Preparation of Poly(L-lactide) Film Having High Elastic Recovery

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ABSTRACT: Triacetin (TAC) is known as a lubricant of poly(L-lactide) (PLLA), and it is used to improve the mechanical properties of PLLA. However, the compatibility of TAC with PLLA and the morphological changes induced by the addition of TAC to PLLA have not been clarified. This study investigates the effects of the addition of TAC on the morphological changes and physical properties of PLLA. We prepared the PLLA films containing a given amount of TAC by solvent-cast blending with chloroform under a low temperature. From the investigation of the mechanical properties of the blends, it is found that the glass-transition temperature of PLLA is remarkably decreased with an increasing amount of TAC, the blend films exhibit high elastic recovery, and the degree of the recovery increases linearly with the amount of TAC. The morphological changes exhibiting high elastic recovery are discussed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 474–480, 2003

Key words: poly(L-lactide); triacetin; blends; mechanical properties; thermal properties

INTRODUCTION

Conventional plastics are made from polyolefin or other nondegradable polymers. The high consumption of these polymers has brought about serious environmental problems. Therefore, replacing these polymers with biodegradable polymers has been expected.

Poly(L-lactide) (PLLA) is an ecofriendly and biodegradable material. That is, the polymer is hydrolyzed, degraded by microbes, and finally changed to carbon dioxide and water under natural circumstances. When PLLA is burned in waste incinerators, toxic gases are not generated. In addition, the furnace is not damaged because the heat of combustion of PLLA is low. Therefore, the use of PLLA as a conventional plastic material would lessen waste problems. Moreover, considering the depletion of fossil resources, PLLA is eminently suitable for use in household and engineering applications because PLLA is synthesized from lactic acid, which is made from plant resources.

PLLA is innocuous and biocompatible with human tissues. Therefore, the polymer has been used not only in the packaging field but also in the orthopedic surgery field.[1,2] Moreover, a further advantage of PLLA is that highly transparent films are obtained from the polymer. Although PLLA has several advantages as described above, it has the disadvantage of indicating poor flexibility for use as conventional plastics. This drawback is ascribed to its high glass-transition temperature (T_g, 58–62°C), compared to that of other biodegradable aliphatic polymers such as poly(ϵ-caprolactone) and poly(butylene succinate).[3,4] To overcome this drawback, one can add lubricants into PLLA. Triacetin (TAC), whose chemical structure is $(CH_3CO_2)_2CH(O_2CCH_3)$, is an ester of oxyacid and a typical lubricant of PLLA.[5] Although flexible PLLA can be obtained by the addition of TAC, its compatibility with PLLA and the morphological changes induced by the addition have not been clarified.

In this work, we investigate the effects of the addition of TAC on the thermal/mechanical properties and morphological changes of PLLA.

EXPERIMENTAL

Materials

The PLLA that was used was supplied by Shimadzu (Kyoto, Japan); its trade name is PLLA 5000. The weight-average molecular weight (M_w) of the PLLA was 19.4×10^4, and its optical purity was 99.0%. The chemical structure of the repeat unit is $[OCH(CH_3)CO]_n$. Reagent grade TAC (Nacalai Tesque, Tokyo) was used as a lubricant. Preliminary experiments revealed that the density of TAC at 17°C was 1.13 g/cm³. Reagent grade chloroform (Nacalai Tesque) was used as a cosolvent of PLLA and TAC without further purification.

Preparation of blends

The PLLA (1 g) was placed in a beaker, and 20 mL of chloroform was added. After being stirred vigorously

for about 4 h, the mixture became a homogeneous solution. A given amount of TAC was added to the solution. After being stirred for about 1 h, the solution was cast in a glass petri dish. A homogeneous film of about 0.15-mm thickness was obtained after the chloroform was vaporized at a temperature below 0°C; the casting temperature is 0°C unless otherwise noted. Highly transparent films were obtained from the neat PLLA that did not contain TAC. However, we obtained opaque films from the neat PLLA cast at room temperature. These results suggest that the crystallization of the neat PLLA is dependent on the casting temperature. In other words, the physical properties of the blends seem to be very sensitive to the casting temperature. After being dried *in vacuo* for 5 days or more, the films were examined to investigate the structure and physical properties. Furthermore, annealed films were obtained by heating for 1 h in an oven at a given temperature. The blends containing X microliters of TAC will be referred to as TACX. Namely, TAC0 and TAC100 denote the neat sample not containing TAC and the blend containing 100 μL of TAC, respectively.

Characterization of blends

In order to measure the transparency of the blend films, we performed a light transmittance test with a Shimadzu UV-2100 spectrometer at a wavelength of 500 nm. Wide angle X-ray scattering curves of the blends were obtained with a Rigaku RINT2000 X-ray diffractometer with nickel-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^{-1}. The melting temperature (T_m) and heat of fusion (ΔH_m) of PLLA were evaluated from the maximum position of the endothermic peak and its area on the DSC curves, respectively.

Mechanical properties of blends

Dynamic mechanical analyses (DMA) of the blends were performed with a Rheometric Scientific RSAII viscoelastic analyzer. Temperature scans at a 1-Hz frequency were carried out with a heating rate of 2°C min^{-1}. We used the annealed samples for the measurements to avoid crystallization during the heating scans. The samples annealed for 1 h at 120°C were used. The storage modulus (E') and the loss modulus (E'') were measured for the annealed samples. The T_g was evaluated from the peak position of the tan δ ($=E''/E'$) versus temperature curve.

The tensile tests for the blends were performed at room temperature with a Tensilon UTM-II-20 tensile tester (Toyo Baldwin Co. Ltd.); the crosshead speed was 10 mm min^{-1} and the initial gauge length was 50
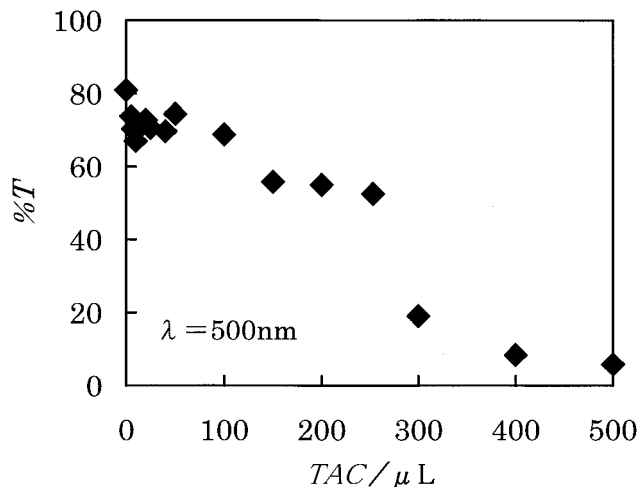
Figure 1   The effect of the amount of TAC on the transparency of blend films.

mm. To estimate the amount of elastic recovery of the blends, we obtained the loading and unloading stress–strain curves. That is, the blends were strained up to 40% and then the load was taken off using the constant crosshead speed. However, we applied the small strain (20%) to the annealed samples to avoid breakage of the blends during elongation. From the data on the applied strain (ε_a) and the measured recovery strain (ε_e), we estimate the degree of the elastic recovery of the blends by using the following equation:

$$E_r = \varepsilon_e / \varepsilon_a$$

Molecular weight distribution of blends

The molecular weight distribution of the blends was evaluated in chloroform at 40°C with a Tosoh gel permeation chromatography (GPC) system (HLC-8220GPC); three TSK(HM-N) gel columns were used. The measured molecular weights were calculated by the universal calibration method using nine polystyrene reference materials. The blend films (10 mg) were dissolved in 5 mL of chloroform, and the solution (20 μL) was injected into the GPC system.

RESULTS AND DISCUSSION

Structure and thermal properties of blend films

Figure 1 shows the effects of the addition of TAC on the transparency of the blend films. The transparency decreases gradually with an increase in the TAC content up to about 250 μL, above which it decreases abruptly. The abrupt decrease may be caused by the formation of large PLLA crystallites in the blends, even at a low casting temperature. The weight percentage of TAC in the blend was estimated from the data on the specific gravity of TAC. Its value in the
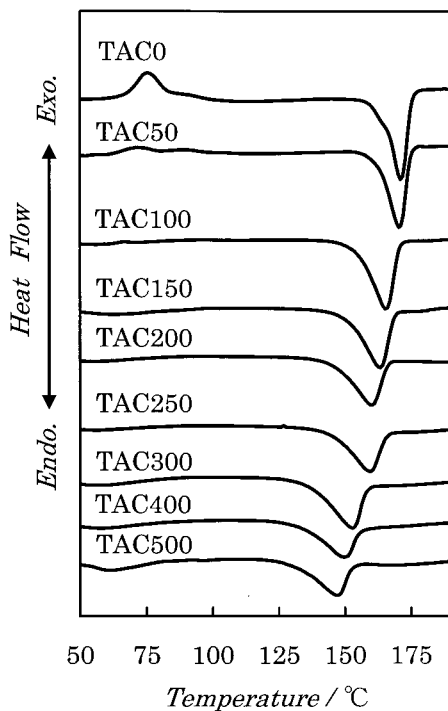
Figure 2 DSC curves of blend films.

Figure 3 The effect of the amount of TAC on the T_m and ΔH of blend films.

blend containing 200 μL of TAC was estimated as about 18 wt %. Therefore, we conclude that almost transparent films are obtained from the blends containing TAC in the range from 0 to 18 wt %.

Figure 2 shows the DSC curves of the blend films. Each blend film indicates an endothermic peak at approximately 170°C; this temperature corresponds to the melting point of PLLA. Only the neat PLLA shows a clear exothermal peak at about 80°C due to the cold crystallization. The appearance of the peak means that amorphous-rich PLLA films can be produced only from the neat PLLA solution not containing TAC. In other words, because the blends do not exhibit such an exothermal peak, TAC seems to induce the crystallization of PLLA; this conclusion will be confirmed by X-ray diffractometry. To discuss the effect of the TAC content on the melting behavior of PLLA in detail, we evaluated the values of the T_m and ΔH_m for each sample. Because cold crystallization takes place during the heating scan of the TAC0 blend, the melting of the crystallites formed in the scan also affects the value of ΔH_m. Figure 3 shows the effect of the TAC content on the value of ΔH_m. From the specific gravity value of TAC, we estimated the weight percentage (wt %) of PLLA in each blend. Using the estimated values, we draw a straight sold line through the ΔH_m value of the blend containing 100 wt % PLLA and that of the blend containing 0 wt % PLLA; the ΔH_m of the blend not containing PLLA was naturally zero. It can be seen that the experimental ΔH_m values, which are not corrected for the weight percentage of PLLA, do not
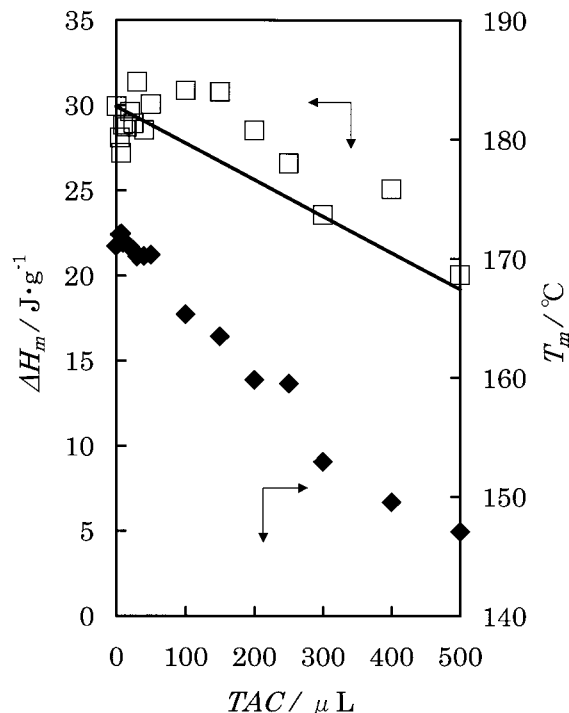
show negative deviations from the straight line, except for the values in the region of a small amount of TAC. Because the negative deviations cannot be seen, the crystallization of PLLA does not seem to be markedly restricted by the presence of TAC. It can be also seen that the T_m decreases linearly with increasing amounts of TAC. This reason will be discussed later.

Figure 4 shows X-ray diffraction curves of the blends. The neat PLLA sample (TAC0) indicates an amorphous pattern, and the blends containing TAC
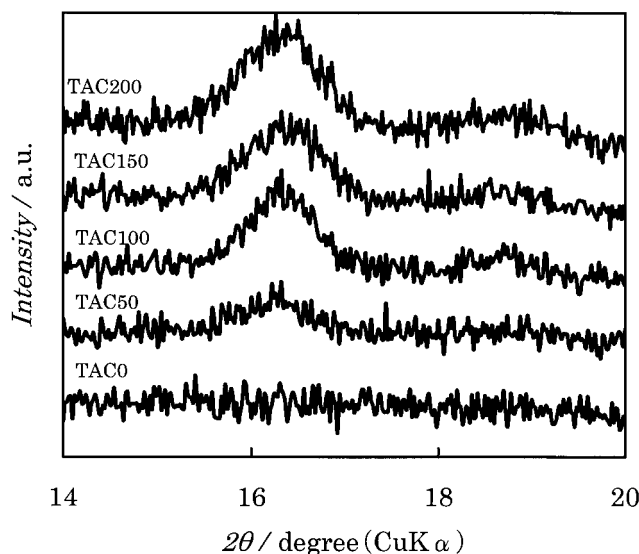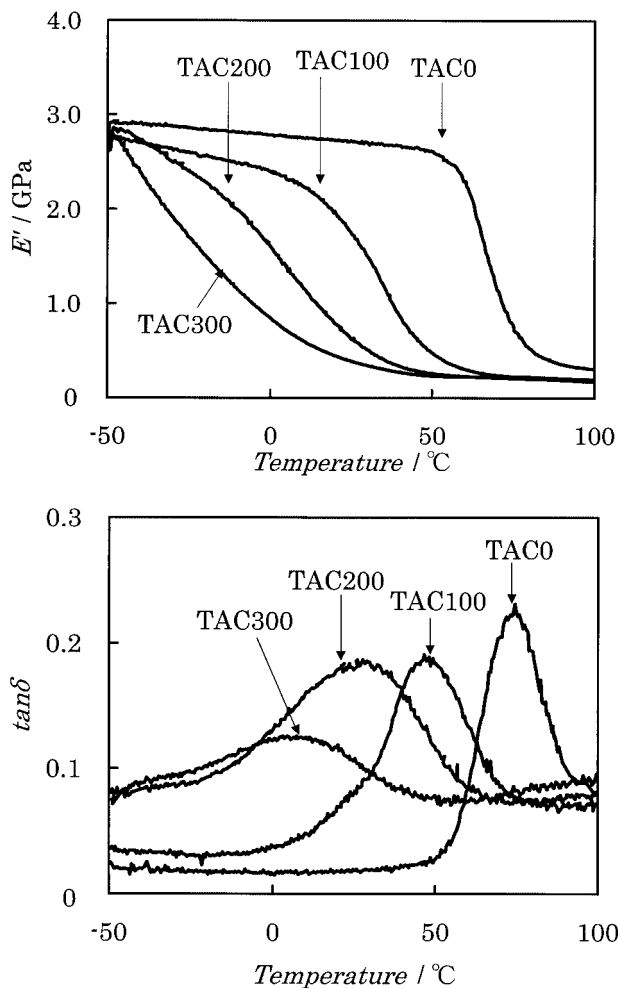

Figure 4 WAXS patterns of blends.

Figure 5 DMA curves of annealed blends.

Figure 6 effect of the amount of TAC on the value of T_g.

PLLA. Figure 6 shows the effect of the amount of TAC on the T_g. The value of the T_g appears to decrease linearly from 57 to 5°C with the amount of TAC. Generally, it is known that, in the miscible blends, only a single T_g is observed and the location of the blend T_g is proportional to the composition of the blend.[10–12] Therefore, our observation would suggest that TAC is miscible in PLLA. That is, the mobility of the amorphous chain of PLLA seems to increase markedly with the TAC content because of the miscibility. Tsuji and Sumida[13] have reported that the T_g of PLLA is decreased with the addition of the swelling solvent whose solubility parameter value is nearly equal to that of PLLA. They have also reported that the T_g of PLLA is changed from 57 to 47°C by immersion in swelling solvents. In comparison to their data, our data should be noted because PLLA films having a wide range of T_g values are prepared by the addition of TAC.

Figure 7 shows the loading and unloading curves of the blends. The shape of the curves appears to be strongly influenced by the TAC content. The TAC0

indicate diffraction peaks originating from crystallites of the α form; the peak positions coincide with those reported by other authors.[6–8] The appearance of the peaks implies that TAC induces the crystallization of PLLA. The peak width of the diffraction plane seen at $2\theta = 16.5°$ seems to be independent of the amount of TAC. This observation suggests that the crystal size of PLLA is not largely influenced by the presence of TAC. Therefore, the decrease in the T_m with increasing TAC content would be caused by the decrease in the chemical potential of amorphous PLLA chains; it is known that the melting point of a crystalline polymer is depressed by low molecular weight diluents.[9]

Mechanical properties of blends

Figure 5 shows the DMA curves of the annealed blends. The E' decreases with increasing temperature, and the decrease in E' appears to be marked with increasing TAC content. This means that TAC acts effectively as a lubricant in the blends. Each blend indicates a peak in the tan δ versus temperature curve. We assume that this peak corresponds to the T_g of
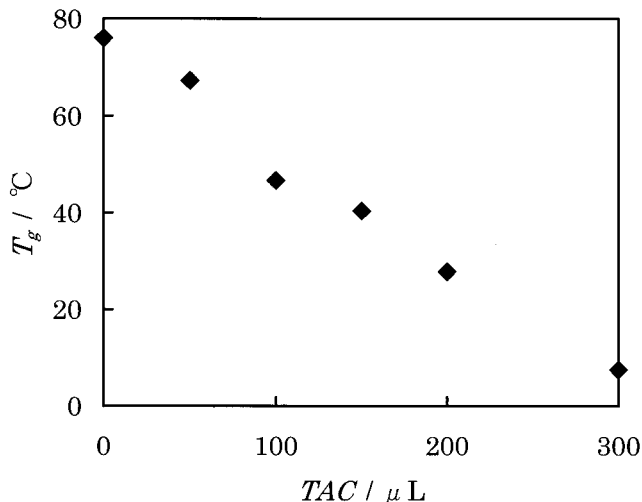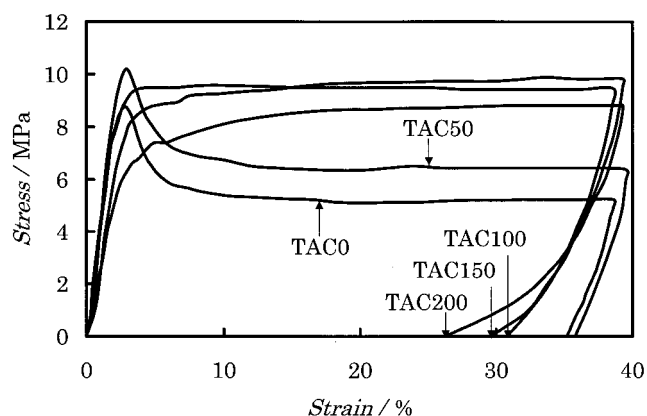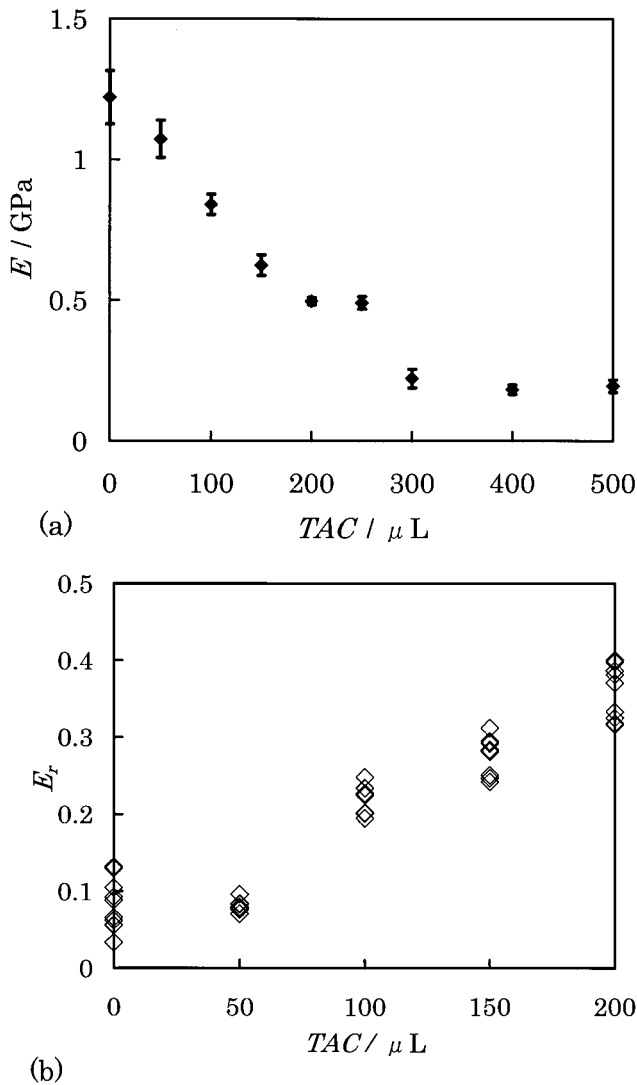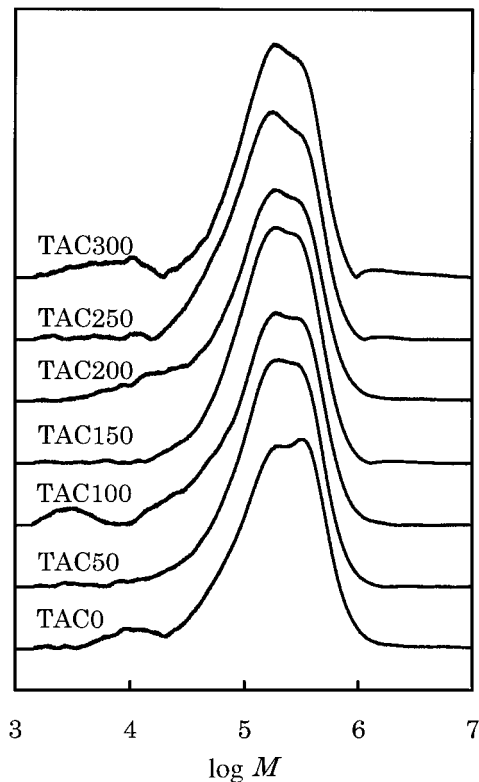

Figure 7 loading and unloading curves of blends.

Figure 8 effect of the amount of TAC on the values of the (a) Young's modulus (E) and (b) elastic recovery ($E_r = \varepsilon_e/\varepsilon_a$).

network structure is made not only by chemical crosslinking reactions but also by molecular entanglements; the entanglements would produce a temporary network structure.[14] In order to obtain more insight into the structure of the network, we measured the molecular distribution of PLLA in the blends with GPC. Figure 9 shows the effect of the addition of TAC on the molecular weight distribution of PLLA in the blend film. It should be noted that the shape of the curve and the peak position appear to be independent of the amount of TAC. This result suggests that TAC does not chemically react with PLLA in the casting process because the molecular distribution is not really changed by the addition of TAC. Thus, the crosslinks, which provide the elastic recovery, would not be chemically formed in the casting process; but quasicrosslinks are supposed to be physically formed during the casting process. This conclusion is also supported by the fact that the blend films are solved in chloroform again.

Now we further discuss the reasons for blends indicating high elastic recovery. As previously described, PLLA crystallites are formed in the blends by the presence of TAC. In blends, there is a large difference in PLLA molecular chain mobility between amorphous and crystalline regions because only the amorphous regions contain TAC molecules having high mobility. It is known that the attainable crystallinity of

sample clearly shows yield behavior, while blends containing a large amount of TAC do not show such behavior. It can be also seen that the Young's modulus (E) decreases with increasing TAC content, and the degree of the e E_r ($=\varepsilon_e/\varepsilon_a$) increases with the TAC content. To quantitatively discuss the effect of the TAC content on the E and E_r values, we evaluated these values for each sample. The result of the evaluation is shown in Figure 8. It can see that the value of E decreases exponentially with the amount of TAC. Note that the value of E_r increases linearly with the TAC content. This increase means that the degree of the elastic recovery increases with increasing TAC content.

For polymers indicating rubberlike properties, not only the high mobility of the amorphous chains but also the formation of crosslinked networks is required. Because our blends behave in a rubbery fashion, the networks would be formed in the blends. In general, a

Figure 9 The effect of the amount of TAC on the molecular distribution of PLLA in the blends.

PLLA is low compared with that of polyethylene. Namely, the crystallinity of the PLLA sample annealed at 140°C for 1 h has been reported as 57%.[15] This may be a reason that large size crystallites may not be formed. The small crystallites formed in the casting process would act as crosslinks. The high mobility of the amorphous chains and the presence of crosslinks provide rubberlike behavior to the blends.

By using the annealed samples, we further investigate the mechanism for blends exhibiting high elastic recovery. Because transparent blend films become slightly opaque with annealing, the crystallites forming crosslinks seem to become large and perfect to some extent. Thus, the morphological change of PLLA induced by annealing seems to affect the degree of elastic recovery. Therefore, we are interested in the effects of annealing on the value of E_r. For this experiment, the blends having a large amount of TAC (TAC150 and TAC200) were prepared by using the low casting temperature of -10°C because the samples containing a large amount of TAC showed marked elastic recovery (see Fig. 8). Furthermore, the reason that the low casting temperature was used was as follows: the smaller PLLA crystallites can be produced at the lower casting temperature, and the size of the PLLA crystallites can be controlled by changing the annealing temperature. Figure 10(a) shows the effect of the annealing temperature of the blends on the value of E. It can be seen that there is no significant difference in the value of E between TAC200 and TAC150 at a given annealing temperature. Furthermore, the value of E for each blend indicates a minimum at 125°C. This result would be caused by the morphological changes during the annealing process. However, considering the scatter in the measured values and the fact that the change in the measured values with annealing is not large, we conclude that E is almost independent of the annealing temperature used.

Figure 10(b) also shows the effect of the annealing temperature on the E_r value of the blends. It can be seen that the E_r value of TAC200 is higher than that of TAC150 at a given annealing temperature. The E_r value for TAC200 is about 70%. The E_r value for each blend appears to show a maximum at 125°C. However, considering the scatter of data and the fact that the amount of the change is small, we conclude that the value of E_r is almost independent of the annealing temperature. From this work it is clear that the annealing temperature that is used does not influence the values of E_r in a large way. As discussed, we conclude that the values of E and E_r are almost independent of the annealing temperature used. This implies that the PLLA crystallites formed in the casting process do not grow on a large scale during the annealing process used in this work. Finally, we can say at least that PLLA films with high elastic recovery are produced by
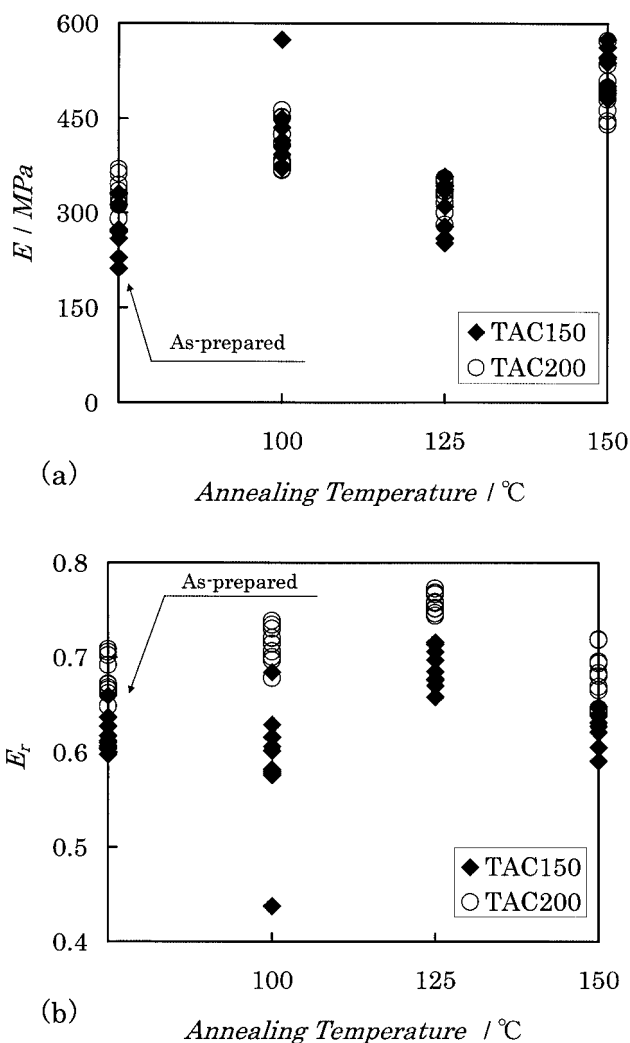

Figure 10 The effect of the annealing temperature on the values of E and E_r.

introducing TAC. From an engineering point of view, the results obtained in this work should be noted because they suggest that there is a possibility of the production of PLLA films and fibers having rubberlike properties by the addition of lubricant during the melt-blending process.

CONCLUSIONS

In order to improve the mechanical properties of PLLA, we add a lubricant to it. The effects of the addition of the lubricant TAC on the morphology and physical properties of PLLA have been investigated. The following conclusions are deduced. First, the presence of TAC accelerates the crystallization of PLLA. The melting point of PLLA is linearly decreased with increasing TAC content. Second, the glass-transition temperature decreases remarkably with increasing TAC content. This means that TAC is miscible in PLLA. Third, the Young's modulus of the blend de-

creases with increasing TAC content. Fourth, rubber-like mechanical properties appear in PLLA films with the addition of TAC. The properties are ascribed to the high mobility of the amorphous PLLA chain produced by the addition of TAC and to the formation of the quasicrosslinks made from PLLA crystallites. Fifth, the degree of elastic recovery is almost independent of the annealing temperature used.

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