

Nylon 6 Microfiber Prepared by Carbon Dioxide Laser Heating

Akihiro Suzuki, Kaori Kamata

Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, Takeda-4, Kofu 400-8511 Japan

Received 19 February 2003; accepted 9 September 2003

ABSTRACT: A nylon 6 microfiber was easily obtained through carbon dioxide laser heating. The laser heating was carried out in two steps: the first laser heating was performed under an applied tension of 36.7 MPa at a power density of 17.3 W cm^{-2} , and the second was performed under 0.18 MPa at 51.81 W cm^{-2} . The microfiber was obtained by the second laser heating of the fiber. The microfiber prepared under the optimum thinning conditions had a diameter of $1.9 \mu\text{m}$ and a birefringence of 46.2×10^{-3} . Its draw ratio, estimated from the diameter, was $9895\times$ (so far, it has been impossible to achieve such a high draw ratio by

drawing). A (200) reflection and a (002/202) doublet due to an α form were observed on the equator, but no (200) reflection due to a γ form was observed. The morphology of the crystallites existing in the microfiber was only the α form. Laser heating made the microfiber more easily than conventional technologies, such as conjugate spinning, melt blowing, and flash spinning. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1449–1453, 2004

Key words: nylon; fibers; drawing; WAXS

INTRODUCTION

A continuous-wave carbon dioxide (CO_2) laser has already been applied to the drawing and annealing of poly(ethylene terephthalate) (PET)¹ and nylon 6² fibers to improve their mechanical properties. A laser-heating zone-drawing and zone-annealing method has been found to be effective in improving their mechanical properties.

The CO_2 laser has been mainly applied to the welding, cutting, and cladding of ceramics and metals, the annealing of semiconductors, the improvement of the surface properties of carbon and other ceramic fibers, the etching of polymers, and the curing of epoxy resins.^{3–10}

In the laser-heating zone drawing and annealing of a nylon 6 fiber, an original nylon 6 fiber is zone-drawn under an applied tension (σ_a) of 35.4 MPa at a power density of 9.65 W cm^{-2} to highly orient the molecular chains, and zone annealing is subsequently carried out in two steps at a power density of 9.65 W cm^{-2} to develop the molecular orientation and crystallization; the first step is carried out under 423 MPa, and the second is carried out under 517 MPa. The obtained fiber has a birefringence of 65.2×10^{-3} , a degree of

crystallinity of 54%, and a storage modulus of 21 GPa at 25°C.

In preliminary experiments to optimize the zone-drawing conditions for PET fibers, PET microfibers¹¹ were prepared by laser heating carried out under very low σ_a values at a higher power density in comparison with laser-heating zone drawing for PET fibers. Furthermore, PET microfibers¹² with a diameter of $1.5 \mu\text{m}$ were easily obtained through high-power laser irradiation of annealed PET fibers.

Microfibers are now manufactured with highly skilled techniques, such as conjugate spinning (requiring a highly complex spinneret), melt blowing, and flash spinning. Until now, it has been impossible to prepare microfibers by any other method. However, laser heating easily produces microfibers without highly skilled techniques.

We present here the results pertaining to the properties of nylon 6 microfibers obtained by CO_2 -laser heating.

EXPERIMENTAL

Materials

The original materials used in this study were as-spun nylon 6 fiber supplied by Toray, Ltd. (Okazaki, Japan), and a commercial-grade fiber. The original fiber had a diameter of $189 \mu\text{m}$, a degree of crystallinity of 28%, and a birefringence of 6.25×10^{-3} . The original fiber was found to be almost isotropic because a Debye ring could be observed in a wide-angle X-ray diffraction

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

Contract grant sponsor: Japan Society for the Promotion of Science [Grant-in-Aid for Scientific Research (B)].

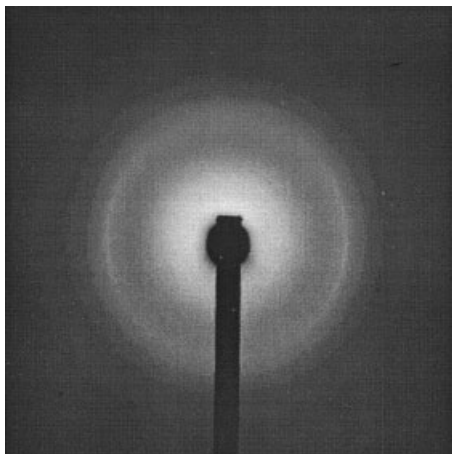


Figure 1 WAXD photograph of the original nylon 6 fiber.

(WAXD) photograph (Fig. 1). However, the original fiber could be considered a poorly oriented fiber because its birefringence was low.

Measurements

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

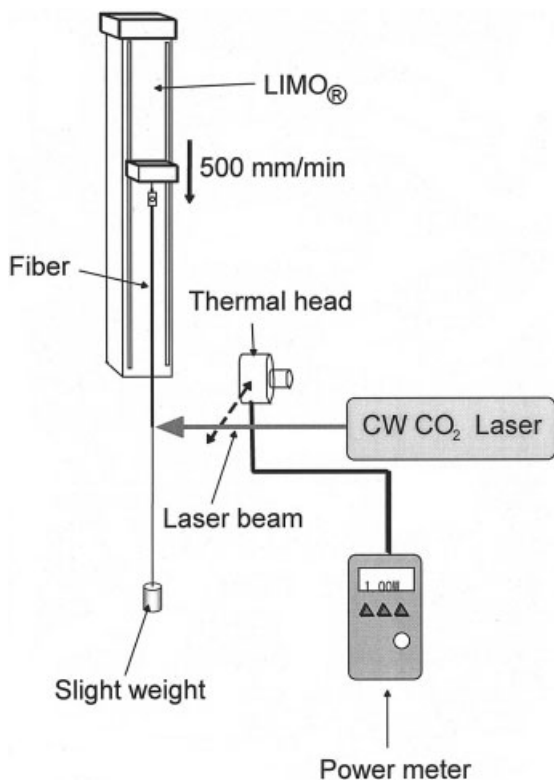


Figure 2 Scheme of the apparatus used for laser heating and laser thinning.

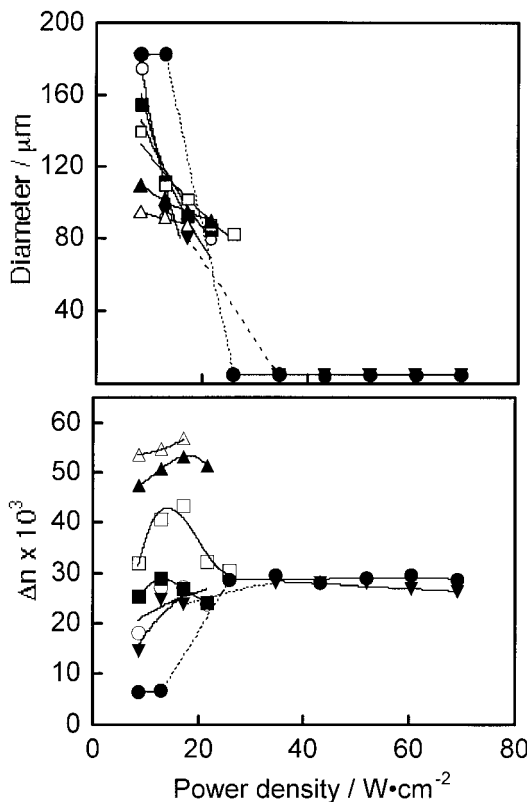


Figure 3 Changes in the diameter and birefringence (Δn) of fibers drawn at various σ_a values with the power density: (●) 0.18, (▼) 0.37, (○) 1.10, (■) 1.83, (□) 3.59, (▲) 18.3, and (△) 36.7 MPa.

The density (ρ) was measured at 23°C by a flotation technique with a mixture of carbon tetrachloride and toluene. The degree of crystallinity, expressed as a weight fraction (X_w), was obtained as follows:

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

where ρ_c and ρ_a are the densities of the crystalline and amorphous phases, respectively. In this measurement, a value of 1.230 g/cm³ was assumed for ρ_c ¹³ and a value of 1.084 g/cm³ was assumed for ρ_a .¹⁴ The density of the amorphous polymer was assumed to be constant and independent of the treatments. However, the density of the microfiber was not able to be measured by the flotation technique because the specimen was very small.

The draw ratio was easily calculated with 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 the diameter of the obtained fiber. The volumes before and after the drawing were assumed to be constant.

TABLE I
Diameter and Birefringence (Δn) of the LH-1 and LH-2 Fibers

First laser heating		LH-1		Second laser heating		LH-2	
Power density (W cm ⁻²)	σ_a (MPa)	Diameter (μm)	$\Delta n \times 10^3$	Power density (W cm ⁻²)	σ_a (MPa)	Diameter (μm)	$\Delta n \times 10^3$
0.37	8.64	179.8	14.4	51.81	0.18	4.90	18.0
	13.0	95.0	24.8			4.79	18.3
	17.3	80.0	23.7			—	—
1.10	8.64	174.5	18.2			4.68	19.3
	13.0	92.3	27.0			2.23	29.5
	17.3	92.5	27.0			—	—
	21.6	80.0	23.9			—	—
1.83	8.64	155.0	25.2			2.26	31.6
	13.0	112.0	28.9			2.40	30.4
	17.3	92.5	26.8			2.34	31.2
	21.6	85.0	24.2			2.97	30.0
3.59	8.64	140.0	31.8			1.99	42.2
	13.0	110.0	40.6			1.98	39.6
	17.3	102.5	43.4			2.14	35.5
	21.6	87.5	32.3			2.15	41.2
18.33	25.9	82.5	30.2			—	—
	8.64	109.8	47.4			1.96	39.4
	13.0	102.5	50.7			1.95	42.7
	17.3	95.0	53.3	2.10	40.1		
36.66	21.6	90.0	53.5	1.97	45.7		
	8.64	95.0	53.6	1.99	44.5		
	13.0	92.3	54.7	2.03	46.3		
	17.3	87.5	56.7	1.93	46.2		

Scanning electron microscopy (SEM) micrographs of the fibers were taken with a JEOL JSM-T20 with an acceleration voltage of 19 kV.

WAXD photographs of the fibers were taken with a flat-film camera. The camera was attached to a Rigaku (Japan) X-ray generator, which was 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 fibers were exposed for 4 h to the X-ray beam from a pinhole collimator with a diameter of 0.4 mm.

Laser heating

The CO₂-laser-heating apparatus used for producing the microfiber consisted of a continuous-wave CO₂-laser emitter (PIN10S, Onizca Glass, Ltd., Japan), a power meter (Nova, Ophir Optonics, Ltd., United States) with a thermal head, and an electric slider (Limo Orientalmotor Co., Ltd., Japan), as shown in

Figure 2, and it was similar to an apparatus with laser-heating zone drawing and zone annealing.¹ The electric slider was used to move the fiber at a constant speed. The continuous-wave CO₂ laser emitted light at 10.6 μm , and the laser beam had a 4.0-mm diameter. The power density was measured by the power meter before the laser heating. One end of the fiber was connected to a jaw equipped with the electric slider, whereas the other was attached to a weight. The fiber was moved downward with the electric slider at a speed of 500 mm/min, and the fiber was irradiated by

TABLE II
Diameter, Birefringence (Δn), and X_w for the Original Fiber, LH-1 Fiber, and LH-2 Fiber

Fiber	Diameter (μm)	$\Delta n \times 10^3$	X_w (%)	Draw ratio
Original	189	6.25	28	—
LH-1	87.6	56.7	37	4.7
LH-2	1.9	46.2	—	9,589

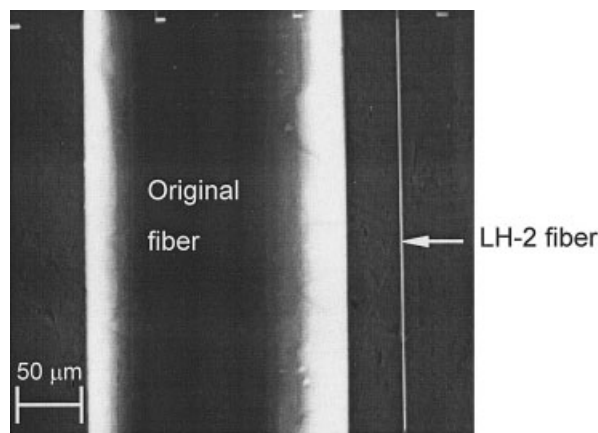


Figure 4 SEM micrographs of the original nylon 6 fiber and the LH-2 fiber.

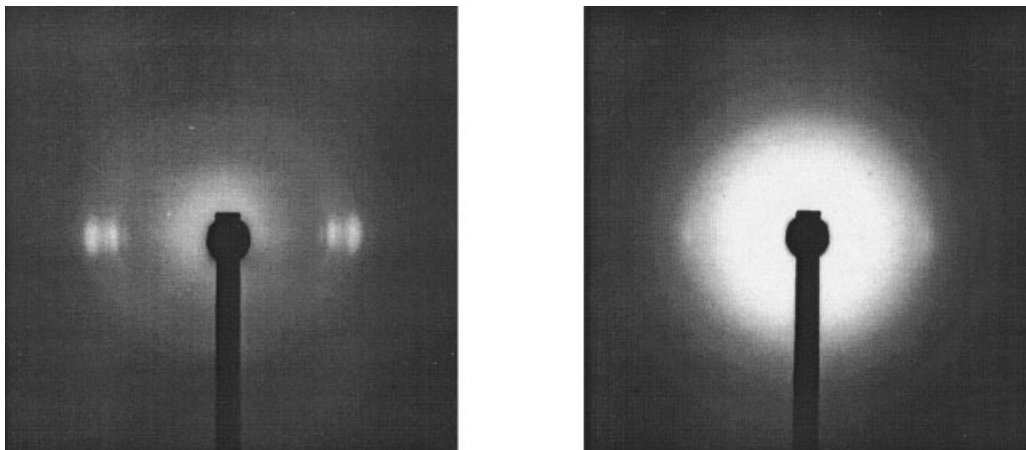


Figure 5 WAXD photographs of the LH-1 (top) and LH-2 (bottom) fibers.

the laser beam. The fiber was drawn rapidly through irradiation with the continuous-wave CO₂ laser at a high power, and a microfiber about 1.5 m long was obtained.

RESULTS AND DISCUSSION

Figure 3 shows the changes in the diameter and birefringence of the fibers obtained by laser heating at various σ_a values with the laser power density. The power density was estimated through the division of the measured laser power by the area of the laser spot. A laser power greater than 90% was obtained in the area of the laser spot. Microfibers were obtained through laser irradiation of the original fiber at $\sigma_a = 0.18$ or 0.37 MPa at a power density greater than 20 W cm^{-2} ; the diameter was about $5 \mu\text{m}$, and the birefringence was about 30×10^{-3} , regardless of the power density. However, no microfiber was obtained from laser heating at $\sigma_a \geq 1.10$ MPa at any power density and at $\sigma_a = 0.18$ or 0.37 MPa at a power density of less than 20 W cm^{-2} . These laser-heated fibers had diameters ranging from 80 to $180 \mu\text{m}$, and their birefringence increased as the power density and σ_a increased.

A second laser heating was carried out for the laser-heated fibers with a diameter of $80 \mu\text{m}$ or more to thin them. To optimize the conditions of the second laser heating, we performed preliminary experiments at various σ_a 's and power densities. The second-laser-heating conditions, 0.18 MPa and 51.81 W cm^{-2} , were determined on the basis of the experimental results.

Table I shows the diameter and birefringence of the second-laser-heating fibers prepared through the CO₂-laser irradiation of the first-laser-heating fibers with a diameter of $80 \mu\text{m}$ or more. The diameter of the second-laser-heating fibers was $5 \mu\text{m}$ or smaller, and the thinnest microfiber was obtained through laser irradiation at 51.81 W cm^{-2} of the first-laser-heating fiber

prepared under 36.7 MPa at 17.3 W cm^{-2} . The first-laser heating and second-laser-heating fibers obtained under the optimum conditions are hereafter abbreviated the LH-1 and LH-2 fibers, respectively. Table II shows the diameter, birefringence, degree of crystallinity, and draw ratio estimated from the diameter for the original, LH-1, and LH-2 fibers. The LH-1 fiber had a degree of crystallinity of 37% and a birefringence of 56.7×10^{-3} . The diameter of the LH-1 fiber was $87.6 \mu\text{m}$, and its draw ratio was $4.7\times$. These values were almost the same as those of the laser-heated zone-drawn fiber. The LH-2 fiber had a diameter of $1.9 \mu\text{m}$ and a birefringence of 46.2×10^{-3} . The draw ratio of the LH-2 fiber reached $9589\times$, and such a high draw ratio has not been attained by any drawing method so far. The birefringence of the LH-2 fiber was almost two-thirds of the intrinsic crystallite birefringence (0.0780).¹⁵

Figure 4 shows SEM photographs of the original and LH-2 fibers. SEM at $10,000\times$ showed that the LH-2 fiber had a smooth surface without a surface roughened by laser ablation and that it was uniform in diameter.

Figure 5 shows WAXD photographs of the LH-1 and LH-2 fibers. In the LH-1 fiber, a (200) reflection and a (002/202) doublet due to an α form¹³ were observed on the equator, but no (200) reflection due to a γ form¹⁶ was observed. The morphology of the crystallites existing in the LH-1 fiber was only the α form. The WAXD photograph of the LH-1 fiber shows that the high level of crystalline orientation was obtained by the first laser heating. The WAXD photograph of the LH-2 fiber shows indistinct reflections due to small crystallites, but the LH-2 fiber was inferior to the LH-1 fiber in its crystalline orientation and crystallinity. Despite the indistinct reflections, the whole orientation was not as low because the LH-2 fiber had a birefringence of 46.2×10^{-3} , as mentioned previously. The indistinct reflections of the LH-2 fiber indicated that

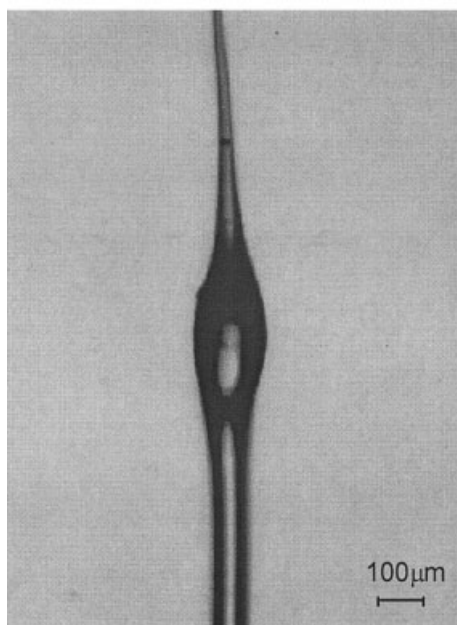
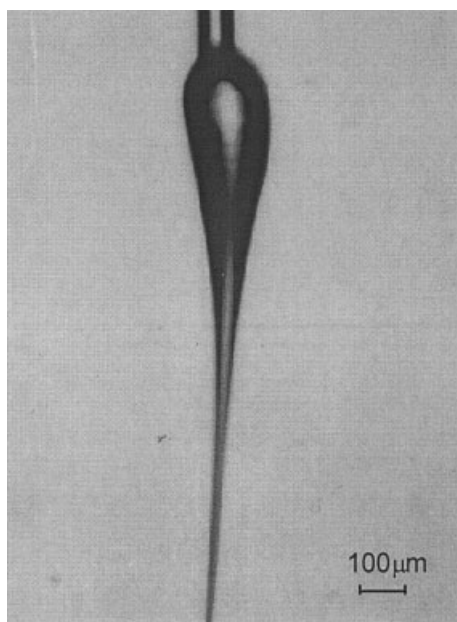


Figure 6 Microphotographs of the upper and lower spindle-shaped necks in the LH-2 fiber.

small amounts of the oriented crystallites were induced by the cold drawing after the melting of the LH-1 fiber with high degrees of crystallinity and orientation.

Figure 6 shows microphotographs of the upper and lower spindle-shaped necks in the LH-2 fiber. The two necks were formed at both ends of a microfiber about 1.5 m long. The formation of the necks suggested that the LH-2 fiber was spun from a molten state. On the basis of

these microphotographs, we hypothesize the following thinning mechanism. The plastic viscosity in part of the fiber during the second laser heating at a high output power became sufficiently low without elongation or cutting because σ_a during the second laser heating was much lower than that during the first-laser-heating zone drawing, and then the heated part became nearly molten; this is clear from the microphotograph of spindle-shaped necking shown in Figure 6. As a result of the second laser heating at an extremely low σ_a value at a high output power, plastic flow occurred at a high strain rate. Drawing at a high strain rate induced molecular orientation and crystallization, despite a large deformation, just as in flow drawing, and produced an oriented nylon 6 microfiber.

CONCLUSIONS

CO₂-laser heating was found to be capable of producing nylon 6 microfibers. The microfibers were prepared via laser heating carried out at extremely low values of σ_a at a higher power density in comparison with laser-heating zone drawing for nylon 6 fibers.

The thinning of the nylon 6 fiber was caused by plastic flow due to a molten state at a high strain rate. Extremely large deformation at the high strain rate induced molecular orientation and crystallization. Thinning with a CO₂ laser is conceivable as dieless spinning. Laser heating could make a microfiber more easily than conventional technologies, such as conjugate spinning, melt blowing, and flash spinning.

The authors are grateful to Toray, Ltd., for supplying the nylon 6 fibers.

References

1. Suzuki, A.; Mochizuki, N. *J Appl Polym Sci* 2001, 82, 2775.
2. Suzuki, A.; Ishihara, M. *J Appl Polym Sci* 2002, 83, 1711.
3. Dadsetan, M.; Mirzadeh, H.; Shari, N. *Radiat Phys Chem* 1999, 56, 597.
4. Scarparo, M. A. F.; Chen, Q. J.; Miller, A. S.; Li, C. J.; Leary, H.; Allen, S. D. *Appl Surf Sci* 1996, 106, 275.
5. Zergioti, I.; Hatzia Apostolou, A.; Hontzopoulos, E.; Zervaki, A.; Haidemenopoulos, G. N. *Thin Solid Films* 1995, 271, 96.
6. Wang, J.; Wong, W. C. K. *J Mater Process Technol* 1999, 95, 164.
7. Hopfe, V.; Jäckel, R.; Schönfeld, K. *Appl Surf Sci* 1996, 106, 60.
8. Paiva, P.; Madelino, F.; Conde, O. *J Lumin* 1999, 80, 141.
9. Panzner, M.; Wiedemann, G.; Henneberg, K.; Fischer, R.; Wittke, T.; Dietsch, R. *Appl Surf Sci* 1998, 127, 787.
10. Hidouci, A.; Pelletier, J. M.; Ducoin, F.; Dezert, D.; El Guerjouma, R. *Surf Coat Technol* 2000, 123, 17.
11. Suzuki, A.; Mochizuki, N. *J Appl Polym Sci* 2003, 88, 3279.
12. Suzuki, A.; Mochizuki, N. *J Appl Polym Sci* 2003, 90, 1955.
13. Holmes, D. R.; Bunn, C. W.; Smith, D. J. *J Polym Sci* 1955, 17, 159.
14. Roldan, L. G.; Kaufman, G. S. *J Polym Sci Part B: Polym Lett* 1963, 1, 603.
15. Kunugi, T.; Yokokura, S.; Hashimoto, M. *Nippon Kagakukaishi* 1976, 29, 128.
16. Richardson, A.; Ward, I. M. *J Polym Sci Part B: Polym Phys* 1981, 19, 1549.