Mechanical Properties and Microstructure of Poly(ethylene terephthalate) Microfiber Prepared by Carbon Dioxide Laser Heating

Akihiro Suzuki, Noriaki Mochizuki

Department of Applied Chemistry and Biotechnology, Faculty of Engineering, University of Yamanashi, Takeda-4, Kofu 400-8511, Japan

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ABSTRACT: We determined that a poly(ethylene terephthalate) microfiber was easily obtained by irradiating a carbon dioxide laser to an annealed fiber. The annealed fiber was prepared by zone drawing and zone annealing. First, an original fiber was zone drawn at a drawing temperature of 90°C under an applied tension of 4.9 MPa, and the zone-drawn fiber was subsequently zone annealed at 150°C under 50.9 MPa. The zone-annealed fiber had a degree of crystallinity of 48%, a birefringence of 218.9×10^{-3}, tensile modulus of 18.8 GPa, and tensile strength of 0.88 GPa. The microfiber prepared by laser heating the zone-annealed fiber had a diameter of 1.5 μm, birefringence of 172.8×10^{-3}, tensile modulus of 17.6 GPa, and tensile strength of 1.01 GPa. The draw ratio estimated from the diameter was 9165 times; such a high draw ratio has thus far not been achievable by any conventional drawing method. Microfibers may be made more easily by laser heating than by conventional technologies such as conjugate spinning. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1955–1958, 2003

Key words: drawing; fibers; mechanical properties; microstructure; polyesters

INTRODUCTION

We previously applied a continuous-wave carbon dioxide (CO_2) laser to the drawing and annealing of poly(ethylene terephthalate) (PET)[1] and nylon 6[2] fibers to improve their mechanical properties. The laser heating was carried out by irradiating the CO_2 laser to the fiber moved at constant speed along a fiber axis. The drawing and annealing using laser heating was designated the laser-heating zone-drawing, and zone-annealing method,[1,2] which was found to be effective in improving their mechanical properties and is excellent from an external heating such as a heating carried out using a heating wire or hot air under very rapid and uniform heating conditions.

The CO_2 laser has been so far applied to welding, cutting, and cladding for ceramics and metals, annealing of semiconductors, and improvement of the surface properties of carbon or other ceramic fibers.[3–8] However, reports in the literature on application of polymers are extremely few.[9,10]

In preliminary experiments to optimize the laser-heating zone-drawing condition for PET fibers it was found that PET microfibers were prepared by laser heating carried out under very low applied tension at higher power density when compared with laser-heating zone drawing. It has already been reported that the original PET fiber with a diameter of 143.6 μm was quickly thinned to 4.5 μm by laser heating, and that its draw ratio estimated from the diameter was 1018 times.[11]

Microfibers are now manufactured with an especially highly skilled technique such as conjugate spinning, which requires a highly complex spinneret. Until now it has been impossible to produce microfibers with any drawing. However, laser heating easily produces microfibers without especially highly skilled techniques.

We present here the results pertaining to the properties of the PET microfibers obtained by applying CO_2 laser heating to the annealed PET fiber.

EXPERIMENTAL

Materials

The original PET fiber used in the present study was a commercial-grade fiber ($\overline{M}_w$= 55,000, $\overline{M}_n$ = 30,000) and had a diameter of 143.6 μm, degree of crystallinity of 4.5%, and birefringence of 0.7×10^{-3}. The original fiber was amorphous and isotropic as shown in Figure 1.

Measurements

The birefringence was measured with a polarizing microscope equipped with a Berek compensator (Olympus Optical Co., Ltd., Japan).

Correspondence to: A. Suzuki (a-suzuki@ab11.yamanashi.ac.jp).

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Figure 1 Wide-angle X-ray diffraction (WAXD) photograph of the original fiber.

Density (ρ) was measured at 23°C by a flotation technique using a carbon tetrachloride and toluene mixture. The degree of crystallinity, expressed as a weight fraction (X_w), was obtained using the relation

$$X_w = [\rho_c(\rho - \rho_a)]/[\rho(\rho_c - \rho_a)] \times 100 \quad (1)$$

where ρ_c and ρ_a are densities of the crystalline and amorphous phases, respectively. In this measurement, a value of 1.455 g/cm^3 was assumed for ρ_c and a value of 1.335 g/cm^3 was assumed for ρ_a.[12] The density of amorphous polymer was assumed to be constant, independent of treatments. However, the density of the microfiber was not measurable by the flotation technique because the specimen was too small.

The draw ratio can be calculated easily using the following equation:

$$\text{Draw ratio} = (d_0/d)^2 \quad (2)$$

where d_0 is the diameter of the original fiber and d is that of the obtained fiber, and the volumes before and after the drawing are assumed to be constant.

Wide-angle X-ray diffraction (WAXD) photographs of the fibers were taken using a flat-film camera. The camera was attached to a Rigaku X-ray generator (Rigaku Co., Japan), operated at 36 kV and 18 mA. The radiation used was Ni-filtered Cu–K_α. The sample-to-film distance was 40 mm. The fiber was exposed for 4 h to the X-ray beam from a pinhole collimator with a diameter of 0.4 mm.

A Tensilon tensile-testing machine (Orientec Co. Ltd., Japan) was used to determine tensile modulus, tensile strength, and elongation at break. A gauge length of 5 cm and elongation rate of 10 mm/min were used. The experimental results are the average of 10 measurements.

The neck profile of the microfiber was photographed with a polarized microscope equipped with a camera.

Laser heating

The CO_2 laser-heating apparatus used for producing the microfiber consisted of the continuous-wave (CW) CO_2 laser emitter (PIN10S; Onizuka Glass Co., Ltd., Japan), a power meter with a thermal head, and an electric slider (Limo Oriental Motor Co. Ltd., Japan), as shown in Figure 2. The electric slider was used to move the fiber at a constant speed. The continuous-wave CO_2 laser emitted light at 10.6 μm, and the laser beam was a 4.0-mm-diameter spot. A power density was measured by the power meter before the laser heating. One end of the zone-annealed fiber was connected to a jaw equipped with the electric slider, whereas the other was attached to a slight weight. The zone-annealed fiber, moving downward at a speed of 500 mm/min, was heated by irradiating the CW CO_2 laser, and drawn instantaneously. The apparatus used in the zone drawing and zone annealing was previously described in detail elsewhere.[13]

RESULTS AND DISCUSSION

We determined that a thinner microfiber could be obtained when the annealed fiber was laser heated at a higher-output power compared with the thinning of the original fiber, and that it is necessary to previously draw and anneal the original PET fiber to obtain a thinner microfiber.

In this study, zone drawing and zone annealing, as described elsewhere,[13] constituted the pretreatment,

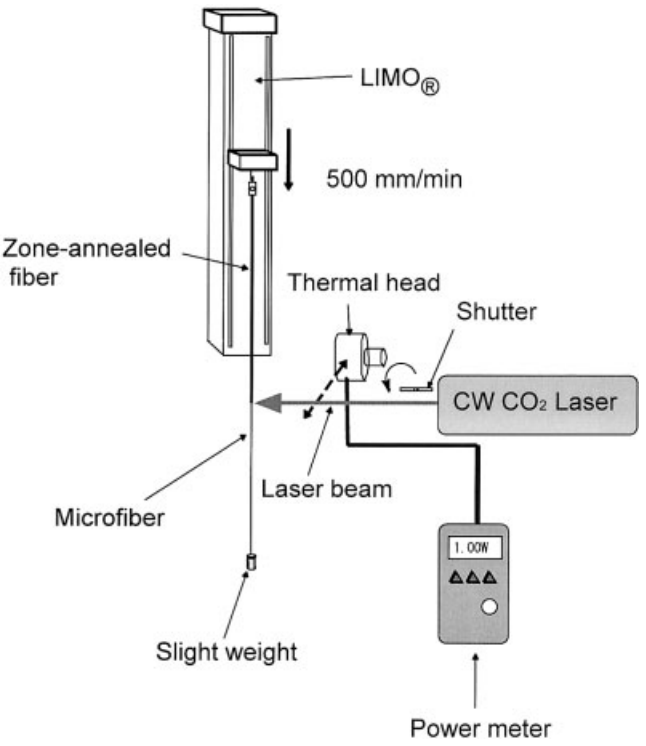

Figure 2 Scheme of apparatus used for laser heating.

TABLE I
Optimum Conditions of Zone Drawing, Zone Annealing, and Laser Heating

Treatment	Applied tension (MPa)	Treating temperature (°C)	Laser power density (W/cm^{-2})
Zone drawing	74.0	90	—
Zone annealing	72.0	150	—
Laser heating	0.0265	—	55.4

given that the zone treatment is an excellent method to prepare the highly oriented fibers with a high degree of crystallinity. The optimum treating conditions to prepare the highly oriented fiber with a high degree of crystallinity were determined in preliminary experiments and are presented in Table I.

First, the original PET fiber was zone-drawn at a drawing temperature of 90°C under an applied tension of 4.9 MPa, and the zone-drawn fiber was subsequently zone-annealed at 150°C under 50.9 MPa. The final fiber obtained by the zone-drawing and zone-annealing process has a degree of crystallinity of 48% and a birefringence of 218.9×10^{-3}, as shown in Table II.

In experiments to determine the optimum condition for laser heating to thin the zone-annealed fiber, the diameter decreased by increasing the laser power density and decreasing the applied tension. When the zone-annealed fiber, to which was added an applied tension of 26.5 kPa, was heated by the CO_2 laser operated at 55.4 W cm^{-2}, the thinnest microfiber was obtained.

The diameter, draw ratio estimated from the diameter, birefringence, and degree of crystallinity for the original fiber, zone-drawn and zone-annealed fibers, and microfiber are also given in Table II. The microfiber obtained under the optimum thinning conditions had a diameter of 1.5 μm and a birefringence of 172.8×10^{-3}, and the draw ratio obtained was 9165 times; such a high draw ratio has thus far not been achievable by any conventional drawing method. Its birefringence is approximately one-half of an intrinsic birefringence (310×10^{-3}).[14] It was suggested that under these conditions, the orientation process is predominant over molecular relaxation processes.

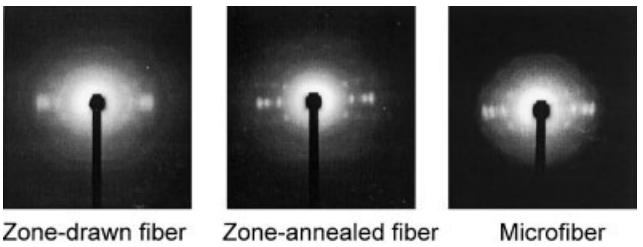

Figure 3 WAXD photographs of the zone-drawn fiber, zone-annealed fiber, and the microfiber.

Figure 3 shows the WAXD photographs of the zone-drawn fiber, zone-annealed fiber, and the microfiber. In the zone-drawn fiber, three principal indistinct reflections (010, $\bar{1}10$, and 100) attributed to crystallites formed by strain-induced crystallization are observed on the equator. Their reflections become more conspicuous at the zone-annealed fiber. The sharpening of the diffraction spots indicates improvements in crystallinity, crystalline orientation, and crystal perfection. The degree of crystallinity of the zone-drawn fiber is 32%, and that of the zone-annealed fiber is 48%, as given in Table II. The WAXD photograph of the microfiber shows that high levels of crystallinity and crystalline orientation are obtained in the thinning by the laser heating. This fact indicates that not only the molecular flow but also the molecular orientation and crystallization are induced by the high strain rate during the thinning process and that agrees approximately with the result of birefringence mentioned above.

Figure 4 shows SEM micrographs of the original fiber and the microfiber. The microfiber has a smooth surface without a surface roughened by a laser ablation and is uniform in diameter.

The mechanical properties for the original fiber, the zone-drawn and zone-annealed fibers, and the microfiber are shown in Table III. The microfiber has a tensile modulus of 17.6 GPa and a tensile strength of 1.01 GPa, and its tensile properties are almost the same as those of the zone-annealed fiber. In spite of an extremely large deformation from the molten state, the microfiber has a high degree of molecular orientation and excellent mechanical properties.

TABLE II
Diameter, Draw Ratio Estimated from Diameter, Birefringence, and Degree of Crystallinity for Original Fiber, Zone-Drawn and Zone-Annealed Fibers, and Microfiber

Fiber	Diameter (μm)	Draw ratio $(d_0/d)^2$	Birefringence ($\times 10^3$)	Degree of crystallinity (%)
Original fiber	143.6	—	0.4	4.5
Zone-drawn fiber	74.0	3.8	196.4	32
Zone-annealed fiber	72.0	4.0	218.9	48
Microfiber	1.5	9158	172.8	—

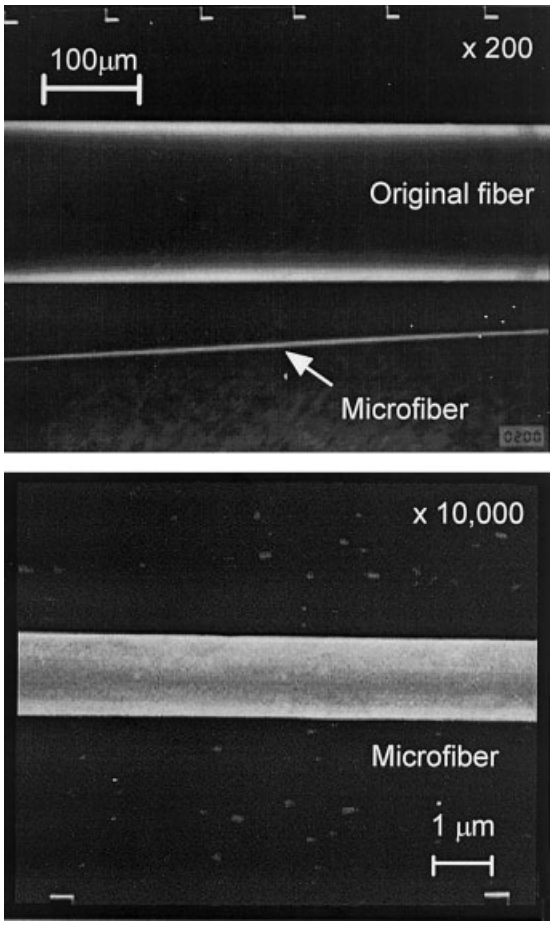

Figure 4 SEM micrographs of an original PET fiber and the microfiber with a diameter of 1.5 μm.

The thinning mechanism is conceivable as follows. Because the higher crystallinity and crystal perfection in the annealed fiber make it possible to irradiate a higher output laser to the fiber as compared to the thinning for the original fiber, the plasticity viscosity in the part heated by a high output laser becomes extremely low. However, the fiber was not stretched or broken because of an extremely low applied tension, and the heated part becomes nearly molten, that is, a sintering state. The microfiber was spun from the sintering state. This is clear from the microphotograph of a spindle-shaped necking as shown in Figure 5. As a result of the laser heating under extremely low applied tension at the higher power, the plastic flow occurred at the higher strain rate. The deformation at the higher strain rate induced the molecular orientation and crystallization in spite of a large deformation just like in the flow drawing and gives the oriented PET microfiber.

TABLE III
Tensile Modulus, Tensile Strength, and Elongation at Break for Original Fiber, Zone-Drawn and Zone-Annealed Fibers, and Microfiber

Fiber	Tensile modulus (GPa)	Tensile strength (GPa)	Elongation at break (%)
Original fiber	2.1	—	—
Zone-drawn fiber	5.8	0.37	62.1
Zone-annealed fiber	18.8	0.88	7.6
Microfiber	17.6	1.01	43.4

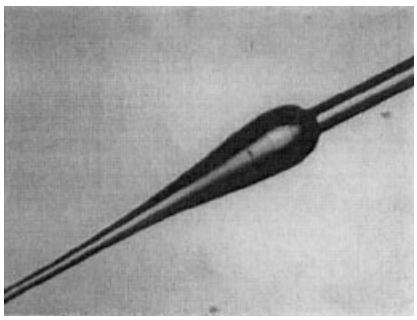

Figure 5 Microphotograph of a spindle-shaped necking in the laser-heated fiber.

CONCLUSIONS

It was found that the CO_2 laser-heating process is capable of producing PET microfibers. The thinning of PET fibers becomes possible by irradiating the high-output laser to the fiber applied at an extremely low load. The PET microfiber obtained under the optimum thinning condition had a diameter of 1.5 μm and birefringence of 172.8×10^{-3} and showed a highly oriented amorphous region and the existence of the crystallites resulting from the strain-induced crystallization. Tensile properties of the microfiber were almost the same as those of the zone-annealed fiber. The draw ratio obtained was 9165 times, and such a high draw ratio has thus far not been achievable by any conventional drawing method. Microfibers may be made more easily by laser heating than by conventional technologies such as conjugate spinning.

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