Mechanical Properties of Poly(ethylene terephthalate) Fiber Produced by Conjugate Melt Spinning with Polystyrene and CO₂ Laser-Heated Drawing

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Abstract: Poly(ethylene terephthalate) (PET) fiber is obtained by polystyrene (PS)/PET sheath/core conjugate melt spinning and removal of the PS component. The fiber is drawn under heating using a carbon dioxide (CO₂) laser. The drawn PET fibers, obtained by PS/PET (80/20) conjugate melt-spinning with take-up velocity of 7 km/min, exhibit higher tensile strength for a given birefringence than that of the corresponding single-component spun and drawn PET fiber.

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1. Introduction

Sheath/core conjugate fibers are formed by co-extrusion of two polymers arranged concentrically. On the spin-line of the conjugate melt-spinning process, the thinning behavior is different from that for single-component spinning due to differences in the elongational viscosity, activation energy of the viscosity, and solidification temperature of the two polymers. As a result, by controlling the stress histories applied to each component, fibers with specific structures, which have higher whole molecular chain orientation than segmental orientation, can be produced. Such special fibers cannot be obtained by single-component spinning. For example, in the PS/PET system, because the PS component solidifies first, no large stress is applied to the PET component, and the applied stress is relaxed after solidification of the PS component. This prevents orientation-induced crystallization even for take-up at 7 km/min [1].

To analyze the effect of conjugate melt spinning, it is desirable that the drawing process is chosen such that the structural characteristics of the as-spun fiber formed in the spinning process reflect those of the drawn fiber as far as

possible. CO₂ laser-heated drawing is a suitable drawing process to achieve this goal, as the as-spun fiber can be drawn instantaneously after rapid and uniform heating by laser irradiation [2]. In this study, PET fiber is produced by this PS/PET sheath/core conjugate melt-spinning process and drawing under CO₂ laser heating followed by removal of the PS sheath. The mechanical properties of the resulting fiber are investigated based on the birefringence and network draw ratio as structural parameters expressing the molecular orientation behavior.

2. Experimental

2.1 Sample

A fiber with PET (IV=0.95 dl/g, Toray) core and PS (57057U, Showa Denko) sheath was produced by conjugate melt-spinning. Polymers were extruded from a 0.5 mm-diameter, single-hole, sheath-core spinneret at 295 °C. The PS/PET weight fraction was varied from 80/20 to 50/50 and 0/100 while maintaining the mass flow rate of the PET component at 2.98 g/min. The fibers were taken-up at 1 and 7 km/min. The PS sheath was later removed by running immersion of the as-spun fiber in a carbon tetrachloride bath for about 90 s.

A CO₂ laser generator with emission wavelength of 10.6 μm (PIN-20S, Onizca Glass Co. Ltd.) was used for laser-heated drawing. The beam diameter at the running fiber was set at 4.0 mm, and the laser power was maintained at

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Table 1 Structure and tensile properties of spun/drawn PET fiber

Sample No.	PET Fraction	Take-Up Speed	Draw Ratio	Feed Speed	Δn	Initial Modulus	Tensile Strength	Elongation	Boil-off Shrinkage Factor
	/ wt%	/ km min ⁻¹		/ m min ⁻¹	$\times 10^3$	/GPa	/GPa	$\times 100\%$	$\times 100\%$
1	20	1	-	-	1.8	2.5	0.13	454	14
2	20	1	3.5	12	134.7	9.2	0.60	88	10
3	20	1	4.0	12	159.2	10.9	0.66	63	10
4	20	1	4.5	12	173.7	12.7	0.70	41	9
5	20	1	5.0	12	180.6	16.4	0.99	28	10
6	20	1	5.5	12	186.6	17.8	1.15	19	9
7	20	1	5.6	12	188.9	18.3	1.16	17	9
8	20	7	-	-	18.4	2.5	0.24	198	53
9	20	7	2.5	12	134.6	11.7	0.75	42	8
10	20	7	3.0	12	149.0	13.0	0.80	31	15
11	20	7	3.5	12	178.5	17.6	1.13	14	10
12	20	7	2.0	3	104.7	6.7	0.58	77	5
13	20	7	2.5	3	130.7	10.8	0.74	36	6
14	20	7	3.0	3	151.8	16.0	0.98	13	8
15	20	7	3.5	3	174.4	17.2	1.11	10	8
16	50	1	-	-	4.0	1.8	0.14	451	40
17	50	1	3.5	12	146.5	10.1	0.57	54	10
18	50	1	4.0	12	164.3	12.2	0.67	42	12
19	50	1	4.5	12	173.7	14.1	0.78	26	10
20	50	1	5.0	12	180.3	15.3	0.92	18	8
21	50	7	-	-	27.4	2.2	0.31	191	35
22	50	7	2.0	12	114.9	6.6	0.52	50	10
23	50	7	2.5	12	169.6	9.7	0.66	20	16
24	50	7	3.0	12	187.4	11.5	0.90	10	18
25	100	1	-	-	6.4	2.3	0.20	419	51
26	100	1	3.5	12	161.1	10.5	0.63	34	8
27	100	1	4.0	12	164.2	14.0	0.87	25	8
28	100	1	4.5	12	181.8	15.2	0.89	27	12
29	100	1	5.0	12	196.3	16.1	1.03	14	13

17 W [3]. The draw ratio and fiber feed speed were as listed in Table 1.

2.2 Refractive Indices

The refractive indices parallel ($n_{\parallel}$) and perpendicular ($n_{\perp}$) to the fiber axis were measured using an interference microscope (Interphako, Carl Zeiss Jena). A mixed solution of diiodomethane and tricresyl phosphate was prepared as an immersion medium. The birefringence (Δn) was calculated as follows.

$$\Delta n = n_{\parallel} - n_{\perp} \quad (1)$$

2.3 Tensile Testing

Each fiber sample (40 mm gauge length) was extended at an initial strain rate of 100% min⁻¹ at room temperature on a tensile tester (RTC-1250, Orientec Tensilon). True stress–true strain curves were obtained from the nominal stress–

strain curves under the assumption of constant volume.

2.4 Boil-Off Shrinkage

Samples with an initial length of 500 mm were immersed in boiling water for 30 min, and the resultant length was measured. The shrinkage factor was calculated as follows:

$$S = \frac{l_0 - l}{l_0} \quad (2)$$

where S is the boil-off shrinkage factor, l_0 is the initial length, and l is the length after shrinkage.

3. Results and discussion

Stress–strain curves were compared to investigate the effect of sheath/core conjugate spinning on the mechanical properties of the as-spun fiber. Figure 1 shows the true

Fig.1 Shifted true stress-strain curves of as-spun fibers

stress-true strain curves shifted to fit the endpoint of the natural drawing region. The true stress-true strain curves of the 50/50 7 km/min sample are omitted as the samples did not exhibit a distinct endpoint of the natural drawing region. The 80/20 7 km/min fiber exhibited the shortest natural drawing region. For the fibers taken up at 1 km/min, higher PS fraction fiber exhibited a larger natural drawing region. In addition, the fibers with 80% PS fraction appear to display a steeper stress increase from the endpoint of the natural drawing region. These results demonstrate that it is possible to produce as-spun fibers with different network structures by changing the strain-rate on the spin-line.

The mechanical and thermal properties of conjugate-spun and laser-drawn PET fibers are listed in Table 1. The PET fibers melt-spun with 80% PS exhibit the highest strength of the fibers prepared in this study. The fiber which had a tensile strength of 1.38 GPa, initial modulus of 18.2 GPa, and elongation of 8% was obtained under the conditions of sample No. 15 using a drawing system that have a reduced fiber friction.

It is interesting that the 80/20 7 km/min fibers drawn to the maximum draw ratio have smaller birefringence values than any of the other fibers drawn to maximum draw ratio. Figure 2 shows the relationship between tensile strength and birefringence of the drawn fibers. The 80/20 7 km/min samples have higher tensile strength for a given birefringence compared to the other fibers, demonstrating that it is possible to obtain PET fibers with high strength for their birefringence by high-speed conjugate spinning and laser-heated drawing. However, the result is not systematic because the 50/50 7 km/min samples do not display such relatively high strength. Therefore, although high-speed conjugate spinning can be used to improve the strength of the drawn fiber, more experimental results are needed in order confirm this result.

The possible effect of immersion in carbon tetrachloride for removal of the sheath was investigated by comparing

Fig. 2 Tensile strength plotted against birefringence

the mechanical properties of 80/20 1 km/min fibers after immersion in carbon tetrachloride for 2 min and 1 h. No significant differences in strength or elongation were identified, indicating that the effect of carbon tetrachloride on the mechanical properties of the resulting PET fiber can be ignored.

The network draw ratio (λ_{net}) [4] was employed to investigate the fiber structure that determines the tensile strength. The network draw ratio can be obtained as follows:

$$\lambda_{net} = \lambda_s \cdot \lambda_{rel} \quad (3)$$

where λ_{rel} is a relative network draw ratio (the effective draw ratio attained by drawing) obtained by the following method. By the shifting of each true stress-strain curve along the true strain range for each sample [5], was calculated from true strain shift (γ_s):

$$\lambda_{rel} = \exp(\gamma_s) \quad (4)$$

Figure 3 shows an example of such shifted true stress-true

Fig.3 Shifted true stress-strain curves of spun and drawn fibers

strain curves. According to the method proposed by Long and Ward [6], the true stress–true strain curves of drawn fibers are shifted toward the true strain direction, overlapping in the vicinity of the break point. As-spun PET fiber taken up at 200 m/min was used as the standard low-orientation fiber. The true stress–true strain curves coincide well in the high-strain region. Where λ_s is the network draw ratio of a standard low-orientation fiber. In this study, was calculated from a thermal shrinkage factor. That was 1.35.

Figure 4 shows the correlation between the network draw ratio and birefringence. The 80/20 7 km/min samples have higher network draw ratios for a given birefringence compared to the others fibers. As the network draw ratio was obtained by shifting the true stress–true strain curves such that the stress coincides in the high strain region, a higher network draw ratio was given by a higher average modulus up to the breaking point. Therefore, a higher network draw ratio at the same birefringence suggests the formation of a larger number of stress-bearing structures for the same molecular segmental orientation. However, similar to the case for tensile strength, the 50/50 7 km/min samples do not exhibit such relatively high network draw ratios.

Fig. 4 Network draw ratio plotted against birefringence

The network draw ratio is defined as the total draw ratio of an imaginary network structure extended through the spinning and drawing process. Accordingly, when the PET fiber was extended in a very short time at high temperature and high draw ratio, then frozen at high temperature, there is the possibility of obtained a fiber structure with higher network orientation than molecular segmental orientation (expressed by birefringence). That is, the PET core fiber deforms at higher temperature and in shorter time, and relaxes

more after solidification in the sheath-core conjugate spin- [1]. As a result, PET fiber obtained by sheath-core conjugate spinning allows for a long natural drawing region. Particularly for fiber taken up at high velocity, only the small segments can relax with a short relaxation time. This tends to form a fiber structure with higher whole molecular chain orientation than segmental orientation [7], resulting in fewer entanglements [8]. This explains the steeper stress increase after the natural drawing region (Fig. 1). Narrower tie-chain-length distributions [9] and thus higher tensile strength can be obtained by sheath/core conjugate melt spinning compared to the single-component spun fiber. And CO₂ laser drawing can reflect that the structural characteristics of the as-spun fiber formed in the spinning process because of drawing the fiber instantaneously with rapid and uniform heating. That is, the drawn fiber appears to contain more load bearing structures, such as taut-tie chain or shish crystal, and less lamellar crystal, which bears a relatively low stress at the breaking point, giving rise to a fiber with higher tensile strength.

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