Porous Poly(L-lactic acid)/Poly(ethylene glycol) Blend Films

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ABSTRACT: Poly(L-lactic acid) (PLLA: $M_w = 19.4 \times 10^4$)/ poly(ethylene glycol) (PEG: $M_w = 400$) blend films were formed by use of a solvent-cast technique. The properties and structures of these blend films were investigated. The Young's modulus of the PLLA decreased from 1220 to 417 MPa with the addition of PEG 5 wt %, but the elongation at break increased from 19 to 126%. The melting point of PLLA linearly decreased with increases in the PEG content (i.e., pure PLLA: 172.5°C, PLLA/PEG = 60/40 wt %: 159.6°C). The PEG 20 wt % blend film had a porous structure. The pore diameter was 3–5 μm. The alkali hydrolysis rate of this blend film was accelerated due to its porous structure. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 965–970, 2004

Key words: biodegradable; blends; films

INTRODUCTION

Poly(lactic acid) (PLA) is a biodegradable thermoplastic polyester that has been extensively investigated due to its biocompatibility and also because its mechanical properties outperform those of both polyethylene and polystyrene. The full-scale production of PLA has recently been established, which will render PLA a more commonly used material in daily life in the near future. To date, there have been a number of investigations focusing on the modification of the properties of PLA, including those that involve the creation of polymer blends and the addition of plasticizer.[1–3]

Poly(ethylene glycol) (PEG) is frequently used in the production of polymer blends, as it is an amphipathic polymer; many varieties (molecular weights) of PEG specimens have been marketed thus far. There have been a number of studies reporting the modification of PLA using PEG. Lee et al.[4] and Huh et al.[5] synthesized the multiblock copolymers of PLA and PEG and investigated the thermal properties and the structures of the copolymers. Younes and Cohn[6] prepared poly(L-lactic acid) (PLLA)/ PEG physically blended materials, and the structure of this type of blend was examined by DSC and IR spectra. They reported that the melting point depression of both PLLA and PEG occurs with a decrease in the concentration of components in the mixture, especially at PLLA or PEG contents below 20 wt %. Nakafuku et al.[7,8] investigated the crystallization of a PLLA/PEG blend system in detail. They concluded that the cocrystal of PLLA and PEG is not formed in the blend, but rather the interaction between PLLA and PEG takes place in an amorphous region. Furthermore, in an examination of the biocompatibility of PLLA/PEG blends, Zoppi et al.[9] demonstrated that PLLA/PEG blends are as biocompatible as pure PLLA, with the advantage of the possible control of the implant degradation rate.

We confirmed in the present study that porous PLLA/PEG blend films could be formed using a solvent-cast technique. In this paper, we report the structures and the properties of these blends. Tsuji et al.[10] formed porous PLLAs by the water extraction of PEG from PLLA/PEG blends. The alkali hydrolysis rate of this biodegradable polymer was accelerated due to the porous structure of this polymer. In contrast, our PLLA/PEG blend film is porous in structure, but without the water extraction of PEG from the blend.

EXPERIMENTAL

Materials

PLLA was supplied by Shimadzu (Kyoto, Japan); its trade name is LACTY (#5000). The weight-average molecular weight (M_w) of the PLLA was 19.4×10^4, and its optical purity was 99.0%. PEG ($M_w = 400$) was purchased from Wako Pure Chemicals Ind., Ltd., Japan. Reagent grade chloroform (Nakalai Tesque Inc., Kyoto, Japan) was used as a cosolvent of these poly-
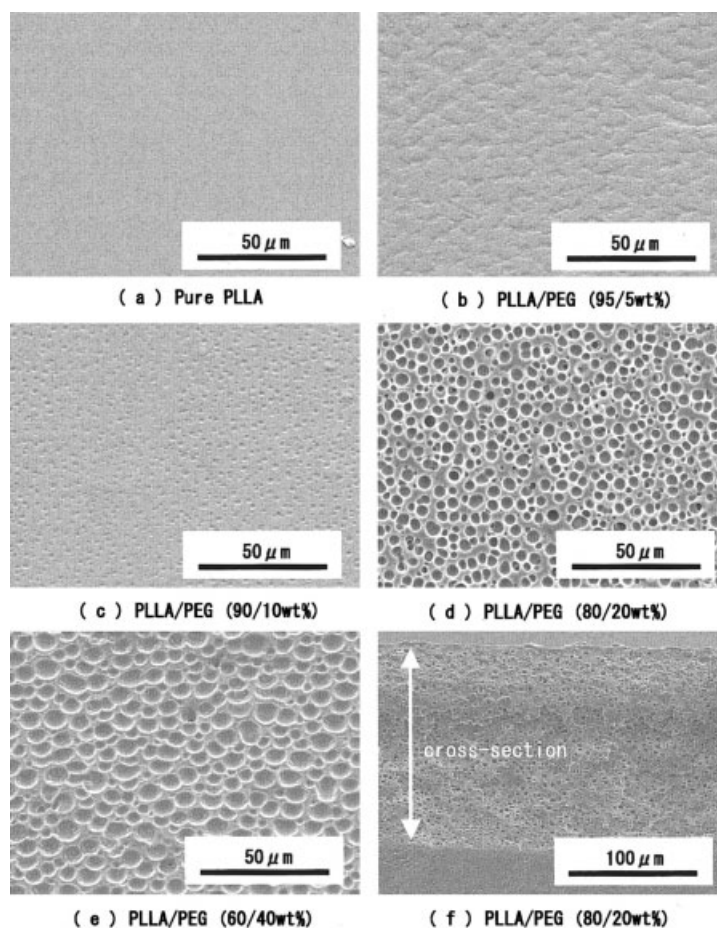
Figure 1 SEM micrographs of as-cast pure PLLA and PLLA/PEG blend films.

mers. All reagents were of commercially available reagent grade.

Formation of blend films

Specified amounts of PLLA and PEG were placed in a beaker; the total amount of these polymers was 1 g. Thirty milliliters of chloroform was then added to the beaker. After stirring the mixture for about 2 h, the mixture became a homogeneous solution. The solution was cast in a glass Petri dish. After the chloroform was vaporized at near 0°C, homogeneous films (ca. 160 μm in thickness) were obtained. The reason for the low casting temperature was to obtain a flexible film close to an amorphous state. The films were stored in a desiccator for 1 week, and their properties were measured.

Characterization of blends

To measure the transparency of the blend films, the light transmittance test was performed with a Shimadzu (Kyoto, Japan) UV-2100 spectrometer; a wavelength of 500 nm was used.

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 tensile machine (Toyo Baldwin, Tokyo, Japan); the crosshead speed was 10 mm/min, and the initial gauge length was 30 mm.

The water vapor permeability of the blends was measured at 30°C with a Yanako (Kyoto, Japan) GTR-20XP. The humidity was 90% and the carrier gas was nitrogen. The effective film area was 15.2 cm². The principle of measurement is to evacuate the downstream side of the film, provide the upstream side with a water vapor at 1 atm, and monitor the increase in pressure in a fixed downstream receiving volume. The permeability coefficient (P) was calculated from the slopes of time–pressure curves in the steady state where Fick's law held. The diffusion coefficient (D) was determined by the time lag method using the following equation: $D = l^2/6\theta$. Here, l is the film thickness, and θ is the time lag, which is given by the intercept of the asymptotic line of the time–pressure curve to the time axis. The
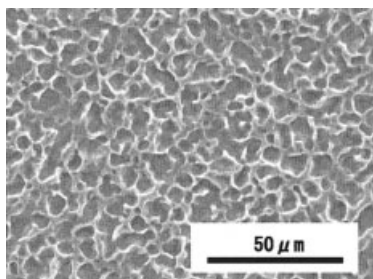
Figure 2 SEM micrograph of water-extracted PLLA/PEG (80/20 wt %) blend film.

solubility coefficient (S) was calculated by using equation $S = P/D$.

Alkali hydrolysis of blends

About 0.1 g of the blend film was hydrolyzed at 40°C by using 0.05N NaOH aqueous solution (30 mL). The samples were removed from the solution after a prescribed time, and they were dried at room temperature and then *in vacuo*. The weight of the dried remaining samples was measured.

Molecular weight distributions of the remaining samples were 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.

RESULTS AND DISCUSSION

SEM observation of blends

Figure 1(a)—(e) shows the SEM micrographs of the surface (solvent evaporation side) of pure PLLA and PLLA/PEG blend films. Pure PLLA has a smooth surface. The addition of PEG to PLLA changed the surface structure of the blend films. Undulation and depressions (diameter: ca. 1–2 μm) were observed on the surface of the blends after the addition of PEG 5 and 10 wt %, respectively. In the case of the sample containing PEG 20 wt %, the blend became very porous (pore diameter, ca. 3–5 μm). The numerous pores increased in size (ca. 7–8 μm) with the addition of PEG 40 wt %. Few differences were observed between the surface structure of the solvent evaporation side and that of the glass dish side. At this stage of investigation, there is still no clear explanation for the formation of the porous structure, but this result does appear, at least in part, to be due to changes in the solvent (chloroform) vaporization rate or might also be due to the mobility of the PEG molecular chain during the process of

film formation. Figure 1(f) shows the SEM micrograph of the cross section of a sample PLLA/PEG (80/20 wt %) blend film. The pores were found to be homogeneously present throughout the film, i.e., from the surface to the center.

The PLLA/PEG blend films were immersed in distilled water at 40°C for 48 h. The films lost weight after immersion. The percentage of mass remaining against the initial weight of each film was 97.9 (pure PLLA), 92.1 (PEG 5 wt %), 90.6 (PEG 10 wt %), and 79.9 wt % (PEG 20 wt %). These values indicated that almost all of the blended PEG was dissolved in water during the immersion procedure. Figure 2 shows an SEM micrograph of the blend films (PEG 20 wt %) after immersion in water (40°C, 48 h). When these findings are compared to the results shown in Figure 1(d), it can be seen that the shape of the pore is rendered more complex by the removal of the PEG region. Thus, it was confirmed that PLLA and PEG are mixed together at the level of a few microns.

Properties of blends

Figure 3 shows the DSC curves of the blends. The crystallization and melting temperatures of pure PLLA were 78.7 and 172.5°C, respectively. The crystallization peak of PLLA did not appear at a PEG content of 5 or 10 wt %. It is likely that the crystallization of PLLA was accelerated by the addition of PEG below 10 wt %. However, the crystallinity of each cast sample was estimated to be very low, as determined by wide-angle X-ray diffraction. The crystallization peak was again observed at a PEG
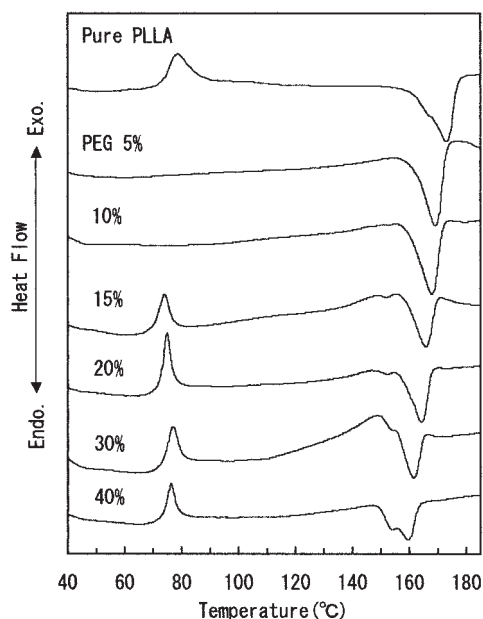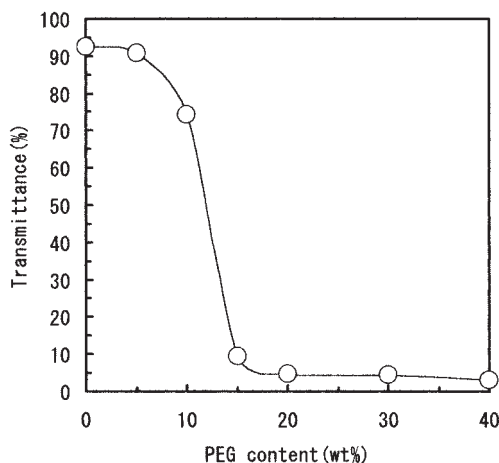

Figure 3 DSC curves of as-cast PLLA/PEG blends.

Figure 4 Effect of PEG content on transparency of as-cast PLLA/PEG blend films (λ = 500 nm).

Figure 5 Effect of PEG content on Young's modulus ($\bigcirc$) and elongation at break ($\bullet$) of as-cast PLLA/PEG blend films.

content exceeding 15 wt %. PEG molecules are expected to have moved in the blend during the heating process, and further crystallization of PLLA occurred at PEG contents above 15 wt %. Moreover, the crystallization temperature (approximately 76°C) did not change at PEG contents exceeding 15 wt %. On the other hand, the melting temperature of PLLA decreased in a linear fashion with increases in the PEG content, i.e., 159.6°C at PEG 40 wt %. A double melting peak appeared at levels above PEG 15 wt %. The higher temperature peak is thought to have been due to the melting of PLLA crystals formed in the process of film formation. The lower temperature peak appears to have been due to the melting of new PLLA microcrystals formed during the process of heating the samples. The intensity of the lower peak increased with increases in the PEG content. The crystallization of PLLA during the heating process would be expected to occur easily with increases in the PEG content, because the mobility of the PLLA segment would increase with increases in the PEG microdomain in the PLLA matrix.

Figure 4 depicts the relationship between the components of the blends and the light transmittance (wavelength: 500 nm). Pure PLLA is transparent. The transmittance of the films steeply decreased at PEG contents from 10 to 15 wt %. This is due to the increasing the crystallinity of PLLA and the formation of pore structure by the addition of PEG to PLLA.

The stress–strain curves of the blend films showed a typical curve having a yield point. Figure 5 shows the plots of Young's modulus and the elongation at break, as obtained from the stress–strain curves for each sample. The Young's modulus drastically decreased with the addition of PEG 5 wt %, but the elongation at break of the blend (PEG 5 wt %) was sevenfold that of pure PLLA. These values changed with increases in the PEG
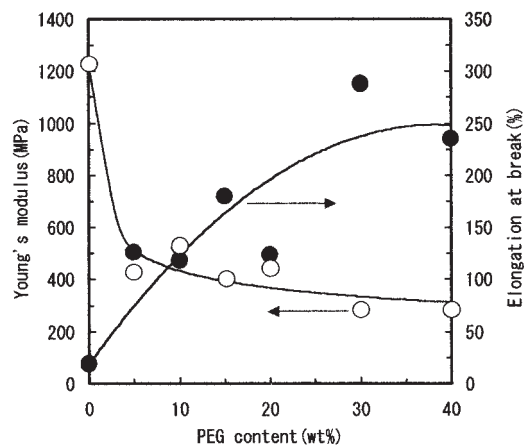
content, namely, the elongation at break was approximately 300% when the PEG content was 30 wt %. These results demonstrated that the dispersion state of PEG in a PLLA matrix would be favorable; moreover, PEG was found to act as a plasticizer of PLLA. It should also be noted that the pore structure of the blends exerted an additional influence on these results.

Figure 6 shows the water vapor permeability of these blend films. The permeability and diffusion coefficients revealed minimum values at a PEG content of 5 wt %. On the other hand, the solubility coefficient increased in a linear manner with increases in the PEG
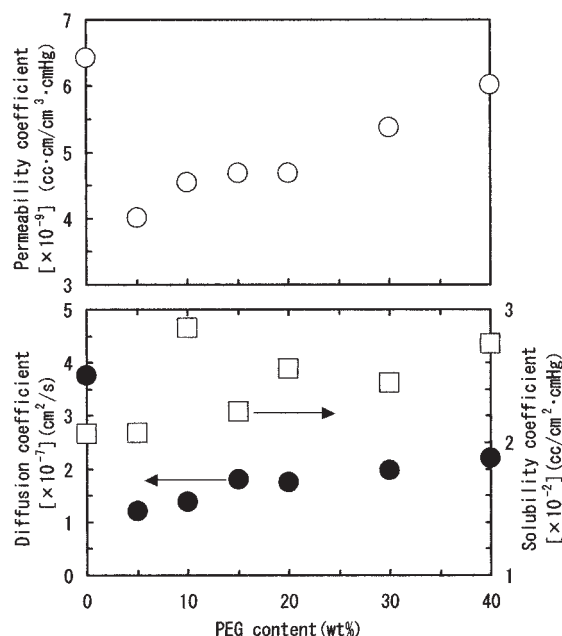

Figure 6 Effect of PEG content on water vapor permeability coefficient ($\bigcirc$), diffusion coefficient ($\bullet$), and solubility coefficient ($\square$) of as-cast PLLA/PEG blend films.
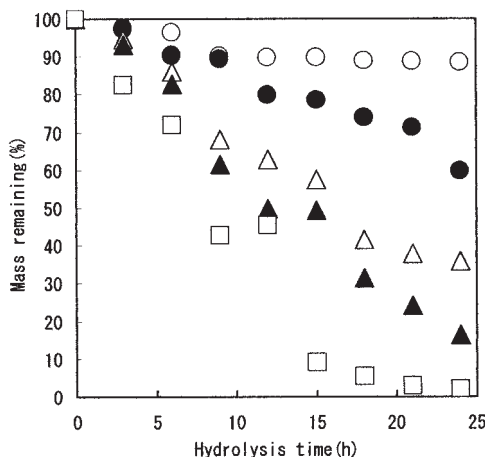
Figure 7 Mass remaining of PLLA/PEG blend films as a function of alkali hydrolysis time in 0.1N NaOH aqueous solution.○, pure PLLA; ●, PLLA/PEG (95/5 wt %); △, 90/10 wt %; ▲, 85/15 wt %; □, 80/20 wt %.

Figure 9 Molecular weight distribution curves of PLLA/PEG (80/20 wt %) blends before and after alkali hydrolysis for different times.

content. Based on these results, it appears that the addition of PEG was mainly influenced by the diffusivity of water molecules inside the blend films. It is possible that the toturosity in the blends in terms of the diffusion of water molecules increases due to the crystallization of PLLA by the addition of PEG; this would account for the finding that the diffusion coefficient of the blend (PEG 5 wt %) became lower than that of pure PLLA. The pores and the continuous phase of PEG, which is a water-soluble polymer, were formed in blends with PEG contents above 10 wt %, and the permeability (diffusion) coefficients increased. In general, no drastic increase in water vapor permeability was observed. Thus, it is likely that the pores formed as a result of the addition of PEG were not continuous, as can be seen in Figure 1(f).

Alkali hydrolysis of blends

Figure 7 depicts the residual weight of blends as a function of alkali hydrolysis time. The hydrolysis rate of pure PLLA is slow; the weight loss amounts to only
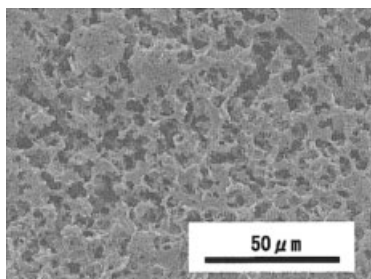

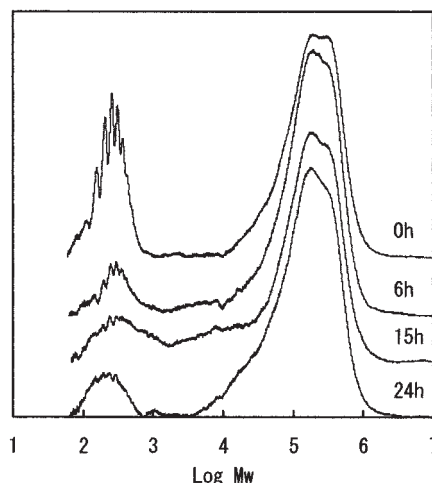**Figure 8** SEM micrograph of PLLA/PEG (80/20 wt %) blend film after alkali hydrolysis (24 h).

about 10% of the initial weight after immersion in NaOH aqueous solution for 24 h. The rate is promoted by the addition of PEG; this effect was due to the increase in the specific surface area, which was the result of the extraction of PEG. The films containing PEG at 20 wt % were hydrolyzed for almost 24 h. Figure 8 shows an SEM micrograph of the residue of a PLLA/PEG (80/20 wt %) blend film after immersion in NaOH aqueous solution for 24 h. Figure 8, compared to Figures 1(d) and 2, reveals that the pore collapsed due to immersion in the NaOH aqueous solution. This effect was the result of the dissolution of PEG and the hydrolysis of the surface of the PLLA matrix.

Figure 9 shows the effect of hydrolysis time on the molecular weight distribution of the PLLA/PEG (80/20 wt %) blends. The peak at the higher molecular weight range corresponds to PLLA, and the peak at the lower molecular weight range corresponds to PEG. It should be noted that the shape of the peak and the peak position of PLLA appear to be independent of the hydrolysis time. This means that the hydrolysis of the PLLA film proceeded by a surface erosion mechanism. The PEG peak decreased due to the dissolution of PEG into the aqueous NaOH solution, but the peak was observed, even after 24 h of immersion in the solution. Some of the PEG was incorporated in the structure of the PLLA matrix, even after 24 h.

As mentioned above, the blend film with a PEG content of 20 wt % was porous in structure. The porosity then accelerated the rate of PLLA alkali hydrolysis due to an increase in the specific surface area of the PLLA. We suggest here that the enzymatic decomposition rate of PLLA was also accelerated for the same reason.

CONCLUSION

PLLA/PEG (M_w = 400) blend films were formed using a solvent-cast technique. The properties and structures of these blend films were investigated. The Young's modulus of PLLA was found to decrease with the addition of PEG, but the elongation at break increased. In addition, the melting point of PLLA decreased in a linear manner with increases in the PEG content.

The structure of the blend film with a PEG content of 20 wt % was porous; the diameter of the pores in this blend was on the level of a few microns. The rate of alkali hydrolysis of the blend film was increased due to its porous structure (i.e., the high specific surface area of PLLA). As a subsequent step for analysis, control of the size of the pores in such blend films will be needed to achieve control of the bio and alkali hydrolysis rates of PLLA.

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