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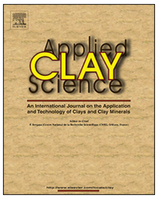

Research paper

Effect of clay treatment on the thermal degradation of PHB based nanocomposites

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ABSTRACT

A detailed understanding of the thermal degradation processes taking place during the melt processing of bio-nanocomposites is crucial in order to increase the processing window of these materials. In this work, the influence of the content of neat clay and modified-clay on the thermal degradation of a biodegradable bacterial poly(3-hydroxybutyrate) (PHB) matrix, was studied. The modified clay consisted in a multi-treated organo-bentonite, which was first acid-activated, then silylated and further modified by cationic exchange treatment. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) tests were carried out to investigate the thermal behavior of the different nanocomposites as a function of temperature, whereas size exclusion chromatography (SEC) runs were performed to analyze the changes on the molecular weight distribution of the PHB. The obtained results reveal that the organic modifiers of the muti-treated clay promote the thermal degradation process leading to a dramatic decrease in the molecular weight of PHB. It was demonstrated that the degradation mechanism of PHB was not modified by the incorporation of neat clay or modified-clay, and that the process can be well described by the Avrami–Erofeev random nucleation model ($m = 4$), in which the reaction is controlled by initial random nucleation followed by overlapping growth.

1. Introduction

Biodegradable polymers, in particular polyhydroxyalkanoates (PHA), represent an interesting alternative to synthetic polymers due to many advantages related with their biodegradability and biocompatibility, and also because they are produced from renewable resources (Hablot et al., 2008). Nevertheless, they have several disadvantages related to their mechanical and barrier properties. In order to overcome such disadvantages one alternative is the preparation of bio-nanocomposites, (Pandey et al., 2005; Chivrac et al., 2006) since the nanofillers are able to enhance the material properties. There are several studies in the literature focalized on PHB or PHBV/Montmorillonite (Mt) based bio-nanocomposites (Chen et al., 2002; Lim et al., 2003; Mook Choi et al., 2003; Chen et al., 2004; Wang et al., 2005).

The main drawback of PHB is its thermal instability during melt processing. Due to this limitation, most of the works use the environmentally unfriendly route of solvent intercalation (Chen et al., 2002; Lim et al., 2003; Chen et al., 2004; Wang et al., 2005). Therefore, great interest has been shown in the thermal degradation of PHB and other related PHA. Since degradation is assumed to occur by random chain excision with or without surfactants, as recently demonstrated for PHB (Hablot et al., 2008), the lower the initial Mw, the faster the short chains are obtained, and therefore, the less thermally stable is the PHA. In the last years, it has been proved that PHB is a chemically recyclable polymer with several end products such as crotonic acid, linear oligomers, having a crotonate end group (Morikawa and Marchessault, 1981), and a cyclic trimer (Melchiors et al., 1996). Many studies have been dedicated to thermal (Grassie et al., 1984c; Grassie et al., 1984b; Grassie et al., 1984a; Kunioka and Doi, 1990; Aoyagi et al., 2002; Li et al., 2003; Abe, 2006; Carrasco et al., 2006) and thermomechanical (Melik and Schechtman, 1995; Renstad et al., 1997) degradation of neat PHB and polyhydroxybutyrate-*co*-valerate (PHBV). These studies have revealed that the degradation occurs rapidly near the melting point mainly through a random chain scission process based on typical structures of pyrolysis products, i.e. crotonic acid and oligomers with a crotonate end group (Morikawa and Marchessault, 1981; Kawalec et al.,

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2007). On the other hand, they have also shown that the parameters of melt processing have to be optimized in order to avoid or restrict this phenomenon that reduces the processing window.

During the last decades, the development of nanocomposites by incorporating nanoscaled fillers into a polymer matrix has been believed to become a key technology on advanced composite materials. It is known that nanocomposites obtained by the incorporation of low amounts of clay into polymeric matrices displayed, among others, enhanced thermal and oxidative barrier properties as compared with traditional composites (Huang et al., 2005; Cyras et al., 2008; Bordes et al., 2009b).

Kinetic data obtained from thermogravimetric (TGA) measurements are very useful for understanding thermal degradation processes and also to identify whether the filler helps to improve the thermal stability of the material. There are several reports about the thermal degradation of PHB-based bio-nanocomposites filled with Mt. Maiti et al. (Maiti and Batt, 2003) have reported that the presence of aluminum Lewis acid sites in the octahedral sheet of the silicate layers enhances the thermal degradation of PHB by catalyzing the hydrolysis of ester linkages. (Xie et al., 2001) have pointed out the complex degradation reactions that could exist in organically modified Mt. and consequently, in nanocomposite with that kind of clays.

The aim of this work was to investigate the influence of the incorporation of the clay, the processing technique and the addition of clay modifiers (silane and phosphonium salts) on the thermal degradation of PHB. A kinetic analytical model (Criado et al., 1989) was applied to non-isothermal TGA measurements trying to identify the possible mechanism of PHB degradation in the presence of neat and modified bentonite.

2. Materials and methods

2.1. Materials

The natural clay employed in this work was a bentonite (Bent), supplied by Minarmco S.A. (Neuquén, Argentina). It consisted predominantly of montmorillonite as evidenced by X-ray diffraction (XRD) analysis (D'Amico et al., 2014). It contained quartz and feldspar as major impurities, as well as traces of gypsum and sepiolite. Dimethyloctadecylchlorosilane (DMOCS) and tributylhexadecylphosphonium bromide (TBHP) organic modifiers as well as pyridine (anhydrous, 99.8%) were purchased from Aldrich and used as received. PHB polymer ($Mw = 246{,}000\ g.mol^{-1}$), was supplied by PHB Brazil and tributyrin (TBL) was provided by Fluka.

2.2. Preparation of the organoclay

Bent was firstly activated by treatment with mineral acid, then it was silylated with DMOCS and finally it was modified by cationic exchange reaction with TBHP (D'Amico et al., 2014). A 5 g portion of clay was dispersed in 200 mL of water. Then 10 mL of 98% (*w*/w) H_2SO_4 was added and the mixture was stirred at room temperature for 6 h. The wet acid activated clay was separated by centrifugation, washed with distilled water and centrifuged at 10,500 rpm for 10 min. This procedure was repeated 5 times. Finally, the wet product was frozen for 24 h and then lyophilized at 100 mTorr and − 50 °C for 72 h. Subsequently, the activated-Bent was silylated with DMOCS. For this treatment, 1.5 g of A-Bent was dispersed in 350 mL of anhydrous n-butanol, together with an excess of DMOCS (5 g). The mixture was heated at 100 °C and kept under stirring. After 15 min, 3.5 mL of pyridine was added and it was refluxed for 24 h. The product was separated by filtration and then washed three times with n-butanol and once with ethanol. Finally, the product (S-A-Bent) was dispersed in 20 mL of ethanol and dried in an oven at 80 °C for 24 h. Finally, ion exchange was performed by dispersing a 2.5 g S-A-Bent in 100 mL of distilled water and 1.1 g of TBHP was added. The dispersion was kept under stirring at the temperature of 70 °C for 4 h. The clay was then filtered and washed several times with distilled water. The exchanged clay was dispersed in ethanol and dried in an oven at 80 °C for 24 h. The resulting sample was designated *E*-S-A-Bent.

2.3. Preparation of the PHB/organoclay nanocomposites

PHB films and PHB/organoclay nanocomposites were prepared by melt compounding method. Different clay contents (2, 4 and 6 wt%) and 20 wt% of a natural hydrophobic plasticizer, TBL, was incorporated to facilitate the polymer processability. TBL is a natural triglyceride present in fats and oils that has shown to be a good candidate as plasticizer for bio-based polymer were added to the PHB (D'Amico et al., 2016). In order to obtain the nanocomposites, raw PHB pellets were mechanically mixed with TBL and the clay prior to melt them in a Haake mixer at 185 °C and a rotation speed of 50 rpm for 3 min. Blends were then molded into films at 190 °C in a hot press. The materials were kept between the plates at atmospheric pressure for 1 min until melting and then for 2 min at 5 MPa. Both clays (original and modified) and PHB pellets were previously dried in a vacuum oven at 80 °C overnight.

2.4. Characterization techniques

X-ray diffraction (XRD) analysis was performed on the clay powders using an X-Pert pro diffractometer, operating at 40 kV and 40 mA, with CuKα radiation (λ = 1.5406 Å), at a scanning speed of 1.5°/min. To calculate the interplanar basal distance (d_{001}), the 2θ angle corresponding to the maximum value of the 001 reflection was used in the Bragg equation. The X-ray diffraction pattern of the raw Bent was analyzed using the X'Pert HighScore 2.2d software.

Size exclusion chromatography (SEC) was used to determine the molar mass distribution and the average molar mass. The tests were performed in a LKB-2249 instrument at 25°C. A series of four μ-Styragel® columns, ranging in pore size 105, 104, 103, 100 Å, was used with chloroform as an eluent. The sample concentration was 4–5 mg/mL and the flow rate was 0.5 mL/min. The polymer was detected by the carbonylic absorption of the ester group (5.75 μm), using an infrared detector (Miram 1A Infrared Analyzer) and the calibration was done with poly(methyl methacrylate) (PMMA) standards supplied by Polymer Laboratories and Polysciences.

Differential Scanning Calorimetry (DSC) measurements were performed in a Perkin Elmer Pyris calorimeter, operating from − 50 to 200 °C at a heating rate of 10 °C/min using nitrogen as a purge gas flow (ASTM D3417–83). The samples (average weight 10 mg) were placed in standard aluminum pans. The degree of crystallinity (X_{cr}) of each sample was calculated from the following equation, with the assumption that the heat of fusion is proportional to the crystalline content:

$$X_{cr}\,(\%) = \frac{\Delta H_{m,}}{w_{PHB} \times \Delta H_{100}} \times 100 \tag{1}$$

where ΔH_m is the experimental heat of fusion, w_{PHB} is the PHB weight fraction and ΔH_{100} is the heat of fusion of 100% crystalline PHB and its value is 146 J/g (Barham et al., 1984).

Thermogravimetric analysis (TGA) was carried out on a TA Q500 thermogravimetric analyzer, the mass of each sample was 5–7 mg and the carrier gas was nitrogen at a flow rate of 50 mL/min. Each sample was heated from room temperature to 700 °C at various heating rate values (5, 10, 15, 20, and 25 °C/min). The organic content was determined as the mass loss in the temperature range between 200 and 500 °C, where no additional thermal events occur for the pristine clay.

3. Theoretical Background

3.1. Isoconversional methods

Any solid state decomposition kinetic can be expressed as a single