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Enzymatic degradation of poly(ε-caprolactone)/poly(DL-lactide) blends in phosphate buffer solution

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Abstract

Blend films of poly(ε-caprolactone) (PCL) and poly(DL-lactide) (PDLLA) with 0.5 weight fraction of PCL were prepared by means of solution casting and their degradation behavior was studied in phosphate buffer solution containing Pseudomonas (PS) lipase. Enzymatic degradation of the blend films occurred continuously within the first 6 days and finally stopped when the film weight loss reached 50%, showing that only PCL in the blends degraded under the action of PS lipase in the buffer solution. These results indicate the selectivity of PS lipase on the promotion of degradation for PCL and PDLLA. The thermal properties and morphology of the blend films were investigated by differential scanning calorimetry, wide-angle X-ray diffraction and scanning electron microscopy (SEM). The morphology resulting from aggregate structures of PCL in the blends was destroyed in the enzymatic degradation process, as observed by SEM. These results confirm again the enzymatic degradation of PCL in the blends in the presence of PS lipase.

Keywords: PCL/PDLLA blends; Enzymatic degradation; Morphology

1. Introduction

Because of their biodegradation in the human body and the environment, aliphatic polyesters such as polyglycolide (PGA), poly(DL-lactide) (PDLLA), poly(L-lactide) (PLLA), poly(β-hydroxybutyrate) (PHB) and poly(ε-caprolactone) (PCL) have attracted much attention recently. These aliphatic polyesters have different properties such as mechanical strength, biodegradation rate, morphology, etc. For example, PDLLA is amorphous and in the glassy state at room temperature, with its glass transition temperature (T_g) around 37°C, while PCL is crystalline and in the rubbery state at room temperature with T_g of ca. − 60°C [1]. For practical applications, however, these biodegradable polymers should have good mechanical strength and biodegradability. Many methods have been developed to improve the final properties of biodegradable polymers, such as random and block copolymerization of lactide and ε-caprolactone, which improves both biodegradation rate and mechanical properties [2–5]. Meanwhile, physical blending of aliphatic polyesters is also a simple way to prepare biodegradable composites with different morphologies and physical characteristics. In fact, many blend pairs have been investigated such as PLLA and PDLLA [1,6], PLLA and poly(L-lactide-*co*-glycolide), PCL and poly(L-lactide-*co*-glycolide), and PLLA and poly(L-lactide-*co*-ε-caprolactone) [7]. PCL/PDLLA blends have also been studied. It was shown that a homogeneous phase is formed when the molecular weights of PCL and PDLLA are low [8]. Tsuji and Ikada investigated the effect of the mixing ratio of PDLLA and PCL on the thermal and mechanical properties and morphologies of the blend. PCL can crystallize at any mixing ratio and form spherulites over PDLLA contents ranging from 0.1 to 0.6 [1]. However, the change in properties of the PCL/PDLLA blends during the course of biodegradation were not studied.

In our previous paper, the degradation of an ε-caprolactone homopolymer film was studied in phosphate buffer solution containing Pseudomonas (PS) lipase [9]. The results showed that enzymatic degradation is a rapid method to study the degradation of PCL. The aim of this work is to study the morphology and thermal properties of PCL/PDLLA blend films during the enzymatic degradation process.

2. Experimental

2.1. PCL/PDLLA blend films

PCL and PDLLA were synthesized by ring-opening polymerization of ε-caprolactone and DL-lactide, respectively,

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with a novel rare-earth coordination catalyst composed of yttrium trifluoroacetate [$Y(CF_3COO)_3$] and triisobutylaluminum [$Al(i\text{-}Bu)_3$] [10]. The viscosity-average molecular weights (M_v) of PCL and PDLLA were 134 000 and 7000, respectively. PCL/PDLLA blend films, in which the weight fraction of PCL was 0.5, were prepared by solution casting. PCL and PDLLA were dissolved in toluene, and the solution poured onto a glass plate. Toluene was evaporated completely within 7–10 days. Then the PCL/PDLLA blend films were washed with distilled water and finally dried under vacuum. The thickness of the films was around 0.1 mm.

2.2. Enzymatic degradation

The enzymatic degradation of PCL/PDLLA blend films was carried out at 37°C in a 0.025 M, pH 7.0 phosphate buffer solution containing PS lipase. The PS lipase was purified before use. PCL/PDLLA blend films with an initial weight ca. 10 mg and dimensions 10 mm × 10 mm were placed in a bottle containing the buffer solution. The composition of the solution in the bottle was 0.50 mg PS lipase per ml of phosphate buffer solution, and 1500 ml buffer solution containing the PS lipase per gram of PCL/PDLLA film. The bottle was incubated at 37°C in a water bath. The film was picked up after a fixed time interval, washed with distilled water and then dried to constant weight.

2.3. Characterization

The surface and cross-sectional morphologies of the PCL/PDLLA blend films before and after enzymatic degradation were observed by scanning electron microscopy (SEM) (JEOL JXA-840). The electron gun voltage was 10 kV. The film samples were coated with gold before examination. Differential scanning calorimetry (d.s.c.) analysis was performed on a Perkin–Elmer DSC-7 instrument. The blend films were heated from − 60°C to 100°C at a rate of 10°C min^{-1}. Wide-angle X-ray diffraction (WAXD) patterns of the blend films were recorded with a Philips diffractometer using nickel-filtered Cu K_α radiation.

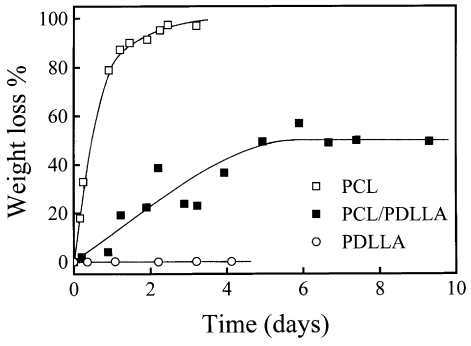

Fig. 1. The weight loss of PCL/PDLLA blend films, PCL and PDLLA films during the course of enzymatic degradation.

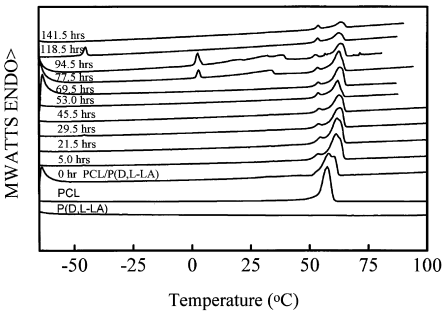

Fig. 2. The d.s.c. thermograms of PCL/PDLLA blend films after degradation in the phosphate buffer solution containing PS lipase for different times. Heating rate = 10°C min^{-1}.

3. Results and discussion

The enzymatic degradation of PCL/PDLLA blend films, as well as PCL and PDLLA films, in the phosphate buffer solution is shown in Fig. 1. Enzymatic degradation of the the blend films continued for the first 6 days but stopped when the weight loss reached 50%. For ε-caprolactone and DL-lactide homopolymers, however, only the PCL film showed complete degradation within 4 days and the PDLLA film did not undergo any change in weight. Our previous works showed that only Pseudomonas (PS) lipase can promote the degradation of PCL in the phosphate buffer

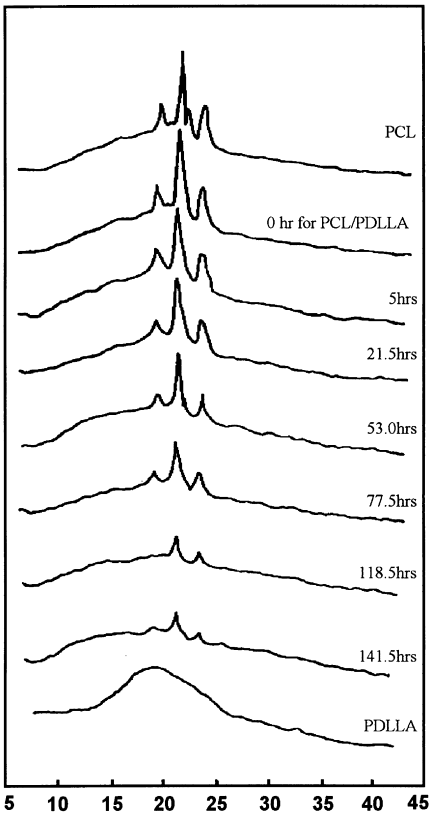

Fig. 3. WAXD patterns of PCL/PDLLA blend films after enzymatic degradation for different times.

solution, porcine pancreatic (PP) lipase and *Candida cylindracea* (AY) lipase having no such action [9]. This shows the selectivity of the lipases to the polymers in the degradation. On the other hand, the results in Fig. 1 confirm the selectivity of PS lipase to the degradation of aliphatic polyesters.

For the PCL/PDLLA blend films, no chemical interactions exist between the PCL and PDLLA components. Therefore, when these blend films were placed in the phosphate buffer solution containing PS lipase, PCL degraded continuously and finally the residue was only PDLLA, the residual weight being just the initial weight of PDLLA in the blends.

The degradation of PCL in the PCL/PDLLA blend films could also be observed by d.s.c., WAXD and SEM. PCL is a semicrystalline polymer but PDLLA is amorphous. When they are mixed together, PCL may form crystalline structure under proper conditions. Tsuji and Ikada found that the presence of amorphous PDLLA did not disturb the crystallization of PCL over the range of PDLLA content from 0.1 to 0.9 [1]. For our blend films in which the PCL content is 0.5, PCL crystallized in the blends; the change in crystallinity of the blend films during the enzymatic degradation process is shown in Figs 2 and 3. The melting curves and WAXD patterns show the occurrence of PCL crystallization in the blends. It is found that there is no obvious shift of the melting peaks during enzymatic degradation, but the areas of the melting peaks decreased gradually and so did the diffraction peaks of the PCL/PDLLA blend films. This reflects the degradation of the crystalline PCL component in the blends. A very interesting phenomenon was observed in the d.s.c. thermograms at 77.5, 94.5 and 118.5 h after degradation, i.e., a new peak at a temperature of ca. 5°C. We believe that this should be attributed to the crystallization of some fractional macromolecules resulting from the degradation process, as the lamellae assembled by the fractions were much thinner than those of macromolecules in the bulk before the degradation process. The melting temperature depends on the crystal core thickness. So the melting point of these new lamallae was also much lower than the original one. This phenomenon will be investigated further in detail by means of other experiments and methods, so as to support our assumption.

The enzymatic degradation of PCL in the blends also can be followed by means of SEM. Fig. 4 presents scanning electron micrographs of the PCL/PDLLA blend films before

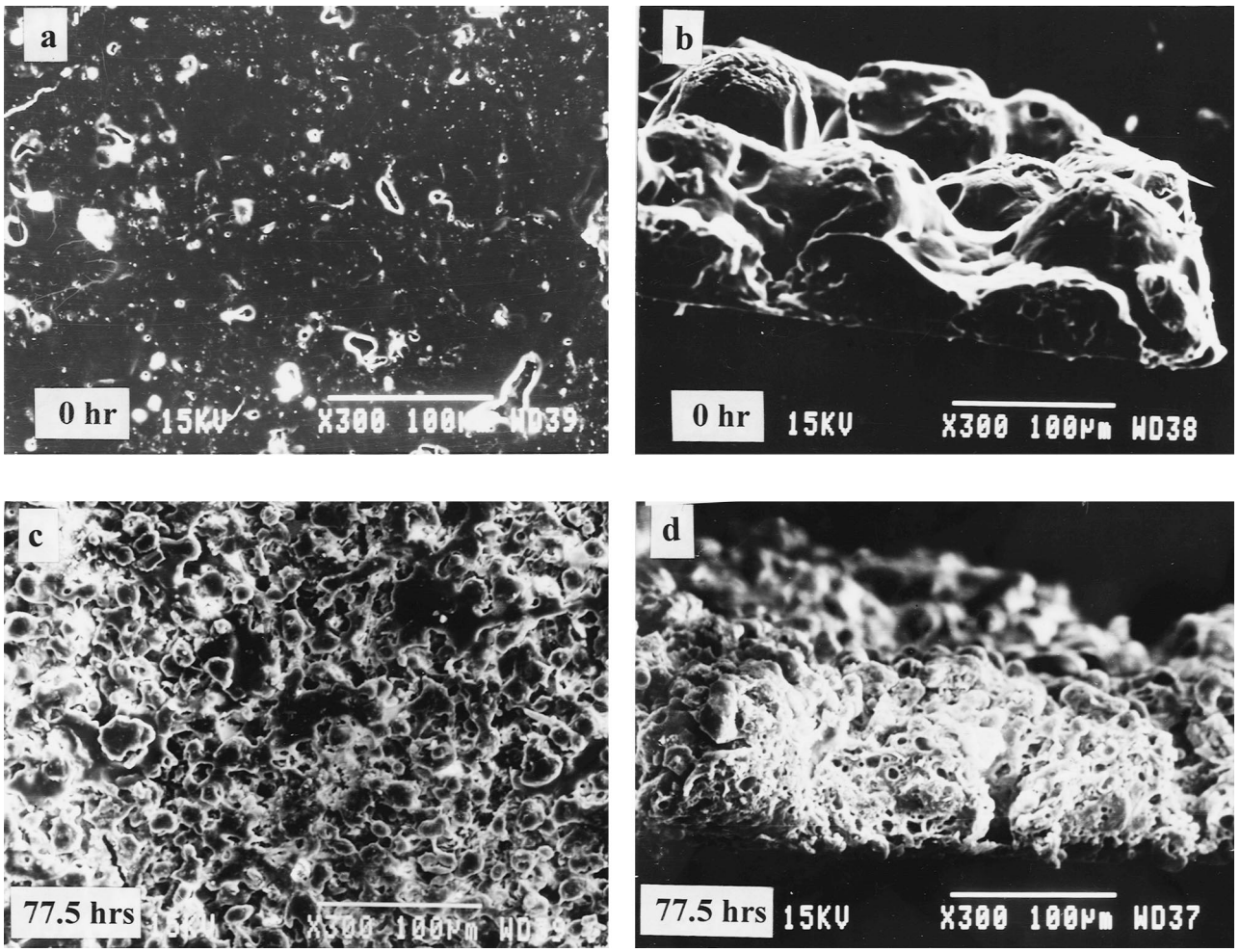

Fig. 4. Scanning electron micrographs of the surface (a,c) and cross-section (b,d) of PCL/PDLLA blend films before and after enzymatic degradation.

and after degradation. The surface of the films before degradation was smooth with small holes due to the evaporation of the solvent (Fig. 4(a)); however, the cross-sectional picture clearly shows regular structure (Fig. 4(b)). After degradation for 77.5 h the structure of the PCL aggregates was destroyed, the morphology changing from a regular structure into a vigorous up-and-down fluctuation (Fig. 4(d)). The smooth surface of the blend films also changed to become cracked (Fig. 4(c)). These results show that enzymatic degradation of the PCL/PDLLA blend films occurred not only on the film surface, but also inside the film. Both morphology changes (on the surface and inside the film) were due to degradation of the PCL component in the film.

4. Conclusions

The degradation of PCL/PDLLA blend films in phosphate buffer solution containing PS lipase was investigated. Only the PCL component degraded completely. Enzymatic degradation of the PCL resulted in morphology changes both on the surface and inside the PCL/PDLLA blend films.

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