Communications

Stereocomplex-Induced Surface Structure of Fluorocarbon End-Capped Polylactide/Enantiomeric Polylactide Blends

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Introduction

The properties and composition of polymer surfaces play an essential role in many commercial applications of polymers, including wetting, printing, biomaterials and adhesives.[1-10] In many of these applications the successful design of polymeric materials is facilitated by modification of surface properties. Several techniques have been developed for modifying polymer surfaces.[11] The common approaches to modify the surface properties of polymeric systems involve either pre- or post-treatments of materials. The latter includes flame treatments,[1] chemical surface reactions,[2] and plasma treatments,[4,6,10] which are useful in producing hydrophilic, hydrophobic, or functionalized surfaces. The former approach may involve synthesis of specific architectures in multicomponent polymeric systems, copolymers and blends. Among synthetic architectures, those having a small amount of a low surface energy component, such as silicon or fluorine-containing polymers have been widely studied. This is because the low surface energy component in multicomponent polymeric systems is usually preferentially concentrated at the air surface region in order to minimize the air/material interfacial free energy.[3,5,7,11-13] Other variables affecting the surface structure in multicomponent polymeric systems have been revealed, including composition,[3] intermolecular interaction,[3,14] morphology,[14-16] molecular weight,[14,17] and sampling method.[3,12,15] Recently, Liu et al.[16] investigated the surface structure of poly(styrene-co-p-hexafluorohydroxyisopropyl-α-methylstyrene)/poly(4-vinylpyridine) (PSOH/PVPy) blends which span a wide range of structure, through immiscibility-miscibility-complexation transitions, by varying the hydroxyl content of PSOH. It was revealed that the formation of interpolymer complex in this blend system dramatically decreased the surface excess of PSOH.

The degradability of poly(lactide)s (PLAs) has been widely investigated for commercial biotechnological applications, controlled-release devices in the areas of biomedical devices and disposable degradable plastic articles because of their nontoxic products in metabolism caused by hydrolytic chain scission, eventually leading to lactic acid. Since the lactide monomer has a chiral center, the property of PLAs can be easily controlled by adjusting d- and l-lactide compositions in the polymer. Since Ikada et al.[18] reported the stereocomplexation between enantiomeric l-PLA and d-PLA, numerous studies have been performed on the crystallization, physical properties, and crystalline structure of the stereocomplex.[19-22] In the stereocomplex crystallites formed as a result of stereo-complexation, equimolar l- and d-lactide unit sequences are packed side by side.[18-20] The stereocomplex exhibits a melting temperature almost 50 °C higher than that of each homopolymer. In this communication, we attempt to preliminary obtain insight into the stereocom-

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plex-induced surface structure of enantiomeric PLA blend films. The design of the blend systems is based on the principle of surface segregation of a modified PLA with a low surface energy (in this case, fluorocarbon end-capped *l*-PLA (F-*l*-PLA)) first synthesized in our laboratories.[13]

Experimental

l- And *d*-lactide (LA) were obtained from Aldrich and Purac, respectively and were recrystallized from anhydrous ethyl acetate. 2-(Perfluorodecyl) ethanol (F-OH) was dried in a vacuum oven at room temperature before use. $CF_3(CF_2)_9$-CH_2CH_2O-*l*-PLA (F-*l*-PLA) was synthesized by ring open polymerization of *l*-LA by stannous octoate as a catalyst in the presence of F-OH. The details of synthesis and characterization of F-*l*-PLA were discussed elsewhere.[13] The characteristics of materials used in the study are shown in Table I. All other chemicals were of reagent grade and were used without further purification. Each 1 wt% solution of *d*-PLA, *l*-PLA, and F-*l*-PLA in chloroform was separately prepared. The mixture solutions were prepared from each homopolymer solution and cast into aluminum weighing dishes, and then allowed to air dry slowly at ambient temperature. They were further dried in a vacuum oven (ca 10 torr) to a constant weight at room temperature. The film thickness was found to be 5 ± 1 μm.

The surface chemical compositions of (F-*l*-PLA/enantiomeric PLA) blend films were obtained using Perkin-Elmer Physical Electronics Model 5300 electron spectrometer for chemical analysis (ESCA). ESCA measurements were performed with an achromatic $MgK\alpha$ X-ray source (1253.6 eV) at 15 kV and 20 mA. High-resolution scans of the C 1s, O 1s, and F 1s were acquired at a take-off angle of 90°, which led to the sampling depth of the C 1s region of 10.3 nm.[23] To minimize the effect of X-ray induced defluorination, short exposure times (typically a total of 4.4 min) were determined from the relationship between exposure time and atomic ratio for poly(vinylidene fluoride) as a standard material. All C 1s spectra were referenced to the neutral carbon of PLA at 285 eV to correct charging effects.

Results and Discussion

In our previous paper,[13] we reported that F-*l*-PLAs are synthesized by the ring open polymerization of *l*-LA using

F-OH as a functional initiator and stannous octoate as a catalyst. These materials improve the controllable biodegradability of *l*-PLA at initial stages by controlling the concentration of surface fluorocarbon groups. The surface segregation of fluorocarbon groups produced a chemical barrier between the *l*-PLA and the hydrolyzing solution. Here, F-*l*-PLA of which chain end groups were labeled by short fluorocarbon groups was used as a model material in order to measure the surface segregation of enantiomeric PLA blends when they form a stereocomplex.

Since the blend of equimolar *l*-PLA and *d*-PLA forms a new crystal structure, stereocomplex packed side by side, the surface compositions of (F-*l*-PLA/*l*-PLA) and (F-*l*-PLA/ *d*-PLA) blend films with 50/50 by wt. are investigated by ESCA. Figure 1 shows the high-resolution ESCA spectra of C 1s regions of both blend films at the 30° takeoff angle. From the intensity of C-F_2 from fluorocarbon compared to that from O=C-O or C-O from PLA, the intensity of (F-*l*-PLA/*l*-PLA) blend film is much higher than that of (F-*l*-PLA/*d*-PLA) blend film. Figure 2 shows the theoretically
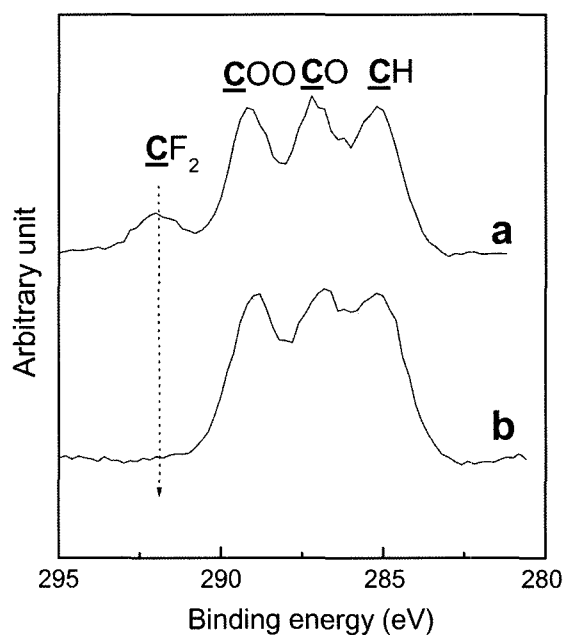

Figure 1. High resolution C 1s spectra of (F-*l*-PLA/*l*-PLA) (a) and (F-*l*-PLA/*d*-PLA) (b) blend films measured at a takeoff angle of 30°. The compositions of blends were 50/50 by wt%. The peak at 292 eV is due to CF_2 in the fluorocarbon end group.

Table I. Characteristics of the Poly(lactide)s Used in This Study

Code	$M_w{}^a$	$M_w/M_n{}^a$	T_g (°C)^b	T_m (°C)^b	Sources
F-*l*-PLA	56,000	2.1	-	164	synthesized^c
l-PLA	66,000	2.0	-	168	Polysciences^c
d-PLA	40,000	1.4	-	165	synthesized^c

^{a}Calculated from direct PS calibration of SEC. ^{b}For as-cast samples. ^{c}Purified from chloroform/methanol system as a solvent/non-solvent.

calculated C 1s peak of F-*l*-PLA on the basis of the calculated M_n (27,000) of F-*l*-PLA. The calculated M_n value of F-*l*-PLA using Mark-Houwink values for PLA measured by size exclusion chromatography was similar to those found from ^{1}H-NMR and ESCA analysis.[23] The theoretically calculated C 1s curve of F-*l*-PLA is very similar to those of (F-*l*-PLA/ *d*-PLA, 10/90 and 50/50 by wt%) blend films. This result suggests that the fluorocarbon chains homogeneously exist in bulk, not in surface segregation.

Figure 3 shows the F 1s/C 1s ratio of F-*l*-PLA and its blends with enantiomeric PLAs. These ratios are plotted as a function of the sine of the photoelectric takeoff angle. As found in many blend systems, the surface composition in multicomponent systems containing small amounts of low surface energy components is dramatically different from
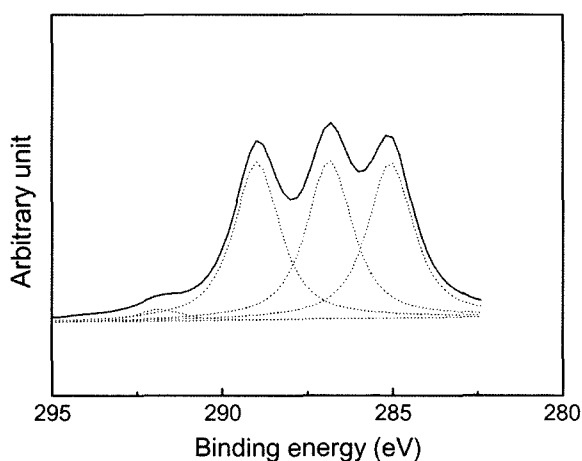

Figure 2. Theoretically calculated C 1s spectrum of F-*l*-PLA on the basis of number-average molecular weight by SEC. The degree of polymerization of *l*-PLA in F-*l*-PLA was 360.
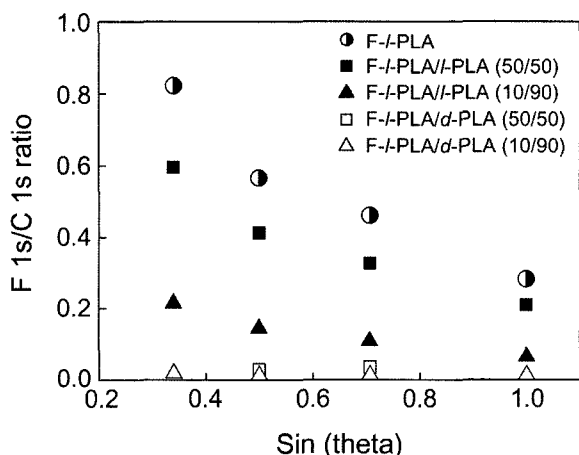

Figure 3. Surface atomic ratio profiles of (F-*l*-PLA/*l*-PLA) and (F-*l*-PLA/*d*-PLA) blend films with two wt% compositions at different takeoff angles.

the bulk composition due to surface segregation which minimizes the surface energy. In the case of (F-*l*-PLA/*l*-PLA) blend films with two different compositions of 10/90 and 50/50 by wt%, the F 1s/C 1s ratios are proportional to the composition of F-*l*-PLA in the blend and the surface segregation of fluorocarbon groups is observed if we consider that the theoretical bulk value of F 1s/C 1s ratio of F-*l*-PLA is ca. 0.019. However, the values of both (F-*l*-PLA/*d*-PLA, 10/90 and 50/50 by wt%) blends are within limits of bulk composition, regardless of takeoff angles and compositions. Since equimolar amounts of *d*- and *l*-PLA form stereocomplexes and leave excess *d*- or *l*-PLA crystals, blends with less than 50 wt% F-*l*-PLA are composed of uncomplexed *d*-PLA and stereocomplex phases. The T_m of (F-*l*-PLA/*l*-PLA, 50/50) blend measured by DSC is similar to *l*-PLA but the T_m of (F-*l*-PLA/*d*-PLA, 50/50) blend shifts to higher temperature by 50 °C than that of *l*-PLA due to the formation of stereocomplexes (DSC data are not shown here). F-*l*-PLA in the blend with less than or equal to 50 wt% F-*l*-PLA is complexed with the same amount of *d*-PLA. Thus, we conclude that the interchain interaction to form stereocomplexes between *l*- and *d*-PLA is strong enough to overcome the driving force of fluorocarbon groups to the surface. We are continuing this study to further characterize the surface composition of blends with different compositions and thermal treatments. Stereocomplex may be an important factor or indeed, a strategy in the synthesis and formulation of biodegradable membranes or devices with surface segregated components.

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