High Temperature Zone-Drawing of Nylon 66 Microfiber Prepared by CO$_2$ Laser-Thinning

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ABSTRACT: A high temperature zone-drawing method was applied to a nylon 66 microfiber, obtained by using CO$_2$ laser-thinning, to develop its mechanical properties. The microfiber used for the high temperature zone-drawing was prepared by winding at 150 m min^{-1} the microfiber obtained by irradiating the laser at 4.0 W cm^{-2} to an original fiber with a diameter of 50 μm, and had a diameter of 9.6 μm and a birefringence of 0.019. The high temperature zone-drawing was carried out in two steps; the first drawing was carried out at a temperature of 230°C at supplying and winding speeds of 0.266 and 0.797 m min^{-1}, the second at 250°C at supplying and winding speeds of 0.266 and 0.425 m min^{-1}, respectively. The diameter of the microfiber decreased, and its birefringence increased stepwise with the processing. The high temperature zone-drawn microfiber finally obtained had a diameter of 4.2 μm, a birefringence of 0.079, total draw ratio of 4.8, tensile modulus of 12 GPa, and tensile strength of 1.0 GPa. The wide-angle X-ray diffraction photograph of the drawn microfiber showed the existence of highly oriented crystallites. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 42–47, 2006

Key words: nylon 66; fibers; mechanical properties; drawing

INTRODUCTION

The microfibers are now manufactured by highly skilled techniques such as a conjugate spinning, an island-in-a-sea-type fiber spinning, a melt blowing, and a flash spinning.[1–4] The mechanical properties of the microfibers obtained by the conventional method are not sufficient because of the lack of the molecular orientation and degree of crystallinity without the microfiber produced by the melt blowing. Although the mechanical properties are improved by drawing and annealing fiber, it is difficult to draw and anneal the microfibers produced by the conventional method because of the special spinning.

A laser-thinning method producing microfiber by irradiating a carbon dioxide (CO$_2$) laser to fibers was developed by us, and an apparatus for the CO$_2$ laser-thinning is able to wind the microfiber as a monofilament, at winding speeds ranging from 100 to 2500 m min^{-1}. The laser-thinning method has already been applied to a poly(ethylene terephthalate) (PET),[5] nylon 6,[6] isotactic polypropylene (i-PP),[7] nylon 66,[8] and poly(L-lactic acid) fibers,[9] and the microfibers with diameter range of 1.5–5 μm were obtained.

The microfiber wound up on a spool can be drawn and be annealed in the forms of multifilament and monofilament to improve its mechanical properties. The obtained PET microfiber was zone-drawn and zone-annealed by bundling the microfiber, and its mechanical properties reached a tensile modulus of 17.9 GPa and tensile strength of 1.1 GPa.[5] However, the high performance microfiber obtained was microfiber bundle about 0.5 m long because the drawing and annealing was a batch processing. It is difficult to continuously draw only a microfiber obtained since its diameter and its tensile strength are too small. We tried to continuously draw the microfiber to improve its mechanical properties.

In this study, the continuous zone-drawing method[10] was applied to the nylon 66 microfiber prepared by the CO$_2$ laser-thinning to prepare high-modulus and high-strength nylon 66 microfibers. We present here the results pertaining to the superstructure and mechanical properties of the zone-drawn and zone-annealed nylon 66 microfibers obtained by the laser-thinning method.
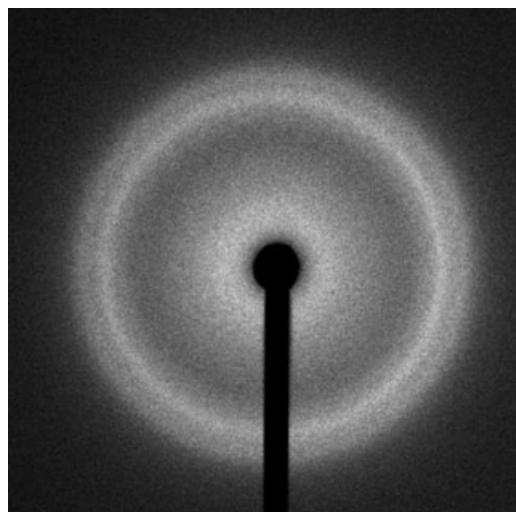
EXPERIMENTAL

Materials

Original nylon 66 fibers were produced from commercial grade nylon 66 pellets by using a laboratory-scale

Figure 1 Wide-angle X-ray diffraction pattern of nylon 66 original fiber.

melt extruder and take-up unit. The original fibers were spun into monofilaments at a spinning temperature of 285°C. As-spun fiber had a diameter of 50 μm, and birefringence of 1.65×10^{-3}. The as-spun fiber was found to be isotropic from a wide-angle X-ray diffraction pattern, as shown in Figure 1.

Measurements

Diameter of microfiber was measured with a scanning electron microscopy (SEM). SEM micrographs of the microfibers were taken with a JSM6060LV (Tokyo, Japan) with an acceleration voltage of 15 kV.

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

Weight average molecular weight (M_w) and number average molecular weight (M_n) were measured with gel permeation chromatography (GPC-14, Waters Co.). The GPC analysis was performed at 23°C in hexafluoroisopropanol and differential refractive index detector. Two 30-cm gel columns (Shodex HFIP-806M) were used at a flow rate of 0.5 mL/min.

Infrared measurements were made on a Fourier transform infrared (FTIR, IR ms/SIRM) microscope (Spectratech, Ltd.) at a resolution of 4 cm^{-1}. Each spectrum resulted from an accumulation of 1024 scans.

Wide angle X-ray diffraction (WAXD) patterns of the fibers were taken with an imaging-plat (IP) film and an IP detector R-AXIS DS3C (Rigaku Co., Akishima, Japan). The IP film was attached to an X-ray generator (Rigaku Co.) operated at 40 kV and 35 mA.

The radiation was Ni-filtered Cu Kα. The sample-to-IP film distance was 65 mm. The fibers were exposed for 30 min to the X-ray beam from a pinhole collimator with a diameter of 1.0 mm.

The degree of crystal orientation (π) was estimated from the half-width (H) of the meridian reflection peak. The H value was estimated from WAXD pattern measured by the imaging-plate through the software for analyzing data.

The π value is given by the equation

$$\pi(\%) = [(180 - H)/180] \times 100$$

The DSC measurements were carried out using a THERM PLUS 2 DSC 8230C calorimeter (Rigaku Co.). The DSC scans were performed within the temperature range of 25–280°C, using a heating rate of 10°C min^{-1}. All DSC experiments were carried out under a nitrogen purge. The DSC instrument was calibrated with indium.

The degree of crystallinity (X_c) was determined from heat of fusion (ΔH_m) as follows

$$X_c(\%) = (\Delta H_m/192) \times 100$$

where 192 J g^{-1} is used as the heat of fusion of the crystalline phase of nylon 66.[11]

Tensile modulus and tensile strength were measured at 23°C and a relative humidity of 50% with EZ Graph (Shimadzu Co. Ltd., Kyoto, Japan). A gauge length of 20 mm and elongation rate of 10 mm min^{-1} were used. The experimental results are the average of 10 measurements.

Continuous high temperature zone-drawing of microfiber obtained by CO_2 laser-thinning

The nylon 66 microfibers used for the high temperature zone-drawing were prepared by irradiating the
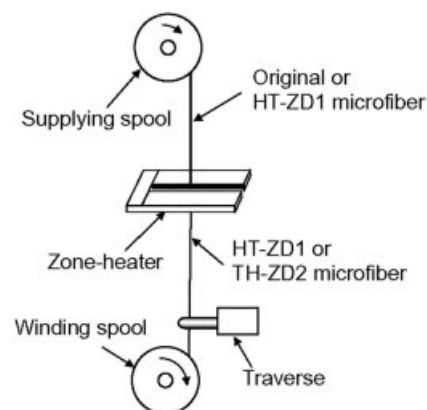
Figure 2 Scheme of apparatus used for the first and second zone-drawings.

Step	Heater temperature (°C)	Supplying speed (m min⁻¹)	Winding speed (m min⁻¹)
1st high temperature zone-drawing	230	0.266	0.797
2nd high temperature zone-drawing	250	0.266	0.425

CO_2 laser to the original nylon 66 fiber. The CO_2 laser-thinning method was described previously.[5–9] The zone-drawing in this study was continuously carried out in the form of a monofilament at the high temperature near the melting point (about 260°C). To enable the continuous high temperature zone-drawing, we assembled the apparatus to zone-draw the microfibers wound up on the spool. The apparatus used for the continuous zone-drawing of the microfiber consists of supplying and winding motors with spools with a diameter of 90 mm, zone-heater, and a traverse, as shown in Figure 2. The spool winding the microfiber obtained by the laser-thinning was attached to the supplying motor. The monofilament microfiber pulled out of the spool is drawn by the zone-heater that was set up to an arbitrary temperature, and the zone-drawn microrfiber is wound up on the winding spool.

RESULTS AND DISCUSSION

The purpose of the high temperature zone-drawing is to increase the mechanical properties of the laser-thinned microfiber by recrystallizing a fold chain crystal (FCC) into an extended chain crystal (ECC) and increasing the orientation of crystallites and amorphous chains in the drawing direction. The drawing was carried out near the melting point (T_m) to achieve the purpose. The recrystallization of FCC into ECC induces the increase in tie molecular chains, which increases the mechanical properties.

The preparatory experiment to determine the optimum drawing condition of nylon 66 microfiber was carried out under various conditions. The microfibers used for the preparatory experiment were the microfibers with a diameter of 9.6 μm, which was prepared

by the laser-thinning carried out at supplying speed of 0.23 and winding speed of 652 m min⁻¹.

The optimum condition for the continuous zone-drawing were the conditions under which the highest birefringence and mechanical properties was obtained. The drawing carried out at two steps, as illustrated in Table I, was found to be effective in the improvement of the mechanical properties. The first high temperature zone-drawing was carried out at a temperature of 230°C at supplying and winding speed of 0.266 and 0.797 m min⁻¹, and the second at a temperature of 250°C at supplying and winding speed of 0.266 and 0.425 m min⁻¹, respectively. The first high temperature zone-drawn and second zone-drawn microfibers obtained under each optimum condition are hereafter abbreviated the HT-ZD1 and HT-ZD2 microfiber, respectively. The microstructure and mechanical properties of the microfiber obtained under each optimum condition will be discussed later.

Table II lists a draw ratio, diameter, birefringence (Δn), degree of crystallinity (X_c), degree of crystal orientation (π), and ratio of trans (936 cm⁻¹) and gauche (1146 cm⁻¹)[11] for the original, the HT-ZD1, and the HT-ZD2 microfibers. The origin of these bands has tentatively assigned to a C—CO stretching and a CO twisting movement.[11]

The fiber diameter decreased with twice zone-drawings, and that of HT-ZD2 microfiber was 4.1 μm. The Δn value increases stepwise with increasing processing, the Δn value of the HT-ZD2 microfiber was 78.9 × 10⁻³, and its value was almost equivalent to the intrinsic crystallite birefringence (78 × 10⁻³).[12]

The X_c increased with twice drawings at the high temperature, the X_c value of the HT-ZD2 microfiber was 38%, and is almost equivalent to that (= 37%) of the continuously zone-drawn nylon 66 fiber reported

TABLE II
Draw Ratio, Diameter, Birefringence, Degree of Crystallinity, Degree of Crystal Orientation, and Ratio of Trans and Gauche for the Original Microfiber, the First High Temperature Zone-Drawn (HT-ZD1) Microfiber, and the Second High Temperature Zone-Drawn (HT-ZD2) Microfiber

| Fiber	Daw ratio	Diameter (μm)	Birefringence (10³)	Degree of crystallinity (%)	Degree of crystal orientation (%)	Ratio of trans/gauche
Original microfiber	–	9.6	19.3	29	10	1.44
HT-ZD1 microfiber	3.0	5.5	71.4	36	89	1.81
HT-ZD2 microfiber	4.8	4.1	78.9	38	90	2.12
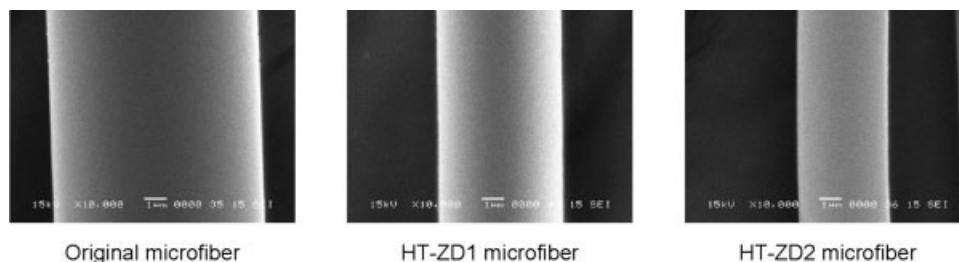
Figure 3 SEM photographs of 10,000× magnifications for the original microfiber, the first high temperature zone-drawn (HT-ZD1) microfiber, and the second high temperature zone-drawn (HT-ZD2) microfiber.

previously.[10] The π value reached 89% at the HT-ZD1 microfiber and further increased to 90% with the second drawing. The high temperature zone-drawing was effective in developing the low orientation level of the crystallites formed by the laser-thinning.

The ratio of trans and gauche increased stepwise with increasing processing. The increase in the ratio of trans and gauche shows the increase in extended chains of amorphous and crystal regions. The amorphous molecular chains were highly oriented along the drawing direction because the birefringence value was extraordinarily high in spite of the lower X_c value.

Figure 3 shows the SEM photographs at 10,000× for three different microfibers. It can be confirmed visually from the SEM photographs that the fiber diameter decreases with increasing processing. The observation by the SEM photographs shows that the microfibers have smooth surfaces not roughened by laser ablation that were uniform in diameter.

It is well known that the molecular weight decreased by the thermal degradation occurred during the melt spinning. To examine whether the thermal degradation during the laser-thinning occurred or not, the GPC measurements were carried out for the microfiber obtained by laser-thinning. Figure 4 shows the
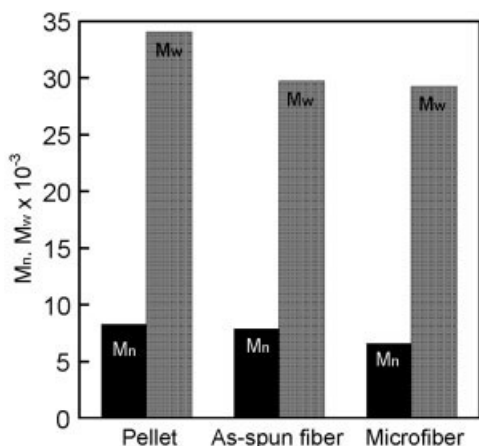

Figure 4 Weight average molecular weight (M_w) and number average molecular weight (M_n) for pellet, as-spun fiber, and original microfiber obtained by the CO_2 laser-thinning.

M_w and M_n of nylon 66 pellet, as-spun fiber, and original microfiber obtained by the CO_2 laser-thinning. The M_w and M_n values decreased with a melt spinning, but hardly decreased by the laser-thinning. The changes in the M_w and M_n with the processing showed that the thermal degradation hardly occurred during the laser-thinning. The experimental results imply that the plastic flow without the thermal degradation immediately induces from the molten state after the only point laser-irradiated by the high output power laser was locally molten.

Figure 5 shows WAXD patterns of original microfiber, HT-ZD1, and HT-ZD2 microfiber. The nylon 66 has two known crystal modifications: an α form and a β form,[13] but no reflection due to the β form was observed in their WAXD patterns. The shapes of the diffraction patterns due to (100) reflection and (010)/(110) doublet of the α form in the original microfiber were almost the Debye ring. With the first drawing, the equatorial diffraction patterns due to the[100] reflection and (010)/(110) doublet changes into the arc-shaped pattern. The equatorial diffraction pattern becomes sharp with the second drawing.

Figure 6 shows DSC thermograms of the original, the LH-ZD1, and the LH-ZD2 microfibers. The original microfiber shows a broad melting endotherm peaking at 260°C. The melting peaks can be attributed to melting of an extended chain crystal formed flow-induced crystallization by laser irradiation and/or to melting of a folded chain crystal recrystallized during the DSC measurements.[14]

The LH-ZD1 microfiber has a melting endotherm peaking at 258°C and the trace of shoulder on the higher temperature side of its peak, and the trace is observed at the same temperature as that at the higher melting peak of the original microfiber. The appearance of a low-temperature melting peak is attributable to the morphological transformation of crystallite; the chain-folded crystalline structure in the original microfiber changes partially into a fringed-micelle one with an unfolding of the chains. Elenga et al.[15] suggested from the standpoint of kinetics that the low-temperature melting peak was ascribed to the fringed-micelle crystals built up by chain unfolding, and the
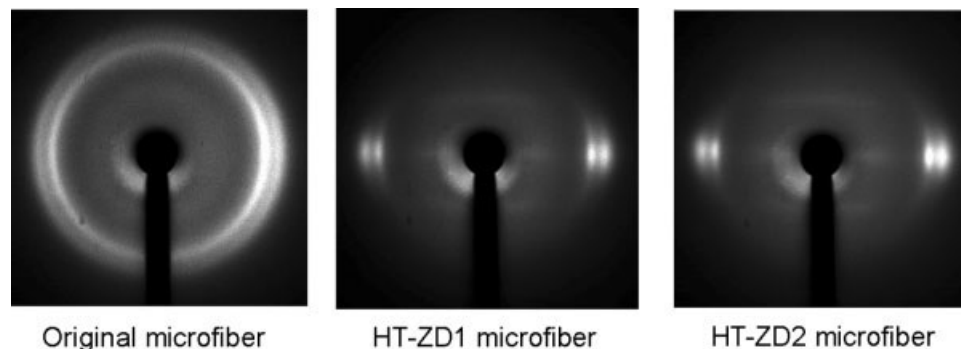
Figure 5 Wide-angle X-ray diffraction patterns of the original microfiber, the first high temperature zone-drawn (HT-ZD1) microfiber, and the second high temperature zone-drawn (HT-ZD2) microfiber.

high-temperature one corresponds to the untransformed fraction of the lamellar crystals that undergo reorganization during the heating scan.

The LH-ZD2 microfiber had a melting endotherm peaking at 261°C. The appearance of the single melting peak supposes that the folded chain crystal remained in the LH-ZD1 microfiber changed into the fringed-micelle crystals during the second zone-drawing, and that the recrystallization of the crystals induced by the zone-drawing did not occur during the DSC scan. A sharpening of the melting peak and

shifting to the higher temperature in the melting temperature are caused by an increase in the degree of perfection of the crystallites.[16,17]

Mechanical properties for the original microfiber, the HT-ZD1 microfiber, and the HT-ZD2 microfiber are shown in the Table III. The tensile modulus and tensile strength increase stepwise with increasing processing. The tensile modulus and tensile strength of the HT-ZD2 microfiber are 11.8 and 1.0 GPa, respectively. The mechanical properties of the HT-ZD2 microfiber are almost equal to the values of high-temperature zone-drawn nylon 66 fibers reported previously.[10] The mechanical properties are directly related to the birefringence and degree of crystallinity. From the viewpoint of superstructure, the improvement of mechanical properties is attributable to the increase in the degree of orientation of the amorphous chain and in the apparent crosslinking density of the physical network built up the crystallites.

CONCLUSIONS

The nylon 66 microfiber obtained by the CO_2 laser-thinning was zone-drawn at the higher temperature to improve its mechanical properties. The microfiber used for the zone-drawing had a diameter of 9.6 μm and a birefringence of 0.019. The high temperature zone-drawing was carried out in two steps; the first
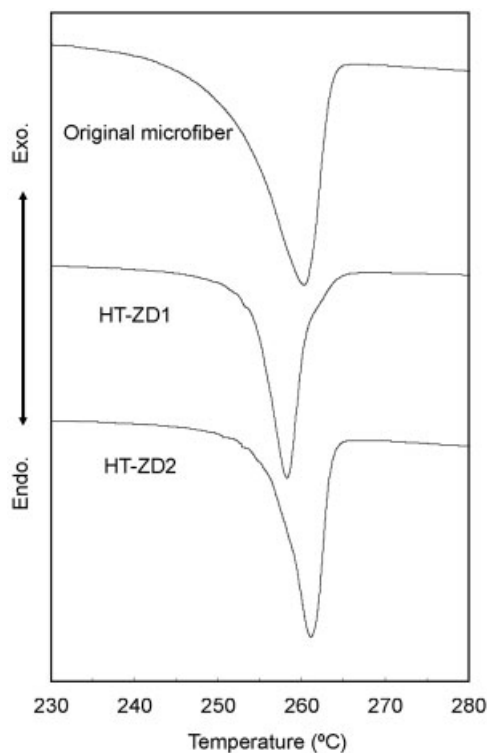
Figure 6 DSC thermograms of the original microfiber, the first high temperature zone-drawn (LH-ZD1) microfiber, and the second high temperature zone-drawn (LH-ZD2) microfiber.

TABLE III
Mechanical Properties for the Original Microfiber, the First High Temperature Zone-Drawn (HT-ZD1) Microfiber, and the Second High Temperature Zone-Drawn (HT-ZD2) Microfiber

Fiber	Tensile modulus (GPa)	Tensile strength (GPa)	Elongation at break (%)
Original microfiber	0.6	0.2	427
HT-ZD1 microfiber	3.3	0.6	75
HT-ZD2 microfiber	11.8	1.0	17

high temperature zone-drawing was carried out at a temperature of 230°C and the second at 250°C. The zone-drawn microfiber finally obtained had a diameter of 4.2 μm, a birefringence of 0.079, a tensile modulus of 12 GPa, and a tensile strength of 1.0 GPa. The continuous zone-drawing method was found to be effective in producing the nylon 66 microfiber with high-modulus and high-strength.

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