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Control of properties of PLA-PFPE-PLA triblock copolymers using stereocomplex between *l*-LA and *d*-LA sequences

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ABSTRACT

Two type of triblock copolymers [poly(l-lactide)-b-perfluoro polyether-b-poly(l-lactide) (fluoro l-PLA) and poly(d-lactide)-b-perfluoro polyether-b-poly(d-lactide) (fluoro d-PLA)] (fluoro PLAs) were synthesized by ring-opening polymerization. The synthesized triblock copolymers showed more hydrophobic properties than pristine l-PLA due to the perfluoro polyether (PFPE). To control the surface properties, the blends were prepared by mixing fluoro PLAs with l-PLA. The degradation rates of the fluoro PLAs/l-PLA blends were retarded due to the surface segregation of PFPE which has lower surface energy. In case of the fluoro d-PLA/l-PLA blends, however, the stereocomplex formation between the l-lactide and d-lactide sequences enhanced the thermal and enzymatic stabilities of l-PLA. As a result, the biodegradability of l-PLA can be controlled by copolymerization or the formation of a stereocomplex.

KEYWORDS

poly(*l*-lactide); poly(*d*-lactide); stereocomplex; perfluoro polyether; biodegradation

Introduction

Recently there has been growing interest in the surface properties of polymeric materials in many commercial applications such as wetting, printing, biocompatibility, and adhesives [1,2]. For many of these applications, some desired surface properties of materials can be obtained via chemical or physical modification. Among synthetic architectures, silicon and fluorine-containing polymers have been widely studied [3,4]. The accumulation of low surface energy components on the surface enhances hydrophobicity, and the initial degradation process is affected by the surface concentration of these species [5].

In recent years, there has been an increasing demand for biodegradable polymers to reduce the environmental pollution caused by large amounts of plastic wastes and to reduce carbon dioxide emissions [6]. Because their mechanical properties are rapidly lost during the initial degradation, the control of the surface degradation of biodegradable polymers is a key factor in determining their commercialized life. Poly(lactides) (PLAs) have been widely used in various applications due to their biodegradability, biocompatibility and good mechanical

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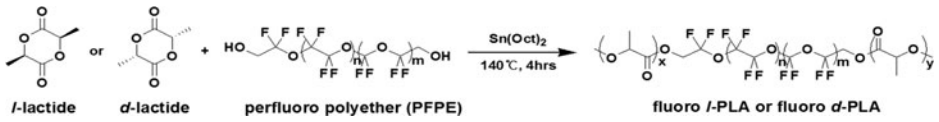

Scheme 1. Synthesis of the triblock copolymer from *l*-lactide, *d*-lactide and PFPE.

properties [7]. PLA is an enantiomeric polymer including poly(*l*-lactide) (*l*-PLA), poly(*d*-lactide) (*d*-PLA), and *dl*-PLA. Because the interaction between two enantiomers with different configurations is stronger than that between two of the same, the *l*-PLA/*d*-PLA blends form stereocomplexes [8,9]. The main objective of this work is to control the degradation rate of *l*-PLA. This control could be achieved by the copolymerization and formation of PLA stereocomplexes. Perfluoro polyether (PFPE) is a hydrophobic material that contains terminal hydroxyl groups. Two types of triblock copolymers [*l*-PLA-PFPE-*l*-PLA (fluoro *l*-PLA) and *d*-PLA-PFPE-*d*-PLA (fluoro *d*-PLA)] (fluoro PLAs) were synthesized. The various blend films were prepared and their properties, such as the surface structure, blending properties, and biodegradation behavior, were studied.

Experimental

Materials

l-Lactide (*l*-LA) and *d*-lactide (*d*-LA) were obtained from Purac (Netherlands) and were recrystallized from ethyl acetate and dried in vacuum to remove the solvent and moisture. α,ω-Diol-poly[(tetrafluoroethylene oxide)-co-(difluoromethylene oxide)], a PFPE, with molecular weight (M_n) of 1400 g/mol, was purchased from Solvay-Solexis (Italy). Stannous octoate was purchased from Sigma Aldrich. All other chemicals were used without further purification. *l*-PLA (M_n = 33,273 g/mol, PDI = 1.28) was synthesized by the ring-opening polymerization of *l*-LA using stannous octoate as a catalyst. In a similar method, fluoro *l*-PLA (M_n = 33,905 g/mol, PDI = 1.20) and fluoro *d*-PLA (M_n = 34,559 g/mol, PDI = 1.16) were synthesized with LA (3 g) and a small amount of PFPE (0.129 g) (Scheme 1). Each 5 wt% solution of *l*-PLA and fluoro PLAs in chloroform was separately prepared and then homogeneously mixed. To investigate the blending effect on the properties, two blend systems were prepared by mixing *l*-PLA with fluoro *l*-PLA or fluoro *d*-PLA. Thin films were prepared by spin coating (2000 rpm, 1 min) on a glass substrate (1 cm × 1 cm).

Measurements

The functional groups of *l*-PLA and fluoro *l*-PLA were analyzed by Fourier-transform infrared spectroscopy (FT-IR, Thermo Scientific, Nicolet iS10). The surface chemical compositions of *l*-PLA, fluoro PLAs and their blends were obtained using X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific, MultiLab2000). XPS measurement was performed with a twin anode X-ray gun (15 W) at 15 kV and 1 mA. The surface wettability of the samples was measured by a drop shape analysis system (DSA, Krüss GmbH, DSA 100). The static contact angle (SCA) was measured using a 500 μL syringe and a needle, 0.5 mm in diameter and 38 mm in length, and 3 μL of liquid (water) at a flow rate of 600 rpm. The thermal properties of the samples were investigated by differential scanning calorimetry (DSC, Mettler Tolledo, DSC 1) under nitrogen, with pure indium as a standard material. The melting temperature (T_m) was

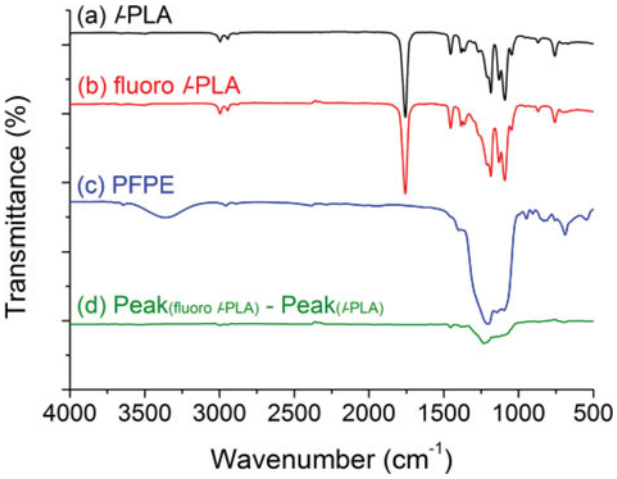

Figure 1. FT-IR spectra of the *l*-PLA, fluoro *l*-PLA, PFPE, and their subtraction.

determined from −10°C to 250°C in the first run at a heating rate of 10°C/min. The glass transition temperature (T_g) was determined in the second run after melt quenching. The surface morphology of the samples before and after enzymatic degradation was obtained by atomic force microscopy (AFM, SII Nano Technology Inc., SPA400) in tapping mode using a cantilever tip with a scan rate of 1 Hz. For the enzymatic degradation test, samples were soaked in 1 mL of Tris-HCl buffer solution followed by the addition of 0.1 mg proteinase K.

Results and discussion

FT-IR was used to identify the functional groups of PFPE, *l*-PLA and fluoro *l*-PLA (Figure 1). The pristine *l*-PLA showed a strong C=O stretching peak at 1745 cm^{-1}, and C-O-C and O-C-C peaks of the ester groups at 1178 cm^{-1} and 1080 cm^{-1}, respectively (Figure 1(a)). Although the fluoro *l*-PLA showed similar functional groups to *l*-PLA (Figure 1(b)), a broad strong peak from PFPE was observed from 1450 cm^{-1} to 1000 cm^{-1} due to the C-F stretching bond (Figure 1(c)). To confirm the occurrence of PFPE in the copolymer, the *l*-PLA spectra were subtracted from the fluoro *l*-PLA spectra using a compensating factor, which was calculated by the intensity of the C=O stretching peak. The result showed a weak and broad peak at 1450∼1000 cm^{-1} from the PFPE chain.

Chemical ratio of *l*-LA and PFPE in fluoro *l*-PLA was investigated by ^{1}H-NMR, as shown in Figure 2. Two peaks, *a* at 5.17 ppm and *b* at 1.60 ppm were assigned to C-H and C-H_3 in *l*-PLA, respectively. The small peak, *c* at 4.35 ppm, was from -CF_2CH_2O- in PFPE. The concentration of PFPE block in fluoro *l*-PLA was about 0.44 mol% which is calculated by integration of peaks.

XPS was used to determine the surface composition of fluoro *l*-PLA and its blend, and the results are shown in Figure 3. The C1s region of *l*-PLA had three peaks at 285, 287.5 and 290.5 eV, assigned to neutral carbon (-CH_3), ether carbon (-CO-) and ester carbon (-COO-), respectively (Figure 3 (a)). In the C1s region of fluoro *l*-PLA, a strong fluoro carbon (-CF_2-O-) peak at 293.8 eV was newly observed (Figure 3 (b)), which suggests that the surface concentration of fluoro chains is much higher than the bulk concentration. To investigate the surface composition of blends, two the blends, fluoro *l*-PLA/*l*-PLA and fluoro *d*-PLA/*l*-PLA at 50/50 wt%, were prepared. From the C1s regions, the relative intensity of the -CF_2-O-

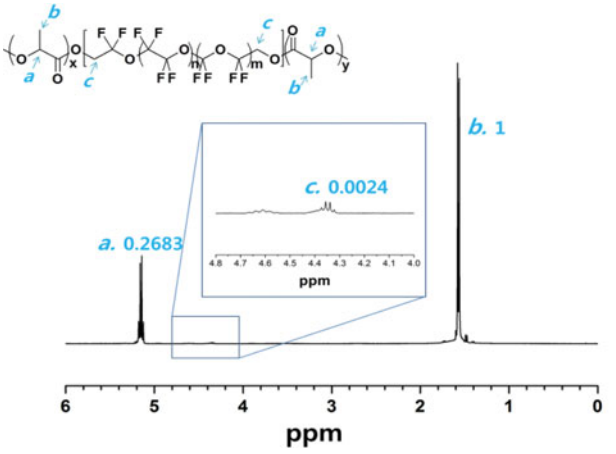

Figure 2. ^{1}H-NMR spectrum of fluoro *l*-PLA.

peak in the fluoro *l*-PLA/*l*-PLA blend is stronger than that of the fluoro *d*-PLA/*l*-PLA blend (Figure 3 (c) and (d)) because the stereocomplex formation between the *l*-LA and *d*-LA unit sequences disrupts the movement of fluoro chains to the surface [3,8,9]. These results indicate that stereocomplex energy is stronger than the surface-moving one of fluoro group which is lower surface free energy.

Figure 4 shows the SCA values of *l*-PLA, fluoro PLAs and the fluoro PLAs/*l*-PLAs blend films. The *l*-PLA film showed the 71.15° ± 1.0° property. The prepared fluoro *l*-PLAs and fluoro *d*-PLA films showed increased hydrophobic properties, 109.30° ± 1° and 108.95 ± 1°, respectively, due to the surface segregation of PFPE. To confirm the stereocomplex effect on the surface properties, fluoro *l*-PLA and fluoro *d*-PLA were blended in different compositions. At a low content of fluoro PLAs (< 5 wt%), the SCA values of the blend films sharply increased. However, at over the 5 wt%, most of the blend films showed similar SCA values. It is well known that a component with lower surface energy in multicomponent polymeric systems is preferentially segregated at the air region in order to minimize the interfacial free energy [3]. The stereocomplexed fluoro *d*-PLA/*l*-PLA showed lower hydrophobicity than fluoro *l*-PLA/*l*-PLA. These results are again in accordance with XPS one.

The thermoproperties of *l*-PLA, fluoro PLAs and fluoro PLAs/*l*-PLA blend (20/80 wt%) films were analyzed by DSC. *l*-PLA had a T_g and T_m at 60.8°C and 174.6°C, respectively (Figure 4 (b)). The T_m of the fluoro PLAs decreased due to the relatively short PLA blocks

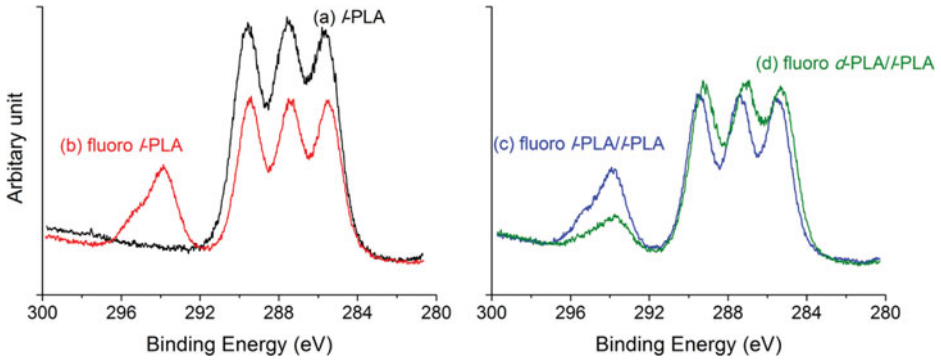

Figure 3. C1s spectra of homopolymers and blend films; (a) *l*-PLA, (b) fluoro *l*-PLA, (c) fluoro *l*-PLA/*l*-PLA, (d) fluoro *d*-PLA/*l*-PLA.

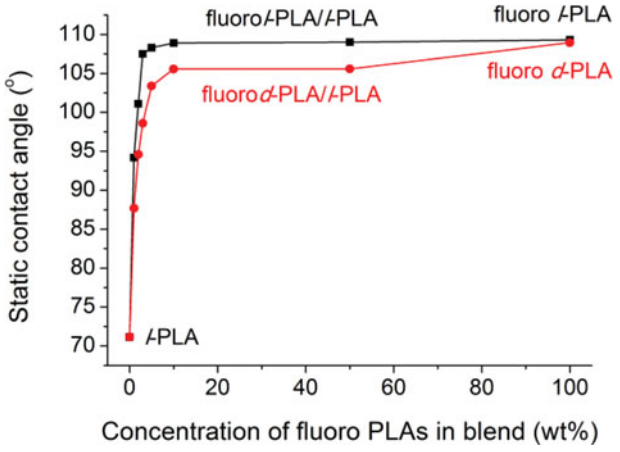

Figure 4. SCA data of *l*-PLA, fluoro PLAs and fluoro PLAs/*l*-PLAs blend films.

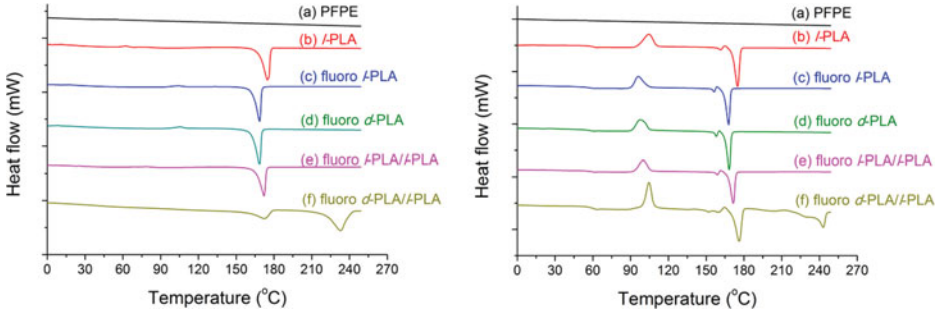

Figure 5. DSC thermograms of *l*-PLA, fluoro PLAs and fluoro PLAs/*l*-PLA blends; (left) in the first run, (right) in the second run.

(Figure 4 (c) and (d)). The T_m of the fluoro *l*-PLA/*l*-PLA blend was similar to that of *l*-PLA (Figure 4 (e)). However, fluoro *d*-PLA/*l*-PLA blend showed two T_ms, at 172.2°C and 232.5°C (Figure 4 (f)). The higher T_m is due to partial complexation between the equimolar *l*-LA and *d*-LA sequences.

Figure 6 shows the morphology and roughness profile of the spin-coated *l*-PLA and fluoro PLAs/*l*-PLA blends (by 20/80 wt%) before and after 1 hr of enzymatic degradation. The level of degradation was inferred from the surface roughness change which is a result of surface

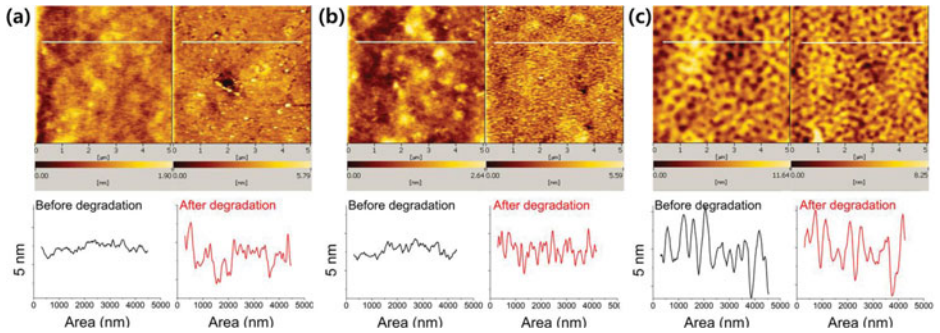

Figure 6. AFM images and Δheight graphs of *l*-PLA and fluoro PLAs/*l*-PLA blend before (left) and after (right) enzymatic degradation. (a) *l*-PLA, (b) fluoro *l*-PLAs/*l*-PLA, (c) fluoro *d*-PLA/*l*-PLA.

erosion. The smooth surface of *l*-PLA became porous structures after enzymatic degradation (Figure 6 (a)). Although the fluoro *l*-PLA/*l*-PLA blend also showed a similar trend with *l*-PLA, the change in the surface roughness before and after degradation was smaller than that of *l*-PLA due to the surface hydrophobic properties of fluoro *l*-PLA, which was segregated on the surface (Figure 6 (b)). However, the partially stereocomplexed fluoro *d*-PLA/*l*-PLA blend showed little difference before and after enzymatic degradation (Figure 6 (c)). These results indicate that the degradation rate of *l*-PLA was controlled by the mixing of fluoro *l*-PLA and fluoro *d*-PLA.

Summary

The triblock copolymers, fluoro *l*-PLA and fluoro *d*-PLA were successfully synthesized, and the obtained copolymers showed hydrophobic properties despite their low PFPE content. To control the surface properties of *l*-PLA, blends were prepared by mixing in a small amount of fluoro *l*-PLA or fluoro *d*-PLA. The stereocomplexed fluoro *d*-PLA/*l*-PLA showed decreased hydrophobic surface properties compared to fluoro *l*-PLA/*l*-PLA because the stereocomplex between *l*-LA and *d*-LA units disrupted the movement of fluoro chains to the surface. The degradation rates in the fluoro PLAs/*l*-PLA blends were retarded due to the surface segregation of PFPE and the stereocomplexing between *l*-LA and *d*-LA.

Acknowledgments

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