Research paper

Vermiculite/poly(lactic acid) composites: Effect of nature of vermiculite on hydrolytic degradation in alkaline medium

M. Dolores Fernández *, M. Jesús Fernández

Departamento de Ciencia y Tecnologia de Polímeros, Facultad de Química, Universidad del País Vasco (UPV/EHU), Paseo Manuel Lardizábal 3, 20018 San Sebastián, Spain

ARTICLE INFO

ABSTRACT

Unmodified and different organomodified vermiculites were used for the preparation of poly(L-lactide) (PLLA) composites via melt mixing. The effect of the clay mineral surface modification, the type of organic modifier of the vermiculite and sample thickness on the degradation of PLLA in alkaline medium at 37 °C was studied. The degradation was evaluated by analyzing mass loss, pH, molecular weights, and morphological changes. Alkaline hydrolysis of PLLA was accelerated by the presence of clay mineral and the degradation rate was very much dependent on type of clay mineral and state of dispersion. Morphological changes suggested that the erosion mechanism of polymer matrix occurred at the film surfaces and started at the interface of polymer and clay minerals. The results presented here show that the hydrolytic degradation of PLLA can be controlled through the preparation of nanocomposites introducing the appropriate organomodified nanoclay mineral.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Polymers based on renewable and biodegradable resources have attracted much attention recently due to the environmental concerns. The most popular and important biodegradable polymers are aliphatic polyesters, and among them poly(lactic acid) (PLA), a linear aliphatic thermoplastic polyester, have received the most attention due to its renewable resources (Tsuji and Ikada, 1998b), biocompatibility, biodegradation, excellent thermal/mechanical properties, and superior transparency of the processed materials (Urayama et al., 2002; Iwata and Doi, 1998). One of the main characteristics of PLA, which is responsible for many of its applications, is its susceptibility to hydrolytic degradation (Hideto and Yoshito, 2000). PLA undergoes hydrolysis of the ester link by a non-enzymatic two step reaction in vivo and in water. In the first step, the ester linkages located in the main chain undergo hydrolysis randomly, and scission of PLA into smaller chains takes place. In the second step, water-soluble monomer and oligomers are released, and an onset of weight loss is observed. Finally, the decomposition products are naturally metabolized to yield carbon dioxide and water. The first reaction step is the rate determining step for the whole hydrolysis process as it is very slow. The hydrolytic degradation of PLA is extremely slow due to its hydrophobicity and water resistance, which will limit the PLA applications. As PLA-based materials should have an appropriate hydrolytic degradation rate in accordance with their applications, several approaches have been used to control the hydrolytic degradation rate of PLA (usually accelerate). The polymerization of lactic acid with other monomers in order to obtain copolymers with less hydrophobicity than PLA is a common way to increase hydrolysis rate of PLA (Li et al., 1997; Zhu et al., 1991; Li, 1999). Degradation rates can also be controlled by blending PLA with other hydrophilic and water sensitive polymers as well as with additives, plasticizers and inorganic fillers (Tsuji and Muramatsu, 2001; You et al., 2005; Mauduit et al., 1996; Sheth et al., 1997; Schwach et al., 2002; Shikinami and Okuno, 1999; Zhang et al., 1997).

PLA/clay nanocomposites have received much attention, in recent years, in both academic and industrial areas due to the excellent enhancement of mechanical and barrier properties, thermal stability and modify its degradation rate (Zeng et al., 2005; Ray and Bousmina, 2005; Ray and Okamoto, 2003; Ray et al., 2002; Ray et al. 2003; Fukushima et al., 2009; Nieddu et al., 2009; Fukushima et al., 2011; Fukushima et al., 2013; Stloukal et al., 2015). Polymer nanocomposites based on layered silicates can be classified into three types, based on the interactions between the organic polymer and inorganic filler: phase-separated, intercalated and exfoliated nanocomposites (Alexandre and Dubois, 2000). In each case, the physical properties of the resultant composite are significantly different (Mittal, 2007).

Montmorillonite, hectorite and saponite, have been the most commonly used layered silicates for the preparation of PLA nanocomposites (Pandey et al., 2005). Thus far, a relatively small number of studies have been reported on the preparation of PLA nanocomposites based on vermiculite (VMT) (Fernández et al., 2013a,b; Zhang et al., 2007; Ye et al., 2016). VMT is a clay mineral that occurs extensively in nature. Like montmorillonite, it belongs to the general family of 2:1 layered silicates. It consists of an Al octahedral sheet, sandwiched between two Si

* Corresponding author.
E-mail addresses: mariadolores.fernandez@ehu.es (M.D. Fernández), mjesus.fernandez@ehu.es (M.J. Fernández).

tetrahedral sheets, and these three sheets form a layer. VMT is much cheaper and has larger cation exchange capacity (CEC) (100–150 meq/100 g) as compared with montmorillonite (60–100 meq/100 g), hectorite (120 meq/100 g) and saponite (80 meq/100 g).

The incorporation of nanoclays in polymer is known to increase the thermal stability and to decrease the photostability and weathering resistance of the polymer (Araújo et al. 2014, Bocchini et al. 2010, Kaynak and Sari, 2016). Though biodegradable polymer nanocomposites based on clay minerals have already been extensively studied in terms of mechanical strength, fire retardancy or crystallization behavior, biodegradation and hydrolytic degradation has been investigated to a lesser extent. Paul et al. (2005), reported the hydrolytic degradation of micro and nanocomposites based on polylactide and natural unmodified montmorillonite, and montmorillonites modified with dimethyl-2-ethylhexyl (hydrogenated tallowalkyl) ammonium cations or with bis-(2-hydroxyethyl) methyl tallowalkyl ammonium cations in buffer phosphate medium at 37 °C. Zhou and Xanthos (2008) investigated the hydrolytic degradation of polylactide/organomodified and unmodified montmorillonite composites in NaOH solution at pH 10.5 over a temperature range of 50–70 °C. Chen et al. (2012) reported the effect of organic montmorillonite on the hydrolytic degradation behavior of poly(L-lactide)/organic montmorillonite nanocomposites in a solution of sodium hydroxide solution (pH = 13) at 35 °C. Rapacz-Kmita et al. (2015) examined the degradation capacity of neat PLA and the PLA/not activated smectite nanocomposites in a water environment at pH 6.55 at different temperatures (25–80 °C). In these studies, the results indicated that the degradation of nanocomposites was faster than that of unfilled PLA, and that both the composite structures and the relative hydrophilicity of the clay played a determining role in the hydrolytic degradation process. The effect of the degree of clay dispersion on the degradation rate depended on the hydrolytic medium. Thus, in phosphate buffered solution, the lower the degree of clay dispersion, the faster was the hydrolysis, while in alkaline medium, the opposite behavior was observed. As far as the hydrophilicity of the clay is concerned, the more hydrophilic the clay, the faster was the degradation, irrespective of the pH of the medium. However, Wu and Wu (Wu and Wu, 2006) studied the degradation of poly(lactic acid) and poly(lactic acid)/chitosan-modified montmorillonite nanocomposites in buffered phosphate saline solution (pH 7.20), and found that the degradation rates of the nanocomposites were slower than that of PLA matrix.

The aim of this study was to prepare unmodified vermiculite and different types of organically modified vermiculite nanocomposites based on PLLA by melt blending, and investigate the effect of clay mineral surface modification and the type of organic modifier used in the vermiculite modification on the hydrolytic degradation of vermiculite/PLLA composites. This study was undertaken using an alkaline aqueous solution as a hydrolysis medium. The morphology and thermal properties of the organo-VMT/PLLA nanocomposites were characterized by X-ray diffraction, microscopy, and differential scanning calorimetry.

2. Experimental

2.1. Materials

Poly(L-lactide) (PLLA) with a D-content of 3.7–4.3% was obtained from NatureWorks LLC (3051D). Thermally expanded vermiculite with a cationic exchange capacity of 150 meq/100 g was purchased from Sigma-Aldrich. VMT was grounded, to obtain particles < 40 μm in size, using an ultracentrifugal mill (Retsch ZM-200). The surfactants used were octadecyltrimethylammonium bromide ($C_{21}H_{46}NBr$, FW: 392.5, >98%) (Fig. 1), labeled ODTMA, supplied by Sigma-Aldrich, oleyl bis(2-hydroxyethyl) methyl ammonium chloride (Ethoquad O/12) (99%), denoted as ETO (FW: 406.1) (Fig. 1), supplied by Akzo Nobel as active solution in isopropyl alcohol (24 wt%), and the
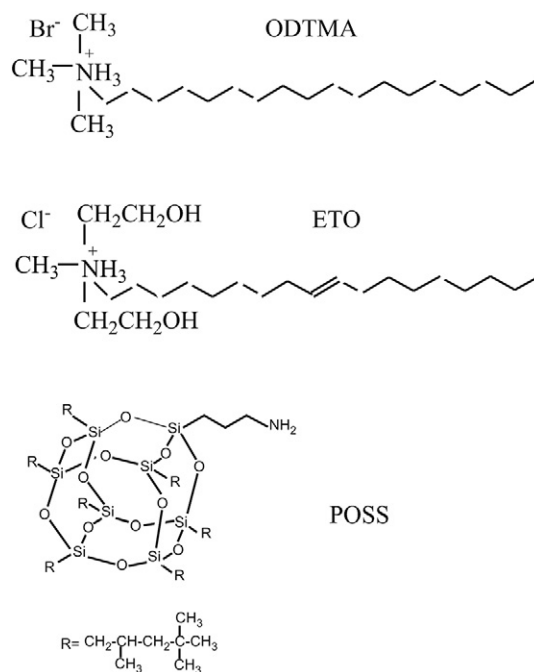

Fig. 1. The chemical structures of surfactants used in this work.

polyhedral oligomeric silsesquioxane derivative aminopropylheptaisooctyl-POSS (99%), purchased from Hybrid plastics, labeled POSS, (Fig. 1) which were used without any further purification.

2.2. Preparation of organovermiculite samples

The VMT was organically modified by a cation-exchange reaction between VMT and the alkylammonium salts according to Fernández et al. (2013a). In a typical experiment, VMT (10 g) was dispersed in deionized water (in the case of ETO) or in a 50/50 (v/v) mixture ethanol/deionized water (in the case of ODTMA and POSS). Separately, the required amount (1.25 equivalent of the CEC) of the alkylammonium salt was dissolved in deionized water at 50 °C in the case of ETO or in ethanol at room temperature for ODTMA. In the case of POSS, 0.4 equivalent of the CEC of the aminoPOSS was dissolved in THF (50 mL), and then hydrochloric acid (HCl, 10% aq., 20 mL) was added. Then, the alkylammonium solutions were added to the dispersion of the clay mineral particles. The reaction mixtures were exchanged for 24 h at 60 °C for ODTMA and POSS, and at 85 °C for ETO. The resulted organoclay minerals denoted as ETOVMT, C18VMT and POSSVMT. ETOVMT and C18VMT were collected by filtration and repeatedly washed with hot deionized water. C18VMT was subsequently subjected to a Soxhlet extraction with ethanol for 1 day and then ethanol acidified with acetic acid of pH = 4 under reflux for 12 h, to ensure complete removal of the excess of surfactant (i.e. unbound surfactant) (Fernández et al., 2013a). POSSVMT was collected by filtration and repeatedly washed with a 50/50 (v/v) mixture ethanol/deionized water. Finally the products were dried under reduced pressure at 60 °C to constant weight. The characteristics of the different types of clay minerals used in this study are presented in Table 1.

2.3. Preparation of composite materials

Composites were prepared by melt compounding at 5 wt% clay loading similarly to the previously reported procedure (Fernández et al., 2013a). Mixtures of dried PLLA pellets and clay minerals were fed to a Minilab II, Haake Rheomix CTW5 mini twin-screw extruder at 185 °C for 10 min with a screw speed of 50 rpm, then the extruded products were processed in a hot-plate hydraulic press to produce plaques. The