower atmosphere that we breathe, is considered a pollutant and is harmful to human health and vegetation [14]. Ozone causes oxidative degradation of different materials, whereby in most cases they initially lose color and eventually decay. At the same time ozonation, is an effective recycling process used for treating wastewater containing refractory organics. For this reason it is regarded as one of promising alternatives for solving the problem of pollution [15]. Ozonation is expected to become increasingly popular in the disinfection market [14,16]. Furthermore it should be noted that ozone exposure seems to be a particularly promising in terms of disinfection and sterilization. Humidified gaseous ozone is already being employed for example in hospitals in a low-temperature sterilizers [17,18]. Ozone has also found application in surface modification. Surface modification of polymers via ozone treatment is a convenient and efficient method for introducing specific functionalities, such as hydrophilicity or hydrophobicity, into existing polymers [19–21]. Obtained results indicate that ozone treatment is the most efficient method of improving surface

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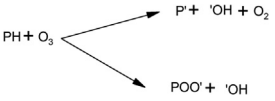
layer adhesive properties [22].

On the other hand ozone influences properties of many types of polymers. The reaction of ozone with organic and inorganic compounds results in a formation of harmful products, such as free radical peroxide, hydroxide or hydroperoxide [23]. It should be mentioned that both the ozone and atomic oxygen, which is a product of the decomposition of O_3 are very reactive. For this reason the reaction (1) presented below is possible in the case of direct reaction of polymer materials with ozone: [24].



(1)

It is also well known that ozone is an unstable gas and in the air the half-time of ozone at 20 °C is about 3 days (2):

$$O_3 \rightleftharpoons O_2 + O \quad (2)$$

Degradation process initiated by ozone was discussed in relation to different kinds of polymers such as gelatin, DNA, chitosan, polycarbonate, polypropylene as well as conducting polymers [20,25–30] Recently a number of researchers analysed influence of ozone on the composite materials such as polypropylene fiber composites or carbon/carbon composites [31,32].

In the case of degradable materials and its composites their utility depends on their resistance to aging processes. For this reason degradation occurring in the presence of ozone is another important mechanism worth focusing on. In the present paper, the main aim is to determine the impact the ozone as well as an additive such as montmorillonite have got on the degradation of polylactide. In spite of extensively documented study devoted to ozone-induced degradation of different types of polymers there has been no focus on the research into the influence the ozone has got on polylactide nanocomposites. Structural changes in the polymer caused by ozone were determined by means of FTIR spectroscopy. The thermal properties, during ozonolysis, were studied by means of differential scanning calorimetry (DSC) and thermogravimetry (TG) techniques. The molecular mass of the samples was calculated by using ^{1}H NMR technique. Atomic force microscopy (AFM) was used in order to observe the morphology and structural changes during exposure to ozone. The changes in the properties of investigated materials were measured after 1, 2, 3 and 4 months of being in the ozone atmosphere.

2. Experimental studies

2.1. Materials

Polylactide, type 2002D (NatureWorks®, USA), with melt flow rate of 5–7 g 10min^{-1} (2,16 kg; 190 °C) and density of 1,24 g cm^{-3} was used as the polymer matrix. Montmorillonit K-10 (Acros Organics, Belgium) was used as the nanofiller. The composites were obtaining by melt processing. The gravimetric dosing system and the twin-screw extruder type TSK 20 (Buhler, Germany), with screw diameter of 20 mm and length/diameter ratio of 40, were used to prepare all nanocomposites [33]. Composition of investigated materials has been presented in Table 1.

2.2. Condition of ozonization

Samples in the shape of films consisting of neat polylactide, filled MMT polylactide at the 1, 3 and 5% weight ratio were subjected to ozone-induced degradation. The influence of nano-additive on the ozone-induced degradation of polylactide composites was studied with an increased quantity of ozone compared to tropospheric conditions. The samples were studied in the presence of ozone, under atmospheric pressure, at room temperature and shielded from light. The stream of air was ozonized using an electric discharge ozone generator. Concentration of ozone was 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.

Table 1
Compositions of investigated materials (L – polylactide; S-Montmorillonite) [36].

Sample symbol	Sample composition (mass parts)	
	PLA	S
L	100	–
LS1	100	1
LS3	100	3
LS5	100	5

2.3. Methods of analysis

2.3.1. FTIR

Infrared spectra were recorded using Nicolet iS10 (Thermal Scientific) spectrometer in range of 400–4000 cm^{-1}. All spectra were recorded at the resolution of 4 cm^{-1} and 64 scan passes. All FTIR spectra were obtained in transmission mode. The Films thickness was 0.048 mm ± 0.003.

2.3.2. ^{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. DSC method

DSC was carried out on a Polymer Laboratories, Epson, UK differential scanning calorimeter under nitrogen screening. Thermal behavior of PLA and PLA/clay nanocomposites was investigated in a temperature range of 25–180 °C with a heating rate of 10 °C/min according to PN-EN ISO 11357:2002. The degree of crystallinity (X_m) was evaluated by applying the following equation (3), also used by other authors [34,35]:

$$X_m = \frac{\Delta H_m}{\Delta H^0 \times X_{PLA}} \times 100\% \quad (3)$$

where ΔH_m is the measured heat of fusion of sample, ΔH^o is the heat of fusion of a 100% crystalline polylactide and $\Delta H^o = 109$ mJ/mg [34], X_{PLA} is the mass fraction of polylactide.

2.3.4. Thermogravimetric analysis (TG)

TA Instruments, SPT 2960 simultaneous DSC-TGA was used for studying thermal behavior of investigated materials. TGA traces were monitored from room temperature to 600 °C at 10 °C/min under air according to the procedure specified in PN-EN ISO 11358:2004.

2.3.5. AFM measurements

AFM has been chosen to visualize the topological morphology during ozonolysis and to gather information on the surface roughness. The photograph of the nanocomposite film surface topography was made 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. The roughness parameter such as the root mean