PET 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

ABSTRACT: In preliminary experiments to optimize the condition of a laser heating, zone drawing for poly(ethylene terephthalate) (PET) fiber, a microfiber was prepared by a continuous-wave carbon dioxide (CW CO_2) laser heating. CW CO_2 laser heating was carried out at an extremely low applied tension (σ_a) at a higher laser power density (PD) as compared to the optimum condition for the laser heating, zone drawing of PET fiber reported previously. The microfibers were obtained by CO_2 laser heating carried out at a PD of 15.8 W cm^{-2} and under a σ_a of 0.66 MPa or lower. The diameter of the fiber decreased with a decreasing σ_a and increasing PD. The smaller the diameter, the higher was its birefringence. The smallest diameter fiber obtained at σ_a = 0.17 MPa at PD = 21 W cm^{-2} had a diameter of 4.5 μm and a birefringence of 0.112, and its draw ratio estimated from the diameter reached 3086 fold. Such a high draw ratio was not previously attained by any drawing method. In a wide-angle X-ray diffraction photograph of the smallest diameter fiber, indistinct reflections due to oriented crystallites were observed. An SEM micrograph of the smallest diameter fiber showed a smooth surface without any crack and was uniform in diameter. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 3279–3283, 2003

Key words: drawing, fibers; polyesters; FT-IR; differential scanning calorimetry (DSC)

INTRODUCTION

A carbon dioxide (CO_2) laser has been applied to the welding, cutting, and cladding of ceramics and metals, the annealing of semiconductors, and the improvement of the surface properties of carbon or other ceramic fibers.[1–6] However, the CO_2 laser has been hardly applied to polymers, and there is only little literature in this field, for example, for the etching of polymers[7] and the curing of epoxy resin.[8]

We applied a continuous-wave carbon dioxide (CW CO_2) laser to the drawing and annealing of fibers to improve their mechanical properties. Laser heating is excellent for an external heating such as a zone heating for a very rapid and uniform heating. The laser-heating zone-drawing and annealing method was applied to poly(ethylene terephthalate) (PET)[9] and nylon 6 (ref. 10) fibers and was found to be effective in improving their mechanical properties.

In the laser-heating zone-drawing of PET fibers, as-spun PET fibers were zone-drawn under an applied tension (σ_a) of 4.44 MPa at a power density (PD) of 6.08 W cm^{-2}, and then the laser-heated zone-drawn fiber was zone-annealed to crystallize the fiber with the highly oriented amorphous regions. The laser heating, zone annealing was carried out in three steps: The first annealing was carried out under σ_a = 139 MPa at 4.83 W cm^{-2}, the second under σ_a = 283 MPa at 4.83 W cm^{-2}, and the third under σ_a = 432 MPa at 3.45 W cm^{-2}. The zone-annealed fiber obtained had a final birefringence of 0.239, a degree of crystallinity of 55%, a tensile modulus of 19.8 GPa, and a storage modulus of 25.7 GPa at 25°C.

In preliminary experiments to optimize the condition of laser-heating zone drawing for PET fiber, a PET microfiber was prepared by laser-heating carried out under a very low applied tension at a higher PD when compared with the condition of laser heating zone-drawing for as-spun PET fiber. The microfibers are now manufactured with an especially highly skilled technique such as a conjugate spinning requiring a highly complex spinneret. Therefore, the productivity of the microfiber using conjugate spinning is low and its production cost is high.

In using the method, we found that the microfiber is easily obtained by laser-heating without especially highly skilled techniques. We present here the results pertaining to the properties of the PET microfibers obtained by CW CO_2 laser heating carried out under various conditions. The properties of the microfiber were investigated using differential scanning calorimetry, wide-angle X-ray diffraction, Fourier transform infrared, and SEM measurements.

EXPERIMENTAL

Material

The original material used in the present study was as-spun PET fiber supplied by Toray Ltd. (Okazaki,

Japan). The original fiber was a commercial-grade fiber ($\bar{M}_w$ = 55,000, $\bar{M}_n$ = 30,000) and had a diameter of about 0.25 mm, degree of crystallinity of 4.5%, and birefringence of 0.7×10^{-3}. The original fiber was amorphous and isotropic.

Measurements

The birefringence was measured with a polarizing microscope equipped with a Berek compensator (Olympus Optical Co., Ltd. Japan). Wide-angle X-ray diffraction (WXRD) photographs of the fibers were taken using a flat-film camera. The camera was attached to a Rigaku X-ray generator (Rigaku Co., Japan) which was operated at 36 kV and 18 mA. The radiation used was Ni-filtered CuKα. 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.

Fourier-transform infrared (FTIR) spectra of the fibers were obtained at room temperature on a Perkin–Elmer *i*-Series FTIR microscope connected to a Perkin–Elmer Paragon 1000 spectrometer (Perkin–Elmer Co.). The spectra were measured at a 4-cm^{-1} resolution and 64 scans.

Differential scanning calorimetry (DSC; Rigaku Co., Japan) measurements were carried out using a Rigaku DSC 8230C calorimeter. The DSC scans were performed within the temperature range of 25 to 300°C, using a heating rate of 10°C/min. All DSC experiments were carried out under a nitrogen purge. The DSC instrument was calibrated with indium.

Laser heating

A schematic diagram of the CO_2 laser-heating apparatus used for producing the microfiber is given in Figure 1. The apparatus consists of a CW CO_2 laser emitter (PIN10S, Onizuka Glass Co., Ltd., Japan), a power meter with a thermal head, and an electric slider (Limo$_{TM}$ Orientalmotor Co. Ltd., Japan). The electric slider was used to move the fiber at a constant speed. The CW CO_2 laser emitted light at 10.6 μm, and the laser beam was a 4.0-mm-diameter spot. A PD was measured by the power meter before the laser heating. One end of the as-spun monofilament was connected to a jaw equipped with the electric slider, while the other is attached to a weight. The fiber was moved downward with the electric slider at a speed of 500 mm/min, and the laser beam was irradiated to the fiber. The fiber was drawn rapidly by irradiating the CW CO_2 laser.

RESULTS AND DISCUSSION

Figure 2 shows the changes in the diameter (d) and birefringence (Δn) of the fibers laser-heated at four
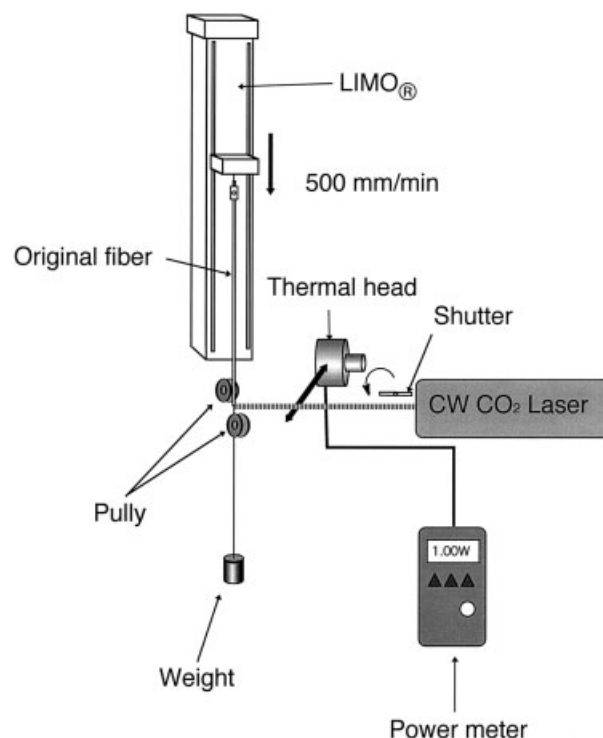

Figure 1 Scheme of laser-heating apparatus used for producing microfiber.

different PDs with the σ_a. The diameters of the fibers laser-heated at PD = 11.8 and 14.2 W cm^{-2} decreased monotonously with a decreasing σ_a, and the diameters of the fibers heated at σ_a = 0.17 MPa reached about 20 μm. On the other hand, the diameters of the fibers obtained at PD = 15.8 and 21.0 W cm^{-2} slowly decreased with a decreasing σ_a to 1.65 MPa, but the fiber was not drawn in the σ_a range of 0.66–1.65 MPa (broken line in Fig. 2). In the σ_a range of 0.66 and below, the diameter decreases discontinuously with a decreasing σ_a, and the fiber heated under 0.17 MPa at 21.0 W cm^{-2} has a very small diameter of 4.5 μm. The draw ratio of the smallest diameter fiber reached 3086-fold. The draw ratio was estimated by the following equation:

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

where d_0 is the diameter of the original fiber and d is that of the obtained fiber, and the density is assumed to be constant. Such a high draw ratio was not previously attained by any drawing method.

In laser heating at PD = 10.3 and 12.4 W cm^{-2}, the Δn values of the fibers decrease monotonously with a decreasing σ_a, and the Δn of the fiber heated under the lowest σ_a is about 20×10^{-3}. The lower the σ_a, the lower is the Δn. It was suggested that in laser heating under these conditions molecular flow processes predominate over the orientation process and that the intermolecular linkage is broken down, and as a re-
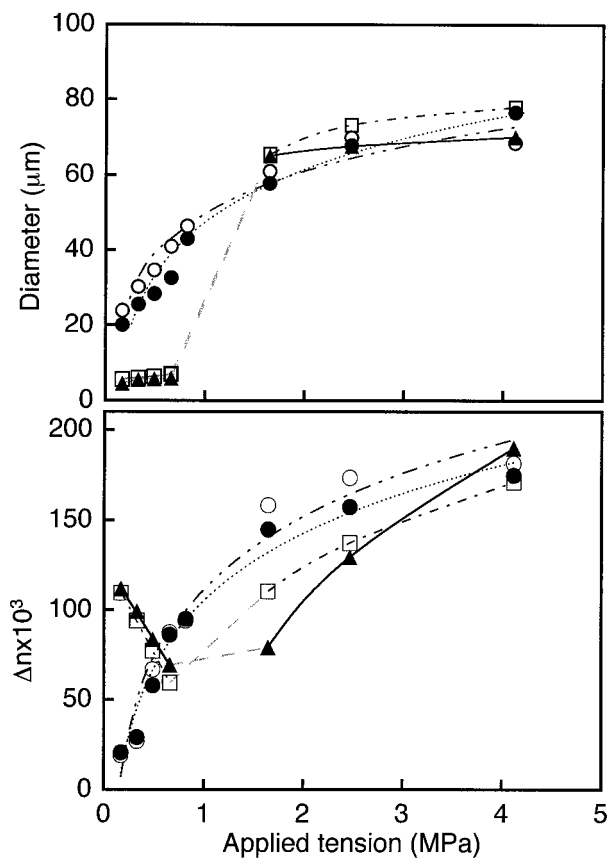
Figure 2 Changes in diameter and birefringence (Δn) of the fibers heated at three different PDs with various applied tensions: (○) 11.8; (●) = 14.2; (□) 15.8; (▲) PD = 21.0 W cm^{-2}.

sult, the polymer molecules may slip past one another and flow individually, exhibiting a large deformation without inducing molecular orientation and crystallization.

In heating at PD = 15.8 and 21.0 W cm^{-2}, the Δn values of the fibers decrease linearly with a decreasing σ_a to 0.66 MPa, but below which value the Δn increases rapidly, unlike the treating in the higher σ_a range. The smallest-diameter fiber heated under σ_a = 0.17 MPa at 21.0 W cm^{-2} has $\Delta n = 112 \times 10^{-3}$. The Δn value of the smallest diameter fiber is almost half that of the intrinsic cry stallite birefringence ($\Delta n_c^0 = 0.22$–0.251) that was reported by a number of authors[11–15] and is the same value as the laser-heated zone-drawn PET fiber reported previously.[9] The laser heating, zone drawing was carried out at PD = 6.1 W cm^{-2} under σ_a = 4.44 MPa, and then the obtained fiber had a draw ratio of 3.8, $\Delta n = 112 \times 10^{-3}$, and a degree of crystallinity of 33%. The optimum condition of the zone drawing differs remarkably from the conditions used (the PD and the σ_a) to prepare the microfiber.

In the laser heating carried out at PD = 15.8 and 21.0 W cm^{-2} under 0.66 MPa, the rapid increase of the Δn shows that the stress-induced crystallization and mo-

lecular orientation processes occur during the heating in the lower σ_a range at the higher PD, unlike that carried out in the higher σ_a range. It was hitherto impossible to prepare microfiber by any drawing and usual spinning. However, it has become possible to easily obtain microfiber by only laser heating once.

Figure 3 shows SEM micrographs of the as-spun PET fiber and the microfiber obtained at PD = 21.0 W cm^{-2} under σ_a = 0.17 MPa. The smallest diameter fiber has a smooth surface without a surface roughened by laser ablation and is uniform in diameter.

Figure 4 shows WAXD photographs of the fibers heated at PD = 21 W cm^{-2} under four different σ_a's. Three principal reflections (010, $\bar{1}$10, and 100) are observed on the equator, and the reflections due to crystallites become more conspicuous at the higher σ_a. In the WAXD photographs of the fibers heated under σ_a = 0.17 and 0.66 MPa, that is, the condition used to obtain the microfiber, indistinct reflections due to crystallites formed by strain-induced crystallization are observed.

On the other hand, those of the fibers under σ_a = 1.65 and 4.12 MPa display clear arcs and show the
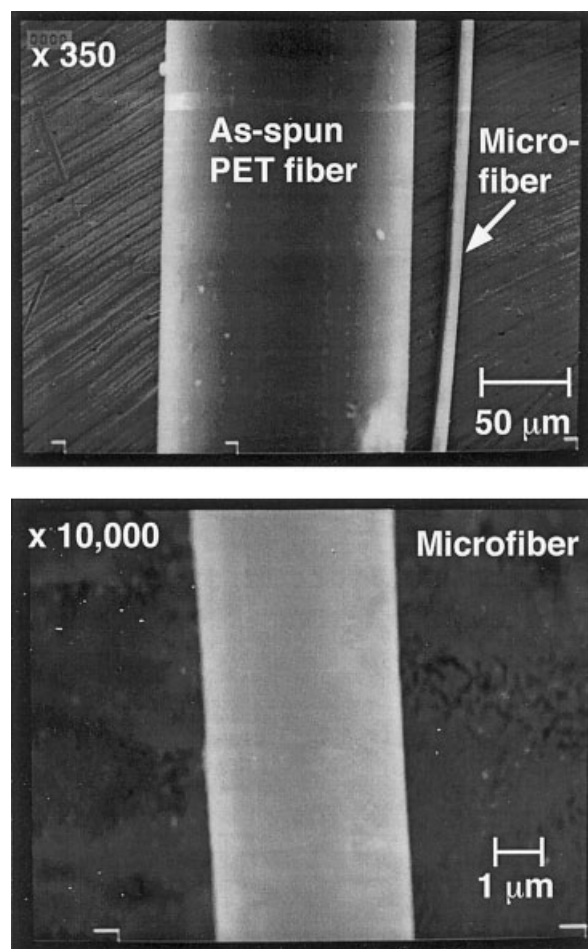

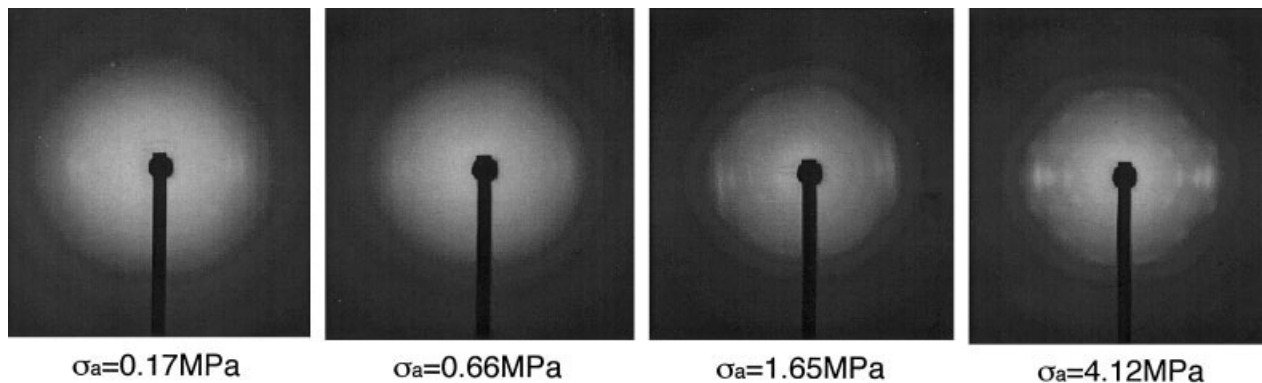**Figure 3** SEM micrographs of an as-spun PET fiber and the fiber heated under 0.17 MPa at 21.0 W cm^{-2}.

Figure 4 WXRD photographs of the fibers heated at PD = 21 W cm^{-2} under four different applied tensions.

existence of the highly oriented crystallites. However, the Δn of the fiber heated under σ_a = 0.17 MPa is higher than that of the fiber obtained under 1.65 MPa, as shown in Figure 2. This fact implies that the smallest diameter fiber heated under σ_a = 0.17 MPa has a highly oriented amorphous phase among the microfibers obtained.

To obtain more information about the molecular orientation of the microfibers, conformational changes were investigated by FTIR measurements. To study the changes in proportion of *trans* and *gauche* conformation of the glycol residue of the fibers heated at four different σ_a's at PD = 21 W cm^{-2}, the bands situated at 848, 898, 973, and 988 cm^{-1} were used.[16–18] The bands at 848 and 973 cm^{-1} are attributed to a *trans* conformation; the bands at 898 cm^{-1}, to a *gauche* conformation; and the bands at 988 cm^{-1}, to a *fold* conformation. The *trans* conformation can be involved in the crystalline and the amorphous phases, but the *gauche* conformation can be found only in the amorphous phase. In this study, the band at 793 cm^{-1} was used as an internal reference band.[19] Figure 5 shows FTIR spectra for the original fiber and the fibers heated under four different σ_a's at PD = 21 W cm^{-2}. The *trans* conformation increases with an increasing σ_a, whereas the *gauche* and folding conformations decrease. The increase of the *trans* and the decrease of the *gauche* are observed in the microfibers obtained under σ_a = 0.17 and 0.66 MPa. This fact indicates that not only the molecular flow but also the molecular orientation and crystallization are induced during laser heating under lower σ_a at higher PD and that agrees approximately with the result of Δn mentioned above.

Figure 6 shows DSC curves for the original fiber and the fibers heated under four different σ_a's at PD = 21 W cm^{-2}. The original fiber shows a change in slope in the specific heat at 81°C, which corresponds to the glass transition, an exothermic transition at 138°C caused by a cold crystallization, and a broad melting endotherm peaking at 256°C. The fibers, except the fiber heated under σ_a = 4.12 MPa, have a broad exothermic transition due to the cold crystallization and

single melting endotherm peaks about 256°C. The cold-crystallization temperature shifts to a lower temperature with an increasing σ_a. The shift is attributed to the existence of oriented crystalline nuclei formed during a rapid large deformation.

The melting peaks can be attributed to melting of the folded chain crystal (FCC) recrystallized from an
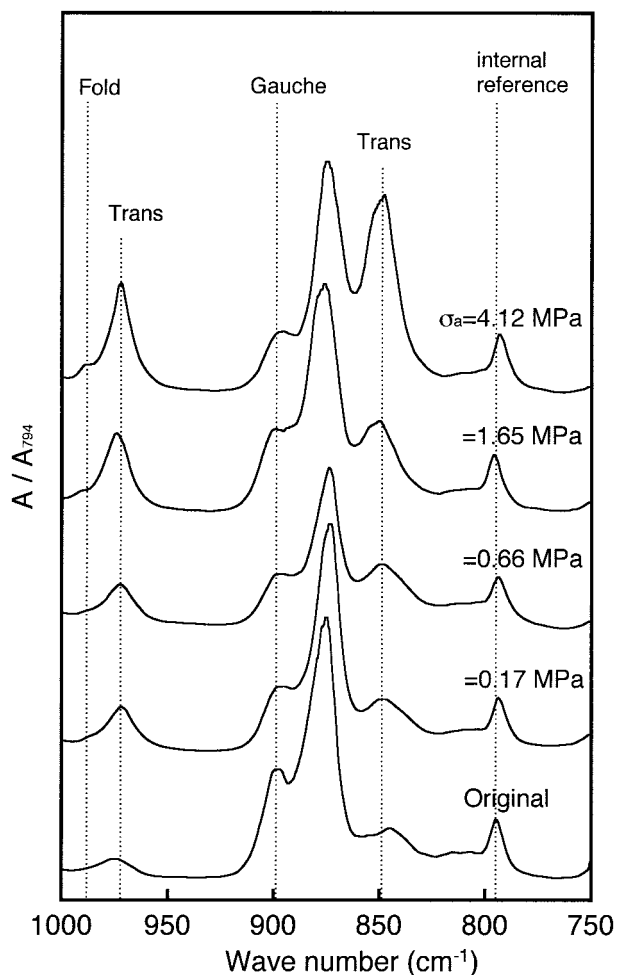

Figure 5 FTIR spectra for the original fiber and the fibers heated at four different applied tensions (σ_a) at PD = 21 W cm^{-2}.
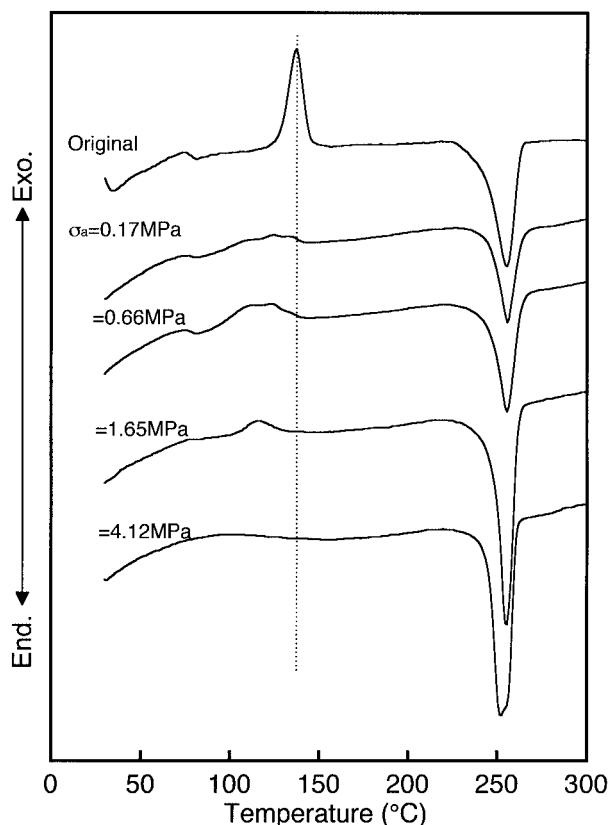
Figure 6 DSC curves for the original fiber and the fibers heated at four different applied tensions (σ_a) at PD = 21 W cm^{-2}.

extended chain crystal (ECC) with low levels of the crystal perfection during the DSC measurement.[20] The fiber heated under 4.12 MPa has single melting endotherm peaks about 250°C and a shoulder on the high-temperature side of its peak. The shoulder is observed at the same temperature as that of the melting peaks of the original fiber and the fibers heated under 1.65 MPa and below.

CONCLUSIONS

It was found that CO$_2$ laser heating is capable of producing PET microfibers. The thinning of PET fibers becomes possible by irradiating the high laser power to the fiber-added extremely low load. The condition

to obtain the microfibers differs largely from the drawing condition to prepare high-modulus and high-strength fiber. The PET microfiber obtained under the optimum condition for thinning had a diameter of 4.5 μm and a birefringence of 112 $\times$ 10^{-3} and showed a highly oriented amorphous region and the existence of the crystallites due to strain-induced crystallization. The draw ratio of the smallest diameter fiber reached 3086-fold. Such a high draw ratio was not previously attained by any drawing method. Laser heating can allow the microfiber to be more easily compared with conventional technology such as conjugate spinning.

The thinning mechanism is conceivable as follows: After the plasticity viscosity in the part of the fiber irradiated by a high output laser becomes sufficiently low, the part that irradiated the laser becomes a nearly molten state, and the plastic flow occurred at a high strain rate. As a result, laser heating carried out under the extremely low applied tension at high power gives an oriented PET microfiber.

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