Glass Transition and Mechanical Properties of PLLA and PDLLA-PGA Copolymer Blends

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ABSTRACT: The change of the glass transition temperatures (T_g) in the blend of poly(L-lactic acid) (PLLA) and the copolymers of poly(D,L-lactic acid) and poly(glycolic acid) (PDLLA-PGA) with different D,L-lactic acid and glycolic acid composition ratio (50 : 50, 65 : 35, and 75 : 25) was studied by DSC. Dynamic mechanical measurement and tensile testing were performed at various temperatures around T_g of the blend. In the blend of PLLA and PDLLA-PGA50 (composition ratio of PDLLA and PGA 50 : 50), T_g decreased from that of PLLA (about 58°C) to that of PDLLA-PGA50 (about 30°C). A single step decrease was observed in the DSC curve around T_g between the weight fraction of PLLA (W(PLLA)) 1.0 and 0.7 (about 52°C) but two-step changes in the curve are observed between W(PLLA) = 0.6 and 0.3. The T_g change between that of PLLA and that of PDLLA-PGA and the appearance of two T_gs suggest the existence of PLLA rich amorphous region and PDLLA-PGA copolymer rich amorphous region in the blend. A single step decrease of E' occurs at around T_g of the pure PLLA but the two-step decrease was observed at W(PLLA) = 0.6 and 0.4, supporting the existence of the PLLA rich region and PDLLA-PGA rich region. Tensile testing for various blends at elevated temperature showed that the extension without yielding occurred above T_g of the blend. Partial miscibility is suggested for PLLA and PDLLA-PGA copolymer blends. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2164–2173, 2004

Key words: glass transition temperature; DSC; mechanical properties; PLLA; PDLLA-PGA copolymer; blends

INTRODUCTION

In recent years, blend properties of biodegradable aliphatic polyesters such as poly(L-lactic acid)(PLLA), poly(D,L-lactic acid)(PDLLA), poly(glycolic acid) (PGA), and their copolymers are reported by many authors. Tsuji and Ikada[1] classified the recently reported blend pairs of these biodegradable polymers and copolymers including poly(ε-caprolactone).

Among these blends, effects of blending amorphous homo-polymer (PDLLA) on the melting and crystallization behavior of PLLA are studied by Tsuji and Ikada.[2–4] It was shown that crystallization of PLLA occurs in the blend with amorphous PDLLA above the PLLA content 0.2. Kairong et al.[5] studied the thermal properties of PLLA and PDLLA blends by differential scanning calorimetry (DSC) and reported that these two polymers are immiscible in the amorphous state because two T_gs are observed in the DSC curve.

There are some different types of copolymers composed of PLLA, PDLLA, and PGA. Among them, there are a small number of studies on the blending PLLA and PDLLA-PGA copolymer, although PDLLA-PGA copolymer was used alone in the field of bone repairing. Coombes and Heckman studied the weight loss of the 25 : 75 blends of PLLA and PDLLA-PGA50 (50 : 50 in monomer ratio of PDLLA and PGA) copolymer *in vivo*.[6]

Cha and Pitt[7] studied the hydrolytic chain scission rate for the three PLLA and PLLA-PGA copolymer blends prepared by compression molding, coprecipitation, and solvent evaporation. They reported that the rate of chain scission depends on the blending method and there was no evidence of miscibility between PLLA and PLLA-PGA copolymer. They did not clarify the T_g change of the blend.

Hirakawa and Kobayashi[8] reported the control-released fine particles of PLLA and PLLA-PGA copolymer blend for drug delivery system.

Tsuji and Ikada[9] reported that the stereocomplex is formed in the PLLA and Poly(D-lactide-*co*-glycolide) copolymer blend and PLLA and Poly(L-lactide-*co*-glycolide) copolymer blend.

In these blends including PLLA, much attention was paid to the melting and crystallization behaviors but the amorphous state of the blends was not studied so much. However, to study the glass transition temperature and the amorphous state of the blend is very important, because the mechanical properties change drastically at around T_g. PLLA is crystalline polymer, but PDLLA and PDLLA-PGA copolymer is not crystalline polymer. Therefore, the effects of blending PDLLA-PGA copolymer to PLLA

should appear on the physical properties in the amorphous region.

In this paper, the effects of the blend ratio on the T_g change of the PLLA and PDLLA-PGA copolymer blends were studied by DSC. The dynamic mechanical measurements and tensile testing at various temperatures around T_g of the blends were also performed. Drastic change should be expected in the stress–strain behaviors at around T_g of the blend. There are PDLLA-PGA copolymers with different monomer ratios, so that different thermal and mechanical properties in the blend of PLLA and PDLLA-PGA are expected.

EXPERIMENTAL

The samples of PLLA of the molecular weight 100,000 and three PDLLA-PGA copolymers with different PDLLA and PGA monomer ratio purchased from Birmingham Polymers, Inc. (Birmingham, AL) were used in this work. The monomer ratio (D,L-lactic acid/glycolic acid) of the copolymer was determined by H^1-NMR in hexafluoroisopropanol(HFIP) solution, according to the supplier. The PDLLA and PGA monomer ratio of the copolymers was 51 : 49 (hereafter denoted by PDLLA-PGA50), 65 : 35 (PDLLA-PGA65), and 75 : 25 (PDLLA-PGA75) with increasing PDLLA content, respectively. The inherent viscosity at 30°C determined by using Micro-Ubbelhode viscometer in HFIP solution was 0.63, 0.64, and 0.67dL/g with increasing PDLLA content after the supplier's data.

The samples were mixed at a desired weight fraction (total 200 mg) and dissolved in chloroform at room temperature in the laboratory dish. Film sample was obtained after evaporation of the solvent at room temperature for about 3 days. The solvent was completely taken away in a vacuum oven at 40°C for 1 day.

The film sample was cut, and about 7 mg was packed in aluminum pan for DSC. Then, the aluminum pan was heated to 200°C, which is above 25–30°C higher temperature than T_m of PLLA and quenched to liquid nitrogen. DSC was performed in DSC8230D of Rigaku Co. (Tokyo, Japan) with TAS 200 controller. Heating rate of DSC was 6 Kmin^{-1}. For temperature calibration, indium was used as a standard.

The samples for dynamic mechanical measurement with the thickness about 0.08 mm were formed in a steel mold by pressing the blend film at 200°C. The samples were quenched to ice water and after taking out from the mold, they were cut to 5 mm in width and 20 mm in length. The dynamic mechanical measurement was performed using the SS-TMA machine of Rigaku Co. (TMA 8140C). The period of applied extensional strain was 0.1 s, and the heating rate during measurement was 4 Kmin^{-1}.

Tensile tests were performed using the homemade tensile testing machine described elsewhere.[10] The
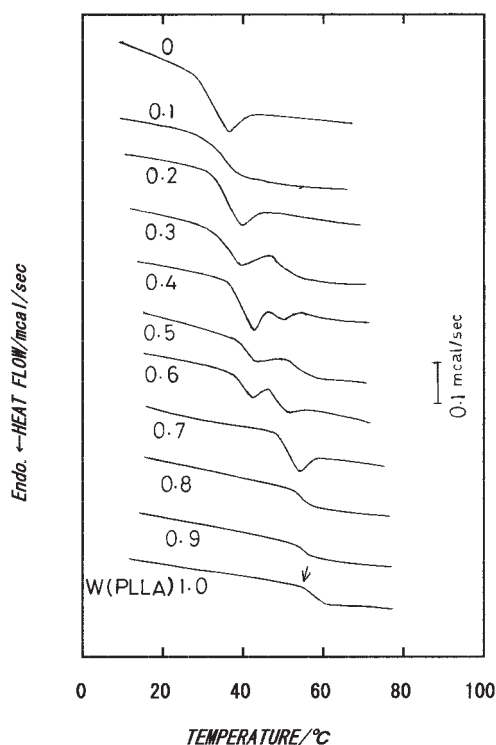

Figure 1 DSC curve of heating of PLLA/PDLLA-PGA50 blend samples around T_g of PLLA and PDLLA-PGA50. Weight fraction is written in the figure.

sample temperature was controlled between –100°C and 100°C by setting an oven. The film sample of the thickness about 0.08 mm was cut 5 mm in width and 25 mm in length and used. Load on the sample was detected by a load cell of the Shinko. Electric Co. (type LBP1; Tokyo, Japan), and the sample elongation was detected by a linear transformer of the Shinko Electric Co. (type 1516). Strain rate in extension was 0.3 min^{-1}. A load-extension curve was drawn in the X-Y recorder and was transferred to a nominal stress–strain curve using an initial sample size, and the distance of the upper and lower grips was measured before testing. Tensile testing was started after the sample temperature became at constant in the oven. The sample temperature was kept at constant within ± 0.5°C during extension.

RESULTS AND DISCUSSION

DSC

Figure 1 shows the DSC heating curves around T_g for the pure PLLA, pure PDLLA-PGA50 copolymer, and the PLLA/PDLLA-PGA50 blend samples. A step due to its glass transition appears at 57.7°C in the curve of W(PLLA) = 1.0. The starting point of the step in the curve as shown by an arrow is taken as T_g in this study. In the sample between the weight fraction of PLLA (W(PLLA)) = 1.0 and 0.7, a single step is ob-
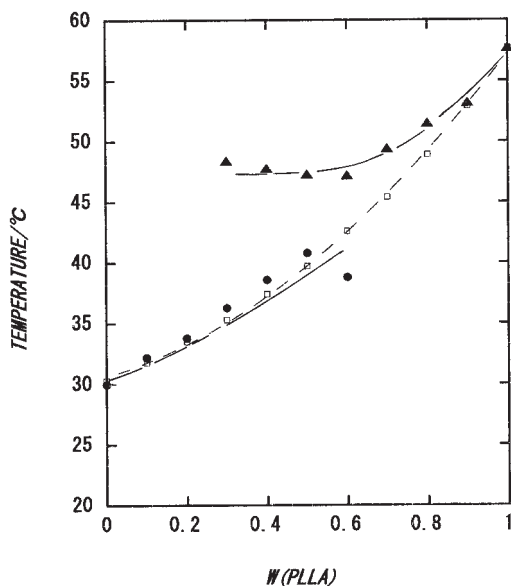
Figure 2 Phase diagram of T_g in the PLLA/PDLLA-PGA50 copolymer blend. ▲, high temperature T_g; ●, low temperature T_g; —□—, Fox equation.

served in the curve. But below the weight fraction 0.6, the two-step changes were observed in the curve around T_g. Below the weight fraction of PLLA 0.2, the single step change was observed again. T_g decreased with decreasing weight fraction of PLLA.

Figure 2 shows the phase diagram of T_g in the blend of PLLA and PDLLA-PGA50 copolymer. T_g changed between that of PLLA (57.7°C) and that of PDLLA-PGA50 copolymer (30.0°C). It decreases from that of W(PLLA) = 1.0 with decreasing PLLA content; but below the weight fraction 0.6, two T_gs appeared. The high temperature T_g (T_{gh}) below W(PLLA) = 0.6 is almost constant at about 48°C. The low temperature T_g (T_{gl}) in the same region decreased continuously to the T_g of pure PDLLA-PGA50.

In the miscible blend of polymers 1 and 2, the change of T_g in the blend is fitted to the well-known Fox equation[11] or Gordon–Taylor equation.[12] The Fox equation is expressed as follows ($1/T_g = W_1/T_{g1} + W_2/T_{g2}$), where W_1 and W_2 is the weight fraction of polymers 1 and 2 in the blend, respectively. T_{g1} and T_{g2} is the glass transition temperature of pure polymers 1 and 2, respectively. In the figure, the obtained data cannot completely fit to the Fox equation, so that PLLA and PDLLA-PGA50 is not completely miscible in the amorphous region. But T_g decreased with decreasing PLLA content in the blend.

If polymers 1 and 2 are completely miscible, then single T_g is observed in the blend for all the blend ratios, and the T_g changes between the high temperature T_g (T_{g1}) of polymer 1 and the low temperature T_g (T_{g2}) of polymer 2 continuously. There are many reports on the continuous T_g change in the miscible

blends.[13–16] On the contrary, if two polymers are completely immiscible, then two T_gs appear corresponding to the high temperature T_{g1} and the low temperature T_{g2}. The temperature position of both T_gs does not change with the weight fraction.

In the PLLA/PDLLA-PGA50 blend in this study, a single T_g is observed between W(PLLA) = 1.0 and 0.7; therefore, it is considered that two polymers are miscible in this region of the weight fraction. Below the weight fraction of 0.6, two T_gs appear so that PLLA and PDLLA-PGA50 is not miscible. However, the low temperature T_g increases with increasing weight fraction of PLLA; therefore, it is recognized that the two polymers are partially miscible. That is, slight amorphous PLLA molecules are included in the PDLLA-PGA50 area and *vice versa*, PDLLA-PGA50 is included slightly in PLLA amorphous region.

In the DSC heating curves for PLLA and PDLLA-PGA65 and PLLA and PDLLA-PGA 75 copolymer blend samples, almost the same change was observed around T_g as appeared in Figure 1. The two-step decrease was observed in the medium weight fraction region of the blend. Figure 3 shows the phase diagram of T_g in the blend of PLLA and PDLLA-PGA65 copolymer blend. In this blend, T_g also decreased from that of PLLA (57.7°C) to that of PDLLA-PGA65 copolymer (33.5°C). It decreases almost continuously from that of W(PLLA) = 1.0; but below the weight fraction 0.7, two T_gs appeared again. The high temperature T_g which appears below W(PLLA) = 0.6 is almost constant at about 48°C. The low temperature T_g decreased continuously to that of pure PDLLA-PGA65 in the same region, but the decreasing rate is low compared with
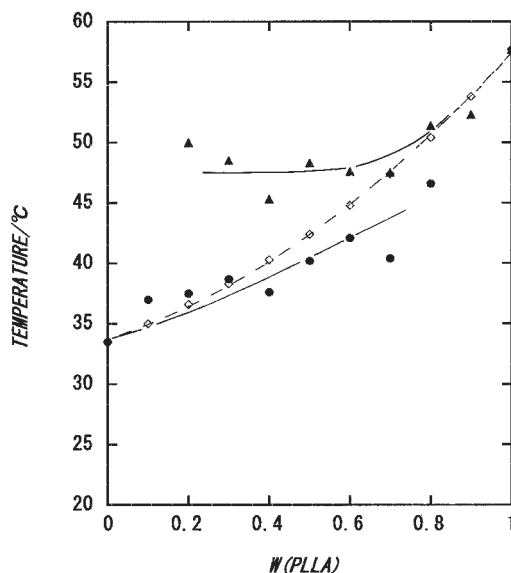

Figure 3 Phase diagram of T_g in the PLLA/PDLLA-PGA65 copolymer blend. ▲, high temperature T_g; ●, low temperature T_g; —□—, Fox equation.
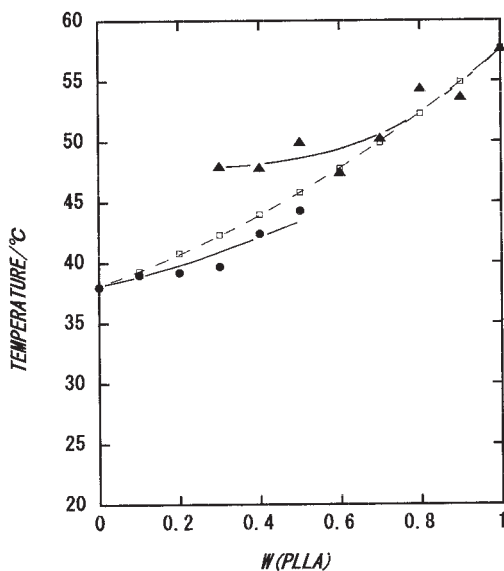
Figure 4 Phase diagram of T_g in the PLLA/PDLLA-PGA75 copolymer blend. ▲, high temperature T_g; ●, low temperature T_g; —□—, Fox equation.

the decreasing rate in the case of PLLA/PDLLA-PGA50 blend. The Fox equation is drawn in the figure, but the obtained data does not fit well.

Figure 4 shows the phase diagram of T_g in the blend of PLLA and PDLLA-PGA75 copolymer blend. T_g decreased from that of PLLA (57.7°C) to that of PDLLA-PGA75 copolymer (38.0°C). It decreases almost continuously from that of W(PLLA) = 1.0 with decreasing PLLA content, and two T_gs appeared below the weight fraction 0.5 in this case. The high temperature T_g below W(PLLA) = 0.5 is almost constant at around 48°C. The low temperature T_g decreased continuously to that of pure PDLLA-PGA75 in the same region. The Fox equation is also drawn in the figure, and it is slightly larger than the obtained data below W(PLLA) = 0.5.

Above results indicate that PLLA and PDLLA-PGA copolymer is partially miscible in the amorphous region. These two polymers should be miscible in the region close to PLLA, but they are not miscible in the medium region of the weight fraction of PLLA and PDLLA-PGA. Taking into account that the low temperature T_g increased with increasing PLLA and the high temperature T_g is almost constant at a temperature (about 48°C) lower than T_g of pure PLLA, the amorphous region of PLLA should include a slightly PDLLA-PGA copolymer chain, on the contrary, the PDLLA-PGA region should include PLLA molecular chain for the three blend systems.

Zhang et al.[17] studied the blend miscibility of PDLLA and Poly(vinyl phenol)(PVPh) by DSC and Fourier transform infrared spectroscopy and reported that there exists pure PVPh and PDLLA-rich phase including PVPh slightly. Two T_gs appeared in the DSC curve, and the T_g value of PDLLA increased slightly with increasing PVPh content.

The miscible region close to PLLA is large for PLLA/PDLLA-PGA75 blend compared with PLLA/PDLLA-PGA50 blend, so that the miscibility of PLLA molecule should be better with PDLLA-PGA75 molecule than PDLLA-PGA50 molecule.

Dynamic mechanical measurements

Dynamic mechanical measurements were performed for the blend samples of the weight fraction of every W(PLLA) 0.2 each. Figure 5 shows the temperature change of E' for the blends of PLLA and PDLLA-PGA50 copolymer at around T_g. In the pure PLLA, E' decreased at about 50°C due to the glass transition, and the value of it keeps 3×10^7 Pa still at 70°C. On the contrary, E' for pure PDLLA-PGA50 decreased from about 3×10^8 Pa at about 35°C to 3×10^6 Pa at 50°C. In the sample of W(PLLA) = 1.0 and 0.8, a single step decrease of E' is observed. But in the sample of W(PLLA) = 0.6 and 0.4, the two-step decrease of E' is observed. This behavior of E' with temperature corresponds to the two-step thermal change in the DSC curve for the blend sample of PLLA and PDLLA-PGA on the weight fraction of PLLA below 0.6.

In the miscible blend of two polymers, E' decreases at one-step around T_g and the E' decreasing curve shifts from the corresponding high temperature T_g to the low temperature T_g with decreasing the content of the high temperature T_g material. On the contrary, if the two polymers are immiscible, two-step decrease of E' occurs.[18,19] In this case, the starting temperature of the first step (low temperature step) corresponds to the decreasing temperature of E' for the low T_g polymer, and the second step (high temperature step) corresponds to the decreasing temperature of the high T_g polymer.

PLLA and PDLLA-PGA50 copolymer blend in this study, two-step decrease appeared at W(PLLA) = 0.6 and 0.4. It is suggested that these two polymers are miscible above 0.8 but not completely miscible below 0.6 as indicated by the DSC study.

Figure 6 shows the temperature change of E' for the PLLA and PDLLA-PGA65 copolymer blends around T_g. E' of the PDLLA-PGA65 copolymer including more PGA compared with PDLLA-PGA50 is large below T_g, and the value of it decreased with decreasing the copolymer content. E' of pure PLLA decreased above 50°C, and the E' decreasing curve shifted to the low temperature side with decreasing PLLA content in the blend. Two-step decrease of E' is observed for the blend of 0.6 and 0.4 corresponding to the thermal behavior at around T_g in the blend of PLLA/PDLLA-PGA65 in Figure 3.

Figure 7 shows the temperature change of E' for the blends of PLLA and PDLLA-PGA75 copolymer at around T_g. E' of the PDLLA-PGA75 copolymer including more PGA is larger than PDLLA-PGA50 and 65 below T_g, and the value of it decreased with decreas-
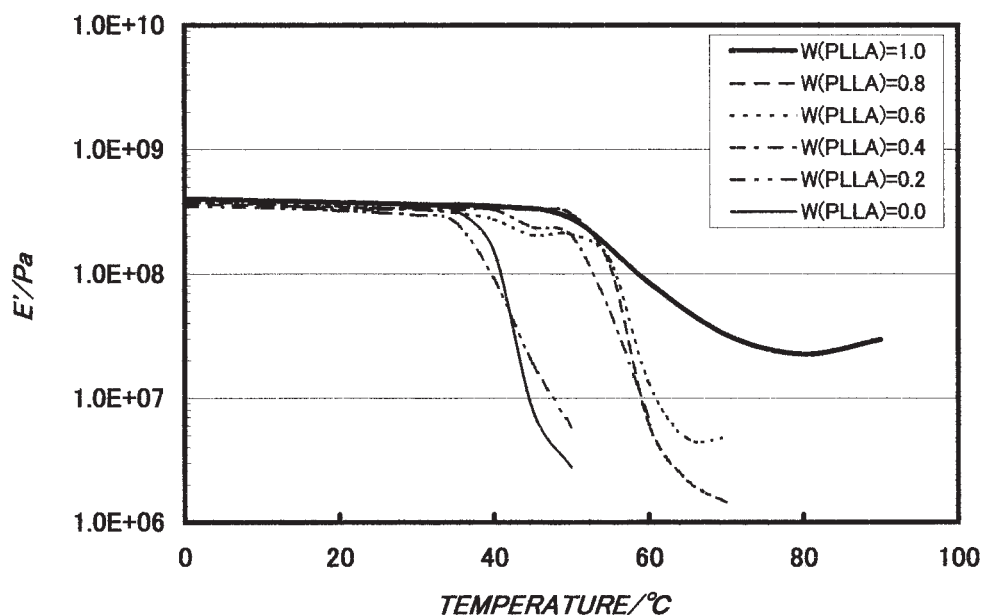
Figure 5 Temperature dependence of storage modulus E' in PLLA/PDLLA-PGA50 blend around T_g. Line style for the corresponding weight fraction is drawn in the figure.

ing the copolymer content below T_g. In this case, the E' decreasing curve shifted also to the low temperature with decreasing PLLA content in the blend. The two-step decrease clearly observed in the blend of W(PLLA) = 0.4. The miscibility of PDLLA-PGA75 with PLLA in the amorphous state may be better than PDLLA-PGA65 and PDLLA-PGA50.

Tensile testing

Figure 8 shows the nominal stress–strain curve of pure PLLA at various temperatures around T_g. It is clearly

seen that the sample breaks without yielding below 30°C. Yield point appears at a few % strain, and the decrease of the stress during extension is observed between 35°C and 55°C. At 35°C, the sample breaks only 17% in the strain. Above 40°C, it is drawn more than 30% in the strain. T_g of PLLA used in this study is 57.7°C, but the sample is drawn at lower temperature than T_g. The density of the sample for tensile testing was 1.248 (g cm^{-3}), which is the same value as that of completely amorphous PLLA. Therefore, it should be brittle below 57.7°C. Slight molecular motion in the amorphous region may occur between 35°C
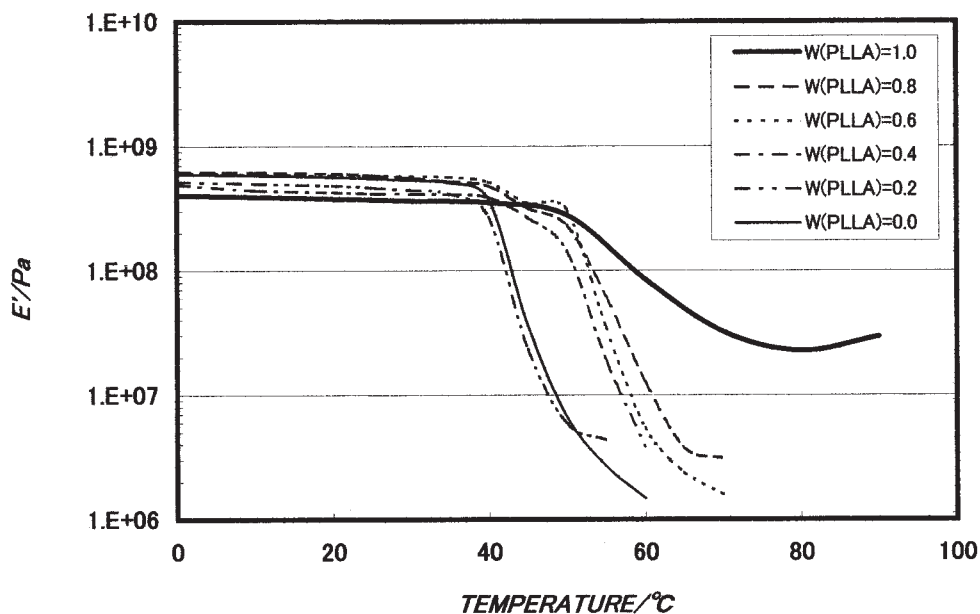

Figure 6 Temperature dependence of storage modulus E' in PLLA/PDLLA-PGA65 blend around T_g.
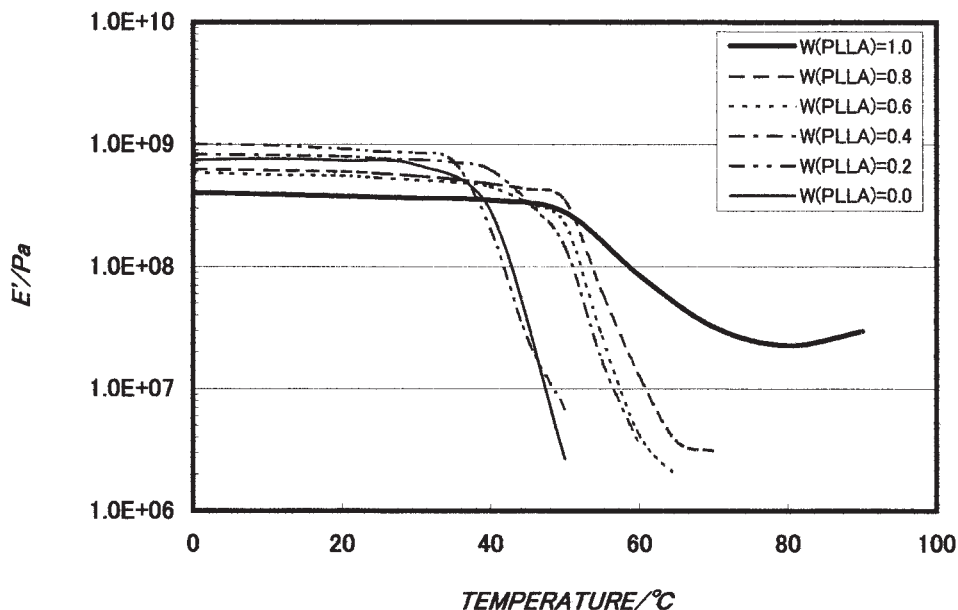
Figure 7 Temperature dependence of storage modulus E' in PLLA/PDLLA-PGA75 blend around T_g.

and 57.7°C; therefore, the drawing after yielding should occur between 35°C and T_g of PLLA.

Another possible explanation of the occurrence of drawing in PLLA after yielding below T_g is the crystallization by drawing. Exothermic peak of crystallization appears at 102°C (above T_g) in the DSC heating curve in the amorphous PLLA sample as shown in Figure 9, but the crystallization by drawing may occur just below T_g. At 60°C just above T_g of pure PLLA, the sample is drawn without yielding because the PLLA amorphous region becomes very soft. The stress level during drawing is very low at this temperature.

Figure 10 shows the nominal stress–strain curves of the W(PLLA) = 0.6 sample at various temperatures

around T_g. The sample is brittle and breaks without showing yield point below 30°C. At 35°C, the yield point appears at about 2% strain and the sample breaks at 22% strain. The yield stress at this temperature is 12.3 MPa, which is only 58% compared with that of pure PLLA at the same temperature. Decreased PLLA content in the blend decreases the yield stress. Decreasing of the yield stress in the tensile testing at 40°C of this blend should be the same reason. The low temperature T_g in this blend is about 40°C, so that the drawing without showing clear yielding begins to occur at this temperature. PDLLA-PGA copolymer should play an important role on the stress–strain behavior below the low temperature T_g in this blend.
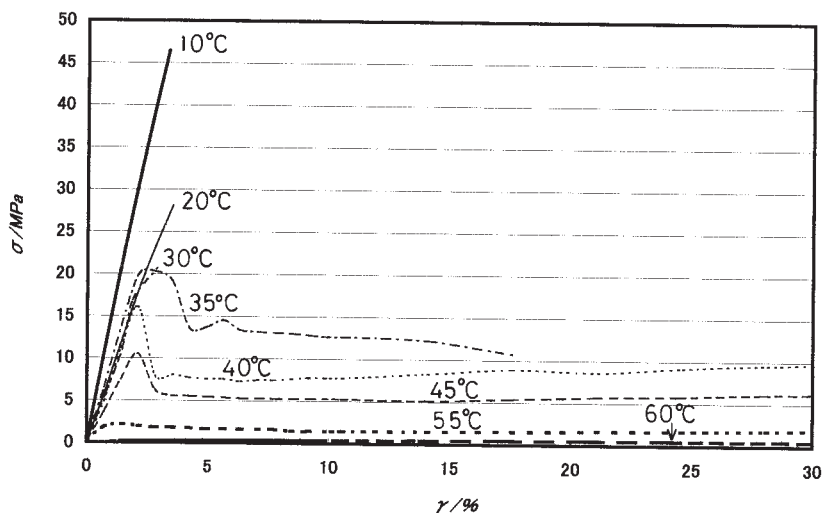

Figure 8 Nominal stress–strain curves of pure PLLA at various temperatures around T_g. Line style for the corresponding temperature is drawn in the figure.
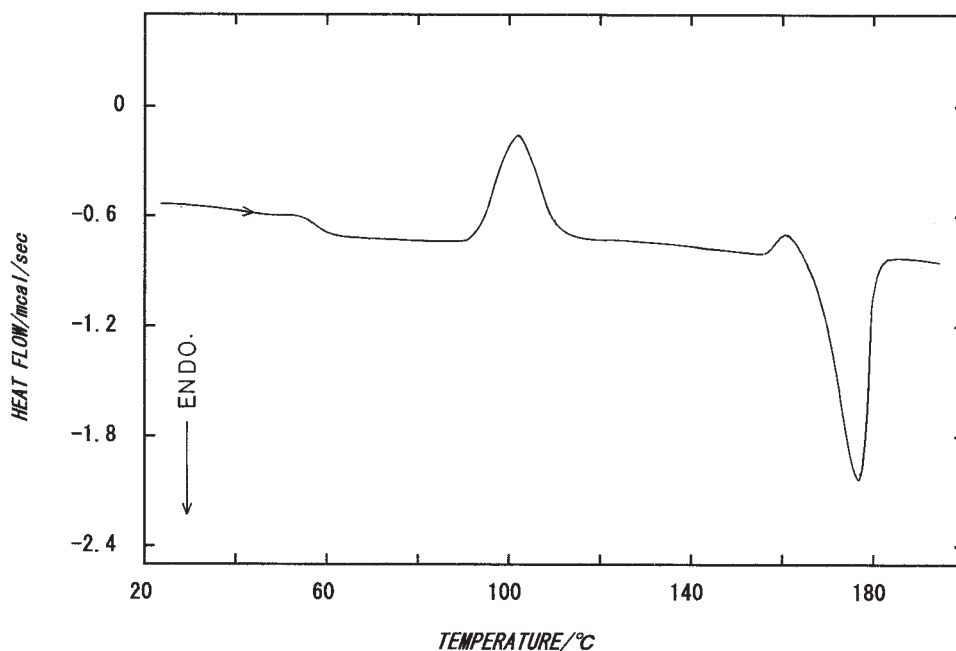
Figure 9   DSC curve of heating for the amorphous PLLA sample.

The sample is drawn more than 30% after showing very slight yielding at 45°C above low temperature T_g.

Figure 11 shows the nominal stress–strain curve of W(PLLA) = 0.4 sample at various temperatures. Below 30°C, the sample is brittle and it breaks within a few % strain. It is drawn after showing yield point at 2% strain at 35°C. Furthermore, stress level during extension after yielding is very low (about 2 MPa). This temperature is slightly lower than the low temperature T_g of this blend; therefore, the sample is drawn after yielding. The stress–strain behavior at 40°C is close to the behavior at 45°C in the W(PLLA) = 0.6 sample, which does not show clear yield point.

Figure 12 shows the nominal stress–strain curve of pure PDLLA-PGA50 copolymer at various temperatures. The sample is glassy and brittle below 30°C (T_g of pure PDLLA-PGA50), and it breaks without showing yield point. It is drawn after showing broad peak around yield point at about 35°C, which is around T_g in this sample. Drawing without yielding occurs at 40°C and 45°C, because the sample is very soft at this temperature, which is above T_g.

It was observed that the tensile modulus determined by the stress–strain curve drastically decreased above 55°C for pure PLLA, corresponding to the decrease of E' with temperature.
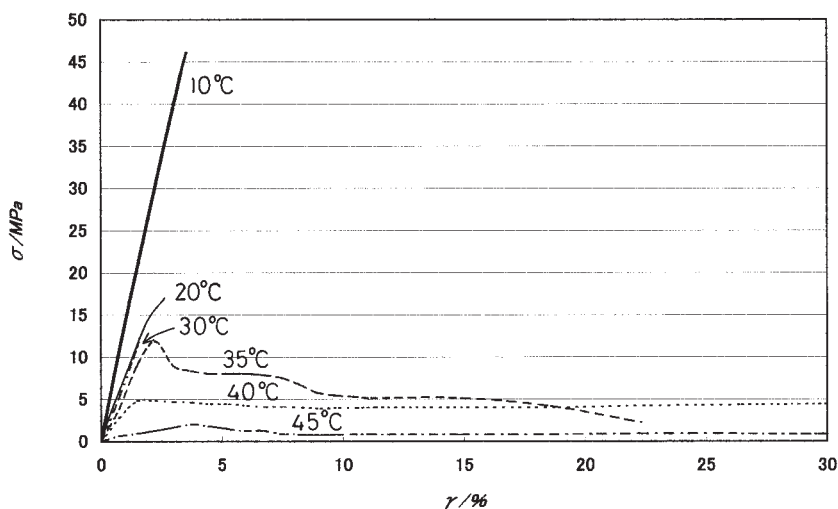

Figure 10   Nominal stress–strain curves of W(PLLA) = 0.6 in PLLA/PDLLA-PGA50 at various temperatures around T_g. Line style for the corresponding temperature is drawn in the figure.
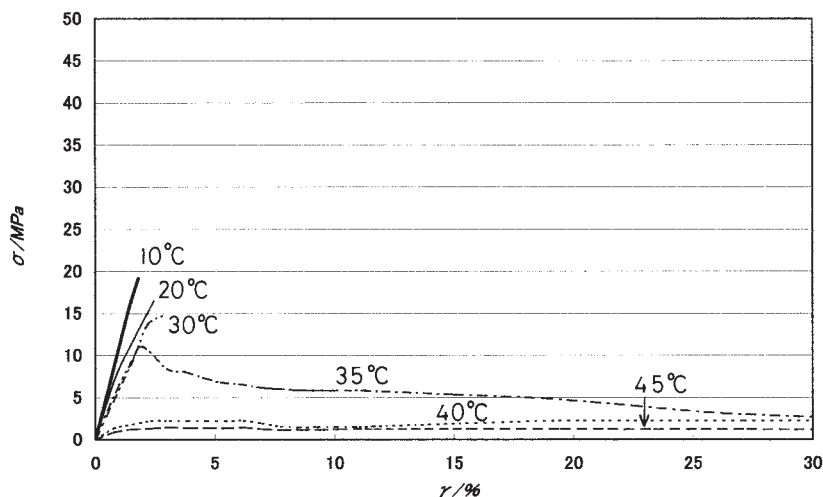
Figure 11 Nominal stress–strain curves of W(PLLA) = 0.4 in PLLA/PDLLA-PGA50 at various temperatures around T_g. Line style for the corresponding temperature is drawn in the figure.

The stress–strain behavior for the blends of PLLA/PDLLA-PGA65 and PLLA/PDLLA-PGA75 copolymers at various temperatures around T_g shows basically the same results as obtained in PLLA/PDLLA-PGA50 copolymer blend. Figure 13 shows the nominal stress–strain curves of PLLA/PDLLA-PGA75 of W(PLLA) = 0.4 blend samples at various temperatures around T_g. Breaking without yielding occurs below 35°C. At 40°C, broad yielding occurs at about 2% strain, and then the drawing is followed. In this sample, T_g is about 43°C; therefore, 40°C is about 3°C lower than T_g. Yielding and the following extension in the stress–strain curve is observed at about 3–5°C lower temperature than low T_g of the blend as observed in the case of PLLA/PDLLA-PGA50 copoly-

mer blends. Drawing without yielding is observed at 45°C (above low temperature T_g of this blend).

Figure 14 shows the nominal stress–strain curves of pure PDLLA-PGA75 sample at various temperatures around T_g. T_g of this sample is 38°C, but drawing after yielding occurs at 35°C, just below T_g of this polymer. Below 30°C the sample is brittle and it breaks without yielding. At 40°C and 45°C (above T_g of pure PDLLA-PGA75), it is very soft and is drawn without showing clear yield point. In this sample, drawing after yielding begins to appear at about 3°C lower than T_g. This behavior is the same as appeared in pure PLLA/PDLLA-PGA50 copolymer.

The stress–strain behavior for the three blends (PLLA/PDLLA-PGA50, 65 and 75 copolymer) at various
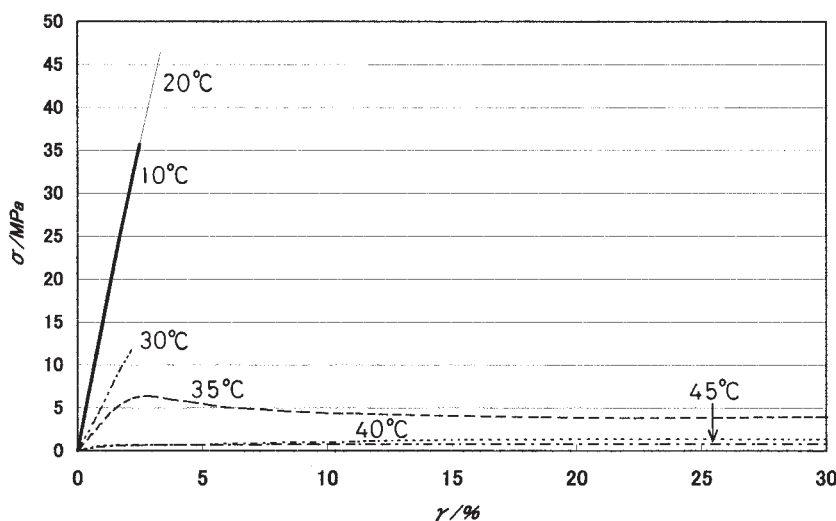

Figure 12 Nominal stress–strain curves of pure PDLLA-PGA50 at various temperatures around T_g. Line style for the corresponding temperature is drawn in the figure.
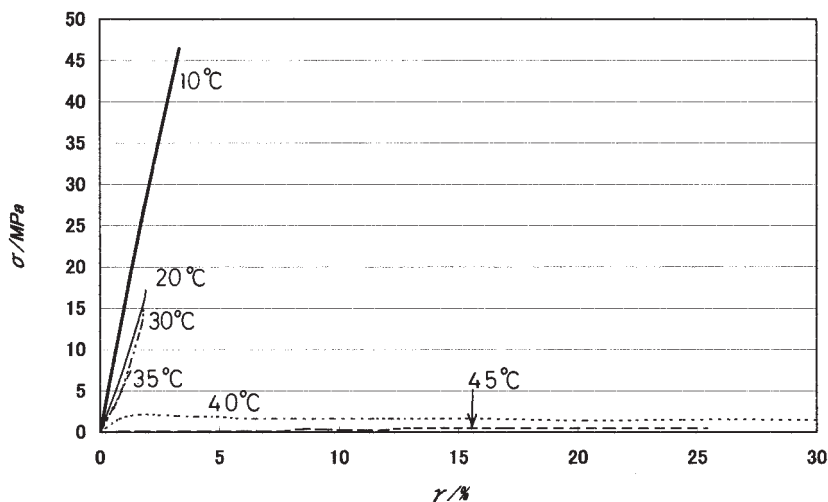
Figure 13 Nominal stress–strain curves of W(PLLA) = 0.4 in PLLA/PDLLA-PGA75 at various temperatures around T_g. Line style for the corresponding temperature is drawn in the figure.

temperatures around T_g showed the following results. The peak in stress (yield stress) and the following extension in the stress–strain curve appears at a lower temperature close to T_g. Drawing without yielding occurs above the testing temperature higher than low temperature T_g of the blend. In pure PLLA or in the blend of PLLA-rich region in the weight fraction, drawing after yielding occurs far below T_g due to the crystallization by drawing or beginning of the precursory molecular motion before T_g in the amorphous region.

CONCLUSION

In the experimental study on T_g of the blend of PLLA and PDLLA-PGA copolymers with the composition

ratio of PDLLA and PGA 50 : 50, 65 : 35, and 75 : 25, the following results are obtained.

1. T_g of the blend determined by DSC changes from the T_g of PLLA to that of PDLLA-PGA copolymer with the weight fraction change. Miscible regions exist close to pure PLLA on the weight fraction of the blend. Two T_gs appear in the semimiscible region. The high temperature T_g in this region is almost constant at about 48°C, but the low temperature T_g increased from that of PDLLA-PGA copolymer with increasing PLLA content.
2. The miscible region on the weight fraction is wider in PDLLA-PGA75 copolymer, which
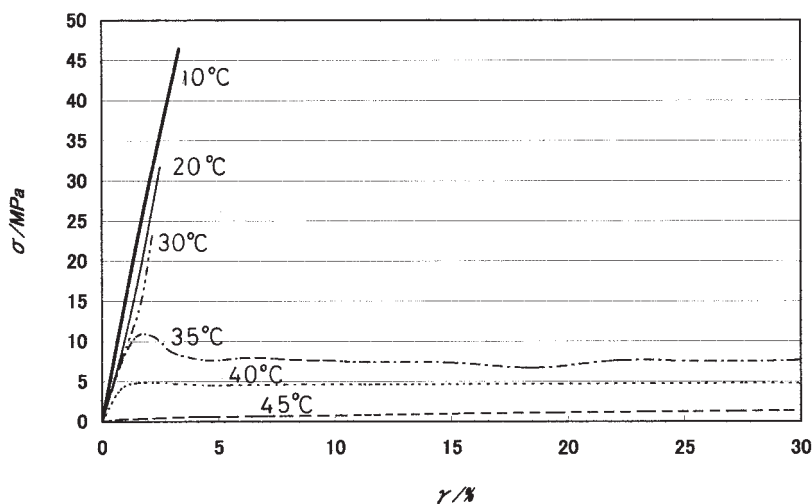

Figure 14 Nominal stress–strain curves of pure PDLLA-PGA75 at various temperatures around T_g. Line style for the corresponding temperature is drawn in the figure.

contains more PDLLA than PDLLA-PGA50 and PDLLA-PGA65. It is suggested that PLLA rich region and PDLLA-PGA copolymer rich region exist in the blend.

3. Two-step decrease of E' appears around T_g in the semimiscible region, corresponding to the two-step thermal change appearing in DSC.

4. Tensile testing of the blend around T_g shows that the drawing without yielding occurs above T_g depending on the weight fraction of the blend. In pure PLLA, drawing without yielding occurs also above T_g, but yielding and drawing is observed between 30°C and the T_g.

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