Blends of Poly(L-lactic acid) with Poly(ω-pentadecalactone) Synthesized by Enzyme-Catalyzed Polymerization

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ABSTRACT: Poly(ω-pentadecalactone) (PPDL) was synthesized by enzyme-catalyzed polymerization. The molecular weight of the PPDL was about 35,000. Opaque poly(L-lactic acid) (PLLA)/PPDL blend films were created by the solvent casting technique. The addition of PPDL led to PLLA crystallization. Furthermore, the addition of PPDL with PLLA increased both the Young's modulus [pure PLLA : 0.67 GPa, PLLA/PPDL (70/30 wt %) : 1.01 GPa] and the PLLA glass transition temperature. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2139–2143, 2008

Key words: poly(ω-pentadecalactone); lipase-catalyzed polymerization; poly(L-lactic acid); blend film; thermal/mechanical property

INTRODUCTION

Much attention has been paid to enzyme-catalyzed polymerization as an environmentally benign method of polymer synthesis. The enzymatic synthesis of various polymers has been reported, and biodegradable polyesters can also be synthesized using enzymes.[1] Uyama and coworkers performed the lipase-catalyzed ring-opening polymerization of ε-caprolactone (ε-CL).[1–4] Kumar and Gross have reported that poly(ε-CL) with a higher molecular weight was obtained in high yield when toluene was used as an organic solvent.[5] Furthermore, Bisht et al.[6] and Kumar et al.[7] synthesized poly(ω-pentadecalactone) (PPDL) by the lipase-catalyzed ring-opening polymerization of ω-pentadecalactone (PDL).[6,7] The monomer conversion was high, and the PPDL obtained had a high molecular weight (above 20,000).[6]

In this study, we tried to blend PPDL with poly(L-lactic acid) (PLLA), which is the most usable biodegradable polymer, to make efficient use of the polymer synthesized by enzyme-catalyzed polymerization. We then investigated the thermal/mechanical properties of the blended films. There are many reports concerning the ability of PLLA/polymer blend systems, such as PLLA/poly(D-lactic acid),[8–10] PLLA/poly(ethylene oxide),[11–14] PLLA/poly(vinyl alcohol),[15] PLLA/poly[(R)-3-hydroxybutyrate],[16] and PLLA/poly(ethylene succinate)[17] to modify the properties of PLLA. But there is no report on the blending of PLLA and polyester obtained by enzyme-catalyzed polymerization.

EXPERIMENTAL

Materials

PDL was purchased from Aldrich Chemical Co., USA. Novozym-435 (lipase B from *Candida Antarctica* immobilized on a macroporous acrylic resin) was a gift from Novozymes Co. (Denmark). PLLA was supplied by Shimadzu (Kyoto, Japan); its trade name is LACTY (No. 5000). The weight-average molecular weight (M_w) of the PLLA was 19.4 × 10⁴ [the polydispersity index (PDI) = 1.82], and its optical purity was 99.0%. Reagent grade chloroform (Nakalai Tesque, Kyoto, Japan) was used as a cosolvent of PLLA and PPDL. All reagents were of commercially available reagent grade.

Enzymatic synthesis of PPDL

We simplified the synthesis method reported by Kumar et al.[7] Novozym-435 (0.053 g) and PDL (0.53 g) were placed together in Pyrex test tubes (screwcap type, 10 mL). Toluene (0.92 g) was subsequently added to the reaction tube. The tubes were placed into an oil bath at 80°C and shaken at 60 rpm for predetermined times. Reactions were terminated by adding an excess of cold chloroform. The enzyme (Novo-

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zyme-435) was removed by filtration (TOYO Roshi Kaisya, Japan: No. 5A). Methanol (200 mL) was added to the filtrate, and the resultant precipitate (PPDL) was dried under vacuum at room temperature.

Formation of PLLA/PPDL blend films

Specified amounts (PPDL content = below 30 wt %) of PLLA and PPDL were placed in a beaker; the total amount of these polymers was 1 g. Further, 20 mL of chloroform was added to the beaker. After being stirred for about 2 h, the mixture had become a homogeneous solution. The solution was cast in a glass petri dish. After the chloroform was vaporized at room temperature, the homogeneous films (about 150 μm in thickness) were obtained. The films were stored in a desiccator for 1 week, and then their properties were measured.

Characterization of blends

^{13}C-NMR spectrum was measured on a JEOL LA-500 spectrometer (at 500 MHz, Tokyo, Japan) in CDCl$_3$ containing tetramethylsilane (TMS) as the internal reference.

The average molecular weight of PPDL was evaluated in chloroform at 40°C with a gel permeation chromatography (GPC) system (Tosoh HLC-8220GPC, Tokyo, Japan). Three TSK (HM-N) gel columns were used, and the measured molecular weights were calculated by the universal calibration method, using nine polystyrene reference materials. The blend films (5 mg) were dissolved in 5 mL of chloroform, and the solution (20 μL) was injected into the GPC system (flow rate: 0.5 mL/min).

To evaluate the transparency of the blend films, the light transmittance test was performed with Shimadzu (Kyoto, Japan) UV-120-01 spectrometer; a wavelength of 500 nm was used.

Wide-angle X-ray diffraction (WAXD) curves of the blends were obtained with a Rigaku RINT-2100 X-ray diffractmeter (Japan) with Ni-filtered CuKα radiation.

The thermal behavior of the blends was measured with a Shimadzu DSC-60 differential scanning calorimeter (DSC) at a heating rate of 10°C/min.

The tensile test was performed at room temperature with a Tensilon UTM-II-20 tensile machine (Toyo Baldwin, Tokyo, Japan); the crosshead speed was 10 mm/min, and the initial gauge length was 30 mm.

The dynamic mechanical analysis (DMA) was performed with Rheometrics Scientific RSA II viscoelastic analyzer (USA). Temperature scans at 1 Hz frequency were carried out with a heating rate of 2°C/min.
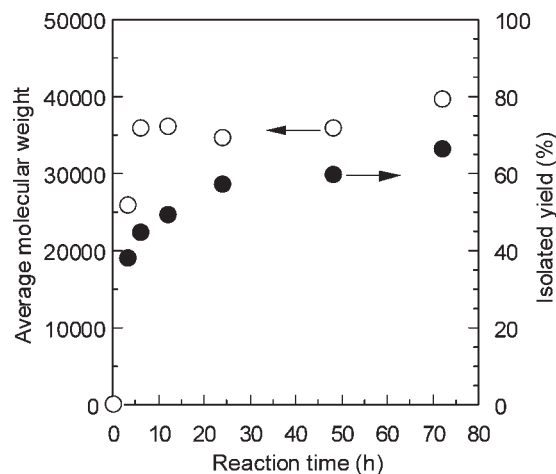
Figure 1 Effect of reaction time on the molecular weight and the isolated yield of PPDL.

RESULTS AND DISCUSSION

Enzymatic synthesis of PPDL

White powder (PPDL) was obtained by enzyme-catalyzed polymerization of PDL. The PPDL obtained was identified by ^{13}C-NMR spectrum. Pure PPDL film could not be formed by using the PPDL powder.

Figure 1 shows the effect of reaction time on the molecular weight (M_w) and the isolated yield of the PPDL obtained. The M_w of PPDL drastically increased within 6 h, reaching about 35,000 and then remaining constant. The yield gradually increased with increasing reaction time, reaching 66.5% at 72 h. This yield is lower than the values reported by Kumar et al.[7] (above 80%). It may have been affected by excess water around the lipase molecules, because we synthesized the PPDL under air rather than nitrogen. However, we obtained PPDL with high M_w. We used the PPDL powder obtained at 12 h for the polymer blend (PPDL weight average M_w = 36,300; PDI = 1.44).

Properties of PLLA/PPDL blend films

Figure 2 shows pure PLLA and PLLA/PPDL blend films. Pure PLLA film is transparent; the blend films become clouded as PPDL content increases. But the macrophase separation of the blend films did not occur by the addition of PPDL to PLLA. Figure 3 shows the relationship between the PPDL contents of the blend films and their light transmittance (wavelength: 500 nm). Pure PLLA is highly transparent (81%). By the addition of PPDL 5 wt % to PLLA, the transmittance of the blend film became 32%. The blend films became opaque above PPDL content 10 wt %. PLLA crystallization might be accelerated by the addition of PPDL.
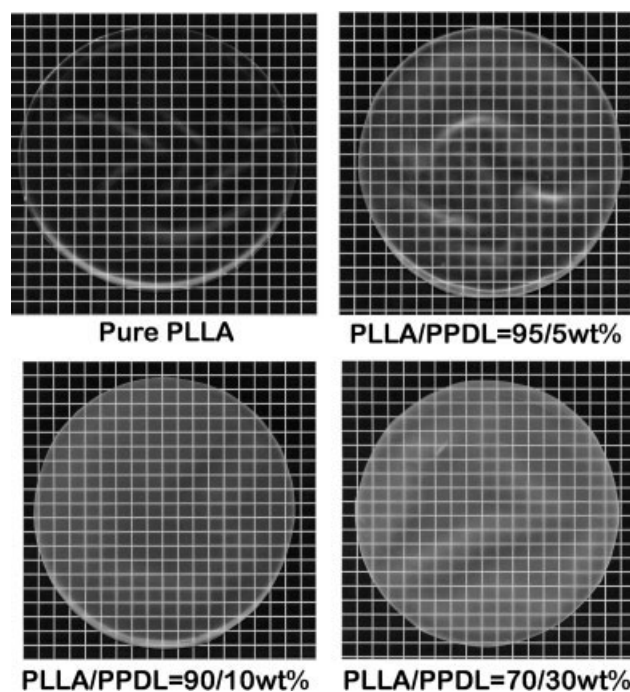
Figure 2 Photographs of pure PLLA and PLLA/PPDL blend films.

Figure 4 shows the WAXD curve of each film. The peaks at around $2\theta = 17°$ and above $20°$ correspond to PLLA and PPDL crystals, respectively. The peak of PLLA crystal increased with increasing PPDL content, despite the decreasing PLLA content in the blends. From this result, it is likely that PPDL microcrystal acts as a nucleating agent for PLLA crystal formation. The peaks of PPDL gradually increased with increasing PPDL content.

Figure 5 shows the DSC curves of the blends. The melting temperatures of pure PLLA and pure PPDL
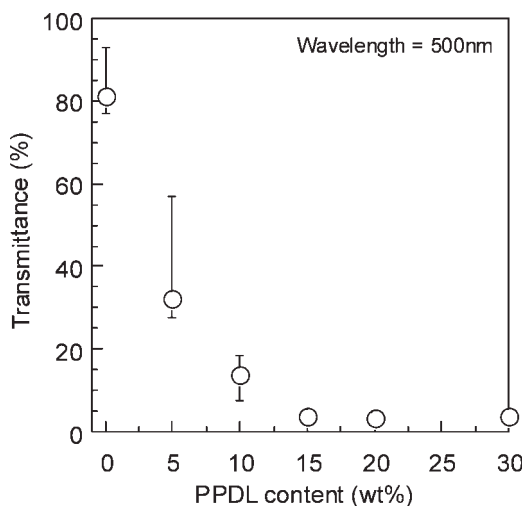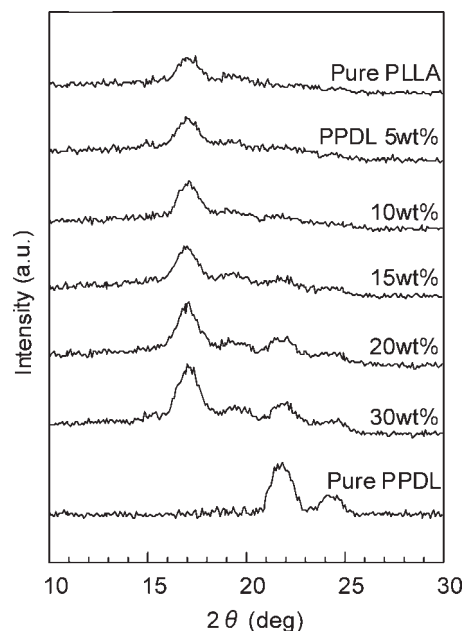

Figure 4 WAXD curves of PLLA/PPDL blend films.

were 171.8°C and 89.0°C, respectively. Two melting peaks are observed for each blend. From this result, it is likely that the mixing state of PLLA and PPDL in the blend would not be on a molecular level or on the level of a few nanometers (however, as can be seen in Figure 2, the macrophase separation is not observed).

The melting temperature (T_m) and the heat of fusion (ΔH_m) of PLLA and PPDL for each blend were evaluated in Figure 5. Figure 6 shows the relationships between these values and the blending ratio. The addition of PPDL to PLLA did not change T_m of
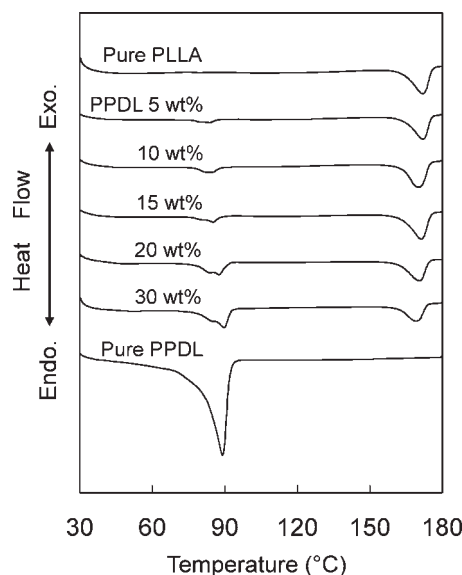

Figure 3 Effect of PPDL content on the transparency of PLLA/PPDL blend films.

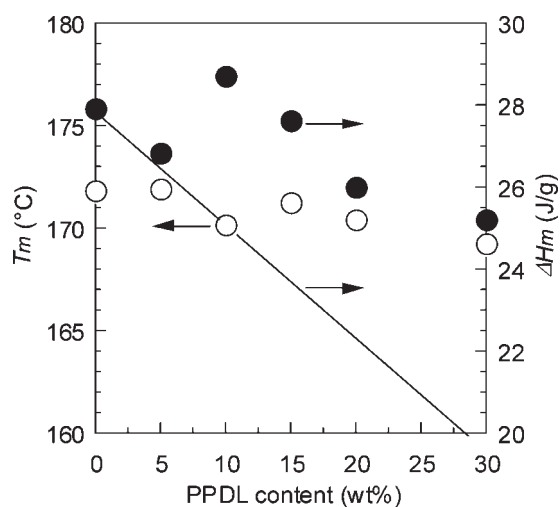**Figure 5** DSC curves of PLLA/PPDL blend films.

Figure 6 Effect of PPDL content on the T_m and the ΔH_m of PLLA/PPDL blend films.
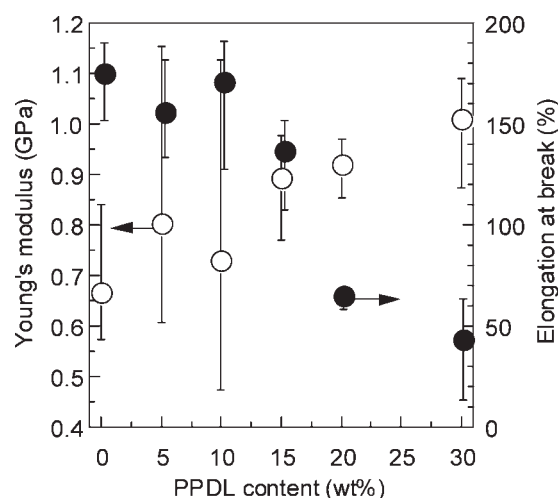

Figure 7 Effect of PPDL content on the Young's modulus and the elongation at break of PLLA/PPDL blend films.

PLLA, but the ΔH_ms of PLLA in the blends were located above the additive line between the value of the pure PLLA (PPDL 0 wt %) and that of pure PPDL (PLLA 0 wt %; $\Delta H_m = 0$). This would be due to the increasing degree of PLLA crystallinity by the addition of PPDL. On the basis of the heat of fusion of 100% crystalline PLLA (93 J/g),[17,18] the degree of PLLA crystallinity was calculated from the melting enthalpies of the sample and normalized with respect to the composition of PLLA in the blends. The degree of crystallinity was found to be 30.0% for pure PLLA, and increased to 34.3% and 38.7% for PLLA/PPDL (90/10 wt %), and PLLA/PPDL (70/30 wt %), respectively. On the other hand, the T_m of PPDL decreased with decreasing PPDL content in the blends: 87.5°C (PPDL 20 wt %), 83.7°C (PPDL 5 wt %). The ΔH_ms of PPDL for each blend showed the additive property between pure PPDL (104.0 J/g) and PPDL 0% (0 J/g).

Each film showed the typical stress–strain (s–s) curve, which has the yield point and the strain after the point. Figure 7 shows the Young's modulus and the elongation at the break obtained from the s–s curve for each film. The Young's modulus increased with increasing PPDL content even though the PLLA content in the blend decreased. This tendency differs from the cases in another PLLA blends.[14,15,17] This would be due to the crystallization of PLLA. The elongation at the break decreased with increasing PPDL content, but it remained above 45% at 30 wt % of PPDL content.

Figure 8 shows the DMA curves of pure PLLA, PLLA/PPDL (80/20 wt %), and PLLA/PPDL (70/30 wt %) [Fig. 8(a): storage modulus, Fig. 8(b): tan δ]. The storage moduli of pure PLLA and PLLA/PPDL blends decreased at around 50 and 60°C, respectively. The temperatures of the blends were higher than that of pure PLLA. Also, the peak of tan δ for

the blends shifted to a higher temperature range than that of pure PLLA. [We considered that this peak corresponds to the glass transition temperature (T_g) of PLLA.[19] The T_g of the PLLA measured by Shimadzu is 62.6°C (Technical Data of Shimadzu Corporation, Japan)]. The crystallinity of PLLA increased by the addition of PPDL, as explained earlier. Thus, the
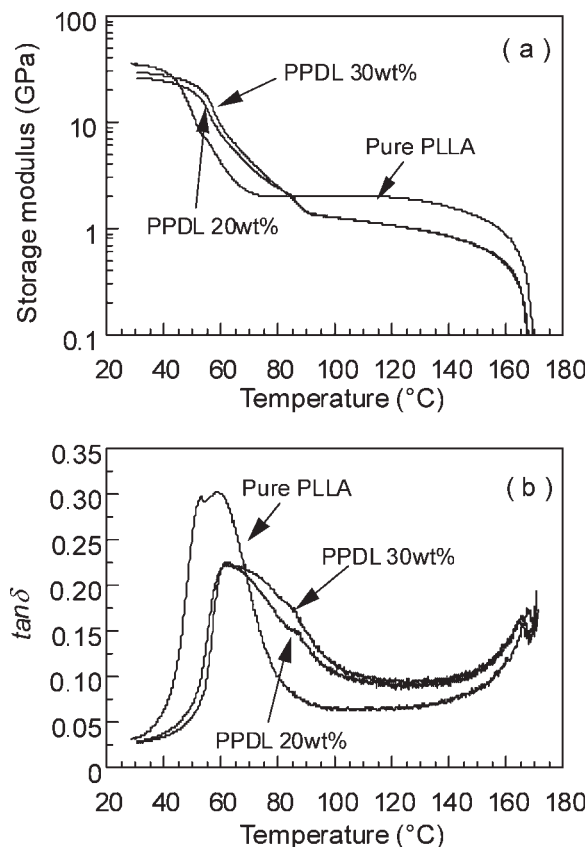

Figure 8 DMA curves of pure PLLA and PLLA/PPDL blend films. (a) Storage modulus, (b) tan δ.

thermal motion of PLLA segments in the blends might be prevented by both PLLA and PPDL crystals and, thus, increase the T_g of PLLA. The moduli of the blends became lower than that of pure PLLA at around 80°C, and the peaks of tan δ for the blends were broadened. It is likely that PPDL in the blend melted at that temperature range.

CONCLUSION

PPDL was simply synthesized using lipase as a catalyst. PLLA/PPDL blend films were created by the solvent casting technique. The blend films obtained were opaque, but the macrophase separation between PLLA and PPDL was not observed. The addition of PPDL led to PLLA crystallization. As the PPDL content in the blends increased, both the Young's moduli of the blends and the T_g of PLLA increased. We found that PPDL would be a useful material for improving PLLA's thermal/mechanical properties.

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