Porous Biodegradable Polyesters. II. Physical Properties, Morphology, and Enzymatic and Alkaline Hydrolysis of Porous Poly(ϵ-caprolactone) Films

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ABSTRACT: Porous poly(ϵ-caprolactone) (PCL) films were prepared by water extraction of poly(ethylene oxide) (PEO) from their solution-cast phase-separated blend films and the dependence of their blend ratio [X_{PCL} = PCL/(PEO + PCL)] and molecular weight of PEO on the porosity, pore size, crystallinity, crystalline thickness, mechanical properties, morphology, and enzymatic and alkaline hydrolysis of the porous PCL films were investigated. The film porosity or extracted weight ratio was in good agreement with the expected values, irrespective of X_{PCL} and molecular weight of PEO. The maximum pore size was larger for the porous films prepared using PEO having a lower molecular weight, compared with films prepared using PEO having a higher molecular weight at the same X_{PCL}. Differential scanning calorimetry of the porous PCL films revealed that their crystallinity and crystalline thickness were almost constant, regardless of X_{PCL} and molecular weight of PEO. The Young's modulus and tensile strength of the porous films decreased, whereas the elongation-at-break increased with decreasing X_{PCL}. The enzymatic and alkaline hydrolysis rates of the porous films increased with a decrease in X_{PCL} and an increase in the molecular weight of PEO. The porous PCL films having Young's modulus in the range of 2–24 kg/mm^2 and enzymatic hydrolysis rate in the range of one- to 20-fold that of the nonporous PCL film could be prepared by altering X_{PCL} and the molecular weight of PEO. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2281–2291, 2001

Key words: poly(ϵ-caprolactone); poly(ethylene oxide); enzymatic hydrolysis; physical properties; porous biodegradable polymers

INTRODUCTION

Porous biodegradable polymeric materials have been attracting the interest of many researchers because they can be utilized as scaffolds for regeneration of tissues.[1,2] The soft biodegradable materials having a low Young's modulus are favorable scaffolds for regeneration of soft tissues such as internal organs, blood vessels, and nerves, in terms of coordination of their mechanical properties. Among the biodegradable aliphatic polyesters, poly(ϵ-caprolactone) (PCL) has a Young's modulus of 20–40 kg/mm^2,[3,4] which is one order lower than 160–210 kg/mm^2 of poly(L-lactide) (PLLA).[5] The soft biodegradable materials from copolymers of ϵ-caprolactone (CL) and L-lactide (LLA) or DL-lactide were previously prepared for the purpose of nerve regeneration.[6,7]

However, the Young's modulus of the copolymer from LLA and CL [LLA/CL (mol/mol) = 54/46] increased from 1.0 to 9.2 kg/mm^2 during storage at room temperature for 2 months because of crystallization of LLA sequences in the copolymer.[8]

Compared to the copolymerization method, altering porosity and pore size is commercially advantageous to prepare soft biodegradable materials having a variety of mechanical properties. Several methods have been proposed to prepare porous biodegradable materials,[1,2] including removal of inorganic salts or organic low molecular weight compounds from melt-molded, solution-cast, gelled, or frozen mixtures of biodegradable polymers and additives or solvents.[1,2] In a previous study, we prepared porous PLLA films by water extraction of poly(ethylene oxide) (PEO) from their solution-cast blends.[9] It became evident that the pore size and porosity of the PLLA films can be controlled by changing their mixing ratio and the molecular weight of PEO. However, the effects of porosity and pore size on the mechanical properties of the porous PLLA films could not be estimated in this study because they were too brittle to measure their mechanical properties.

Numerous studies have been performed on biodegradation[10–14] and both enzymatic[15–19] and nonenzymatic[20,21] hydrolysis of PCL. Tokiwa et al.[15,16] found that the hydrolysis of PCL is accelerated by the presence of lipases. Mochizuki et al.[17] and Pranamuda et al.[18] studied, respectively, the effects of draw ratio (crystallinity) and blending with tropical starches from different plants on the enzymatic hydrolysis of PCL. On the other hand, Gan et al.[19] reported that a pseudomonas lipase can catalyze the hydrolysis of PCL, whereas its hydrolysis in the presence of porcine pancreatic or candida cylindracea lipase was very slow. Most biodegradable aliphatic polyesters are known to be hydrolyzed catalytically in the presence of enzymes[22,28] and alkalis,[13,22–27] mostly via a surface-erosion mechanism. In such cases, increasing their porosity or surface area per unit weight will accelerate the hydrolysis per unit mass, depending on the porosity and pore size. However, there have been no such reports on the enzymatic and alkaline hydrolytic surface erosion of the porous aliphatic polyesters having different porosities and pore sizes.

The purposes of the present study were to prepare soft biodegradable PCL materials having different mechanical properties by changing their porosity and pore size and to elucidate the effects of porosity and pore size on their enzymatic and alkaline hydrolysis via surface erosion. PCL films, having different pore sizes and porosities, were prepared by means of direct solution blending of PCL with PEO in the presence of their cosolvent, followed by water extraction of PEO from the blend films after solvent evaporation. To obtain PCL films with various porosities and pore sizes, PCL and PEOs with different molecular weights were blended at different polymer ratios to vary the domain size and number per unit volume of PCL- and PEO-rich phases in their blends. PCL and PEO were required to yield phase separation into PCL-rich and PEO-rich phases with a large size to prepare porous PCL films. For this requirement, the solvent-casting method was selected because some solvents are known to induce phase separation between the two polymers even if they are partially miscible in the melt or in the amorphous state.[29] In addition, solvent evaporation was allowed to proceed extremely slowly to form a PEO-rich phase with a large domain.

EXPERIMENTAL

Materials

Films of about 100 μm thickness were prepared by casting 1 g/dL mixed solution of PCL (M_w = 2.9 × 10^5, M_w/M_n = 1.6) and PEOs [M_w = 1.5 × 10^3 (M_w/M_n = 1.1) and M_w = 7.0 × 10^4 (M_w/M_n = 1.6), abbreviated as PEO(L) and PEO(H), respectively; Aldrich, Milwaukee, WI] with different polymer compositions using methylene chloride as a solvent, followed by slow solvent evaporation at room temperature for about 1 week, as reported in our previous work.[4,9,14,21] PCL was synthesized by the procedure reported earlier (140°C for 240 h, stannous octoate 0.015 wt %).[4] The blend ratio of the as-cast films (X_{PCL}) is defined by the following equation:

$$X_{PCL}(w/w) = PCL/(PEO + PCL) \qquad (1)$$

The period of time for the solvent evaporation was 1 week, to complete phase separation between the two polymers during solvent evaporation.[4,9,14,21] The cast films were dried in vacuum for another week and stored at room temperature for at least 1 month, to reach the equilibrium state before physical measurements. The as-cast blend films from the pair of PCL and PEO(L) and of PCL and
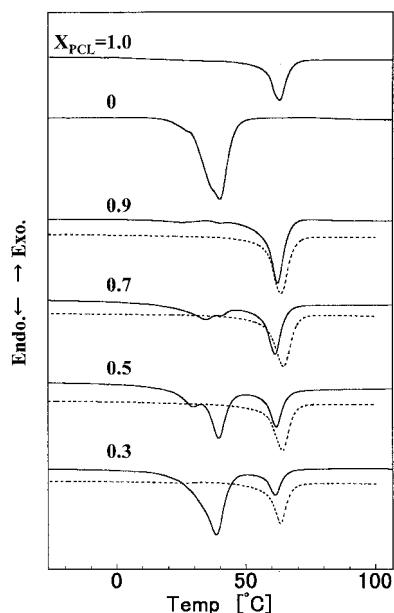
Figure 1 DSC thermograms of as-cast films (—) of PCL-PEO(L) and nonblended PCL ($X_{PCL} = 1$) and PEO ($X_{PCL} = 0$) and water-extracted films (- - -) of PCL-PEO(L) films.

PEO(H) are abbreviated as PCL-PEO(L) and PCL-PEO(H) films, respectively. Extraction of PEO from the films was performed in distilled water (HPLC grade; Nacalai Tesque, Inc., Kyoto, Japan) at room temperature for 1 week and then dried. The water for extraction was exchanged every day.

Hydrolysis

The enzymatic hydrolysis of the water-extracted films (10×10 mm^2) was performed according to the procedure reported by Pranamuda et al.[18] In brief, the film was placed in a vial filled with 10 mL of 0.02M phosphate-buffered solution (pH 7.0) containing 0.005 wt % of the surfactant Plysurf A210G (Dai-Ichi Kogyo Seiyaku Co., Japan), and air in the pores of the porous films was removed under reduced pressure for 5 min. The film was then moved to a vial filled with 20 mL of 0.02M phosphate-buffered solution (pH 7.0) containing 2000 units of lipase [Type XI, Rhizopus arrhizus, suspension in 3.2M (NH$_4$)$_2$SO$_4$/10 mM potassium phosphate solution; Sigma, St. Louis, MO] and 0.005 wt % of Plysurf A210G, which stabilized the suspended state of the lipase. The distilled water used for preparation of the phosphate-buffered solution was of HPLC grade (Nacalai Tesque, Inc.). The enzymatic hydrolysis of the films was performed at 30°C in a rotary shaker up to 20 h.

The alkaline hydrolysis of the water-extracted films (5×5 mm^2) was performed in 20 mL of 4N NaOH solution (Nacalai Tesque Inc.) at 30°C for predetermined periods of time. Air in the pores of the specimens was removed under a reduced pres-
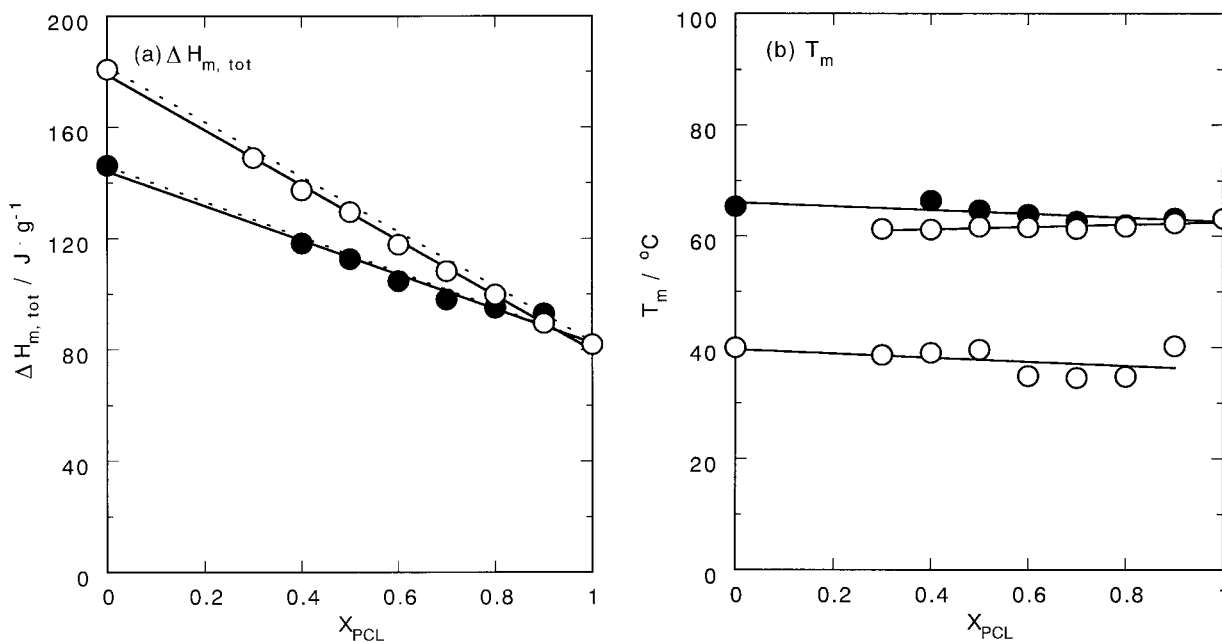

Figure 2 $\Delta H_{m,tot}$ (a) and T_m (b) of water-extracted films of PCL-PEO(L) (○) and PCL-PEO(H) (●) as a function of X_{PCL}; (- - -) expected $\Delta H_{m,tot}$. T_m's of PCL-PEO(L) (○) around 65 and 40°C are ascribed to those of PCL and PEO(L), respectively.
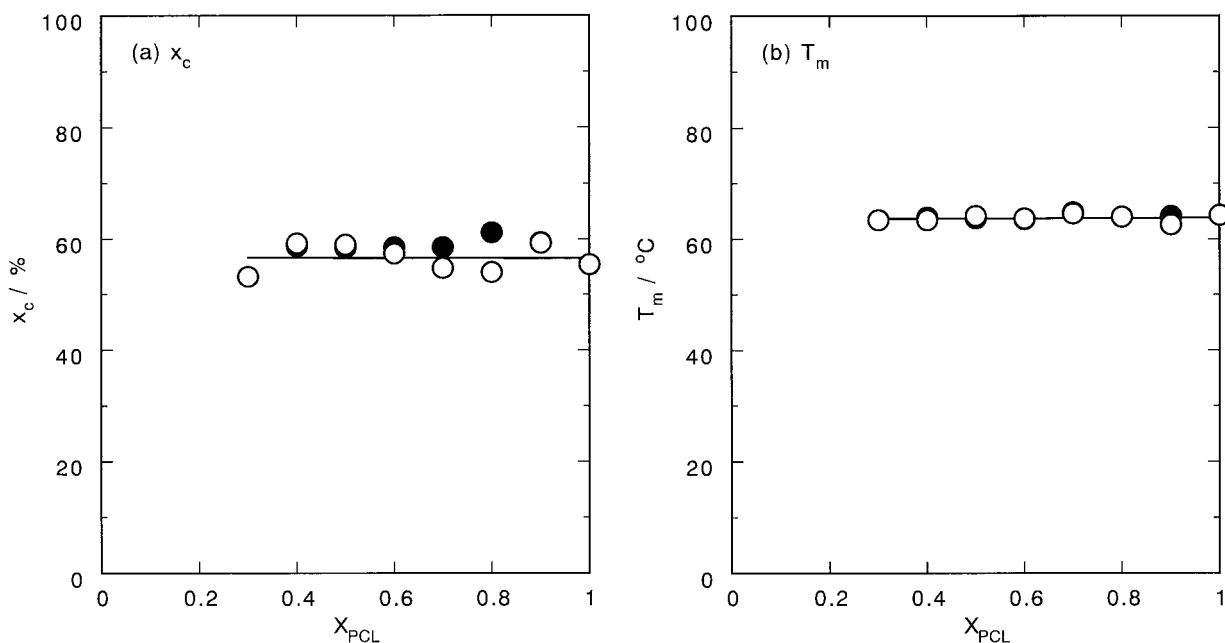
Figure 3 x_c (a) and T_m (b) of water-extracted films of PCL-PEO(L) (○) and PCL-PEO(H) (●) as a function of X_{PCL}.

sure for 5 min immediately after their immersion in $4N$ NaOH solution. The alkaline hydrolysis of the films was performed in a rotary shaker up to 96 h.

The hydrolyzed films were washed intensively with the distilled water, followed by drying under reduced pressure for at least 2 weeks. The films, hydrolyzed enzymatically, were washed at 4°C to stop further enzymatic hydrolysis.

Measurements and Observations

The extracted weight ratio (EWR) of the films by water extraction was calculated using the following equation:

$$\text{EWR (wt \%)} = \frac{W_{\text{before}} - W_{\text{after}}}{W_{\text{before}}} \times 100 \qquad (2)$$

where W_{before} and W_{after} are weights of the dried films before and after extraction with water. EWR can be considered as an index of porosity.

Melting temperature (T_m) and enthalpy of melting (ΔH_m) of the as-cast and water-extracted films (sample weight of about 3 mg) were determined by a Shimadzu DT-50 (Shimadzu Co., Kyoto, Japan) at a heating rate of 10°C/min under a nitrogen gas flow of 50 mL/min. The crystallinity (x_c) of water-extracted films was evaluated according to the following equation, assuming

that all the PEO molecules were removed by water extraction:

$$x_c\ (\%) = \frac{\Delta H_m}{142} \times 100 \qquad (3)$$

where 142 (J/g of polymer) is the enthalpy of melting of PCL crystals having an infinite crystal thickness, as reported by Crescenzi et al.[30]

Tensile properties of the water-extracted films were measured at 25°C and 50% relative humidity using a Shimadzu tensile tester (EZ-Test) with a gauge length of 20 mm at a crosshead speed of 100%/min.

Morphology of the water-extracted films was observed with a Hitachi SEM (S-2300; Hitachi Co., Tokyo, Japan). The films for SEM observation were coated with carbon to a thickness of about 20 nm.

RESULTS AND DISCUSSION

Crystallization during Solvent Evaporation

Figure 1 shows the DSC thermograms of the as-cast PCL-PEO(L) and nonblended PCL $(X_{PCL} = 1)$ and PEO $(X_{PCL} = 0)$ films before water extraction. The melting peaks of PCL and PEO(L) were observed around 65 and 40°C, respectively, for all
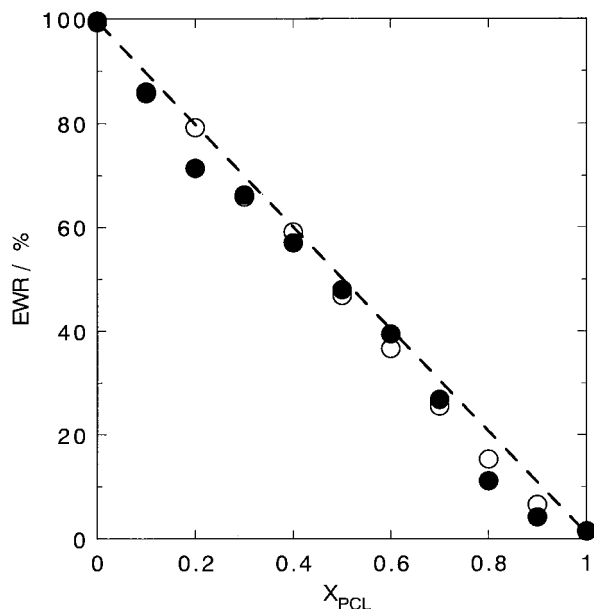
Figure 4 EWR of films of PCL-PEO(L) (○) and PCL-PEO(H) (●) as a function of X_{PCL}; (- - -) expected EWR.

these two polymers at these specific X_{PLLA} values decreased the nucleus density of PLLA crystallites or hindered growth of the crystallites during solvent evaporation, resulting in imperfect crystallization of PLLA.

As seen in Figure 2(b), the T_m of PCL and PEO(L) in their blend films and the T_m of the blend films of PCL-PEO(H) were practically constant, re-
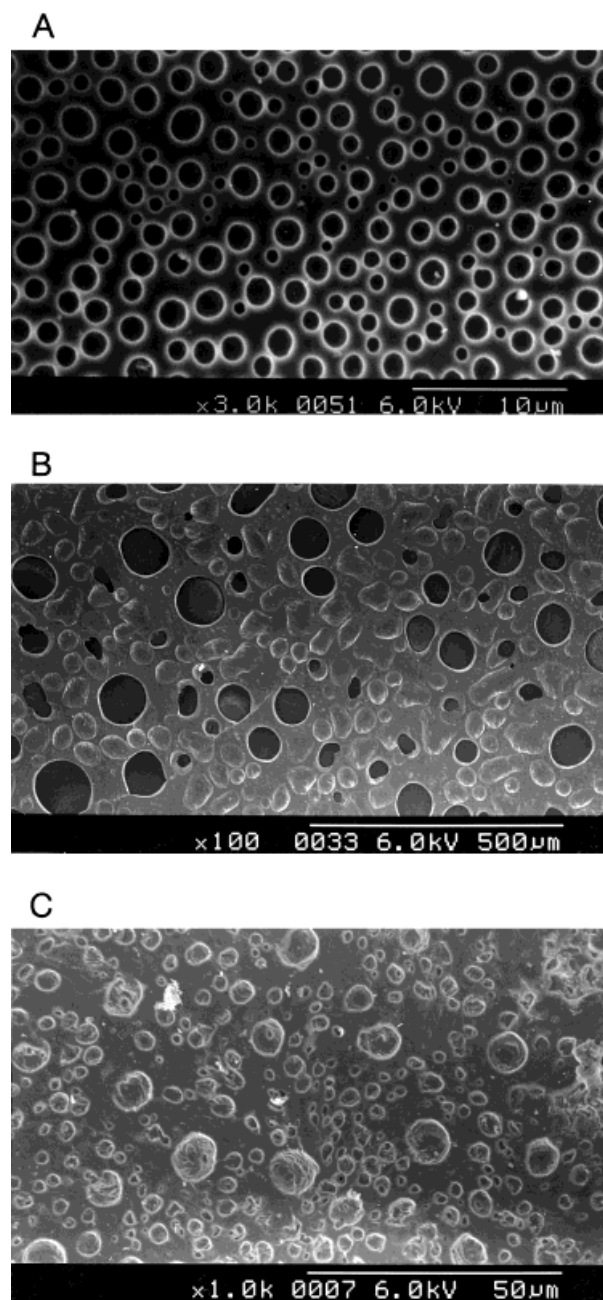
A

B

C

Figure 5 SEM photographs of water-extracted films of PCL-PEO(L) with X_{PCL} of 0.9 (A) and 0.6 (B) and of PCL-PEO(H) with X_{PCL} of 0.6 (C).

the blend films before water extraction. This means that PCL and PEO(L) were crystallizable in the presence of another polymer component during solvent evaporation and also suggests that PCL and PEO(L) were phase-separated after solvent evaporation. The crystallization of PCL and PEO(H) in their as-cast blend films cannot be estimated from the DSC measurements because of the overlap of their melting peaks around 65°C.

The total enthalpy of melting of PCL and PEO ($\Delta H_{m,tot}$) and T_m of the as-cast PCL-PEO(L) and PCL-PEO(H) films were evaluated from the DSC thermograms and are plotted in Figure 2(a) and (b), respectively, as a function of X_{PCL}. Figure 2(a) shows that $\Delta H_{m,tot}$ of the as-cast films agrees well with the expected values, assuming that PCL and PEO crystallized unaffected with each other, irrespective of X_{PCL} and the molecular weight of PEO. This suggests that PCL and PEO crystallized separately after their phase separation, regardless of X_{PCL} and the molecular weight of PEO. If PCL and PEO were kept miscible during solvent evaporation or crystallization, $\Delta H_{m,tot}$ would have become lower than the expected value as a result of the reduced ΔH_m of the polymer component, which crystallized later. A decrease in total enthalpy of melting and crystallization for PLLA was reported for the blend film of PLLA and PEO(H) at a polymer composition $[X_{PLLA}$ (w/w) = PLLA/(PEO + PLLA)] of 0.9 and for the blend film of PLLA and PEO(L) at $X_{PLLA} = 0.6$.[9] It is probable that the relatively high miscibility of
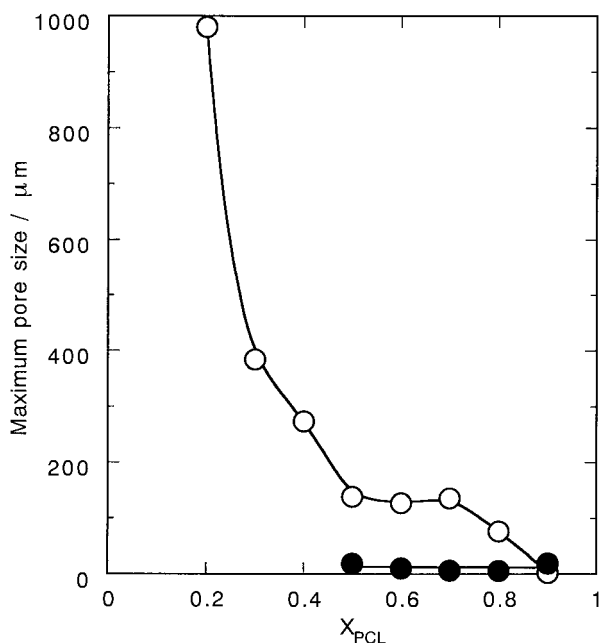
Figure 6 Maximum pore size of water-extracted films of PCL-PEO(L) (○) and PCL-PEO(H) (●) as a function of X_{PCL}.

gardless of X_{PCL}, thus confirming that PCL and PEO were phase-separated before their crystallization. Seemingly the single melting peak was noticed for all the blend films of PCL-PEO(H), irrespective of X_{PCL}, because of the overlapping of the respective melting peaks of PCL and PEO(H), as mentioned earlier. However, the slight decrease in T_m of PCL and PEO(L) with a rise in the fraction of another component may be the result of the imperfect crystallite growth of the major component in the presence of a small amount of the minor component in the respective phases.

Crystallization during Water Extraction

Figure 1 also illustrates the DSC thermograms for the films of PCL-PEO(L) after water extraction (dashed lines). Evidently, the melting peak of PEO(L) observed around 40°C for the as-cast blend films disappeared completely after water extraction, meaning that PEO(L) was completely dissolved and removed from the films. The slight rise in T_m of PCL, around 65°C, of the water-extracted films implies that the crystalline thickness of PCL increased during water extraction or drying. Probably, PEO molecules trapped in the amorphous region between the PCL crystalline regions may have hindered the crystalline growth of PCL during solvent evaporation. It seems prob-

able that the removal of PEO molecules trapped in the amorphous region between the PCL crystalline regions allowed PCL chains in the amorphous region to recrystallize.

Both x_c and T_m of PCL in the water-extracted films evaluated from DSC thermograms are plotted in Figure 3(a) and (b), respectively, as a function of X_{PCL}; x_c and T_m of PCL for the water-extracted films are virtually constant, regardless of X_{PCL} and the molecular weight of PEO. This means that altering the porosity and pore size of the PCL films, which are estimated below, did not vary their highly ordered structures such as fraction of crystalline region and crystalline thickness. In other words, porous PCL films having similar x_c and crystalline thickness can be prepared by the method of solution casting and subsequent water extraction.

Porosity

The EWR of the films, plotted in Figure 4 as a function of X_{PCL}, was in good agreement with that expected under the assumption that all the PEO molecules were completely water-extracted from the as-cast films, irrespective of X_{PCL}. The as-cast PCL-PEO(H) films became small fragments after water extraction when X_{PCL} was lower than 0.5. Almost complete extraction of PEO(L) with water and porous film formation regardless of X_{PCL} means that both the PCL-rich phase and the PEO(L)-rich phase were continuous in all the PCL-PEO(L) films before water extraction, regardless of X_{PCL}.

The small shifts of EWR of the PCL-PEO(H) films at $X_{PCL} = 0.8$ and 0.9 to lower values from those expected imply that part of the PEO(H) molecules could not diffuse out from these as-cast films, probably because the PEO(H)-rich phase was dispersed in the continuous PCL-rich phase in these films.

Morphology

Figure 5 shows typical SEM photographs of the water-extracted blend films of PCL-PEO(L) with $X_{PCL} = 0.9$ and 0.6 and that of PCL-PEO(H) with $X_{PCL} = 0.6$. Pores were noticed on the surfaces of all these films. No pores were noticed on the surface of the water-extracted nonblended PCL film (photo not shown). This finding and the DSC result confirm that PCL and PEO were phase separated after solvent evaporation, as can be expected from their calculated solubility parameter (δ) values [δ (PCL) = 20.8 (J$^{0.5}$ cm$^{-1.5}$),[31] δ (PEO)
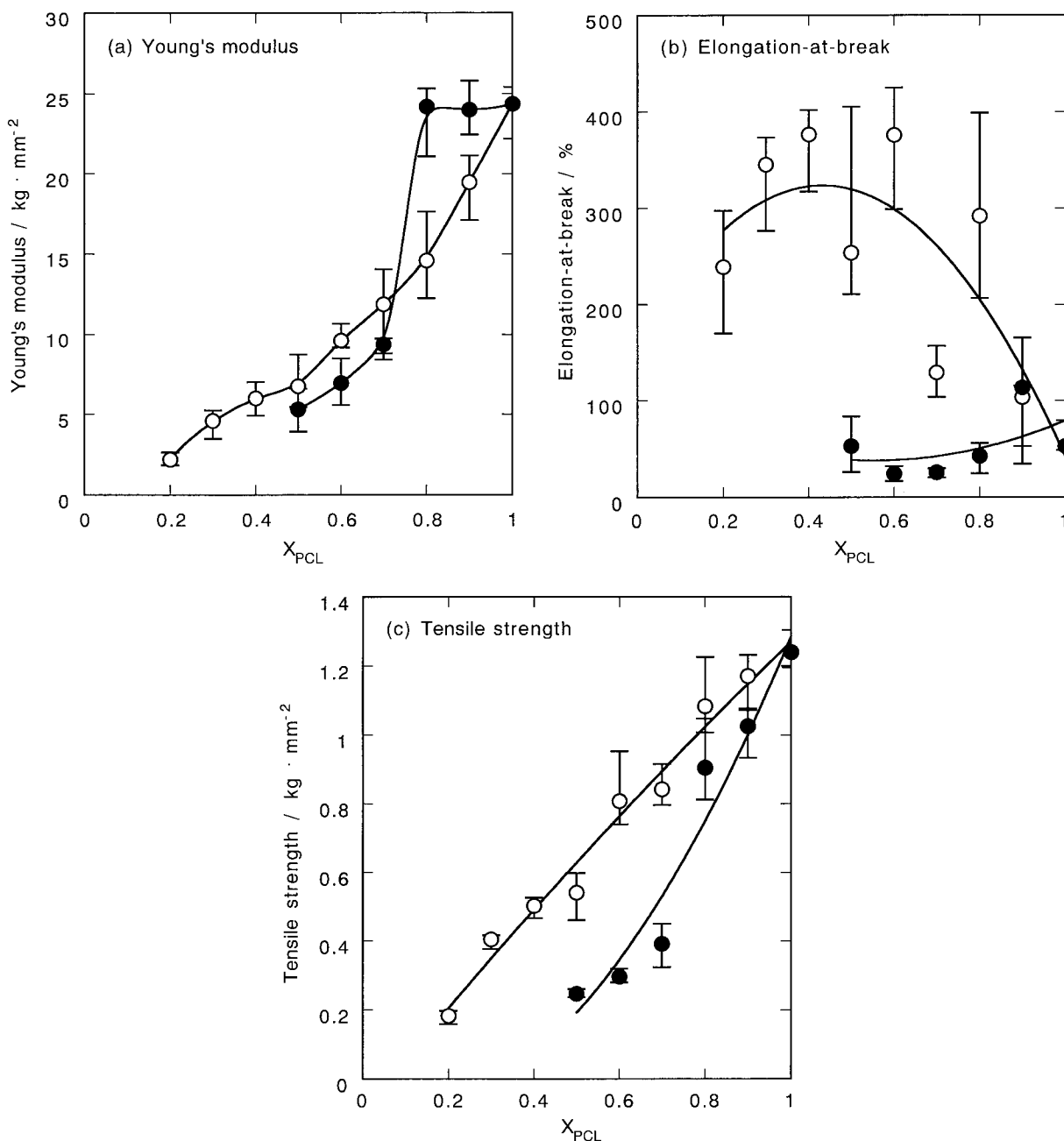
Figure 7 Young's modulus (a), elongation-at-break (b), and tensile strength (c) of water-extracted films of PCL-PEO(L) (○) and PCL- PEO(H) (●) as a function of X_{PCL}.

$= 17.8$ ($J^{0.5}$ $cm^{-1.5})^{32}$]. The water-extracted films of PCL-PEO(L) had round pores with clear edges, whereas the pore shape in films of PCL-PEO(H) was rather strained-round and their edges were indistinct. The maximum pore size for the water-extracted PCL-PEO(L) films increased from 3 to 100 μm when X_{PCL} was reduced from 0.9 to 0.6. The maximum pore size at $X_{PCL} = 0.6$ was higher for the water-extracted film of PCL-PEO(L) than that for the film of PCL-PEO(H).

Pore Size

The maximum pore sizes were evaluated from the SEM photographs of the water-extracted films of PCL-PEO(L) and PCL-PEO(H) and are plotted in Figure 6 as a function of X_{PCL}. It can be seen that the maximum pore size increased with a decrease in X_{PCL} and reached around 1000 μm at $X_{PCL} = 0.2$ for the water-extracted PCL-PEO(L) films, whereas that of water-ex-
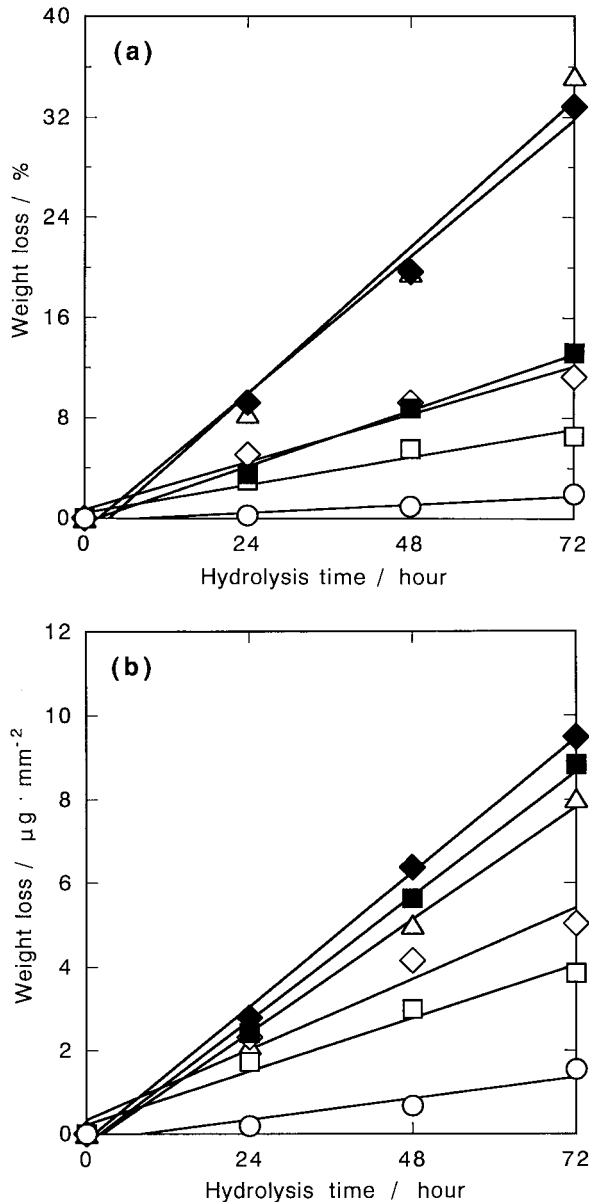
Figure 8 Percentage weight loss (a) and weight loss per unit apparent surface area (b) of water-extracted films of nonblended PCL (○), PCL-PEO(L) (□, ◇, △), and PCL-PEO(H) (■, ◆) hydrolyzed enzymatically as a function of hydrolysis time: $X_{PCL} = 1$ (○); 0.7 (□,■); 0.5 (◇, ◆); 0.3 (△).

tracted PCL-PEO(H) films did not depend on X_{PCL}. The water-extracted films of PCL-PEO(L) had maximum pore sizes larger than those of PCL-PEO(H) when compared at the same X_{PCL} below 0.8. This suggests that the domain size of the PEO-rich phase in the as-cast blend films decreased when the molecular weight of PEO increased. The high mobility of PEO(L) com-

pared with that of PEO(H) may have enhanced its association to form large domains in the as-cast PCL-PEO(L). The molecular weight effects on the pore size were reversed for the porous PLLA films prepared using the same PEOs utilized in this study.[9] In this case, the entropy of mixing may have stabilized the PLLA–PEO(L)–solvent system compared with the PLLA–PEO(H)–solvent system. Figures 4 and 6 revealed that the porosity and pore size can be controlled by X_{PCL} and molecular weight of PEO, and probably also by the rate of solvent evaporation and the type of solvent.

Tensile Properties

The Young's modulus, elongation-at-break, and tensile strength of the water-extracted films are plotted in Figure 7(a), (b), and (c), respectively, as a function of X_{PCL}. The Young's modulus for the water-extracted films of PCL-PEO(L) decreased monotonously with decreasing X_{PCL} and finally reached 2.2 kg/mm^2 at $X_{PCL} = 0.2$, which is one order smaller than 24 kg/mm^2 of the nonblended PCL and comparable to 1.0 kg/mm^2 of the as-cast poly(L-lactide-*co*-ε-caprolactone) (PLLA-CL) film.[8] This means that pores in the PCL films efficiently enhanced their flexibility, and the soft biodegradable materials having Young's modulus as low as
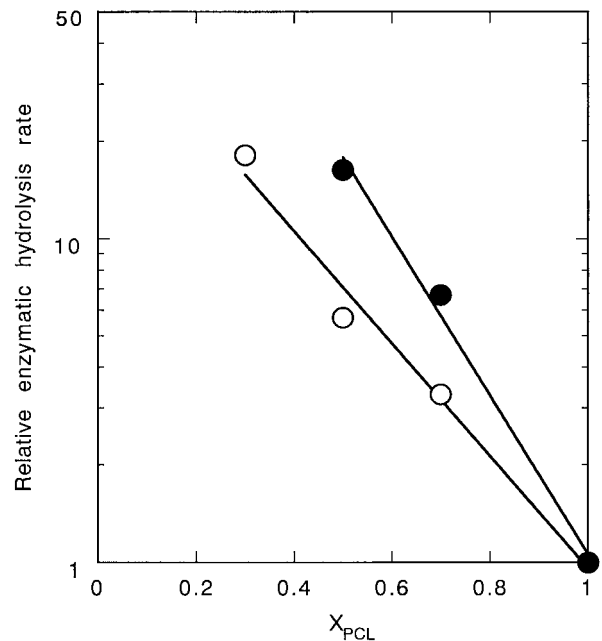

Figure 9 Enzymatic hydrolysis rate of water-extracted films of PCL-PEO(L) (○) and PCL-PEO(H) (●) relative to that of nonblended PCL film.
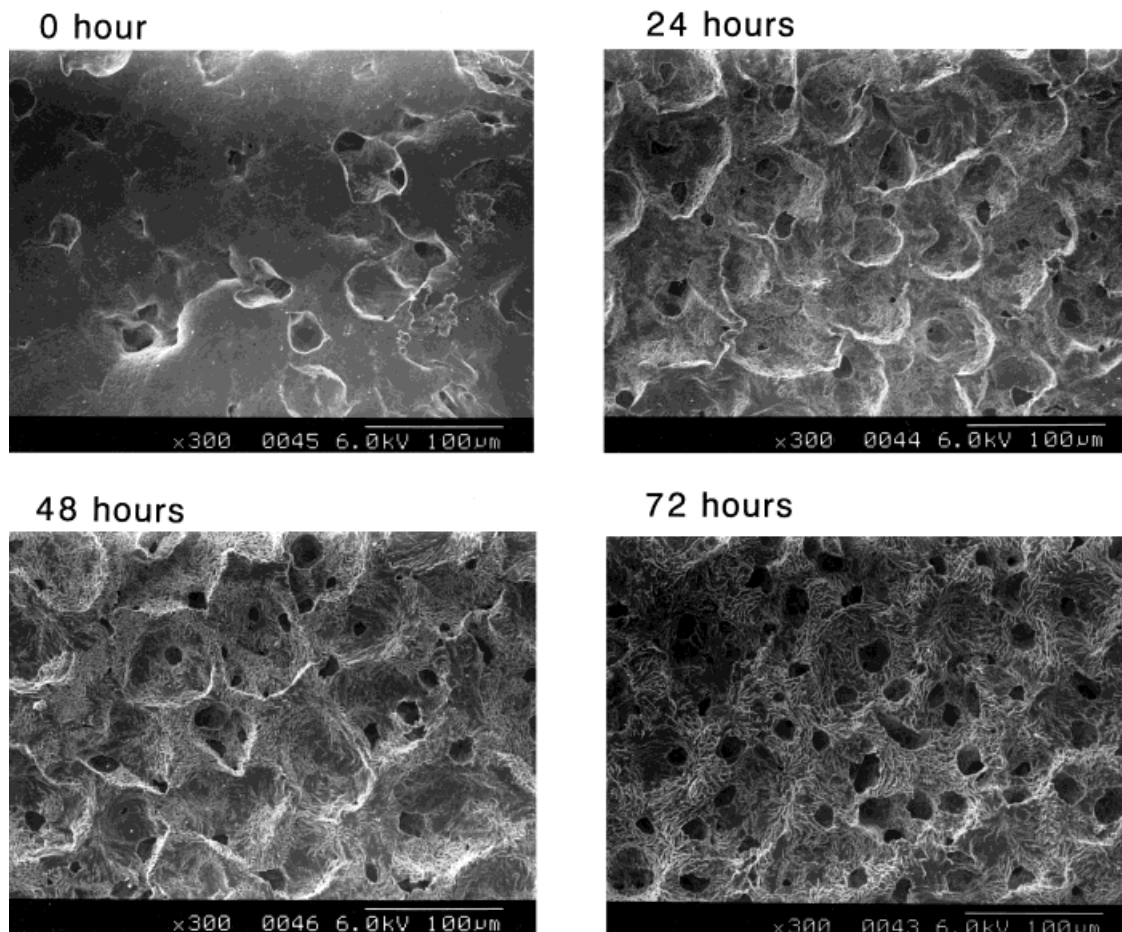
0 hour

24 hours

48 hours

72 hours

Figure 10   SEM photographs of water-extracted films of PCL-PEO(L) with $X_{PCL} = 0.5$ before and after enzymatic hydrolysis for different times.

$2 \ \text{kg/mm}^2$ can be prepared by the pore formation in the films without utilizing the copolymerization method. On the other hand, the Young's modulus of the water-extracted PCL-PEO(H) films remained unchanged for X_{PCL} between 1 and 0.8 and decreased dramatically with a decrease in X_{PCL} below 0.7, finally reaching $5.3 \ \text{kg/mm}^2$ at $X_{PCL} = 0.5$. The Young's modulus of the as-cast PLLA-CL film increased from 1.0 to $9.2 \ \text{kg/mm}^2$ after storage at room temperature for 2 months because of crystallization of L-lactide sequences in the copolymer.[8] Such crystallization during storage would not occur in the water-extracted PCL-PEO films because their crystallization almost completed during solvent evaporation and water extraction.

The elongation-at-break of the water-extracted PCL-PEO(L) films increased with a decrease in X_{PCL} from 1 to 0.5 and then decreased at X_{PCL} below 0.5. In contrast, the elongation-at-break of the water-extracted films of PCL-PEO(H) decreased slightly with decreasing X_{PCL}.

The tensile strength of the water-extracted PCL-PEO(L) and PCL-PEO(H) films decreased slowly and rapidly, respectively, with a decrease in X_{PCL}. In other words, the tensile strength was greater for the water-extracted films of PCL-PEO(L) than for those of PCL-PEO(H), when compared at the same X_{PCL}. The different dependencies of these tensile properties on X_{PCL} between the water-extracted films of PCL-PEO(L) and PCL-PEO(H) may result from the difference in the morphology and size of the pores and in the amount of PEO molecules remaining after water extraction between these two series of films.

Enzymatic Hydrolysis

The results of enzymatic hydrolysis of the water-extracted films are given in Figure 8. As men-

tioned earlier, the x_c's of the porous PCL films were virtually constant, irrespective of X_{PCL} and the molecular weight of PEO used for film preparation; therefore, only the effects of porosity and pore size on their hydrolysis could be investigated using these films. The weight loss of all the films increased linearly with hydrolysis time without any induction periods. The enzymatic hydrolysis rate increased with a decrease in X_{PCL} and an increase in the molecular weight of PEO. As shown in Figures 4 and 6, the porosity increased with decreasing X_{PCL} and the maximum pore size was smaller for the water-extracted films of PCL-PEO(H) than for those of PCL-PEO(L), when compared at the same X_{PCL}. It is well known that the enzymatic hydrolysis of aliphatic polyesters proceeds mainly via the surface-erosion mechanism.[13,22–27] It is probable that the high porosity and small pore size enlarged the surface area per unit weight, resulting in the accelerated enzymatic hydrolysis of the films.

Figure 9 gives the enzymatic hydrolysis rate of water-extracted blend films relative to that of the nonblended PCL film. Evidently, the relative hydrolysis rate of the water-extracted blend films increased dramatically with a decrease in X_{PCL} or porosity and finally reached 20-fold that of the nonblended PCL film. This finding reveals that biodegradable nonporous PCL materials having a hydrolysis rate as high as 20-fold that of the nonblended nonporous PCL can be prepared by increasing the porosity.

Figure 10 shows the SEM photographs of the water-extracted film of PCL-PEO(L) with X_{PCL} = 0.5 subjected to the enzymatic hydrolysis for varying times. It is seen that the initial smooth surface of the film became rough and the pore density increased with hydrolysis time. The wrinkles were formed during the enzymatic hydrolysis, which may be ascribed to preferred enzymatic hydrolysis and removal of the chains in the amorphous region, as reported by Mochizuki et al.,[17] leaving the chains in the crystalline region.

Alkaline Hydrolysis

The result of alkaline hydrolysis of the water-extracted films is given in Figure 11. The weight loss of the films started to increase after a short induction period and the weight loss rate increased with hydrolysis time and then decreased. The weight loss occurred rapidly for the films prepared at low X_{PCL} and using PEO(H). This is very similar to the above-mentioned result for their enzymatic hydrolysis.
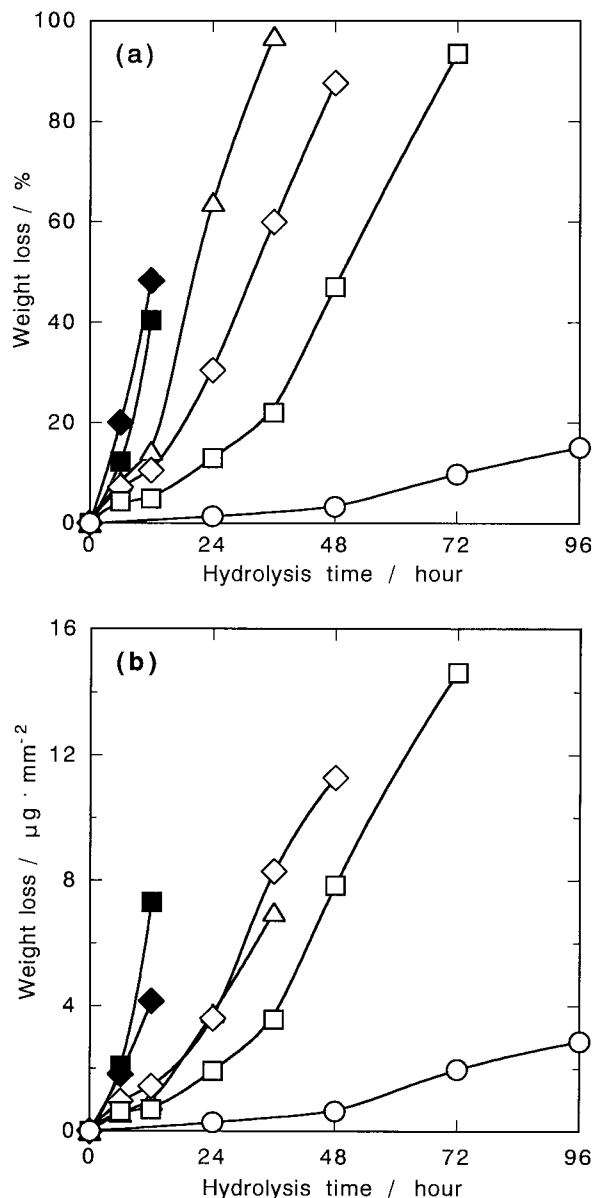

Figure 11 Percentage weight loss (a) and weight loss per unit apparent surface area (b) of water-extracted films of nonblended PCL (○), PCL-PEO(L) (□, ◇, △), and PCL-PEO(H) (■, ◆) hydrolyzed in alkaline solution as a function of hydrolysis time: X_{PCL} = 1 (○); 0.7 (□, ■); 0.5 (◇, ◆); 0.3 (△).

Like PLLA,[28] the alkaline hydrolysis of PCL may have proceeded mostly via the surface-erosion mechanism and, therefore, the alkaline hydrolysis rate was higher for the porous PCL films that were prepared at low X_{PCL} using PEO with the high molecular weight, thus having higher surface areas per unit weight or having high porosities and small pore sizes.

The difference in the weight loss behavior between the films hydrolyzed in these two media must be the result of the difference in the position of the chains where hydrolytic scission occurs. The linear increase of the weight loss of the enzymatically hydrolyzed films strongly suggests that the hydrolytic scission occurs at an end of the polymer chain, whereas the significant induction period for weight loss and the initial increase in hydrolytic rate of the alkaline hydrolysis may be the result of random hydrolytic scission of the polymer chain.

CONCLUSIONS

Porous PCL films were prepared by water extraction of the PEO component from solution-cast blend films from PCL and PEO. Their pore size and porosity were controllable by varying the blend ratio of the two polymers and the molecular weight of PEO. The Young's modulus of the porous PCL films was lowered to one tenth that of the nonblended PCL film and their enzymatic hydrolysis rate per unit weight increased up to 20-fold that of the nonblended nonporous PCL film.

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