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Mechanical properties and higher order structure of bacterial homo poly(3-hydroxybutyrate) melt spun fibers

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Abstract

Bacterial homo poly(3-hydroxybutyrate) (PHB) was melt spun into fibers and the relations among the processing conditions, crystalline structures, and the mechanical properties were investigated. WAXD patterns of PHB fibers indicate a broad reflection which cannot be assigned to any plane in the orthorhombic system of PHB, although most strong reflections can be assigned to the planes in the orthorhombic system. It has been reported that the broad reflection is assigned to be β-zigzag form, which occurs by the stretching of the amorphous tie molecules between lamellae. When annealed under high tension, this broad reflection tended to be stronger, while it became significantly weak when annealed without tension. These results suggest that the annealing without tension makes the amorphous tie molecules crystallized into orthorhombic form, while annealing under high tension makes the molecules in the amorphous region stretched and increased the fraction of the β-zigzag form.

Keywords: Bacterial homo poly(3-hydroxybutyrate); Fibers; β-Zigzag form

1. Introduction

Bacterial poly(3-hydroxybutyrate) (PHB) is produced by various microorganisms as an energy storage product [1]. PHB is a thermoplastic material with a melting point T_m of ~180°C and a glass transition temperature T_g lower than room temperature [2]. On cooling slowly from the melt, PHB crystallizes to form large spherulites. Rapid cooling results in amorphous state and subsequently followed by secondly spherulitic crystallization even at room temperature [3,4]. This sperulitic crystallization of PHB and its copolymer makes cold deformation to enhance crystalline orientation extremely difficult.

Various efforts have been paid to process PHB and PHB copolymer into fibers, films, and other products. Furuhashi et al. [5,6] and Yamamoto et al. [7] succeeded the melt spinning and cold drawing of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) and reported its mechanical properties and detailed higher order structure. More recently, Gordeyev et al. [8] reported the production of the oriented elastic PHB melt spun fibers with high tensile strength and modulus. Unfortunately, the brief report by Gordeyev et al. [8] does not contain either detailed processing condition or higher order structure.

Utilizing a roughly purified sample, we have succeeded the melt spinning and cold drawing of bacterial PHB. Fibers obtained were further annealed to enhance the mechanical properties. The objective of this study is to investigate the effects of drawing and annealing condition on the mechanical properties and higher order structure of bacterial homo PHB melt spun fibers.

2. Experimental

2.1. Materials

Bacterial homo PHB was supplied by MONSANTO Japan Co. and used without further purification. Sample was dried in vacuo at 80°C for 10 h before melt spinning.

2.2. Melt spinning and drawing

Melt spinning of PHB was carried out using a laboratory size screw extruder equipped with a single nozzle with 1 mm in inner diameter. PHB was extruded at a melting zone temperature of 180°C and a nozzle temperature of 170°C. The extrudate was taken up at 28 m/min and directly

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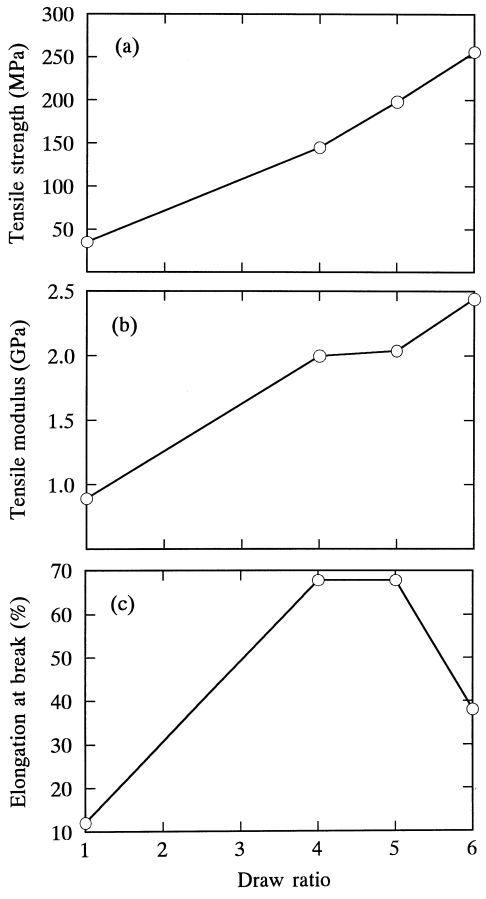


Fig. 1. (a)Tensile strength, (b) modulus, and (c) elongation at break of the PHB fibers as functions of draw ratio.

drawn to various ratios using a drawing machine with two sets of rolls and a hot plate heated at 110°C.

2.3. Annealing

Annealing of fibers drawn to six times was conducted at various temperatures and under various tensions. The drawn PHB fibers were passed through the air heated at 75, 100, 125, and 150°C under the tensile stresses of 0, 50, and 100 MPa. The period for which fibers stayed in the heated zone was set to 2.5 min. Tensile stress applied to the fibers during annealing was controlled by using a tension meter (KE-100, Shinko Tsushin Kogyo Co.).

2.4. Wide angle X-ray diffraction patterns

WAXD patterns of the fibers were taken on a flat film using a JEOL-DX-GE-E X-ray generator operated at 40 kV and 20 mA, and a nickel filtered CuKα ($\lambda = 0.15418$ nm) was radiated for 3 h. WAXS diffractometer scans were obtained using a CuKα radiation (40 kV, 30 mA) with RINT 2100 FSL (Rigakudenki Ltd).

2.5. Thermal analysis

Differential scanning calorimetery (DSC) measurements were carried out on a MAC Science 3100 thermal analyzer, using 1.0–2.0 mg of sample sealed in an aluminum pan. The measurements were done in nitrogen flow at a heating rate of 10°C/min and a cooling rate of 5°C/min.

2.6. Mechanical properties

Mechanical properties of the fibers were evaluated by the tensile tests with a tensile testing machine (CATY-500BH: YONEKURA Ltd). A specimen gauge length of 20 mm was used. The tests were carried out at a cross-head speed of 50 mm/min at room temperature. The results obtained were averaged over five samples for each condition.

2.7. Morphology

Scanning electron micrographs (SEM) were taken by using a JSM-25S (TEOL Co., Ltd) microscope at an electron voltage of 5–20 kV after samples were subjected to Au coating.

3. Results and discussion

3.1. Melt spinning and drawing of PHB fibers

The polymer used in this study is a bacterial homo PHB. Filament with about 300 μm in diameter was easily obtained by melt spinning. As spun fibers can be cold-drawn at 110°C only immediately after melt spinning. The maximum drawn ratio achieved at this drawing temperature was six times. Drawn PHB fibers are stable and no longer change their thermal and mechanical properties upon storage at room temperature significantly.

PHB and its derivatives have a low crystallization rate as a general property of polyesters. Since the melt spinline of PHB quenched at room temperature does not crystallize immediately, as spun fiber is still in the molten state at room temperature and cold drawing is not possible. Aging of this amorphous fiber even at room temperature results in the brittle material, which cannot be drawn even at a higher temperature due to the spherulite formation. Melt spinning process of PHB and PHB copolymers already reported utilized the materials containing some nucleating agent such as boron nitride and the spinline is heated to proceed the crystallization [5]. These processes have been carried out in order to improve the low crystallization rate of PHB.

The bacterial PHB homopolymer as received in this study contain some contaminant such as protein and lipid from the culture medium. This contaminant seems to act as a nucreating agent so that some degree of crystallization is proceeded in the spinline. This crystallization in the spinline makes cold drawing possible immediately after spinning. Aged

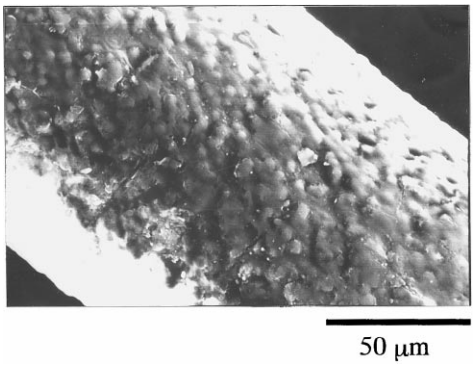


Fig. 2. Surface of PHB as spun fiber aged at room temperature for a day.

as spun fiber was very brittle and cannot be drawn because of the spherulite formation.

3.2. Mechanical properties of the drawn PHB fibers

Fig. 1(a)–(c) shows the mechanical properties of the drawn PHB fibers. Tensile strength and modulus increase monotonously with increasing draw ratio.

As spun PHB fiber is very brittle and the elongation at break is significantly lower than drawn fibers. This is due to the spherulitic crystallization of as spun fiber which occurs after melt spinning. Generally the melt spun fibers have a smooth surface. However, as spun PHB fiber has large sperulitic crystals even on the surface of the fiber as shown in Fig. 2.

3.3. Thermal analysis of the drawn PHB fibers

Typical DSC cooling and second heating traces of PHB powder as received are shown in Fig. 3. The crystallization peak temperature T_c in the cooling process and the melting peak temperature T_m in the second heating process were detected at 90 and 171°C, respectively. Cooling rate in this measurement was 5°C/min, which is believed to be much lower than that achieved in the melt spinning process and it is expected that the as spun fiber just after melt spinning has a fairly low degree of crystal.

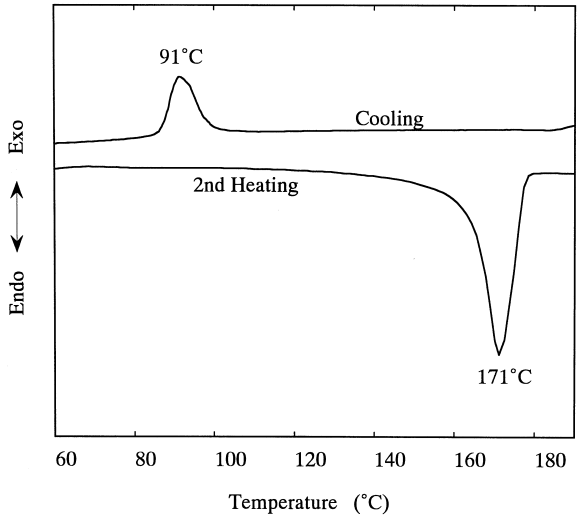


Fig. 3. Typical DSC traces of cooling and second heating traces of PHB powder as received.

Once PHB is melt spun into fibers, the melting peak shifts to higher temperature. This is clearly seen in the DSC heating curves of as spun and drawn PHB fibers shown in Fig. 4. Note that the DSC measurement of as spun fiber was carried out after the crystallization was completed. These fibers show the melting peak around 176°C irrespective of the draw ratio. However, these peaks tend to be sharper with increasing draw ratio, indicating more perfect crystal formation during the drawing process. The crystallinity calculated from the melting peak area increases once the fibers are cold drawn.

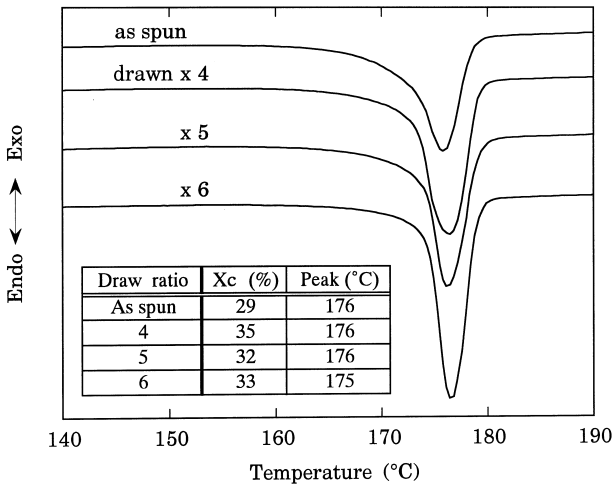
3.4. Higher order structure of the drawn PHB fibers

Yokouchi et al. [9] and Pazur et al. [10] reported that PHB crystallizes into an orthorhombic lattice structure ($P2_12_12_1$: $a = 0.576$ nm, $b = 1.320$ nm and $c = 0.596$ nm (fiber axis), α-form) with their chains in the left-handed 2/1 helix. Fig. 5(a) shows the WAXD pattern of the as spun PHB fiber. Three reflections are detected at $2\theta = 13.4$, 16.0, and 27.0° on the equator and assigned to be (020), (110) and (040) of orthorhombic unit cell, respectively. These reflections indicate the slight *c*-axis orientation of the crystal along the fiber axis even in the as spun fiber.

The WAXD patterns of PHB drawn fibers shown in Fig. 5(b)–(d) indicate the higher crystalline orientation with increasing draw ratio. First and second layer lines are clearly observed in the WAXD patterns of PHB fiber drawn to five or six times. In these fibers, *c*-axis parallel to the fiber axis seems to be the most preferential orientation. It should be noted that there is a broad reflection at $2\theta = 19.7°$ on the equator, which cannot be assigned to be any plane in the orthorhombic system. Furuhashi et al. [5] obtained similar WAXD patterns of poly(3HB-*co*-3HV) fibers and assigned this as a reflection from pseudohexagonal system. This reflection appears even in our homo PHB fiber drawn up to five times. Yokouchi et al. [9] reported the PHB crystalline modification which has a twisted planar zigzag conformation (β-form). Formation of this β-form induced by the cold drawing was demonstrated by Orts et al. [11] who suggested that the β-form chains emanate upon stretching from the amorphous domains between orthorhombic α-form lamellae. The increasing intensity of this reflection with draw ratio of the homo PHB fibers may support their mechanism.

3.5. Mechanical properties of the annealed PHB fibers

PHB fiber drawn up to six times was stretched under various tensile stresses at various temperatures to determine the maximum tensile stress obtainable without breakage. The maximum tensile stress can be applied without



Draw ratio	Xc (%)	Peak (°C)
As spun	29	176
4	35	176
5	32	176
6	33	175

Fig. 4. DSC heating traces of PHB fibers drawn to various draw ratios.

breakage were about 100 MPa at 125°C and 55 MPa at 150°C, respectively.

Fig. 6(a) shows the tensile strength of the annealed PHB fibers. The fibers annealed without tension reduces the strength lower than that of the unannealed fiber. Annealing under 50 MPa in tensile stress at any temperature examined kept the strength of the fibers close to that of the unannealed fiber. Annealing under 100 MPa increased the strength largely and the strength increased with increasing the annealing temperature. Annealing at 125°C under 100 MPa in tensile stress achieved the maximum strength.

Fig. 6(b) shows the tensile modulus of the annealed PHB fibers. The modulus of the annealed fibers tends to be higher

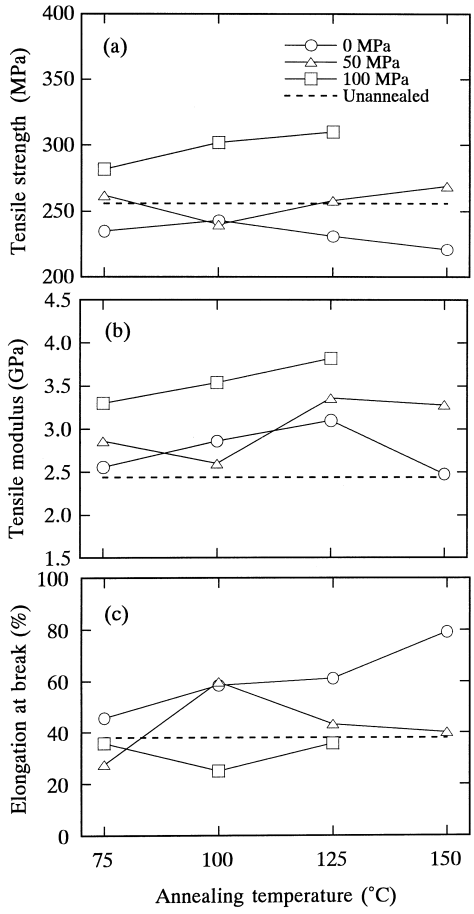


Fig. 6. (a) Tensile strength, (b) modulus, and (c) elongation at break of PHB fibers annealed under various tension at various temperature.

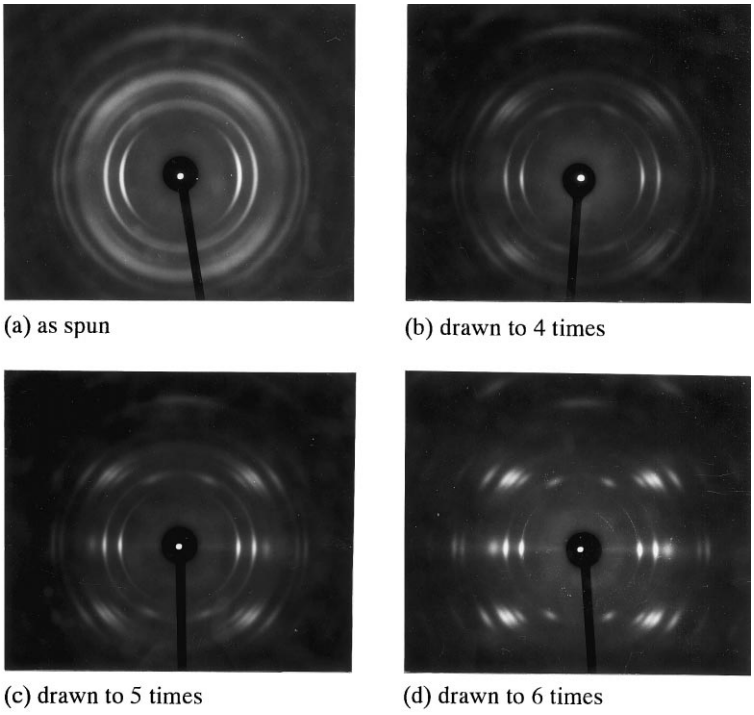
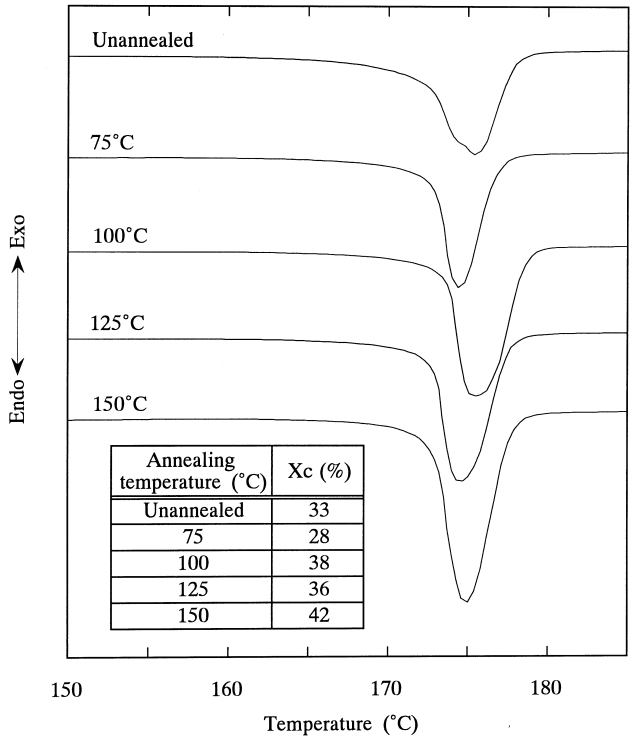
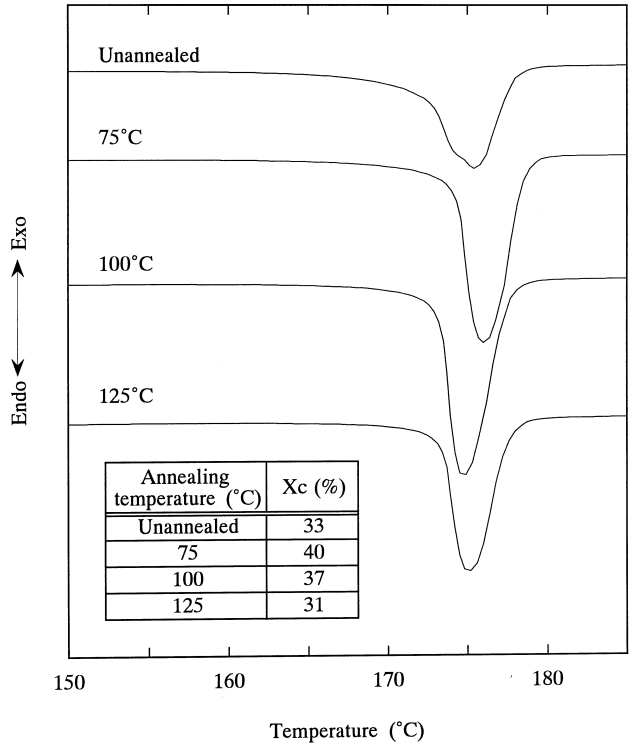


Fig. 5. WAXD patterns of as spun and drawn PHB fibers.



Annealing temperature (°C)	Xc (%)
Unannealed	33
75	28
100	38
125	36
150	42

Fig. 7. DSC heating traces of PHB fibers annealed without tension.



Annealing temperature (°C)	Xc (%)
Unannealed	33
75	40
100	37
125	31

Fig. 8. DSC heating traces of PHB fibers annealed under 100 MPa in tensile stress.

than that of the unannealed fiber, except for the fiber annealed without tension at 150°C. This is due to the crystallization that occurs during the annealing process. The modulus of the fibers under the tensile stress of 100 MPa increased monotonously with increasing annealing temperature and achieved the maximum value.

Fig. 6(c) shows the elongation at break of annealed PHB fibers. The elongation at break of the fibers annealed without tension increased with increasing temperature indicating the relaxation of the crystalline orientation during annealing. The elongation at break of the fiber annealed under 100 MPa at any temperature is lower than that of the unannealed fiber.

3.6. Thermal analysis of the annealed PHB fibers

Figs. 7 and 8 show the DSC heating curves of PHB fibers annealed at various temperatures without tension and under 100 MPa in tensile stress, respectively. Fig. 7 indicates that the melting peaks of fibers annealed without tension are larger than that of the unannealed fiber and tend to be sharper with increasing annealing temperature. Annealing at lower temperature under high tension makes this endothermic peak also sharper than that of the unannealed fiber. However, annealing under high tension at higher temperature (100 MPa in tensile stress at 125°C) makes the peak broader and even smaller. From these results, it is suggested that when annealing without tension, tie molecules and the crystals as formed melt partly recrystallize into a more perfect α-form crystal. This perfect crystal gives a sharp and large melting peak in the heating process. On the other hand, tie molecules between the α-form lamellae in the fiber annealed at high temperature under high tension recrystallize into the β-form. Since this form of crystal seems to be imperfect giving a broad reflection in the WAXD pattern, it does not add much additional melting peak area to that of the as formed orthorhombic crystal and gives some endothermic peak area at a lower temperature range making the melting peak broader.

3.7. Higher order structure of the annealed PHB fibers

Figs. 9–11 show the WAXD patterns of the annealed PHB fibers. These WAXD patterns indicate the crystalline orientation further increased with increasing annealing temperature and applied tension. The fiber annealed at 150°C under the tensile stress of 50 MPa shows the highest crystalline orientation among the fibers examined.

When annealed without tension, the reflection from the β-form on the equator become significantly weaker with increasing annealing temperature (Fig. 9). Under the tensile stress of 50 MPa, similar and less significant tendency was observed (Fig. 10). On the contrary, when the tensile stress is as high as 100 MPa, it becomes stronger with increasing temperature (Fig. 11). Especially, annealing at 125°C under the tensile stress of 100 MPa produced the fiber with the highest β-form content. From these results, it is suggested

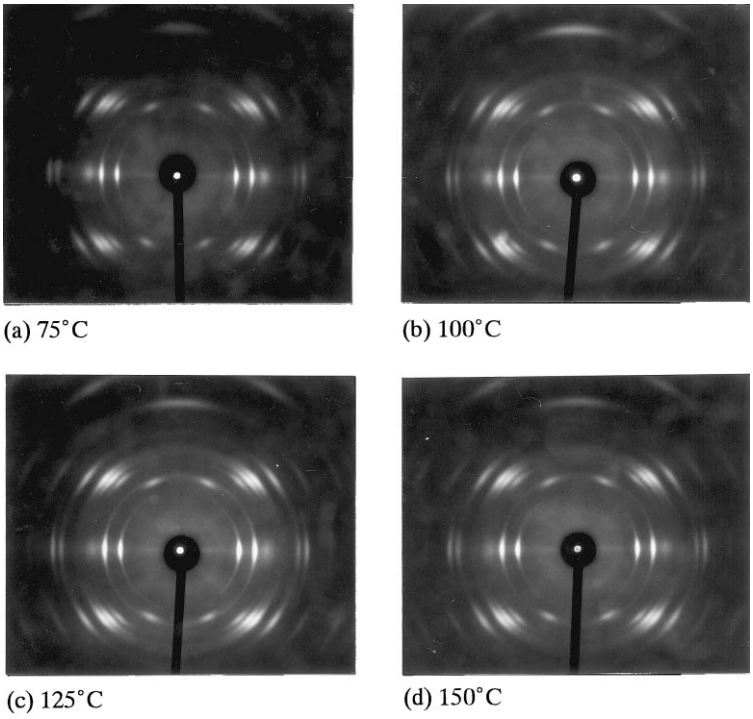


Fig. 9. WAXD patterns of PHB fibers annealed at various temperature without tension.

that the amorphous tie molecules transforms into orthorhombic crystal during the annealing process without tension. When the fibers are annealed under high tension, molecules in the amorphous region are stretched and crystallized into the β-form. This may be consistent with the results of DSC, where annealing without tension increase the melting peak area greatly while annealing under high tension increase it slightly. WAXD studies revealed that the reflection assigned to be the β-form is broad, indicating this crystal is rather imperfect. Orthorhombic crystal recrystallized from the tie molecule add some melting endotherm to that of the as formed crystal, while the β-form imperfect

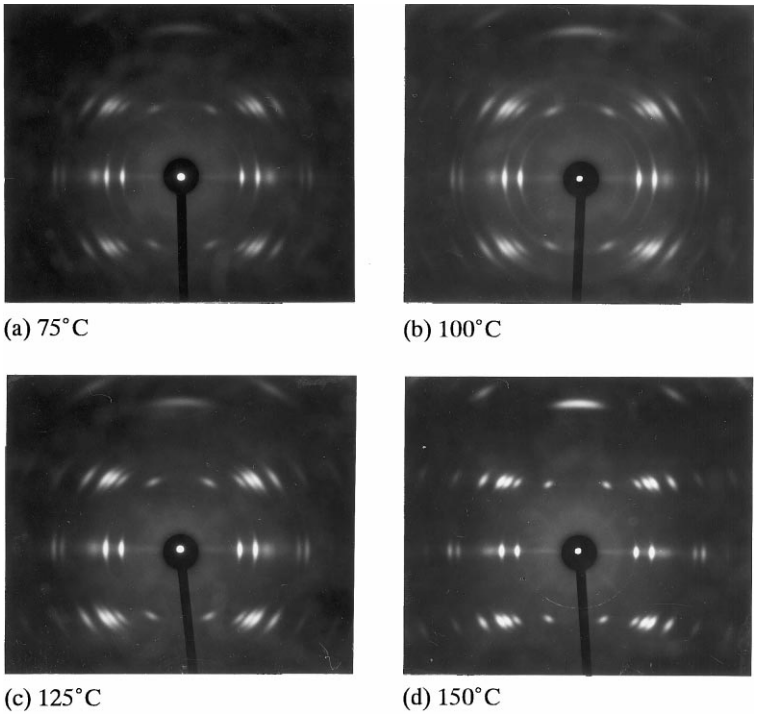


Fig. 10. WAXD patterns of PHB fibers annealed at various temperature under 50 MPa in tensile stress.

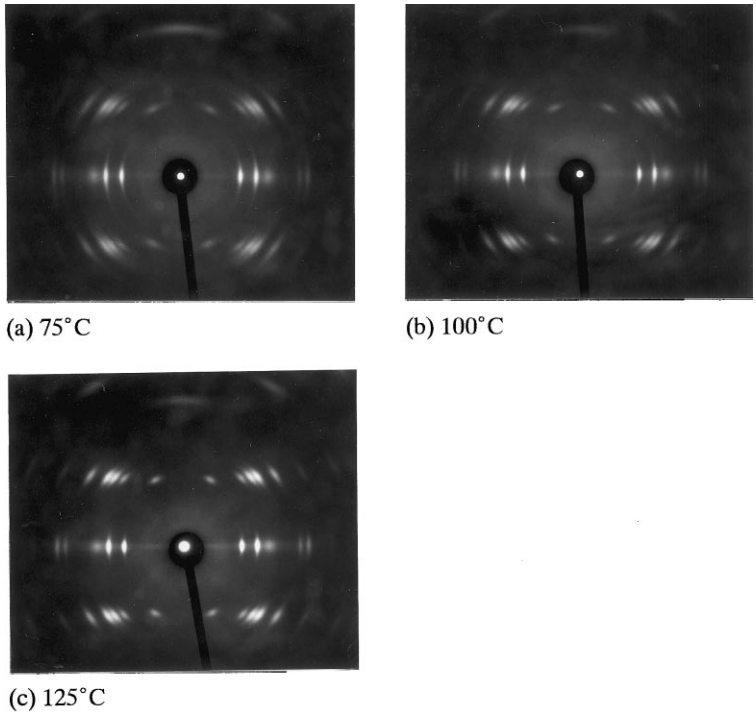


Fig. 11. WAXD patterns of PHB fibers annealed at various temperature under 100 MPa in tensile stress.

crystal recrystallized does not add large endothermic peak area. This mechanism may be further supported by examining the change in the diameter of the PHB fibers during annealing as shown in Fig. 12. When the fibers are annealed under high tension, fiber diameter tended to decrease, indicating the slight stretching of the fiber during annealing. On the other hand, annealing at high temperature without tension increases the diameter, indicating the shrinkage of the fiber during the annealing. The fibers which increased the diameter during annealing tend to have considerably less β-form than the unannealed fiber. On the other hand, the fibers which reduced the diameter during annealing have more β-form.

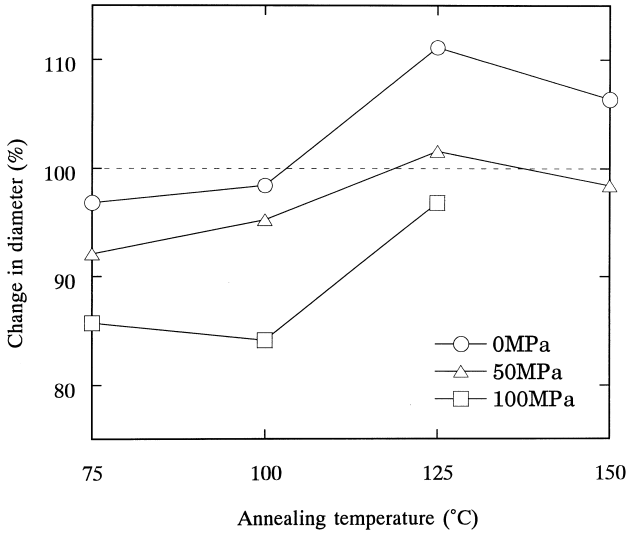


Fig. 12. Change in the fiber diameter during annealing.

4. Conclusion

Bacterial homo PHB was melt spun into fibers. Small amount of contaminant involved in PHB seems to act as a nucleating agent and some degree of crystallization occurred in the spinline. This crystallization made the cold drawing possible immediately after spinning.

WAXD patterns show that two kind of crystalline forms are present in the drawn fibers as already reported for poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) fibers. These are the α-form in the orthorohombic system and rather imperfect β-form with twisted planar zigzag conformation. Fraction of the latter increased with draw ratio. Annealing without tension increased the fraction of α-from and β-form present in the drawn fibers almost disappeared at high temperature. On the other hand, annealing at higher temperature under high tension increased the β-form fraction. Mechanical properties of PHB fiber increased not only with the crystalline orientation of the α-form but also increasing fraction of the β-form.

References

[1] Merrick J. Phtosynth Bact 1978;199:219.
[2] Ellar D, Lundgren DG, Okamura K, Marchessalt RH. J Mol Biol 1968;35:489.
[3] Biddlestone F, Harris A, Hay JN. Polym Int J 1996;39:221.

[4] De Koning GJM, Scheeren AHC, Lemstra PJ, Peeters PJ, Reynears H. Polymer 1994;35:4598.
[5] Furuhashi Y, Ito H, Kikutani T, Yamamoto T, Kimizu M. Sen i Gakkaishi 1997;53:356.
[6] Furuhashi Y, Ito H, Kikutani T, Yamamoto T, Kimizu M, Cakmak M. J Polym Sci Polym Phys 1998;36:2471.
[7] Yamamoto T, Kimizu M, Kikutani T, Furuhashi Y, Cakmak M. Int Polym Process 1997;12:29.
[8] Gordeyev SA, Nekrasov YUP. J Mater Sci Lett 1999;18:1691.
[9] Yokouchi M, Chatani Y, Tadokoro H, Teranishi K, Tani H. Polymer 1973;14:267.
[10] Pazur RJ, Hocking PJ, Raymond S, Marchessault RH. Macromolecules 1998;31:6585.
[11] Orts WJ, Bluhm TL, Hamer GK, Marchessault RH. Macromolecules 1990;23:26.