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Higher-order structures and mechanical properties of stereocomplex-type poly(lactic acid) melt spun fibers

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Abstract

Equimolar blend of poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) was melt spun into fibers and the relations among the processing conditions, crystalline structures, thermal properties, and mechanical properties were investigated. Drawing and annealing were performed in order to obtain fiber mainly consisting of the stereocomplex crystal phase. Fibers drawn at various temperatures exhibited either amorphous, highly oriented homo crystal, or the mixture of homo and stereocomplex with a fairly low orientation depending on the drawing temperature. Annealing of the drawn fibers at an elevated temperature higher than the melting temperature of homo crystal increased the stereocomplex content significantly. The fractions of the homo and the stereocomplex crystals strongly depended on the higher-order structure of the drawn fibers and the annealing temperature.

Keywords: Poly(lactic acid); Stereocomplex; Fiber

1. Introduction

Biopolymers are now of great interest and activity all over the world as a new polymeric material to next generation instead of the synthetic polymers from exhaustible resources such as petroleum. However, there are some problems for practical applications such as their poor physical property, poor processability, and high production costs. Among various biopolymers, poly(L-lactic acid), PLLA, which can be produced by abundant naturally occurring corns, sugars, or beets, is considered to be one of the most promising material for products overcoming these drawbacks. PLLA is a thermoplastic material with a melting point T_m of about 180 °C and a glass transition temperature T_g higher than room temperature [1]. Thus PLLA fibers and films can be obtained in the similar processes for poly(ethylene terephthalate) (PET) and various products with superior mechanical properties can be easily obtained.

Although PLLA has a fairly high melting temperature in comparison with other biodegradable polyesters, its T_m, around 180 °C, is not high enough for some applications. PLLA fibers and cloths have to be dyed at fairly low temperature (~110 °C) and ironing of PLLA cloths at high temperature ruins their softness. One can remember that Carothers in DuPont synthesized various aliphatic polyesters in 1930s as the material for synthetic fibers. Unfortunately he finally gave up because of low thermal stability of these aliphatic polyesters. Most synthetic polymers for the synthetic fibers, such as nylon 66, nylon 6, and PET have a melting point higher than 200 °C.

One of the fundamental techniques to increase the melting point of poly(lactic acid) is to produce so called ''stereocomplex-type crystal'' which is formed by the equimolar blend of PLLA and poly(D-lactic acid) PDLA. This stereocomplex

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crystal melts at a temperature of about 50 °C higher than the melting point of PLLA. There are many reports on the stereocomplexation mechanism, morphologies, spectroscopic, and hydrolysis studies [2–23].

There are some reports concerning the fiber processing of stereocomplex-type PLAs. One of the present authors reported the higher-order structure and mechanical properties of PLLA/PDLA blend melt spun fibers [24]. Glassy as-spun blend fiber drawn up to several times at 110 °C resulting in the oriented fibers consisted of both homo and stereocomplex crystals. Although an annealing process of the drawn fiber under tension at the temperature above T_m of the homo crystal gave a fiber mainly consisting of stereocomplex crystal, the crystal orientation and the mechanical properties were significantly deteriorated.

Tsuji et al. prepared stereocomplex fibers by wet and dry spinning processes from mixed solutions of PLLA and PDLA [25]. Although drawing process of wet spun fiber was not possible even at an elevated temperature, it was possible for the dry-spun fiber and a reasonable strength was obtained. The crystallinity ratio of the stereocomplex to homo crystal increased with the draw ratio of the blend fiber.

Takasaki et al. have published two papers on the high-speed melt spinning of PLLA/PDLA blends with various blend ratios [26,27]. They found that the as-spun blend fibers with up to 16.4 wt% PDLA content have only homo crystals. However, PLLA/PDLA = 50/50 blend high-speed spun fiber obtained under high spinline tension contained a certain amount of stereocomplex crystal, and the annealing gave a fiber mainly consisting of highly oriented stereocomplex crystal.

In this study, we have obtained the stereocomplex-type PLA fibers by the melt spinning of PLLA/PDLA blend followed by drawing and annealing. The objective of this study is to investigate the effects of drawing and annealing conditions on the higher-order structure, the thermal properties and the mechanical properties of equimolar PLLA/PDLA blend melt spun fibers.

2. Experimental

2.1. Materials

A commercial PLLA (Lacty, medical grade, weight-average molecular weight, $M_w = 2.20 \times 10^5$ g/mol and polydispersity, DPI = 1.96) and a PDLA (PURAC, $M_w = 2.63 \times 10^5$ g/mol, DPI = 1.77) were used in this study. Melting, crystallization, and glass transition temperatures of PLLA and PDLA as synthesized were 177, 101, and 55 °C, and 178, 109, and 54 °C, respectively, as measured by differential scanning calorimetry (DSC). PLLA and PDLA were dried in vacuo at 80 °C for 1 h and then at 130 °C for 6 h prior to the melt spinning.

2.2. Melt spinning and drawing

Melt spinning of PLA was carried out using a laboratory size screw extruder equipped with a single nozzle with 0.5 mm inner diameter. PLA was extruded at a melting zone temperature of 230 °C and at a nozzle temperature of 210 °C. The molten extrudate was stretched and quenched in an ice/water bath (5 °C) placed 20 cm below the nozzle. The glassy as-spun fiber was drawn up to 3 times in air at a temperature between 60 and 120 °C using a drawing machine with two sets of rolls and a heating chamber.

2.3. Annealing

Annealing of fibers was conducted between 170 and 200 °C with the fibers drawn at 60, 90, and 120 °C. Annealing was performed under tension in air for 30 min, which leads to 2 times drawing. Fiber preparation conditions and the sample code are listed in Table 1.

2.4. X-ray analysis

Wide-angle X-ray diffraction (WAXD) patterns were obtained at room temperature using a nickel-filtered CuKα radiation with a wave-length of 0.1542 nm, from a Rigaku RAD 2C sealed beam X-ray generator operating at 40 kV and 20 mA. WAXD patterns were recorded using a point-collimated beam and a flat-plate film holder.

2.5. Thermal analysis

Thermal properties of the fibers were determined with a DSC, Shimadzu DSC-50 in a N_2 atmosphere at a heating rate of 10 °C/min. Specimen (1–2 mg) was sealed in an aluminum pan. Melting and crystallizing temperatures were determined from the maximum of the endothermic and the exothermic peaks, respectively.

2.6. Mechanical properties

Mechanical properties of the fibers were evaluated using a tensile testing machine (CATY-500BH: YONEKURA Ltd) at a cross-head speed of 100 mm/min at a room temperature. A specimen gauge length of 20 mm was used. The results obtained were averaged over five samples for each condition.

3. Results and discussion

3.1. Melt spinning and drawing of PLA fibers

Fiber of about 300 μm in diameter was easily obtained by melt spinning. PLA extrudate quenched in an ice/water bath and taken up was a glassy hard fiber. Drawing up to 3 times in air at a temperature ranging from 60 to 120 °C was possible. Since the glass transition temperature was around 60 °C, the glassy fiber was unable to be drawn below 60 °C. Drawing at or above 120 °C, the fiber seems to melt, even though lower than its melting temperature.

Table 1
Drawing conditions and characteristics of melt spun stereocomplex-type PLA fibers

Sample	T_D (°C)[a]	T_A (°C)[b]	T_g (°C)[c]	T_c (°C)/ΔH_c (J/g)[d]	$T_{m,H}$ (°C)/$\Delta H_{m,H}$ (J/g)[e]	$T_{m,S}$ (°C)/$\Delta H_{m,S}$ (J/g)[f]
As-spun	–	–	62	96/18.1	170/15.1	220/20.2
PLA-60	60	–	62	90/17.7	170/12.9	218/24.1
PLA-70	70	–	62	83/5.4	169/11.1	217/15.0
PLA-80	80	–	62	85/10.3	168/16.3	218/26.3
PLA-90	90	–	75	84/1.2	167/20.0	217/30.4
PLA-100	100	–	74	80/7.5	167/18.4	217/28.5
PLA-110	110	–	62	94/12.5	167/13.8	217/19.9
PLA-120	120	–	60	103/20.1	167/14.8	218/18.1
PLA-60–170	60	170	60	–	170/5.0	219/50.2
PLA-60–180	60	180	61	–	170/2.4	219/46.1
PLA-60–190	60	190	60	–	170/1.4	221/55.4
PLA-60–200	60	200	60	–	–	219/57.6
PLA-90–170	90	170	61	–	165/8.5	220/40.6
PLA-90–180	90	180	60	–	165/5.3	220/36.1
PLA-90–190	90	190	60	–	–	220/60.9
PLA-90–200	90	200	62	–	–	220/48.3
PLA-120–170	120	170	61	99/0.5	170/4.5	218/35.9
PLA-120–180	120	180	61	–	165/4.7	218/38.5
PLA-120–190	120	190	60	–	–	218/53.0
PLA-120–200	120	200	61	–	–	218/44.2

[a] Drawing temperature.
[b] Annealing temperature.
[c] Glass transition temperature at which half of the increase of heat capacity.
[d] Crystallization temperature and exotherm.
[e] Melting temperature and endotherm of homo crystal.
[f] Melting temperature and endotherm of stereocomplex crystal.

3.2. Higher-order structure of drawn PLA fibers

Two different crystal structures (α- and β-forms) have been proposed for PLLA, based on X-ray diffraction patterns and conformational energy analysis. The α-form of PLLA is in a pseudo-orthorhombic system with parameters for $a = 1.07$ nm, $b = 0.595$ nm, and c (fiber axis) $= 2.78$ nm [28–30]. Two chains with a 10_3 helix in conformation are contained in a unit cell. The β-form appears in solution spun and drawn fibers at higher drawing temperature and/or at higher draw ratios. An orthorhombic system is proposed for this structure ($a =$ 1.03 nm, $b = 1.82$ nm, and c (fiber axis) $= 0.900$ nm) containing six chains with 3_1 helix in conformation [29]. Okihara analyzed the stereocomplex crystal by X-ray diffraction, electron diffraction and conformational energy analyses [31,32]. This stereocomplex phase shows different crystal structure from that of homo crystal. The stereocomplex crystal system is triclinic ($P1$) with cell dimensions: $a = 0.916$ nm, $b = 0.916$ nm, c (fiber axis) $= 0.870$ nm, $\alpha = 109.2°$, $\beta = 109.2°$, and $\gamma =$ 109.8°. PLLA and PDLA segments are packed laterally in a parallel fashion as a pair in the unit cell. Stereocomplex takes a 3_1 helical conformation, which is extended a little from a 10_3 helix in the homo crystal with the α-form.

WAXD patterns of drawn PLA fibers are shown in Fig. 1. As-spun fiber showed only an amorphous halo (data not shown) and the fiber drawn at 60 °C (PLA-60) kept its amorphous state. The fibers drawn at 70, 80 and 90 °C showed reflections at $2\theta = 17.0°$ on the equator. These can be assigned to the (110) and (200) of α-form homo crystal. WAXD pattern of the fiber drawn at 90 °C indicates the sharpest and strongest reflection of the α-form, suggesting the highest crystallinity of homo crystal. The fiber drawn at 100 °C started to show weak reflections at $2\theta = 11.8°$ and 20.5° on the equator. These are assigned to (100), (010), and (−110), and (110), (−120), and (−210) of stereocomplex phase. The reflections of α-form became equatorial arc, indicating less orientation of the homo crystal. The α-form reflection from the fiber drawn at a temperature above 100 °C became weaker and obtuse, indicating that the amount of α-form crystal becomes less oriented with increasing drawing temperature. On the other hand, the reflections from stereocomplex became stronger but obtuse, indicating that the amount of stereocomplex increases but less oriented with increasing drawing temperature. Accordingly, the fibers drawn at the temperature below homo crystallization temperature have a low crystallinity. The fibers drawn near the homo crystallization temperature consisted of oriented homo crystal. When the fiber was drawn at higher temperature, both homo and stereocomplex crystallizations occurred although the crystalline orientation was rather low.

It has been reported that PLLA was crystallized in a 10_3 helix conformation (α-form) in general, but in some drawing condition a 3_1 helix conformation (β-form) also forms [29]. However, in this study, no reflections corresponding to β-form homo crystal were observed.

3.3. Thermal analysis of the drawn PLA fibers

Fig. 2 shows the DSC thermograms of as-spun fiber and fibers drawn at various temperatures ranging from 60 to 120 °C. Overlapping of small gaps and peaks around 50–80 °C was

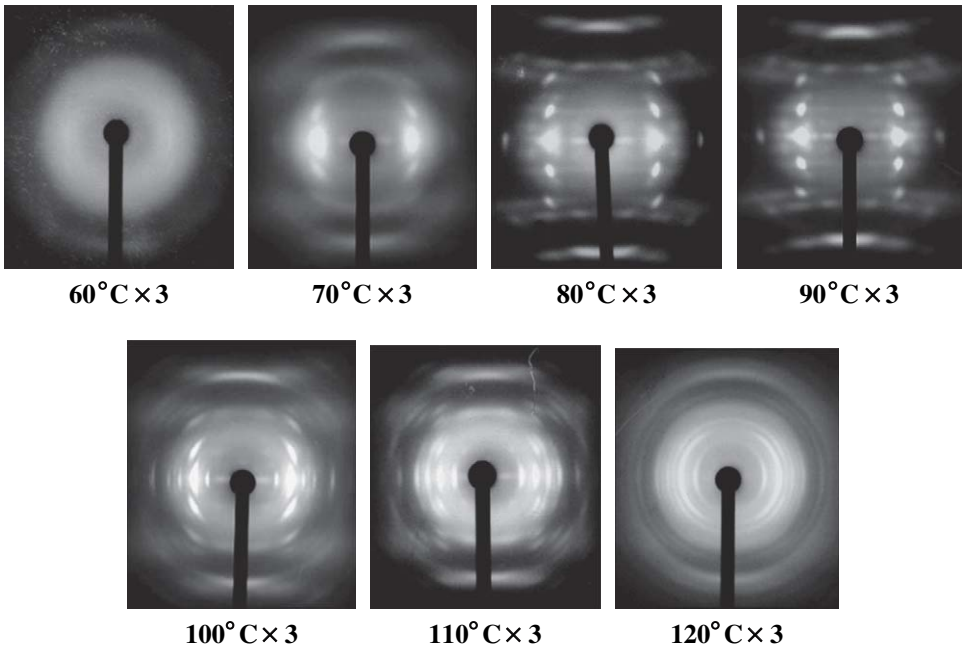

Fig. 1. WAXD patterns of PLA fibers drawn at various temperatures.

observed in the DSC curves of most fibers. These are considered to be a glass transition of PLA as reported to be observed around 60 °C in PLAs [1]. It should be noted that the fibers with high crystallinity (PLA-90 and -100) did not show a clear glass transition.

An exothermic peak at a temperature between 70 and 110 °C, representing a homo crystallization of PLLA and PDLA was observed. This exothermic peak tended to be smaller and shifted to the lower temperature with increasing drawing temperature up to 90 °C, and again became larger when the fiber was drawn at higher temperatures. Tsuji and Ikada reported that the pure PLLA or PDLA shows a crystallization peak around 90 °C, while PLLA/PDLA equimolar blend shows a stereocomplex crystallization around 70 °C [12]. Although it is not possible at this moment to distinguish whether this exothermic peak is due to the crystallization of homo crystal or that of the stereocomplex, the fiber drawn at 90 °C was already highly crystallized and consisted of homo crystal as was detected by WAXD.

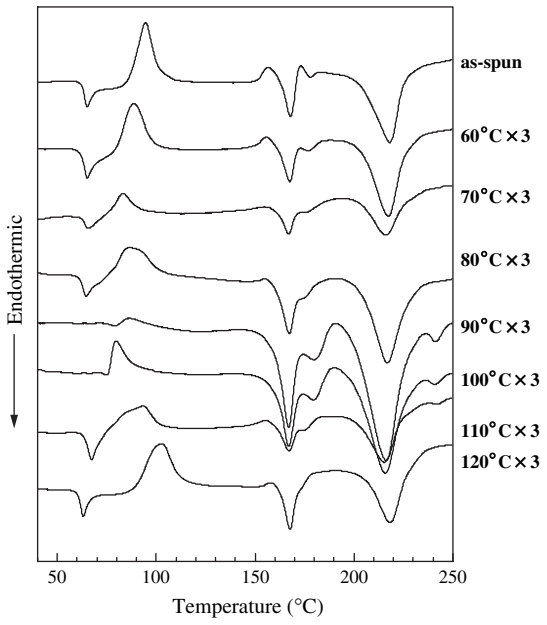

Fig. 2. DSC heating traces of PLA fibers undrawn and drawn at various temperatures.

In the as-spun and drawn PLA fibers, small exothermic and endothermic peaks were observed consecutively at around 160–180 °C. The T_m of homo crystal was detected around 170 °C. This temperature region corresponds to the melting temperature of the α-form of crystal. The melting endotherm increased with increasing drawing temperature up to 90 °C, then decreased again.

It should be noted that most fibers showed two endothermic peaks in the temperature range from 160 to 180 °C, larger peak at a lower temperature followed by a smaller peak at a higher temperature. These two endothermic peaks were considered to be attributable to the melting of homo crystal in two different states. PLLA and PDLA were mixed in a single screw extruder, in which the mixing of PLLA and PDLA was carried out insufficiently. Because of this insufficient mixing, the resulting blend may have three phases, a pure PLLA or PDLA phase unmixed and crystallized into homo crystal showing a higher melting point, a PLLA or PDLA phase mixed insufficiently and crystallized into imperfect homo crystal showing a lower melting point, and a well mixed blend phase which may crystallize into the stereocomplex. Similar result has been observed in PLLA solution blended with small amount of PDLA [33]. It is expected that the PLLA or PDLA imperfect crystalline phase, in which PLLA and PDLA are mixed

fairly well but not in molecular level, can be transferred into the stereocomplex, although the pure PLLA or PDLA phase is not transferred into the stereocomplex after melting. The fibers drawn at the temperature range between 80 and 100 °C near crystallization temperature of homo crystal seem to have a larger amount of pure PLLA or PDLA phase. From these DSC curves shown in Fig. 2, one can notice that the PLA-80, -90, and -100 fibers show a larger endothermic peak at higher temperature region. From these results one can expect that these drawn fibers may have large homo crystal content after annealing at an elevated temperature.

WAXD patterns shown in Fig. 1 indicate that the fibers drawn at lower temperatures are basically amorphous, those drawn at intermediate temperature range consisted of oriented α-phase, and those drawn at higher temperatures seem to have mixture of α- and stereocomplex phases. However, DSC curves of the fibers drawn at any temperature show a large endothermic peak around 220 °C. This indicates that the melting and recrystallization into stereocomplex occurred in any of the fibers investigated.

3.4. Mechanical properties of the drawn PLA fibers

Fig. 3(a)–(c) shows the mechanical properties of drawn PLA fibers as functions of drawing temperature. Tensile modulus and strength showed maxima of 8.5 GPa and 520 MPa, respectively, when the fiber was drawn at 90 °C. This may correlate with the amount of crystal and degree of orientation in this fiber. Elongation at break decreased with increasing drawing temperature up to 90 °C, and increased slightly when the fiber was drawn at higher temperatures. Crystallization and the crystalline orientation proceeded with increasing drawing temperature up to 90 °C. Drawing above this temperature, the rate of crystallization decreased and the high molecular motion did not keep high molecular orientation, resulting in rather brittle character.

3.5. Higher-order structure of annealed PLA fibers

The PLA fibers drawn at 60, 90 and 120 °C in the drawing process were further drawn up to 2 times at a temperature ranging from 170 to 200 °C, higher than the melting temperature of the homo crystal, in the annealing process without breakage. Annealing below 170 °C only enhanced the homo crystallization.

Fig. 4 represents the WAXD patterns of the PLA fibers annealed at various temperatures. Most patterns bear crystalline reflections mainly from stereocomplex crystals. WAXD patterns of the fibers initially drawn at 60 °C and annealed at 170, 180, 190, and 200 °C (PLA-60–170, PLA-60–180, PLA-60–180, and PLA-60–200, respectively) are shown in the upper row. The reflections from both homo and stereocomplex crystals were detected from PLA-60–170 fiber. With increasing annealing temperature, the reflection of homo crystal became weaker, and PLA-60–190 fiber showed only reflections from stereocomplex phase. PLA-60–200 fiber again showed homo crystal reflections. The formation of the highly oriented homo crystal might occur in the cooling process after annealing at as such a temperature higher than T_m of homo crystal.

WAXD patterns of the fibers initially drawn at 90 °C and annealed at 170, 180, 190, and 200 °C (PLA-90–170, PLA-90–180, PLA-90–180, and PLA-90–200, respectively) are shown in the middle row. The fibers drawn initially at 90 °C showed the reflections from both homo and the stereocomplex crystals after annealing at any temperatures investigated. This suggests the existence of pure homo crystal of PLLA or PDLA, which is unable to recrystallize into stereocomplex phase as mentioned in the DSC results.

WAXD patterns of the fibers initially drawn at 120 °C and annealed at 170, 180, 190, and 200 °C (PLA-120–170, PLA-120–180, PLA-120–190, and PLA-120–200, respectively) are shown in the lower row. PLA-120–170 fiber showed the reflections from coexisting homo and stereocomplex crystals. However, the fibers annealed at 180 and 190 °C showed only reflections from the stereocomplex phase. When the fiber was annealed at 200 °C, homo crystal reflection slightly appeared again, and the orientation of both crystal phases relaxed significantly.

3.6. Thermal analysis of the annealed PLA fibers

Fig. 5(a)–(c) shows the DSC heating curves of PLA fibers annealed at various temperatures. Crystallization peaks of homo crystal almost disappeared and the melting peak of stereocomplex crystal appeared around 220 °C. Melting

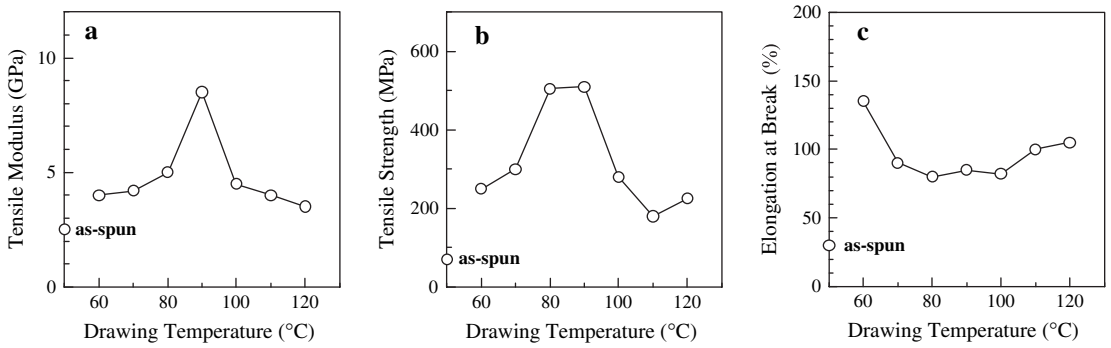

Fig. 3. (a) Tensile modulus, (b) strength, and (c) elongation at break of PLA fibers drawn at various temperatures.

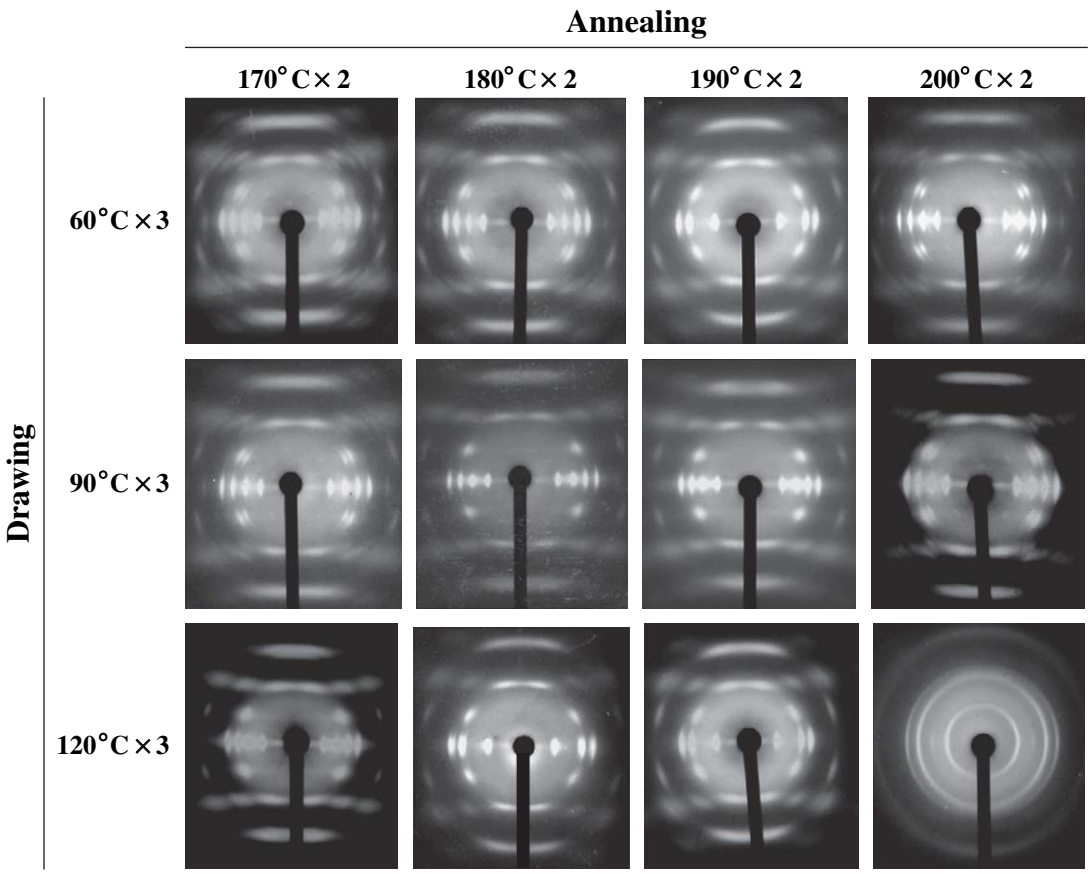

Fig. 4. WAXD patterns of PLA fibers annealed at various temperatures.

endotherm of stereocomplex crystal became sharper while that of homo crystal around 165 °C became smaller and disappeared with increasing annealing temperature. In addition, there existed a small endothermic peak around 190 °C. This peak may be due to the melting of imperfect stereocomplex crystal disturbed by the excess component. This phenomenon is prominent when the fiber was drawn at lower annealing temperatures.

3.7. Mechanical properties of the annealed PLA fibers

Fig. 6(a)–(c) shows the mechanical properties of the PLA fibers annealed at various temperatures. Basically the series of PLA-120 fibers have poor mechanical properties irrespective of the annealing temperature. The fiber drawn at 120 °C has a fairly low crystalline orientation, and annealing of such fiber did not give any improvement of the mechanical properties.

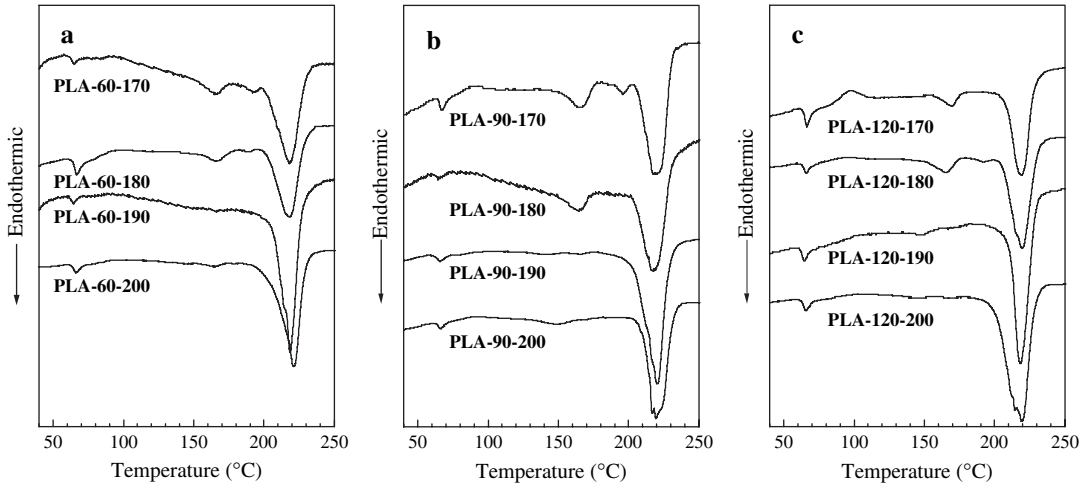

Fig. 5. DSC heating traces of PLA fibers drawn at (a) 60, (b) 90, and (c) 120 °C, and annealed at various temperatures.

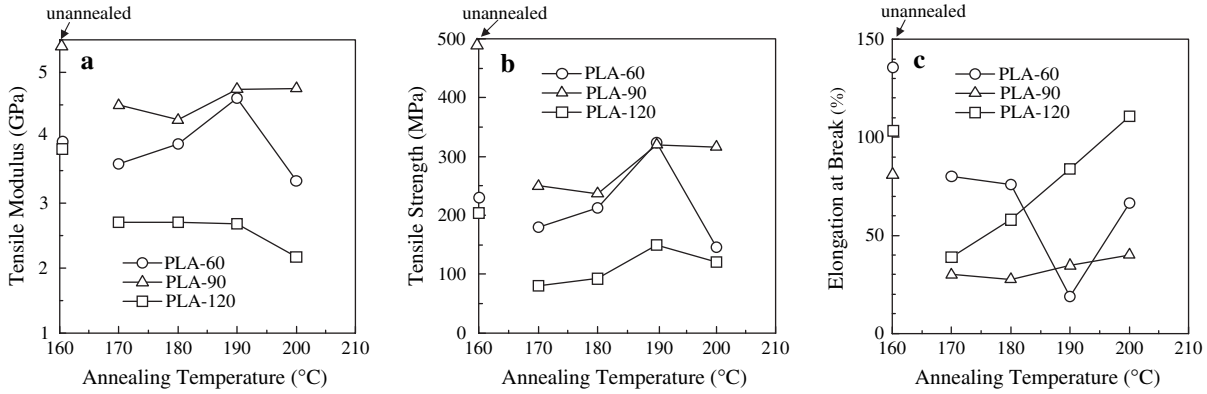

Fig. 6. (a) Tensile modulus, (b) strength, and (c) elongation at break of PLA fibers drawn and annealed at various temperatures.

On the other hand, PLA-90 has a fairly good mechanical property because of the high crystallinity and crystalline orientation even before annealing. Unfortunately the annealing of this fiber slightly deteriorated the mechanical properties, which did not depend on the annealing temperature. PLA-60 was an amorphous fiber and it did not have mechanical properties as high as that of PLA-90 fiber, although this fiber seems to have high amorphous orientation. Similar deterioration of the mechanical properties to that of PLA-90 was observed when PLA-60 was annealed at a lower temperature. However, the mechanical properties increased with annealing temperature up to 190 °C, and then decreased after annealing at higher temperatures. PLA-60 fiber annealed at 190 °C showed better mechanical properties than unannealed one. One of the present authors also reported similar deterioration of PLLA/PDLA blend melt spun fibers [24]. Annealing at 200 °C for 5 min under tension decreased the tensile modulus and strength from 6.85 GPa and 550 MPa to 6.4 GPa and 280 MPa, respectively. During this annealing the reduction of the birefringence was also observed.

In this study, the highest tensile modulus and strength achieved were 4.7 GPa and 335 MPa, respectively, for PLA-90–190. PLA-60–190 showed slightly lower modulus and strength. Tsuji et al. have reported that the Young's modulus and tensile strength of dry-spun complex fiber were 8.6 GPa and 922 MPa, respectively [25]. Takasaki et al. have reported that the maximum tensile modulus and strength achieved by high-speed melt spinning were about 6.0 GPa and 580 MPa, respectively [27]. However, Takasaki's fiber exhibited mainly the homo crystal by DSC and WAXD measurements. Their fiber with the highest stereocomplex content showed the tensile modulus and strength of about 2.86 GPa and 138 MPa, respectively, which are lower than the fiber obtained in this study.

3.8. Stereocomplexation of drawn and annealed fibers

The strategy used in this study to obtain the PLA fiber with highly stereocomplex fraction is to draw the fiber at a condition in which the homo crystal does not form. It is reasonable that the homo crystal does not form above its melting temperature. Since the as-spun amorphous fiber easily melts at a temperature above the melting temperature of the homo crystal, it is necessary to draw at a lower temperature once with homo crystallites and draw again at higher temperature.

The fiber drawn near the T_g of PLA is basically amorphous. The fiber drawn at a temperature higher than the crystallization temperature (higher than 100 °C) has both homo and stereocomplex crystalline phases with low crystallinities. The crystalline orientation of this fiber is rather low. When the fiber was drawn near the homo crystallization temperature (at 90 °C), the fiber tends to have only highly oriented homo crystal phase.

DSC measurements revealed that the fibers seem to have two homo crystalline phases. One with a higher melting temperature is a homo crystal of pure PLLA or PDLA unmixed. This leads to the remaining of homo crystal even when annealed at temperature higher than melting temperature of homo crystal. It is proposed that this phase exists in amorphous region between stereocomplex crystalline regions. The other with a lower melting temperature is a homo crystal of PLLA or PDLA mixed insufficiently so that this phase can be transferred into the stereocomplex easily after drawing at higher temperature. While both of these homo crystal phases formed in the drawing process at 90 °C, mostly the latter phase formed during DSC measurement in the fiber drawn at 60 and 120 °C. This means that the fiber drawn at 90 °C has a phase which is not transferred into the stereocomplex easily.

All of the fibers drawn at 60, 90, and 120 °C were successfully annealed at 190 °C at a temperature above the melting temperature of the homo crystal. Oriented amorphous fiber (PLA-60) with a phase easily transferred into the stereocomplex was drawn at 190 °C and the resulting fiber has only oriented stereocomplex phase. Oriented homo crystalline fiber (PLA-90) changed into fiber with both highly oriented homo and stereocomplex phases after annealing process at 190 °C, which is even higher than the melting temperature of homo crystal. The fiber with the mixture of homo and stereocomplex (PLA-120) turned to the fiber with highly oriented stereocomplex phase. The stereocomplex seems to form effectively when (1) PLLA and PDLA were mixed well so that the fiber has a phase easily transferred into the stereocomplex, and (2) the fiber drawn after the drawing process did not have homo crystal phase. Mixing of PLLA and PDLA chains seemed to occur

not only in the extruder but also during the drawing process. However, when the drawing was carried out near the homo crystallization temperature, homo crystallization occurred rather than mixing resulting in the fiber with only homo crystal. We have also tried melt spinning the cast-film of the mixture of PLLA and PDLA, which showed mixture of homo and stereocomplex crystals, but after spinning, the fibers exhibited almost same as simply as the PLLA and PDLA pellets were set together into the hopper. Accordingly, once melted, the mixture of PLLA and PDLA became random coil with PLLA and PDLA chains individually.

Contrary to our expectations, stereocomplex crystals did not induce high mechanical properties. Similar results have been reported by Takasaki et al. who determined the mechanical properties and the higher-order structure of the high-speed spun PLLA/PDLA blend fibers [27]. It may be due to the difficulty in forming a highly ordered stereocomplex phase. In the stereocomplex phase, PLLA chain and PDLA chain have to stand side by side alternately. Chain folding structure should exist in the stereocomplex lamella for PLLA and PDLA chains, respectively. And if chain folding occurs, the chain folding should have to occur in switchboard model, or the chains should pass to the next lamella. The crystalline phase with this sort of complex structure should have a lot of defect, which suppresses the enhancement of mechanical properties.

4. Conclusions

Equimolecular blends of PLLA and PDLA were melt spun into PLA fibers. Drawing and annealing processes were performed to form stereocomplex crystals. WAXD patterns showed that three kinds of higher-order structure were observed in the drawn fibers depending on the drawing temperature: (1) oriented amorphous state in the fiber drawn at a lower temperature (60 °C), at which crystallization does not occur significantly; (2) highly oriented homo crystal in the fiber drawn at an intermediate temperature (90 °C), at which homo crystallization significantly occurs; (3) coexistence of homo and stereocomplex crystals with a fairly low orientation at a higher temperature (120 °C). DSC measurements revealed that the fiber drawn at an intermediate temperature range seems to have some pure PLLA of PDLA crystal, which cannot be transformed to the stereocomplex crystal by the annealing process.

Annealing process at 190 °C of the fibers drawn at 60 °C and 120 °C gave the fibers mainly consisting of stereocomplex crystals. Rest of the fibers still showed a coexistence of homo and stereocomplex crystals. These results indicate that the higher-order structure of the drawn fiber strongly affects the crystalline form obtained in the annealed fiber. Unfortunately, the annealed fiber with high stereocomplex content did not show the superior mechanical properties.

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