Properties and Enzymatic Degradability of Melt-Spun Fibers of Poly(butylene succinate) and Its Various Derivatives

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Abstract: Chain-extended poly(butylene succinate) (PBS-e) and poly(butylene succinate/adipate) (PBSA-e) as well as high polymers of poly(butylene succinate-co-carbonate) (PBSC) and poly(butylene succinate-co-ε-hydroxycaproate) (PBSCL) were melt-spun into mono-filament fibers by the on-line spinning and drawing technique. The mechanical properties and degradability of these fibers were totally compared in reference to those of the poly(butylene succinate) homopolymer (PBS) and poly(butylene succinate-co-L-lactate) (PBSL). It was found that the tensile strength of the drawn fibers decreases in the order of PBSA-e >> PBS-h > PBSL > PBS-e > PBSC > PBSCL corresponding with the decreasing order of their molecular weight. Their enzymatic degradability was studied with a lipase originated from *Pseudomonas cepacia*. It was found that the rate of enzymatic degradation is in the order of PBSA-e > PBSC > PBSL > PBSCL >> PBS-e ≅ PBS-h. This rate difference can be explained by the difference in crystal size and the polarity effect of the comonomer units that may affect the accessibility of the enzyme to the polymer chains.

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1. Introduction

Recently, biodegradable polymers have been paid much attention, because their use may reduce the environmental problems that are caused by the wastes of synthetic nondegradable polymers[1]. As the biodegradable polymers, aliphatic polyesters such as poly(L-lactic acid) (PLLA), poly(3-hydroxybutyrate) (PHB), and poly(butylene succinate) (PBS) have been developed and are now manufactured in large scale for use as plastic materials. Among them, PBS can readily be synthesized from succinic acid and 1,4-butanediol as the monomers by the use of the conventional petrochemical process[2-5]. The aliphatic polymers of this two-component type, however, have been recognized to be useless to fabricate synthetic fibers because of its low melting point and decreased molecular weight[6]. Recent progress in molecular design and polymerization technique has allowed us

to obtain high polymers of these aliphatic polyesters to improve their physical and mechanical properties. Consequently, PBS and its derivatives having a weight average molecular weight (Mw) higher than 100,000 have been available to replace the ordinary thermoplastic non-degradable polymers that are currently utilized. Recently[7-10], we succeeded in melt-spinning the fibers of a homopolymer of poly(butylenes succinate) (PBS-h) with high molecular weight and its copolymer of poly(butylene succinate-co-L-lactate) (PBSL) to demonstrate that both of the highly drawn fibers of PBS-h and PBSL have a high strength, competing with the ordinary polyamide fibers. We also demonstrated that these fibers can receive enzymatic degradation in spite of a rather slow rate. In the mean time, various PBS derivatives have been developed by introduction of various comonomer units or by chain extension with diisocyanates[11]. Accordingly, their properties and degradability should

be compared on a same basis to deduce the structure-property relationship of the PBS derivatives. On the other hand, we have discovered that a lipase originated from *Pseudomonas cepacia* is very active for degrading PBS derivatives[12,13]. This discovery allows us to evaluate the enzymatic degradability of the various

PBS derivatives to know how the comonomer composition affects their degradability.

In the present study, we prepare melt-spun fibers of various PBS derivatives with different comonomer and chain-extension units and evaluate their mechanical properties and enzymatic degradability to attain an insight into the effects of the structural units on the fiber properties.

2. Experimental

2.1 Materials

In the present study, four PBS derivatives were used, chain-extended poly(butylenes succinate) (PBS-e) and poly(butylene succinate/adipate) (PBSA-e) and polycondensed poly(butylene succinate-co-carbonate) (PBSC) and poly(butylene succinate-co-ε-hydroxycaproate) (PBSCL). Their structures and characteristics are shown in Scheme 1 and Table 1, respectively, in which those of the related derivatives PBS-h and PBSL are involved for comparison. PBS-e and PBSA-e whose chain extension had been done with hexamethylene diisocyanate[14] were supplied by Showa High polymer Co. Ltd. (Tokyo). PBSC was supplied by Mitsubishi Gas Chemical Industries Co. Ltd. (Tokyo) while PBSCL was supplied by Daicel Co. Ltd. (Osaka). A lipase from *Pseudomonas cepacia* (Lipase PS*) was obtained from Amano Seiyaku Co. Ltd. (Nagoya).

2.2 Melt-spinning and drawing

Mono-filament fibers were melt-spun with an extruder having a mono-hole nozzle of 1.0 mm in diameter at the spinning conditions summarized in Table 2. The as-spun filament was directly subjected to 5-fold drawing around 60°C[7].

Fig.1 Chemical structures of the PBS derivatives.

Table 1 Characteristics of various PBS derivatives.

Polymer	Comonomer (Unit mol %)	T _m (°C)	T _g (°C)	M _n (Da)	M _w /M _n
PBS-e	0.7 ^{a)}	112.4	-39.6	82,000	2.75
PBSA-e	2.6	90.6	-44.3	93,000	2.45
PBSC	3.3	98.6	-40.2	37,000	1.91
PBSCL	2.8	109.2	-41.5	31,000	1.86
PBS-h	—	114.0	-34.0	44,000	2.00
PBSL	3.0	111.0	-33.0	57,000	2.50

^{a)} Estimated from the M_n of the final polymer and the prepolymer.

2.3 Measurements

Tensile properties were measured on an AG-1000B tensile tester (Shimadzu Co. Ltd). The cross-head speed was 50 mm / min, and the sample length was 20 mm. Wide-angle X-ray scattering (WAXS) was measured on a JEOL DX-GE-E model diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation at a wave length of 1.542 Å that was generated at 40 kV and 20 mA. The fibers were cut to small pieces to obtain a random arrangement that could allow us to get an average diffraction from the fibers with three dimension. The crystallinity was estimated by the curve fitting of the resultant diffraction diagram. Birefringence of the fibers was measured on a Nikon Type 102 polarizing microscope with a Berek compensator under a sodium radiation. Scanning electron micrographs (SEM) were observed using a Hitachi S-800 microscope by accelerating the electron beam at an electric voltage of 6 kV. The sample was subjected to Pt - Pd coating.

2.4 Method of enzymatic treatment

Sample filaments (100 mm in length, 25 pieces) were dipped in 15 ml of a lipase solution (5 mg / ml) in a buffer (pH = 6) consisting of 28.4 g/l Na_2HPO_4 and 0.24 g/l NaH_2PO_4 at 50°C. After a prescribed time, the

filaments were taken out from the solution, washed thoroughly with water, and dried *in vacuo*. The lipase solution was refreshed after every three days.

3. Results and discussion

3.1 Properties of the melt-spun fibers of the PBS derivatives

As shown in Table 2, the spinning temperature of the PBS derivatives was adjusted to 110-138°C depending on their melt viscosity or molecular weight. The spinning temperatures of the chain-extended PBS-e and PBSA-e were significantly higher than those of the copolymers PBSC and PBSCL and the formerly examined PBS-h and PBSL. The melt draw ratio could be higher only for PBSA-e showing an excellent spinnability, while that of the other polymers was as low as 3 times. The melt-drawn filament was then directly subjected to the 5-fold drawing on line in order to avoid spontaneous crystallization of the polymer in the as-spun state[7]. Accordingly, both the spinnability and the drawability of each polymer were excellent, and a mono-filament fiber having a diameter of 100-310 μm was obtained in each case. Table 3

Table 2 Spinning conditions of mono-filament fibers of PBS derivatives¹⁾.

Polymer	Temperature ²⁾ (°C)	Extruding speed (m/min)	Winding speed (m/min)	Melt draw ratio (times)
PBS-e	138	8.7	25.9	3
PBSA-e	138	11.9	21.5	18
PBSC	110	7.6	23.4	3
PBSCL	128	8.8	27.5	3

¹⁾ The melt-drawn filament was directly subjected to the drawing of 5 times.

²⁾ For the spinneret. Feeding zone : 105°C, Metering zone : 112-132°C.

Table 3 Properties of mono-filament fibers drawn to 5 times¹⁾.

Polymer	Tensile properties			Diameter (μm)	Birefringence ($\Delta n \times 10^3$)	Crystallinity ²⁾ (%)
	Strength (MPa)	Modulus (GPa)	Elongation (%)			
PBS-e	250	0.44	29	250	71	43
PBSA-e	830	0.32	360	310	64	39
PBSC	190	0.44	41	150	69	42
PBSCL	150	0.47	38	100	63	46
PBS-h ³⁾	340	1.10	270	125	40	---
PBSL ³⁾	330	0.66	160	270	32	---

¹⁾ Drawing temperature : 65°C.

²⁾ By WAXS.

³⁾ Lit. 7)

summarizes the properties of the fibers newly prepared in this study, as compared with those of the formerly reported PBS-h and PBSL fibers[7-10]. It is known that the tensile strength is in the order of PBSA-e>> PBS-h> PBSL> PBS-e> PBSC> PBSCL. This order corresponds to the increasing order of molecular weight of the polymers except PBS-e whose drawability was very low. Among them, PBSA-e having the highest molecular weight and spinnability

showed a particularly high strength. The tensile modulus was almost similar among the derivatives, except PBS-h that showed a modulus twice higher than that of the others. The tensile elongation changed from 29 % to 360 % depending on the elasticity beyond the yield point of the stretched filaments. The PBSA-e fiber showed rather peculiar tensile properties among the derivatives, having the highest strength and elongation in spite of its lower modulus. The high strength may be attributed to the high molecular weight of the polymer that is induced by the chain extension reaction of the preformed PBS with diisocyanate. The urethane units involved in this copolymer can also provide the fiber with plasticity to give the lower modulus and higher elongation.

The birefringence values of the fibers were not so different from each other, being in the range from 6.3 to 7.1×10^{-2} that is comparable with that of Nylon 6 fibers[15]. These results suggest that the melt-spun fibers of the PBS derivatives can be strong if their molecular weight is enough high and that the properties of these fibers may compete with the recently developed PLLA fibers[16,17].

Fig.2 WAXS of the drawn fibers of (a)PBS-e, (b)PBSCL, (c) PBSA-e and (d) PBSC.

Fig.3 Typical SEM photoes of the fibers in cubated in the phosphate buffer containing Lipase PS* ((e),(f),(g),(h)) as compared with the corresponding original fibers((a),(b),(c),(d))). (a),(e): PBS-e, (b),(f): PBSCL, (c),(g): PBSA-e, (d),(h):PBSC. The incubation time was 192h, 336h, 48h, and 48h for PBS-e, PBSCL, PBSA-e, and PBSC. respectively at 50°C. Scale bar = 30 μ m

3.2 Crystallinity and morphology of the fibers

Figure 2 shows the WAXS of the drawn fibers of the PBS derivatives. Very sharp reflections due to the PBS crystals are shown, and accordingly, the crystals formed in the highly drawn fibers are monoclinic as reported previously[18]. It was also known that the crystal orientation and crystallinity (see Table 3) are not so different among the four.

Figures 3 (a, b, c, and d) show typical SEM photos of the drawn fibers of the PBS derivatives. It is known that each filament surface displays a texture along the spinning and drawing line. Particularly, the PBSCL fiber shows the most complex texture. As reported previously[7-10], the PBS derivatives are allowed to solidify in the melt-drawing stage with crystallization occurring to give partially crystallized as-spun fibers. The cold drawing of these as-spun fibers makes the preformed crystals orient in the fiber direction with some crystal transformation. However, the preformed crystallites, if enough stable, likely stay in the fiber without crystal transformation and inhibit homogeneous drawing of the fiber with the formation of the textures. Since the PBSA-e with short segmental nature likely forms small crystallites, the crystal transformation/orientation becomes smoother in comparison with other polymers to form little texture in the drawing stage. PBSCL whose fiber contained the most complex texture should become highly crystalline during the melt-drawing. These results also support that the PBS fibers should have as good quality as the conventional synthetic fibers.

3.3 Enzymatic hydrolysis

The filaments of the PBS derivatives were subjected to the enzymatic hydrolysis in the presence of Lipase PS*. Figures 4 and 5 show typical changes in mass and tensile strength of the various fibers as a function of immersion time, respectively. Since in the absence of the enzyme such rapid changes were not observed, the responsibility of the enzyme for the degradation was supported. We had learned before that the activity of this lipase can be kept for at least 5 days of incubation at 50°C [12]. Here, the enzyme solution was renewed every three days after the incubation for safety. In the case of PBSC and PBSA-e, the tensile strength decreased sharply at the initial stage of immersion. The PBSCL and PBSL fibers showed a gradual decrease in strength. Whereas, little

Fig.4 Changes in mass of the fibers of PBS derivatives as a function of incubation time.

Fig.5 Changes in tensile strength of the fibers of PBS derivatives as a function of incubation time.

decrease was observed even after a long immersion of PBS-e. The mass decrease was also very fast in the PBSA-e and PBSC fibers, while it was significantly slow in the PBSCL and PBSL fibers. The PBS-e fiber showed no weight decrease in the enzymatic hydrolysis as the previously examined PBS-h fiber [7-10]. Therefore, the hydrolysis rate is known to decrease in the order of PBSA-e > PBSC > PBSL > PBSCL >> PBS-e $\approx$ PBS-h. The tensile strength of the fibers is allowed to decrease with the mass loss because the tie molecules present in the amorphous phase are hydrolyzed.

Figures 3 (e, f, g, and h) show typical surface

morphologies of the degraded filaments as observed by SEM. The filaments having received the hydrolysis exhibited completely different surface structures compared with their respective original filaments. Apparently, the PBSA-e became outstandingly thinner than the original filament. Since the control experiment conducted without the lipase gave no change in the surface morphology in all cases, the action of the enzyme was known to be effective for the surface degradation of the filaments.

Generally, the degradation rate of polymeric materials is greatly influenced by their crystallinity and crystal size; the rate increases with decreasing crystallinity and crystal size¹⁸⁾ because both nonspecific and enzymatic hydrolyses preferentially initiate from the polymer chains involved in the amorphous region and then enter into those in the crystal surfaces. The large difference in degradation rate among the fibers examined here may be attributed to the different crystal size rather than the different crystallinity. In fact, the crystal size of the PBS derivatives should decrease in the order of PBS-h > PBS-e > PBSL > PBSCL > PBSC > PBSA-e as manifested by their T_m decrease, and this order is almost opposite to the increasing order of the enzymatic degradability of the fibers where the order of PBSL and PBSCL is turned around. On the other hand, the decreasing order of crystallinity among the four examined fibers, i.e., PBSCL > PBS-e $\cong$ PBSC > PBSA-e is not correlated with the degradability. Furthermore, the fact that the highly drawn fibers are more highly resistive to hydrolysis than the less drawn films suggests the importance of the crystal morphology in the degradation. Since the enzymatically degradable PBSA-e, PBSC, PBSL, and PBSCL are all copolymers including a considerable amount of comonomer units, the size growth of their crystals is limited and the polymer chains in the crystal surface are allowed to interact with the lipase. The polar groups such as urethane and carbonate groups involved in PBSA-e and PBSC, respectively, can attract water to stimulate the enzymatic hydrolysis, whereas the hydrophobic ϵ -hydroxycaproate units of PBSCL and the L-lactate units of PBSL cannot have such effect. Furthermore, it is known that PBS undergoes slow nonspecific hydrolysis even in the absence of the enzyme. This non-specific hydrolysis, although its rate is very slow, is faster for

the copolymers with polar comonomer units and thus the number of polymer chains that can interact with the enzyme increases to enhance the enzymatic hydrolysis. These facts lead to a conclusion that the enzymatic hydrolyzability of the PBS derivatives depends on the crystal size and the hydrophilic / hydrophobic nature of the introduced comonomer units.

4. Conclusion

Melt spun fibers were made from various PBS derivatives and subjected to enzymatic hydrolysis with Lipase PS* originated from *Pseudomonas cepacia*. It was found out that the tensile strength of the fibers was in the order of PBSA-e >> PBS-h > PBSL > PBS-e > PBSC > PBSCL and that their degradation rate with this enzyme was in the order of PBSA-e > PBSC > PBSL > PBSCL >> PBS-e $\cong$ PBS-h. This difference in degradation rate can be explained by the difference in crystal size and the polarity effect of the comonomer units that are related with the enzyme accessibility to the polymer units.

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