Structure and Physical Properties of Cellulose Acetate/Poly(L-lactide) Blends

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ABSTRACT: Two biodegradable polymers, poly(L-lactide) (PLLA) and cellulose acetate (CA), were solvent-cast-blended with chloroform. Macrophase separation took place without a compatibilizer. However, homogeneous blend films were obtained with the addition of tetraisopropyl titanate (TP) as a compatibilizer to the blend. We investigated the reasons for the blends exhibiting homogeneity and measured the physical properties of the blends. We reached the following conclusions: (1) the addition of TP produces small PLLA crystallites in the PLLA/CA blends, (2) the addition of TP reduces the thermal decomposition temperature of PLLA/CA blends, (3) Young's modulus of the blends is almost independent of the blend ratio, and (4) the introduction of TP assists with the hydrolysis of the blends. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1219–1226, 2002

Key words: biodegradable; blends; differential scanning calorimetry (DSC)

INTRODUCTION

Nowadays, the recycling and biodegradability of materials are important problems. It is thought that some materials used for disposable purposes should have biodegradability. Biodegradable polymers are promising candidates for these materials. Because many kinds of materials are used in various disposable applications, biodegradable materials should be prepared with various properties suitable for end uses. Although there are many methods of preparation, polymer blending would be the most convenient.

Poly(L-lactide) (PLLA) is a biodegradable polymer, and its melting point (T_m) is higher than that of other biodegradable aliphatic polymers such as poly(ϵ-caprolactone) and poly(butylene succinate) (PBS).[1] PLLA has been used not only in packaging but also in orthopedic surgery; the polymer is biocompatible with human tissues. Because PLLA has several advantages, many studies have been performed.[2–5] In particular, the hydrolysis and biodegradation mechanisms of PLLA films have been extensively studied by many authors.[6–9]

Cellulose acetate (CA) is made from natural resources; some of the three OH groups in a glucose unit of cellulose are substituted for $OCOCH_3$ groups. It is known that the biodegradability of CA depends on the degree of substitution (DS). Biodegradation can be observed in a sample with a DS of less than 2.5;[10] the CA used in this work was biodegradable on the basis of its DS value. It is usually an amorphous and rigid polymer according to its molecular structure. Because there is a large difference in the molecular structures of PLLA and CA, a new material would be produced from the blending of these polymers.

Tetraisopropyl titanate (TP) is a transition-metal alkoxide that has relatively high reactivity;

its chemical structure is Ti[—O—CH—(CH$_3$)$_2$]$_4$. The blending of CA with the alkoxide has been performed, and it has been reported that there is an interaction between these materials.[11,12] Taking account of these reports, we believe that TP could be used as a compatibilizer for a PLLA/CA blend system; there is no study in which a transition-metal alkoxide has been used as a compatibilizer for polymer blends as far as we know.

We have previously reported that cellulose triacetate (CTA) is miscible with PBS.[13] Using this blend system, we investigated the effect of the addition of TP on the structure of PBS/CTA blends.[14] On the basis of this work, we concluded that the addition of TP causes PBS crystallites to become small. Furthermore, we have studied the structure and physical properties of TP/PBS/CA blends.[15] As an extension of that work, we investigated the structures and physical properties of TP/PLLA/CA blends in this study.

EXPERIMENTAL

Materials

The PLLA used was supplied by Shimadzu, Ltd. (Kyoto, Japan); its trade name is PLLA #5000. Its weight-average molecular weight was 19.4 × 10^4, and its optical purity was 99.0%. The chemical structure of the repeat unit is [—O—CH(CH$_3$)—CO—]$_n$. CA was purchased from Wako Pure Chemicals Industries, Ltd. (Tokyo, Japan); its weight-average molecular weight was 45,000, and its acetyl content was 39.78%. From the value of the acetyl content, the DS was calculated and found to be 1.52. According to this value, the CA used in this work was biodegradable.

A reagent grade of chloroform (Nacalai Tesque Inc., Kyoto, Japan) was used as a cosolvent for these polymers without further purification. For the sufficient dissolution of CA in chloroform, we added a small amount of ethanol to the solution. Furthermore, an extrapure reagent grade of TP (Nacalai Tesque) was used as a compatibilizer.

Preparation of the Blends

Specified amounts of PLLA and CA were placed in a beaker; the total amount of these materials was 1 g, and 10–30 mL of chloroform and 2 mL of ethanol were added. The amount of chloroform was usually 30 mL, unless otherwise noted. After being stirred vigorously for about 2 h, the mixture became a homogeneous solution. TP (100 μL) was further added to the solution as a compatibilizer; the function of TP in the solution is discussed later. With the addition of TP, the viscosity of the solution was markedly increased. To control the viscosity, we changed the amount of chloroform. After being stirred for about 15 min, the solution was cast into a glass Petri dish. After chloroform was vaporized at 0°C, homogeneous films about 0.15 mm thick were obtained. The physical properties of the blend films were measured. A blend film containing a given amount of PLLA is denoted $\phi_{PLLA} = X$, where X represents the weight percentage of PLLA in the blend. Samples containing no TP were also made for comparison and are denoted $\phi_{PLLA} = X$ (TP = 0).

Characterization of the Blends

For the measurement of the transparency of the blend films, a light transmittance test was performed with a Shimadzu UV-2100 spectrometer; a wavelength of 500 nm was used. The viscosity of the blend solution was measured with a Yamaichi VM-1G-M viscosity meter (Tokyo, Japan). The evaluated value does not represent an accurate value of the viscosity in a strict sense because the viscosity is evaluated from the induced force on a probe, which vibrates in an immersing solution.

The thermal behavior of the blends was measured with a Shimadzu DSC-60 differential scanning calorimeter at a heating rate of 10°C min^{-1}. The nonisothermal crystallization behavior of the blends was also measured with differential scanning calorimetry (DSC). The blends were heated to 220°C at a heating rate of 20°C min^{-1}, held for 10 min at that temperature for the destruction of all crystallites, and cooled down to room temperature at a cooling rate of 5°C min^{-1}. The crystallization behavior was recorded during the cooling process. T_m and the heat of fusion (ΔH_m) were evaluated from the maximum position of the endothermic peak and its area on the DSC curves, respectively. Similarly, the crystallization temperature (T_c) and the calorific value during crystallization (ΔH_c) were evaluated from the peak position and its area, respectively.

Thermogravimetric analyses (TGAs) of the blends were performed by a piece of the material being placed in a platinum dish and heated from room temperature to 500°C under a nitrogen atmosphere at a heating rate of 5°C min^{-1} with a Shimadzu thermogravimetric analyzer (DTG-60).

Dynamic mechanical analyses (DMAs) of the blends were performed with a Rheometric Scientific RSA II viscoelastic analyzer. Temperature scans at a 1-Hz frequency were carried out at a heating rate of 2°C min^{-1}. The glass-transition temperature (T_g) was evaluated from the peak position of an E''–temperature curve.

The tensile tests for the blends were performed at room temperature on a Tensilon UTM-II-20 tensile tester (Toyo Baldwin Co., Ltd., Tokyo, Japan); the crosshead speed was 10 mm min^{-1}, and the initial gauge length was 50 mm.

Hydrolysis of the Blends

About 0.1 g of a blend film 0.1 mm thick was hydrolyzed at 40°C with a 0.1N NaOH aqueous solution (30 mL) that was shaken at a constant speed; we determined the normality of the solution to finish the hydrolysis of the blends within a week. The samples were removed from the solution after a given time, washed with water for about 5 h, and dried at 50°C. The weight of the remaining dried samples was measured. Molecular weights and their distribution for the remaining samples were also evaluated in chloroform at 40°C with a Tosoh gel permeation chromatography (GPC) system (HLC-8220GPC; Tosoh Co., Tokyo, Japan); three TSK (HM-N) gel columns were used, and the measured molecular weights were calculated by the universal calibration method with nine polystyrene reference materials. The hydrolyzed blend samples (7 mg) were dissolved in 5 mL of chloroform. After the elimination of insoluble matter from the solution by filtration, 20 μL of the solution was injected into the GPC system.

RESULTS AND DISCUSSION

Structure of the Blend Films

Figure 1 shows the effect of the addition of TP on the structural homogeneity of the blend films. The addition of TP seems to prevent the macrophase separation and form homogeneous films. This result suggests that the addition of TP makes the PLLA crystallites small and disperses them homogeneously. A similar effect of TP on the homogeneity of the films has been observed in TP/PBS/CA blends.[15] We have also reported that small PBS crystallites are formed by the addition of TP in PBS/CTA blend systems.[14] From addi-
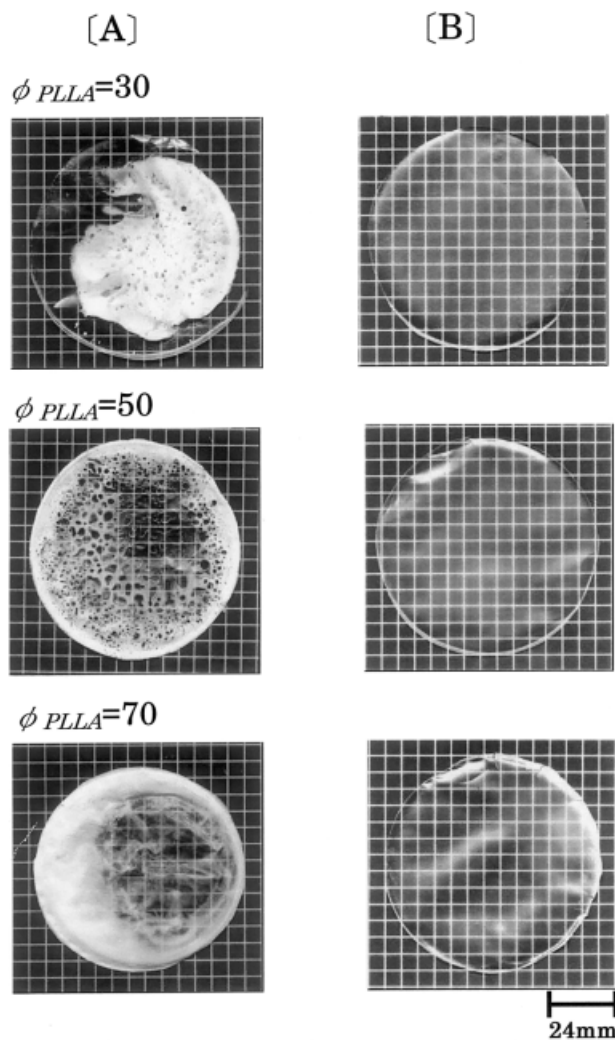

Figure 1 Photographs of the blend films placed on section board: (A) no addition of TP and (B) the addition of TP (100 μL).

tional tests, we found that the homogeneity is influenced by the viscosity and temperature of the solution. Taking account of these results, we suggest that the structure of the TP/PLLA/CA blends is in a pseudostable state. From an engineering point of view, a fine continuous fiber would be made from a TP/PLLA/CA blend with the addition of TP; the inhomogeneous structure prevents the formation of fine continuous fibers. Actually, we obtained a fine homogeneous fiber from the TP/PLLA/CA blends.

Figure 2 shows the effects of the PLLA content (ϕ_{PLLA}) on the transparency and homogeneity of the blend films. The transparency decreases with increasing ϕ_{PLLA} up to about $\phi_{PLLA} = 30$, above which it remains almost constant and then in-
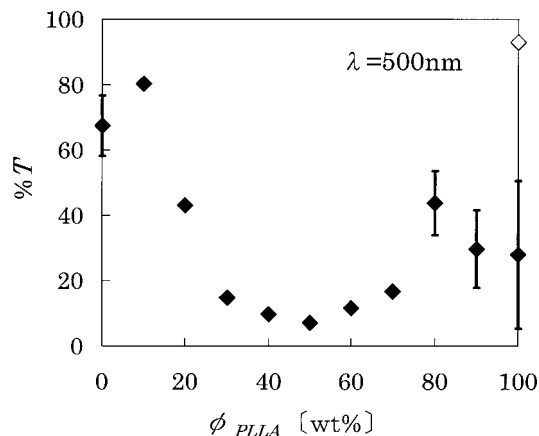
Figure 2 Effect of ϕ_{PLLA} on the transparency of the blend films.

Figure 4 DSC curves of the blends.

creases again. Figure 3 shows the effect of the addition of TP on the viscosity of the blend solutions. The viscosity of the solution containing no TP increases slightly with increasing ϕ_{PLLA}. It is clear that the addition of TP increases the viscosity of the blend solution. The increase in the viscosity of the $\phi_{\text{PLLA}} = 100$ sample is larger than that of the $\phi_{\text{PLLA}} = 0$ sample; the viscosity of the $\phi_{\text{PLLA}} = 100$ sample is increased about three times with the addition of TP. This result suggests that the interaction between PLLA and TP is relatively strong. The characteristics of the interactions were investigated with ^{1}H-NMR and ^{13}C-NMR techniques in a liquid state. However, evidence for the interactions was not obtained. This result may mean that the interactions are not so strong that these interactions cannot be observed with NMR. Anyway, the reaction mech-
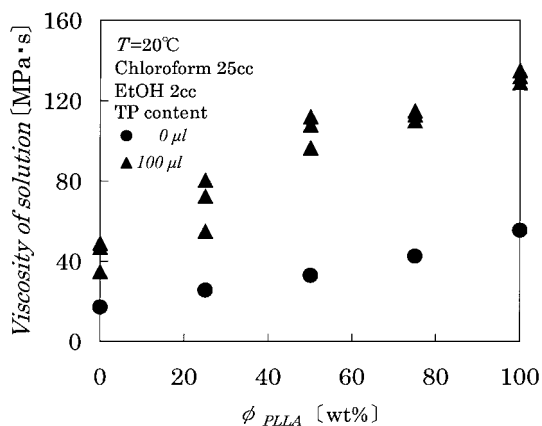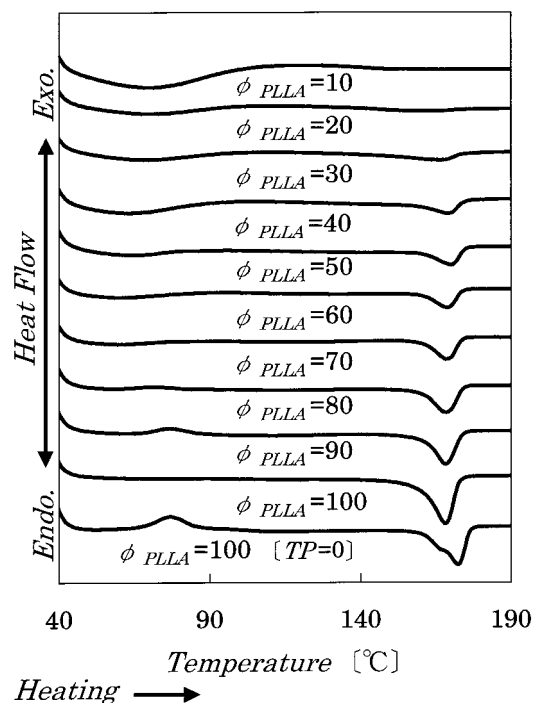
anisms of TP with CA and PLLA are not clear in this stage.

Thermal Properties of the Blend Films

Figure 4 shows the DSC curves of the samples. An endothermic peak can be seen at approximately 175°C in each blend sample; this temperature corresponds to T_m of PLLA. The neat PLLA sample ($\phi_{\text{PLLA}} = 100$, TP = 0) shows an exothermal peak at about 80°C. Because such a peak cannot be seen in the blends, CA and TP seem to induce the crystallization of PLLA. To discuss the effect of ϕ_{PLLA} on the melting behavior of PLLA in detail, we evaluated the values of T_m and ΔH_m for each sample. The results are shown in Figure 5. A straight and solid line is drawn through the values of ΔH_m at $\phi_{\text{PLLA}} = 0$ and $\phi_{\text{PLLA}} = 100$ (TP = 0), where the value of ΔH_m at $\phi_{\text{PLLA}} = 0$ is zero. The T_m values of the blends are lower than those of neat PLLA (TP = 0), and T_m has a maximum at $\phi_{\text{PLLA}} = 50$. Moreover, the experimental ΔH_m values deviate downward from the straight line, except for $\phi_{\text{PLLA}} = 30$ and $\phi_{\text{PLLA}} = 40$. These results imply that the addition of TP and CA causes the formation of small PLLA crystallites.

The nonisothermal crystallization behavior of the blends was also studied. Figure 6 shows the effects of ϕ_{PLLA} on T_c and ΔH_c. A straight and

Figure 3 Effect of ϕ_{PLLA} and the addition of TP on the viscosity of the blend solutions.
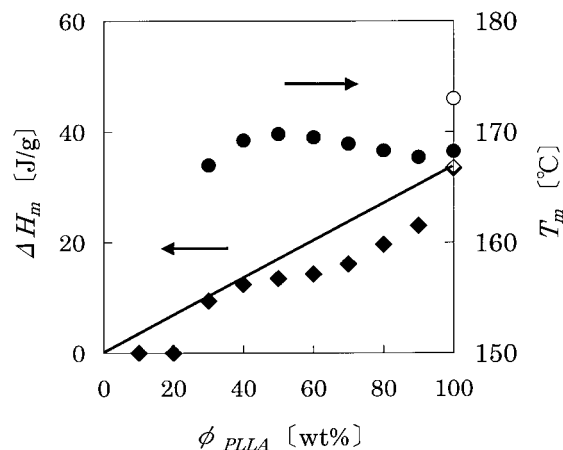
Figure 5 Effect of ϕ_{PLLA} on T_m and ΔH_m of PLLA. Open symbols indicate TP = 0 samples.

solid line is also drawn through the values of ΔH_c at $\phi_{PLLA} = 0$ and $\phi_{PLLA} = 100$ (TP = 0), where the value of ΔH_c at $\phi_{PLLA} = 0$ is zero. The T_c values of the blends are somewhat lower than those of neat PLLA (TP = 0), and T_c has a maximum at ϕ_{PLLA} = 50. The results support the idea that the addition of TP and CA produces small PLLA crystallites. Moreover, the experimental ΔH_c values deviate downward from the straight line, and ΔH_c has a maximum at ϕ_{PLLA} = 50.

Now we discuss the reasons for ΔH_c exhibiting a maximum: ΔH_c originates from the primary crystallization. In PLLA-poor samples, PLLA molecules would form particles, and these particles would be dispersed in the CA matrix. The PLLA molecules in the particles would be confined, even at the melting state, by the CA mole-
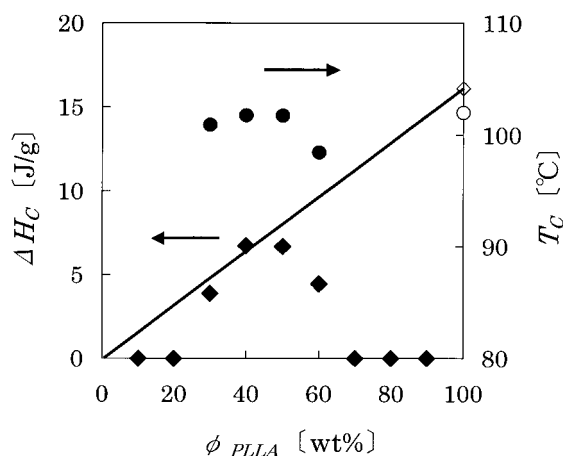

Figure 6 Effect of ϕ_{PLLA} on T_c and ΔH_c of PLLA. Open symbols indicate TP = 0 samples.
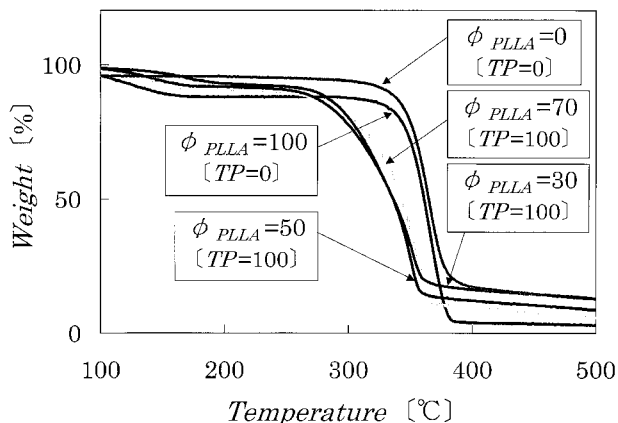

Figure 7 TGA curves of the blends.

cules in the frozen state. Therefore, the PLLA molecules would be freely crystallized during the cooling process from the melt. However, in PLLA-rich samples, CA molecules are supposed to be individually dispersed in the PLLA matrix; of course, there is a possibility that CA molecules form particles in the matrix. The PLLA molecules under the molten state seem to be entangled freely with CA molecules and CA particles. The crystallization rate of polymers is determined by the transport term and the nucleation term.[16] The presence of CA molecules and CA particles may hinder the transportation of PLLA polymer segments to a growing crystal surface. Because T_g of PLLA is high compared with that of other aliphatic polyesters, PLLA molecules are hard to crystallize at a low temperature. Therefore, the aforementioned entanglement may further hinder its crystallization. As described, there is a difference between the crystallization mechanism of PLLA in a PLLA-rich sample and that in a PLLA-poor sample. This difference is likely to responsible for ΔH_c showing a maximum at ϕ_{PLLA} = 50.

We investigated the effect of the addition of TP on the thermal degradation of the blends. Figure 7 shows TGA curves for the blends. The addition of TP seems to reduce markedly the temperature at which decomposition starts. The incorporation of the oxide of TP into the PLLA/CA matrix seems to accelerate the separation of the polymer chains. A similar effect of the addition of alkoxide on the decomposition temperature has been reported for niobium(V) oxide/CA blends.[17]

Mechanical Properties of the Blends

Figure 8 shows the DMA curves of the TP/PLLA/CA blends. The storage modulus (E') de-
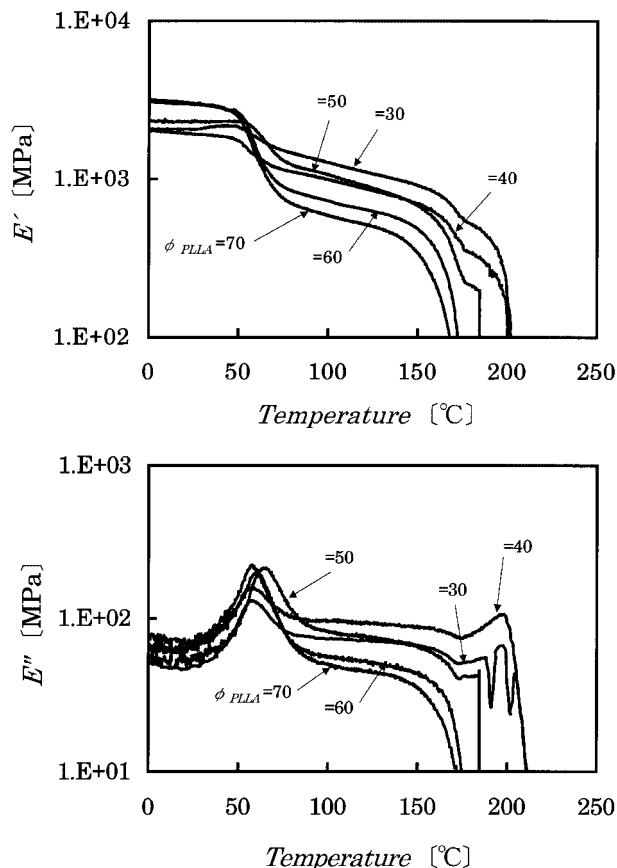
Figure 8 DMA curves of the blends.

creases slightly with increasing temperature and changes abruptly at about 60°C. Above this temperature, it decreases slightly again up to about 170°C and then decreases markedly. The change at about 60°C becomes marked with increasing ϕ_{PLLA}. In curves of the loss modulus (E'') versus the temperature, a peak can be seen at about 60°C in each blend; this peak corresponds to T_g of PLLA. E'' at T_g seems to increase with increasing ϕ_{PLLA}. To discuss the molecular motion of PLLA molecules in detail, we investigated the effects of ϕ_{PLLA} on T_g and E'' at T_g. There is no correlation between T_g and ϕ_{PLLA}. This result implies that the segmental motions of the amorphous PLLA molecules are not largely restricted by the CA and TP molecules. Moreover, E'' at T_g increased with increasing ϕ_{PLLA}. This result means that the amorphous component of PLLA increases with increasing ϕ_{PLLA}.

Figure 9 shows the effect of ϕ_{PLLA} on Young's modulus of the blends. The modulus seems to almost independent of ϕ_{PLLA}. This means that materials with various moduli cannot be obtained from the blend of CA and PLLA.
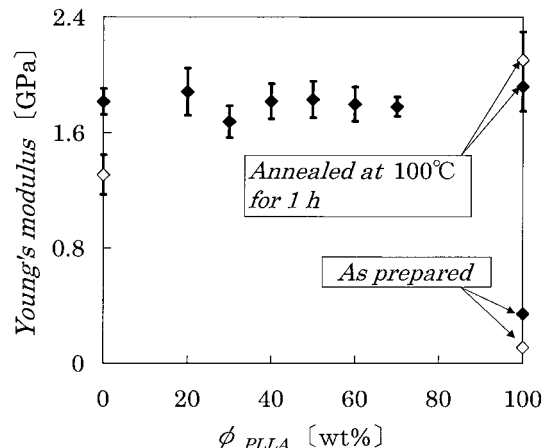

Figure 9 Effect of ϕ_{PLLA} on Young's modulus of the PLLA/CA blends. Open symbols indicate TP = 0 samples.

Hydrolysis of the Blends

Figure 10 shows the mass of the residue of the blends as a function of the hydrolysis time. With an increase in the hydrolysis time, the mass of each sample decreases markedly at first and then indicates a nearly constant value. The sample with high ϕ_{PLLA} indicates a marked decrease. The mass of the residue is thought to decrease with an increase in water-soluble oligomers formed during hydrolysis. If only the PLLA component in the blend were hydrolyzed, the constant value would be determined by ϕ_{PLLA}. However, experimental data demonstrate that the constant value is always lower than that estimated from ϕ_{PLLA}. This means that the CA component is also hydrolyzed
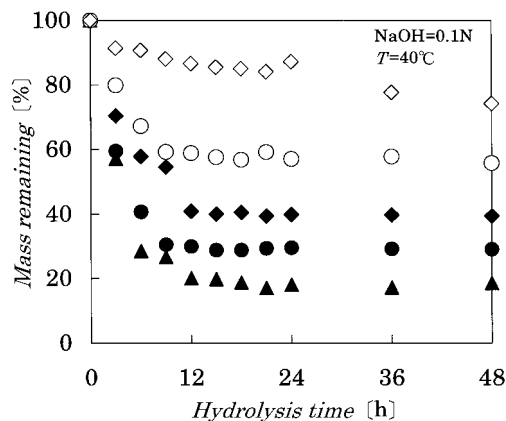

Figure 10 Effect of the hydrolysis time on the mass of the residue of the blends: ($\diamond$) ϕ_{PLLA} = 100 (TP = 0), ($\bigcirc$) ϕ_{PLLA} = 0 (TP = 0), ($\blacklozenge$) ϕ_{PLLA} = 30, ($\bullet$) ϕ_{PLLA} = 50, and ($\blacktriangle$) ϕ_{PLLA} = 70.
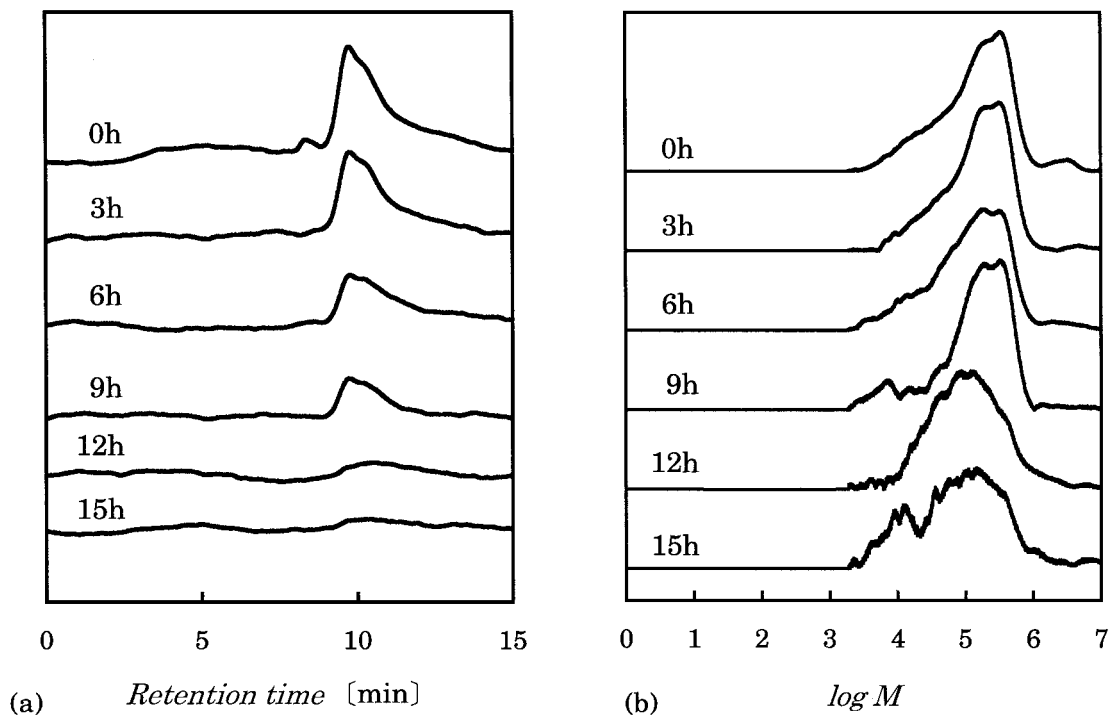
Figure 11   Effect of the hydrolysis time on GPC spectra of $\phi_{PLLA} = 70$ blends.

during the hydrolysis of the blends. It is noted that the mass reduction of the blends is marked with respect to that of the neat PLLA (ϕ_{PLLA} = 100, TP = 0) and CA (ϕ_{PLLA} = 0, TP = 0) samples. This result suggests that the microscopic inhomogeneity of the structure induced by the blend and the introduction of TP assist with the hydrolysis. The aqueous solution could penetrate easily into the phase boundary region of the blends.

Figure 11 shows the effect of the hydrolysis time on GPC spectra of $\phi_{PLLA} = 70$ blends. In Figure 11(a), the peak appearing at a retention time of 10 min becomes flat with an increase in the hydrolysis time. This means that the number of water-soluble oligomers increases with increasing hydrolysis time. Figure 11(b) shows the effect of the hydrolysis time on the molecular weight distribution of $\phi_{PLLA} = 70$ blends; these curves were calculated from Figure 11(a). The peak position is nearly constant up to a hydrolysis time of 6 h, above which the peak shifts to a lower position. The peak position is almost independent of the hydrolysis time up to 6 h even though the mass is reduced to 30% with the hydrolysis time (see Fig. 10). Furthermore, we ascertained that the $\phi_{PLLA} = 70$ blends that were hydrolyzed for 6 h contained the PLLA component, and the T_m

value was independent of the hydrolysis time. On the basis of these results, we propose that the hydrolysis of TP/PLLA/CA blends takes place mainly from the film surface. In our previous works on TP/PBS/CTA[14] and TP/PBS/CA[15] blends, we have proposed that the hydrolysis of these blends occurs uniformly from not only the surface but also the inner part of the blends.

CONCLUSIONS

A new biodegradable polymer composite material was prepared from a blend of PLLA and CA by the addition of TP. The structure and physical properties of the blends were investigated. The following conclusions have been made:

1. There is a possibility that TP is used as a compatibilizer of the PLLA/CA blends. That is, homogeneous films can be obtained from a blend of CA and PLLA by the addition of TP. The viscosity of the PLLA/CA blend solution is increased by the addition of TP. Although TP interacts with PLLA and CA molecules during the solvent blending process, the evidence for interactions cannot be observed with NMR. From

DSC measurements, we conclude that the interactions make PLLA crystallites small in the PLLA/CA blends.
2. The addition of TP decreases the thermal decomposition temperature of PLLA/CA blends.
3. Young's modulus of the blend is almost independent of the CA content.
4. The microscopic inhomogeneity of the structure and the introduction of TP seem to assist with the hydrolysis of the blend materials.

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