

High Pressure Crystallization of Poly(L-lactic acid) in a Binary Mixture with Poly(ethylene oxide)

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ABSTRACT: The effect of pressure on the melting and crystallization behavior of pure poly(L-lactic acid) (PLLA) and PLLA in the semi-miscible binary mixture with poly(ethylene oxide) (PEO) was studied by high pressure DTA up to 250 MPa. A high pressure-crystallized mixture was studied by DSC, polarized microscope and wide-angle X-ray diffraction (WAXD). Pressure dependence of the melting temperature (dT_m/dP) of pure PLLA determined by high pressure DTA was 0.173 K MPa^{-1} which is slightly larger than that of PEO (0.15 K MPa^{-1}). In cooling from the melt under high pressure, pure PLLA did not crystallize above 100 MPa, but in a mixture with PEO, the crystallization of PLLA occurred even at 200 MPa. The crystallization of PLLA under high pressure is discussed as due to increased interactions between PLLA molecules at elevated pressure.

KEY WORDS Poly(L-lactic acid) / Poly(ethylene oxide) / Binary Mixture / Melting / DTA / Crystallization / Miscibility / X-Ray Diffraction / High Pressure /

Poly(L-lactic acid) (PLLA), a biodegradable polymer, is semi-miscible with poly(ethylene oxide) (PEO).¹ Melting point depression of both PLLA and PEO occurs with decrease in components in the mixture, especially at lower contents below each weight fraction of 0.2. Furthermore, ringed spherulites are formed by melt-crystallization in a binary mixture of PLLA and PEO although non-ringed spherulites are formed in pure PLLA crystallized from the melt.²

The behavior of melting and crystallization of crystalline polymers is much affected by pressure because interactions between molecular chains are very weak. The melting points of many crystalline polymers increase several tens of degrees per 100 MPa.³ The pressure effect on the melting and crystallization of the binary mixture of crystalline polymer and amorphous polymer was studied in recent years using poly(vinylidene fluoride)/poly(methyl methacrylate) (PMMA),⁴ poly(ϵ -

caprolactone)/styrene-acrylonitrile copolymer⁵ and PEO/PMMA.⁶ In the crystallization of a crystalline polymer in the binary mixture with an amorphous polymer under high pressure, two different types of behavior were observed, increase of interference effect on the crystallization of the crystalline polymer by the amorphous polymer under high pressure and segregation of the crystalline polymer from the amorphous polymer under high pressure. In this case, the crystallization of the crystalline polymer occurs even at lower content of crystalline polymer in the mixture. It is therefore very interesting to study pressure effect on the crystallization behavior of the semi-miscible crystalline-crystalline polymer mixture.

In this paper, the behavior of melting and crystallization for pure PLLA and the mixture of PLLA and PEO under high pressures up to 250 MPa is studied. A mixture with a weight fraction of PLLA (W_{PLLA}) of 0.4 was chosen

for its representative behavior in the mixture. High pressure DTA was performed to determine pressure change of melting and crystallization temperatures. The samples crystallized at 0.1 MPa and high pressures were studied by DSC and X-ray diffraction measurements at 0.1 MPa. Optical microscopic observation of the samples was also performed to study changes of the morphology by high pressure crystallization.

EXPERIMENTAL

PLLA and PEO used were purchased from Scientific Polymer Products Inc. and Wako Pure Chemical Co., respectively. The molecular weight of PEO was 3000. The Infra-red absorption spectra of solution-grown PLLA film completely corresponded to that of the sample of Younes and Cohn¹ between 650 cm^{-1} and 4000 cm^{-1} .

The viscosity-average molecular weight M_η of the PLLA sample was determined by measuring viscosity in a chloroform solution at 30°C. In the calculation of M_η , the relation of Shindler and Harper⁷ was used. M_η determined by the above method for the original PLLA sample was 2000.

On the thermogravimetric analysis curve of this PLLA sample, a decrease of weight due to thermal degradation appeared between 240°C and 350°C in the heating process. Therefore, DSC measurement was performed below 210°C to avoid thermal degradation.

Mixing of the two polymers was performed by solution-casting and drying according to the method in ref 2. The film of the binary mixture obtained by the above method was pushed in a glass tube of 1.8 mm in diameter and a rod-like specimen was formed by melt-crystallization in an oil bath.

High pressure DTA was performed as described elsewhere.⁵ The rod-like sample 1.8 mm in diameter was cut into pieces 2 mm in length. The sample for X-ray diffraction measurement was prepared by wrapping a

rod-like sample (18 mm in length and 1.8 mm in diameter) with lead foil and covering the foil with epoxy resin. High pressure crystallization of the samples was performed by cooling in a high pressure vessel after heating to about 7–10°C higher than T_m as determined by high pressure DTA. The heating rate of the sample was 6°C min^{-1} and cooling rate, about 4–5°C min^{-1} . DTA experiments were performed under high pressures up to 250 MPa for pure PLLA and the binary mixture to avoid thermal degradation of PLLA, because the melting temperature of PLLA increases with pressure, but for pure PEO the experiment was performed up to 500 MPa.

To prepare samples for optical microscopy, a piece of slide glass (5 mm × 5 mm) was put in a laboratory dish during evaporation of the solvent, and the film attached on the slide glass was observed with a polarized microscope of Nikon Co. DSC measurements were performed using DSC 8230D of Rigaku Co. with a TAS 200 controller. The heating rate of DSC was 6°C min^{-1} and the cooling rate, 1°C min^{-1} .

Wide-angle X-ray diffraction (WAXD) measurements were performed on the rod-like sample by a transmission method using a diffractometer. Nickel filtered Cu- K_α radiation was used as an incident X-ray beam.

RESULTS AND DISCUSSION

Melting Curve of PLLA

Figure 1 shows the DTA curve of the melting and crystallization of pure PLLA at elevated pressure. The endothermic peak of melting shifts to the high temperature side with pressure and the intensity of the peak decreased with increasing pressure. The exothermic peak of crystallization also decreases in intensity with increasing pressure and no peak was observed above 100 MPa. This means that crystallization of PLLA does not occur during cooling above 100 MPa in pure PLLA. Figure 2 shows the pressure change of the peak temperature of melting, T_m , and crystallization, T_c , for PLLA.

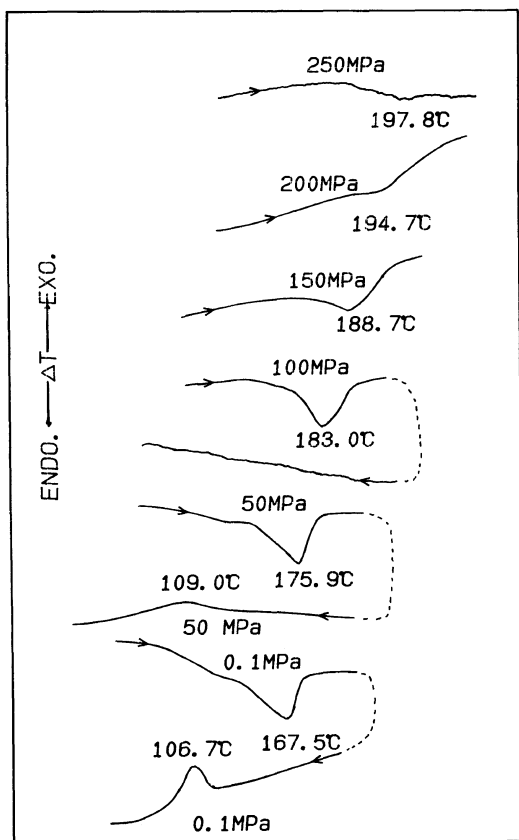


Figure 1. DTA curves of heating and cooling of pure PLLA as a function of pressure.

The curve of T_m versus pressure P fits the quadratic equation, $T_m = A + BP - CP^2$ and the coefficients A , B , and C were determined by the least squares method. The values of A , B , and C for the pure PLLA, PLLA in the mixture with PEO and the pure PEO are listed in Table I. The intensity of the melting peak of PEO did not change up to 500 MPa. In the table, A and B are taken to be the melting temperature at 0.1 MPa and pressure coefficient (dT_m/dP) at 0.1 MPa, respectively. The pressure coefficient of PLLA is larger than that of PEO ($dT_m/dP = 0.15 \text{ K MPa}^{-1}$), but smaller than those of other polymer crystals: 0.30 K MPa^{-1} in poly(ethylene),⁸ 0.367 K MPa^{-1} in isotactic poly(propylene),⁹ and 0.34 K MPa^{-1} in poly(vinylidene fluoride).¹⁰

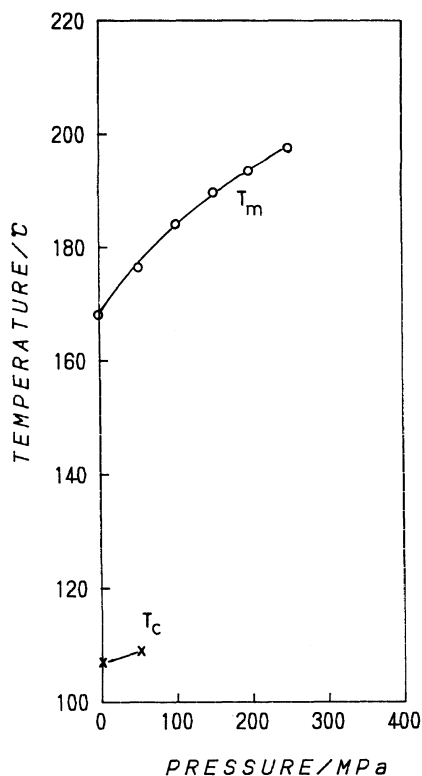


Figure 2. Pressure dependence of melting temperature (T_m) and crystallization temperature (T_c) of pure PLLA. \circ , T_m ; \times , T_c .

Table I. A , B , and C in the equation, $T_m = A + BP - CP^2$ for the melting temperature of pure PLLA, PLLA in the mixture with PEO ($W_{\text{PLLA}} = 0.4$) and pure PEO in DTA

W_{PEO}	A	B	C
	$^{\circ}\text{C}$	KMPa^{-1}	KMPa^{-2}
Pure PLLA	167.7	0.173	1.90×10^{-4}
PLLA in mixture	163.2	0.174	2.04×10^{-4}
PEO	57.2	0.149	1.01×10^{-4}

Figures 3(a) and (b) show the DTA curve of heating and cooling for the mixture of PLLA and PEO ($W_{\text{PLLA}} = 0.4$) at elevated pressure. The intensity of the endothermic peak in the heating process decreases with increasing pressure. The intensity of the exothermic peak

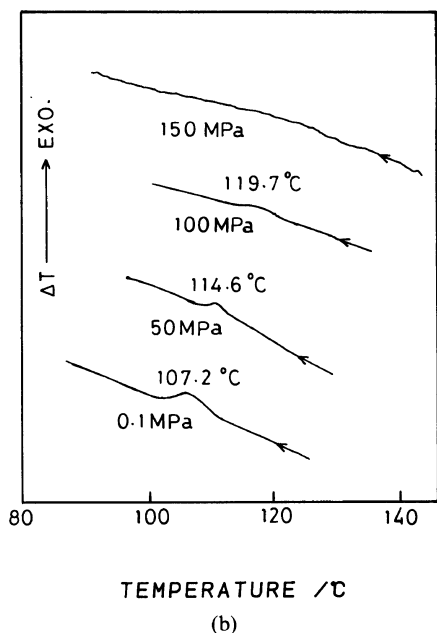
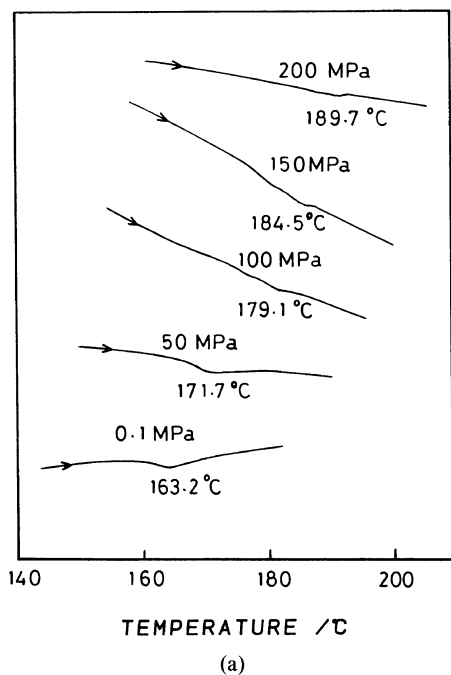


Figure 3. DTA curves of heating and cooling of PLLA in the mixture with PEO ($W_{\text{PLLA}}=0.4$) as a function of pressure. (a), heating; (b), cooling. Melting and crystallization peaks of PEO appeared at lower temperature is omitted.

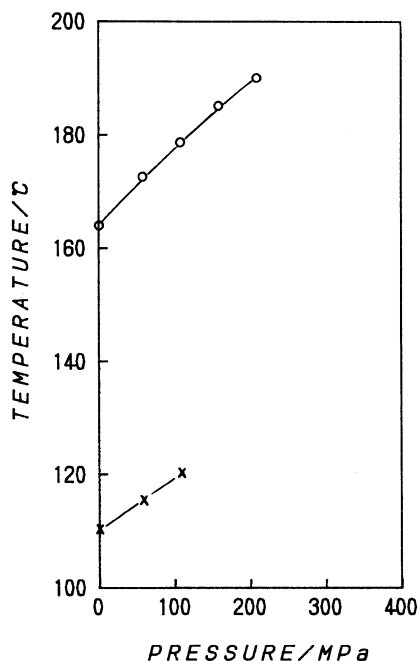


Figure 4. Pressure dependence of melting (T_m) and crystallization temperature (T_c) of PLLA in the mixture. ○, T_m ; ×, T_c .

in the cooling process also decreases at elevated pressure, but a peak still appears above 100 MPa. This indicates that the crystallization of PLLA in the mixture occurs at this pressure except for a large difference in peak temperature. These peak temperatures corresponding to T_m and T_c of PLLA in the binary mixture as a function of pressure are shown in Figure 4. The values of T_m and T_c were obtained up to 200 MPa and 100 MPa, respectively. Their pressure dependence was determined by the least squares method described above and the values of A, B, and C for T_m are listed in Table I.

Figure 5 shows the DSC curve in the heating of pure PLLA samples obtained by solvent-casting at 0.1 MPa and by cooling from the melt at 100 MPa. In the sample obtained by solvent-casting at 0.1 MPa (curve (a)), crystallization occurs about 100°C in heating and then the crystal melts at about 170°C. The sample cooled from above T_m at 100 MPa shows

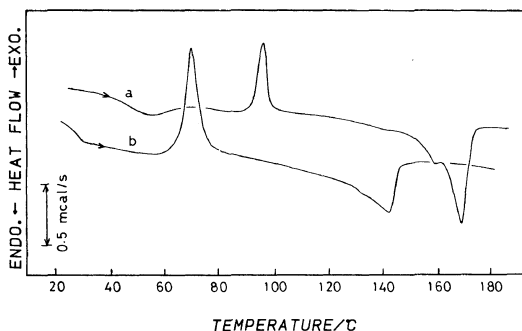


Figure 5. DSC heating curves of pure PLLA samples prepared by solvent-casting at 0.1 MPa (a) and cooling from the melt at 100 MPa (b).

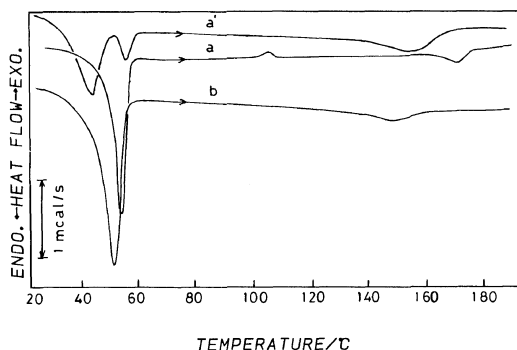


Figure 6. DSC curves of heating of PLLA and PEO binary mixture of $W_{\text{PLLA}} = 0.4$ prepared by solvent-casting at 0.1 MPa (a), cooling from the melt at 0.1 MPa (a') and 100 MPa (b).

basically similar crystallization and melting behavior (curve (b)), except for peak position. The appearance of an exothermic peak of crystallization at about 70°C in heating of the sample cooled from the melt under high pressure indicates that the crystallization of PLLA did not occur during cooling at 100 MPa. The lower melting temperature of the sample cooled from the melt at 100 MPa (about 27°C lower than that of the sample prepared by slow cooling at 0.1 MPa) may be due to thermal degradation under high pressure.

Figure 6 shows the DSC curve of heating of the binary mixture of $W_{\text{PLLA}} = 0.4$ prepared by solvent-casting, cooling from the melt at 0.1 MPa and 100 MPa. In the case of the mixture

obtained by solvent-casting (curve (a)), the melting peak of PEO was observed at 54°C and the crystallization of PLLA occurred at 104°C in heating. The endothermic peak of melting of the PLLA crystal appeared at 170.6°C. In the sample cooled from the melt at 0.1 MPa (curve (a')), endothermic double peak corresponding to the melting of PEO appeared at about 45°C and 55°C and the melting peak of PLLA appeared at 156°C. It is not clear why the double peak of melting of PEO appears in the sample cooled from the melt at 0.1 MPa. In the cooling process after melting of the solvent-cast mixture, two types of PEO crystals different in thickness may be formed in the space between the PLLA crystals. In the sample cooled from the melt at 100 MPa (curve (b)), two endothermic peaks corresponding to the melting of PEO and PLLA appear at 53°C and 145°C, respectively. There appears no exothermic peak of crystallization of PLLA in heating and the melting peak appears in the sample cooled from the melt at 100 MPa. Therefore it is concluded that crystallization of PLLA in the mixture occurred at 100 MPa in cooling. The melting point of this sample is about 8°C lower than that of the sample prepared by cooling from the melt at 0.1 MPa and the heat of fusion is very small, indicating that the small and incomplete crystals are formed under high pressure.

Figure 7 shows the X-ray diffraction patterns of pure PLLA cooled at 0.1 MPa and 100 MPa. The diffraction peak of (110) of PLLA at 16.9° in 2θ angle is very large in the sample cooled from the melt at 0.1 MPa but the peak disappears in the sample cooled from the melt under high pressure. Figure 8 shows the X-ray diffraction patterns of the binary mixture of $W_{\text{PLLA}} = 0.4$ cooled from the melt at 0.1 MPa and 100 MPa. In the diffraction pattern of the sample cooled from the melt at 100 MPa, the moderate intensity diffraction peak of PLLA was observed. The peak was also observed in the sample of the weight fraction of PLLA 0.6 cooled from the melt at 100 MPa. From these

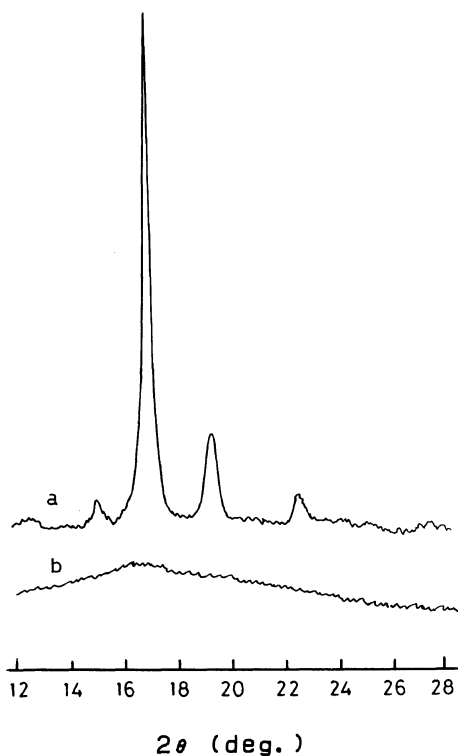


Figure 7. WAXD patterns of the pure PLLA samples prepared by cooling from the melt at 0.1 MPa (a) and 100 MPa (b).

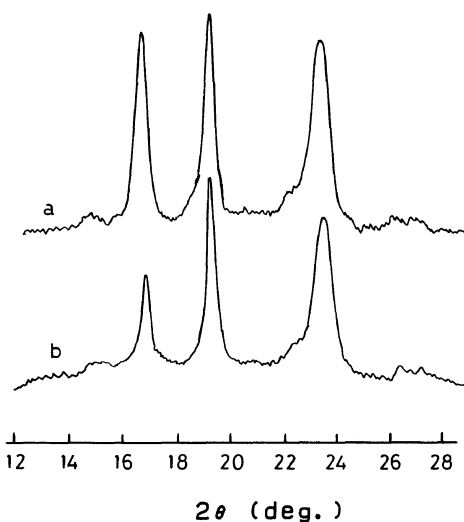


Figure 8. WAXD patterns of samples of $W_{\text{PLLA}}=0.4$ prepared by cooling from the melt at 0.1 MPa (a) and 100 MPa (b). The peaks at 19.3° and 23.4° are those from PEO.

results it is concluded that under high pressure the crystallization of PLLA occurs in the binary mixture with PEO but not in pure PLLA. Molecular interactions should increase with pressure and if the interactions become very strong under high pressure, then the crystallization of PLLA may be hindered. On the other hand, if molten PEO acts like solvent, crystallization of PLLA in the mixture may occur. Segregation of PLLA molecules from the mixed state of PLLA and PEO should occur during cooling.

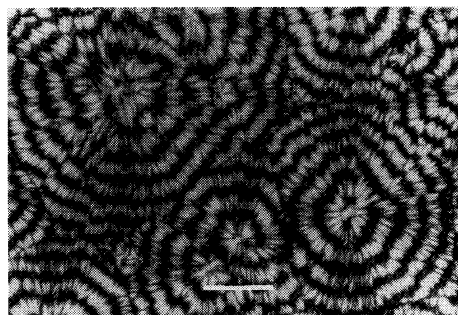
Thermal degradation of PLLA under high pressure was studied by measuring the viscosity-averaged molecular weight of the samples cooled from the melt at 0.1 MPa and 200 MPa. The molecular weight of the sample cooled from the melt at 0.1 MPa was 2000 and that of the sample cooled from the melt at 200 MPa decreased to 900. It should be noted that the degradation of PLLA under high pressure actually occurs at about 200°C , although it occurred above 240°C at 0.1 MPa. Even if it occurs under high pressure, thermal degradation may not be an important factor for the crystallization of PLLA in the binary mixture under high pressure because the effect should occur both in pure PLLA and in the binary mixture.

Optical Microscopic Observation

In pure PLLA cooled from the melt at 0.1 MPa, large non-ringed spherulites were formed as shown in Figure 9(a). When cooled from the melt at 50 MPa, small isolated blocks of PLLA composed of undeveloped spherulites formed as shown in Figure 9(b). No crystalline phase formed in the sample prepared by cooling from the above 100 MPa. Figure 9(c) shows the film sample of PLLA cooled from the melt at 200 MPa. No crystal is observed in the photograph. Optical microscopic observation supports the conclusion from the DSC and X-ray diffraction measurements that crystallization of pure PLLA does not occur during cooling under high pressure.



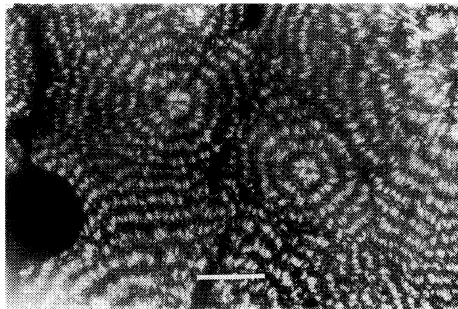
(a)



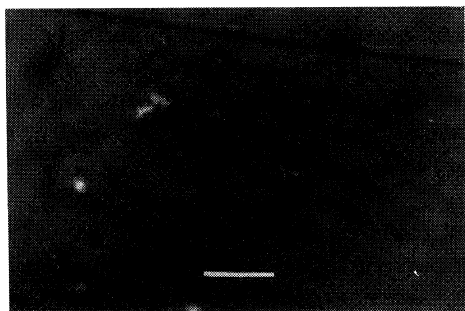
(a)



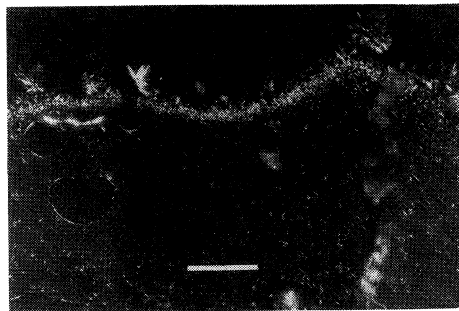
(b)



(b)



(c)



(c)

Figure 9. Optical micrographs of spherulites of pure PLLA prepared by cooling from the melt at various pressures: (a), 0.1 MPa; (b), 50 MPa; (c), 200 MPa. Scale bars mean 100 μm .

Figure 10. Optical micrographs of spherulites of the PLLA and PEO binary mixture of $W_{\text{PLLA}}=0.5$ prepared by cooling from the melt at (a), 0.1 MPa; (b), 50 MPa; (c), 200 MPa. Scale bars mean 100 μm .

In the binary mixture with PEO, the morphological features of PLLA differ from those of pure PLLA. Ringed spherulites are formed in the binary mixture cooled from the melt at 0.1 MPa. Figure 10(a) shows the ringed spherulites of $W_{\text{PLLA}}=0.5$ cooled from the melt at 0.1 MPa. It was concluded from observation

of the heating and cooling process with optical microscope having a heating device that ringed spherulites are composed of PLLA and PEO crystal lamellae.² Figure 10(b) shows a micrograph of the binary mixture of $W_{\text{PLLA}}=0.6$ cooled from the melt at 50 MPa. Ringed spherulites formed but the extinction ring was

not continuous suggesting that the crystals in the spherulite are not well developed. In the sample of $W_{\text{PLLA}}=0.4$ cooled from the melt at 100 MPa, spherulites and small crystals were observed, but most of them melted at 56°C in the heating process, so that these spherulites and crystals are those of PEO. Only very small bright areas of crystals of PLLA remained after the melting of PEO. Figure 10(c) shows a micrograph of the binary mixture cooled from the melt at 200 MPa. Very small crystals are observed in the micrograph. The disappearance of exothermic peak of crystallization of PLLA in the DSC curve of heating and the existence of the diffraction peak of PLLA in the X-ray diffraction pattern of the binary mixture cooled from the melt at 200 MPa indicate that crystallization of PLLA occurs at 200 MPa in the binary mixture with PEO but the crystals of PLLA are too small to be observed clearly in the optical microscopy.

CONCLUSIONS

Through high pressure DTA and high pressure crystallization of pure PLLA and PLLA in the binary mixture with PEO, following conclusion were drawn.

1. PLLA is a pressure-sensitive polymer in the melting and crystallization behavior. Thermal degradation of this polymer is also very sensitive to the application of pressure.
2. Pressure dependence of melting tem-

perature (dT_m/dP) of pure PLLA is 0.173 K MPa^{-1} , which is slightly larger than that of PEO but the value is small among many polymer crystals.

3. Exothermic peak of crystallization of PLLA on the DTA curve did not appear above 100 MPa in pure PLLA, indicating no crystallization of PLLA at high pressure above 100 MPa.

4. By DSC, X-ray diffraction measurement of the high pressure-crystallized binary mixture, the crystallization of PLLA easily occurs in the mixture with PEO under high pressure. Solvent effect of the molten PEO molecule is suggested.

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