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European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Hydrolytic behavior of poly(lactic acid) films with different architecture modified by poly(dodecafluorheptyl methylacrylate)

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ARTICLE INFO

Article history:

Received 8 May 2014

Received in revised form 18 July 2014

Accepted 30 July 2014

Available online 8 August 2014

Keywords:

Poly(lactic acid)

Poly(dodecafluorheptyl methylacrylate)

Hydrolytic degradation

Architecture

ABSTRACT

Poly(lactic acid) (PLA) coated with poly(dodecafluorheptyl methylacrylate) (PFA), namely PLA-coat-PFA, and PLA blended with PFA, namely PLA-blend-PFA, together with neat PLA were subjected in 40 °C water for 100 days to investigate the hydrolytic behavior of the materials with different architectures. The water diffusion rate and hydrolytic behavior were studied by means of water absorption test, morphology observation, monitor of mass loss, pH measurement, thermal analysis and molecular weight determination. The results show that (1) the water permeation in PLA can be hindered by coating with PFA, while water absorption can be enhanced by blending with PFA because the gaps between PLA and PFA, resulting from poor interaction between the two phases, reduce the penetration depth; (2) the neat PLA and PLA-coat-PFA undergo heterogeneous degradation while PLA-blend-PFA behaves as homogeneous degradation, and the degradation rate follows the order: PLA > PLA-blend-PFA > PLA-coat-PFA; (3) coating and blending PFA with PLA can both delay the hydrolytic degradation of PLA by hindering water permeation and decreasing the autocatalysis of the hydrolytic products, respectively.

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1. Introduction

In recent years, the problems of fossil resources depletion and environmental pollution have made an urgent need to develop sustainable materials. Poly(lactic acid) (PLA) seems to be one of the most promising materials which exhibits many advantages, such as renewability, comparable mechanical properties to those of traditional synthetic polymers, energy saving, and eco-friendly [1]. In addition, due to production technology innovation, the price of PLA is reduced, making PLA be more and more competitive [2]. However, PLA is much susceptible to

hydrolysis [3], which is one of the key issues for PLA's application [4–6]. The ease hydrolysis of PLA will lead to unstable properties and limit PLA's application, especially the long-term application [7,8]. Therefore, it cannot show the advantages of PLA completely and there is a need to study how to control or resist the hydrolytic degradation of PLA.

In past years, many works have been done to study the hydrolytic degradation of PLA. The hydrolytic degradation of PLA proceeds at ester groups, resulting in chain scission [9]. The carboxylic end groups produced during hydrolytic degradation will in turn act as catalyst for the hydrolysis, which is called autocatalysis [10,11]. So, the diffusion of hydrolytic products is an important factor for PLA hydrolysis [12]. In addition, acting as one of the reactants in hydrolytic reaction, water's behavior in PLA is another important factor [13]. Basing on these two issues, many

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environmental factors can affect the hydrolysis of PLA significantly, such as pH, temperature and humidity [14–16]. At the same time, copolymerization, blending, cross-linking and surface modification have been applied to tune the hydrolytic rate of PLA by controlling the crystallinity, stereo-chemical structure, molecular weight, hydrophilicity, etc. [6,17–21]. However, most of the modification is for biomedical use, only few studies focus on enhancing hydrolytic resistance for durable application like textiles, automotive interiors and electronics [22–24].

In those studies of hydrolytic resistance of PLA, hydrophobic modification seems to be the most common method. Reddy et al. prepared polyblend fibers with PLA and PP, and the results show that hydrophobic PP resist the hydrolysis of PLA during water treatment, resulting in better mechanical stability than neat PLA fiber [25]. Hydrophobic acetyl tributyl citrate (ATC) plasticizer was introduced into PLA to slow the hydrolytic rate by Höglund et al. [26]. Besides, Haynes's study also shows that the hydrolysis of PLA can be delayed by introducing hydrophobic substance [27]. Taking into account of hydrophobic substance, fluorinated acrylate polymers maybe one of the best choice and they have been widely used to improve other materials' hydrophobicity due to their extremely low surface energy [28–31]. For the purpose of enhancing hydrolytic stability of PLA, in the present article, we will design two PLA films with different architectures, which is realized by the use of poly(dodecafluorheptyl methacrylate) (PFA), i.e., the PLA coated with PFA (PLA-coat-PFA) and PLA blended with PFA (PLA-blend-PFA), and study their hydrolytic behavior by monitoring the changes of mass, molecular weight, pH, crystallinity and cross-sectional morphology during the hydrolysis.

2. Experimental section

2.1. Materials

Poly(L-lactic acid) (PLA) with a melt flow index in the range of 5–7 g/10 min (2.16 kg, 210 °C) and a density of 1.24 g/cm³ was obtained from Nature Works® (2002D). According to the manufacturer, this PLA has a D content of 4.25%. The M_n and M_w of this PLLA, measured by GPC, are 124,000 and 240,000 Da, respectively. Poly(dodecafluorheptyl methacrylate) (PFA) was obtained by the solution radical polymerization of dodecafluorheptyl methacrylate (shown in Fig. 1, XEOGIA Fluorine-Silicon Chemical Company, China) using butyl acetate (from Kelong Chemical Reagent Factory, China) as solvent and 2, 2'-azobisisobutyronitrile (from Kelong Chemical Reagent

Factory, China) as initiator at 70 °C for 8 h. After the polymerization, the reaction solution was precipitated in methanol. Then, the PFA was purified by three precipitation cycles using ethyl acetate as solvent and methanol as precipitant. Finally, the precipitated PFA was dried in vacuum oven at 40 °C for 24 h. The obtained PFA is transparent solid with a glass transition at 53.2 °C, measured by DSC.

2.2. Sample preparation

The flakes of neat PLA (labeled as PLA) and PLA blended with 5 wt% PFA (labeled as PLA-blend-PFA) were prepared by processing at 60 rpm and 170 °C in a Haake internal mixer (Rheocord 90) for 10 min first. Then, the melt mixed samples were melting at 190 °C for 2 min, pressed into 0.8 mm thick films under 10 MPa pressure for 2 min at 190 °C and cooled at room temperature for 3 min under the same pressure. Finally, the obtained films were cut into 1 × 3 cm² specimens. Before the blending and compression process, all the samples were dried in vacuum oven at 40 °C for a week. In addition, the sample of PLA coated with PFA (labeled as PLA-coat-PFA) was prepared by immersing the neat PLA specimens (1 × 3 cm², width × length) into PFA/ethyl acetate solution (4 wt%) for 10 s and drying under natural conditions (at 27 ± 2 °C, 65 ± 5% RH) for 24 h.

2.3. Hydrolysis

First, all specimens were dried in vacuum oven at room temperature for 10 days. Then, each dried and pre-weighed specimen (initial mass was named as M_0) was dipped into a glass vial containing deionized water, and the mass ratio of specimen to water was 380/10 (mg/g). After that, the vials were sealed with screw caps and placed into thermostatically controlled oven at 40 °C. Every 10 days, triplicate specimens of each sample were picked out, dried in vacuum oven at room temperature for 10 days and weighed again (the mass was named as M_d). Residual mass percentage, presenting the hydrolysis result, was calculated from the following formula: residual mass (%) = $M_d/M_0 \times 100\%$, and all values presented were the average value of three specimens.

2.4. Water absorption

Each pre-weighed specimen (M_0) was dipped in a glass vial and then placed in a thermostatically controlled oven at the same conditions as the hydrolytic specimens. At a predetermined time, each specimen was picked out and weighed (M_t) after wiping out the water on the surface.

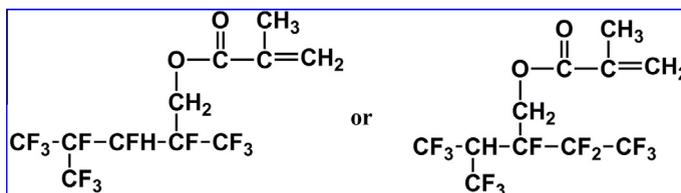


Fig. 1. Molecular structure of dodecafluorheptyl methacrylate.

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