Nylon 6 Microfiber Obtained by a Continuous-Thinning Method with a Carbon Dioxide Laser

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ABSTRACT: We succeeded in producing nylon 6 microfibers with a continuous-thinning method with a carbon dioxide (CO_2) laser. A laser-thinning apparatus used to continuously prepare microfibers was developed in our laboratory; it consisted of spools supplying and winding the fibers, a continuous-wave CO_2-laser emitter, a system supplying the fibers, and a traverse. The laser-thinning apparatus produced microfibers in the range of 100–2500 m min^{-1}. The diameter of the microfibers decreased as the winding speed increased, and the birefringence increased as the winding speed increased. When microfibers, obtained through the laser irradiation (at a power density of 19.8 W cm^{-2}) of the original fiber supplied at 0.32 m min^{-1}, were wound at 848 m min^{-1}, they had a diameter of 3.2 μm and a birefringence of 47×10^{-3}. The draw ratio calculated from the supplying and winding speeds was 2650×. Scanning electron microscopy showed that the microfibers obtained with the laser-thinning apparatus had smooth surfaces not roughened by laser ablation that were uniform in diameter. Wideangle X-ray diffraction photographs of the microfibers wound at 566 and 848 m min^{-1} showed equatorial and meridional reflections due to the γ from. These reflections gradually became clear as the winding speed increased. The developed apparatus more easily produced microfibers than conventional technologies, such as conjugate spinning, islands-in-a-sea fiber spinning, melt blowing, and flash spinning. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1454–1458, 2004

Key words: nylon; fibers; drawing; WAXS

INTRODUCTION

A thinning method with a continuous-wave carbon dioxide (CO_2) laser has already been applied to poly-(ethylene terephthalate) (PET),[1,2] nylon 6,[3] and isotactic polypropylene (i-PP)[4] fibers, and it is effective in preparing their microfibers. When a high-output-power laser is used to irradiate a fiber applied at an extremely low tension, its microfiber is easily obtained. The applied tension in laser thinning is 1/100 to 1/1000 of the applied tension in the laser-heating zone drawing of PET[5] and nylon 6 fibers.[6]

When a laser operated at a power density of 55.4 W cm^{-2} is used to irradiate an annealed PET fiber with an applied tension of 26.5 KPa, a microfiber with a diameter of 1.5 μm is obtained, and its birefringence is 172.8×10^{-3}.

For the thinning of a nylon 6 fiber, laser heating is performed in two steps: the first laser heating is carried out under an applied tension of 36.7 MPa at a power density of 17.3 W cm^{-2}, and the second is carried out under 0.18 MPa at 51.81 W cm^{-2}. The nylon 6 microfiber has a diameter of 1.9 μm, a birefringence of 46.2×10^{-3}, and a draw ratio of 9895×.

The drawn i-PP fiber is heated under an applied tension of 0.3 MPa with a laser operated at 39.6 W cm^{-2}. The obtained i-PP microfiber has a diameter of 1.8 μm, a birefringence of 30×10^{-3}, and a draw ratio of 51,630×.

In the laser thinning of PET, nylon 6, and i-PP fibers, two spindle-shaped necks are formed at both ends of a microfiber about 1.5 m long. The formation of the spindle-shaped neck suggests that a portion of the fiber is locally melted by the irradiation of the high-output-power laser and that instantaneous plastic flow occurs after the melt viscosity becomes sufficiently low. The instantaneous plastic flow induces molecular orientation and crystallization, despite a large deformation, just as in flow drawing and then produces the oriented microfiber. Thinning by laser heating can be considered dieless spinning.

Laser heating easily produces microfibers without highly skilled techniques and is remarkable as a method for producing microfibers. However, only a microfiber about 1.5 m long can be obtained by laser heating. This result is not very valuable from an industrial point of view, even if it is academically interesting.

We tried to develop a method of continuously preparing microfibers with laser heating, and we suc-
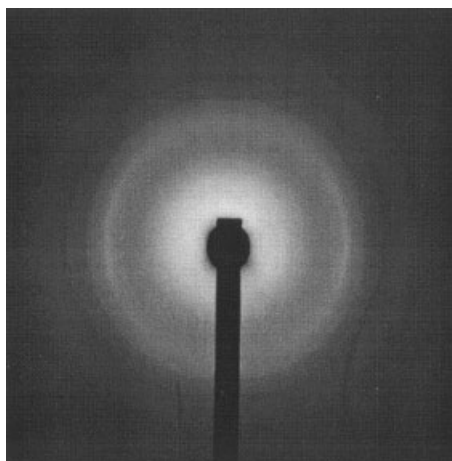
Figure 1 WAXD photograph of the original fiber.

ceeded in producing an apparatus for continuously obtaining microfibers with CO_2-laser heating. The developed apparatus could wind microfibers as monofilaments in the winding speed range of 100–2500 m min^{-1}.

Microfibers are now manufactured with highly skilled techniques, such as conjugate spinning (requiring a highly complex spinneret), islands-in-a-sea fiber spinning, melt blowing, and flash spinning, and it is impossible to prepare microfibers by any other method. The polymers from which microfibers can be produced by these methods are limited in number. However, it is possible to thin all thermoplastic polymers with the developed apparatus without a large-scale instrument.

We present here results pertaining to nylon 6 microfibers obtained with the laser-thinning apparatus.

EXPERIMENTAL

Materials

The original fibers 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 μm, a degree of crystallinity of 28%, and a birefringence of 6.25×10^{-3}. The original fiber was found to be slightly oriented fiber from a wide-angle X-ray diffraction (WAXD) photograph (Fig. 1).

Measurements

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

The draw ratio was calculated easily with the following equation:

$$\text{Draw ratio} = (S_w/S_s) \qquad (1)$$

where S_s is the supplying speed and S_w is the winding speed.

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

WAXD photographs of the fibers were taken with a flat-film camera. The camera was attached to a Rigaku (Akishima, Japan) X-ray generator operated at 36 kV and 18 mA. The radiation was Ni-filtered Cu Kα. 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.

Continuous-laser-thinning apparatus

The laser-thinning apparatus used to continuously produce the microfiber consisted of spools supplying and winding the fiber, a continuous-wave CO_2-laser emitter (PIN10S, Onizca Glass, Ltd., Oume, Japan), a system supplying the fiber, and a traverse (Fig. 2). The continuous-wave CO_2 laser emitted light at 10.6 μm, and the laser beam had a 4.0-mm diameter. The power density was measured with a power meter during the laser irradiation. It was necessary to supply the fiber to a laser-irradiation point at a constant speed to prepare the microfiber in a stable manner. The supplying system pulled the original fiber from the supplying spool and supplied it to the laser-irradiation point at a constant speed. The supplying system played an important role in the continuous-laser-thinning apparatus. The fiber thinned at the laser irradiating point was wound on the spool at a winding speed of 100–2500 m min^{-1}.
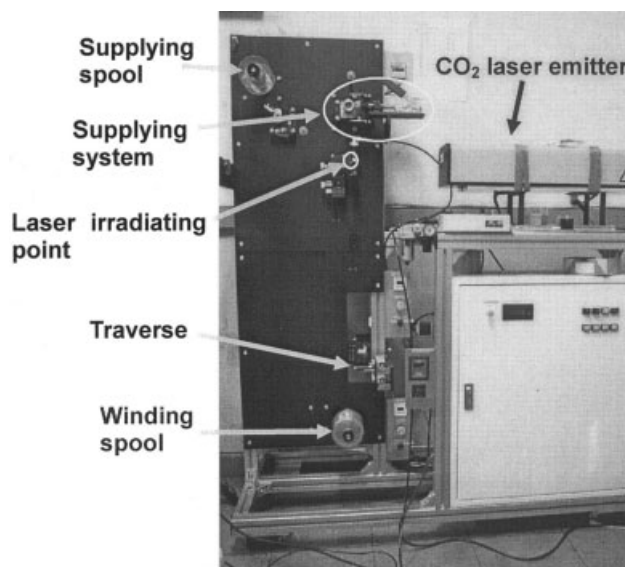

Figure 2 Continuous-laser-thinning apparatus used to produce microfibers.

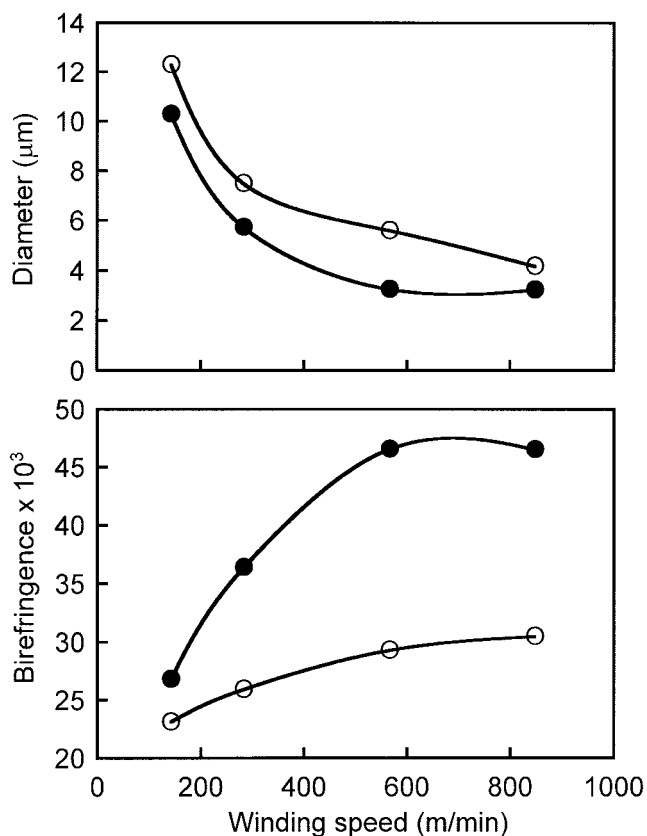**Figure 3** Winding speed dependence of the diameter and birefringence of fibers obtained at two supplying speeds: (●) 0.32 and (○) 0.47 m min^{-1}.

RESULTS AND DISCUSSION

Figure 3 shows the winding speed dependence of the diameter and birefringence of the fibers obtained at two supplying speeds. All irradiation at supplying speeds of 0.32 and 0.47 m min^{-1} was carried out at a power density of 19.8 W cm^{-2}. There was a close relationship between the supplying speed and the laser power density. It was difficult to continuously thin the nylon 6 fiber, except under these conditions. In the winding speed dependence of the diameter at each supplying speed, the diameter decreased as the winding speed increased. When the microfiber, obtained through the laser irradiation of the original fiber supplied at 0.32 m min^{-1}, was wound on the spool at 848 m min^{-1}, the thinnest microfiber, with a diameter of 3.2 μm, was obtained. Its draw ratio, estimated from the supplying and winding speeds, was 2650×. It has been impossible to attain such a high draw ratio with conventional drawing.

The continuous-laser-thinning mechanism was hypothesized as follows. When the original fiber, supplied to the laser-irradiation point by the supplying system, was heated through the irradiation of a high-output-power laser, the plastic viscosity of the fiber irradiated by the laser became sufficiently low, and a

portion of the fiber was nearly molten. The original fiber was continuously thinned by the plastic flow occurring from the nearly molten state, and then the microfiber, having fallen down because of its own weight, was wound on the winding spool. However, the microfiber was not obtained even if the laser irradiated the fiber pulled from the supplying spool with a winding force.

Figure 4 shows a photograph of the thinnest microfiber wound onto the spool; its diameter was 90 mm, and its winding length was about 85,000 m. Until now, there had been no technology able to wind a microfiber as a monofilament.

The birefringence increased as the winding speed increased. The increase in the birefringence of the fiber supplied at 0.32 m min^{-1} depended strongly on the winding speed, and the birefringence of the microfibers wound at 566 and 848 m min^{-1} was 47 × 10^{-3}. The birefringence value was equivalent to about 60% of the intrinsic crystallite birefringence (78 × 10^{-3}).[7] Rapidly winding the microfiber obtained through laser irradiation of the fiber supplied at the lower speed induced large deformation at a faster strain rate, and such deformation increased the degree of molecular orientation.

Figure 5 shows SEM photographs of microfibers wound at 142, 566, and 848 m min^{-1}. These microfibers were obtained through the laser irradiation of the original fiber supplied at 0.32 m min^{-1}. SEM at 1000× and 5000× showed that these microfibers had smooth surfaces not roughened by laser ablation that were uniform in diameter.
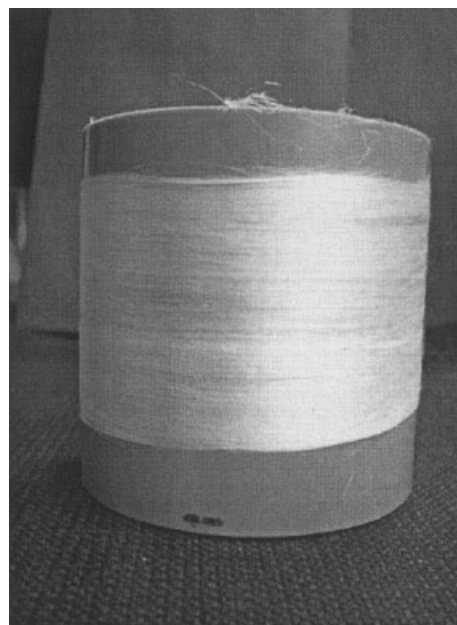

Figure 4 Photograph of a microfiber wound on a winding spool with a diameter of 90 mm.
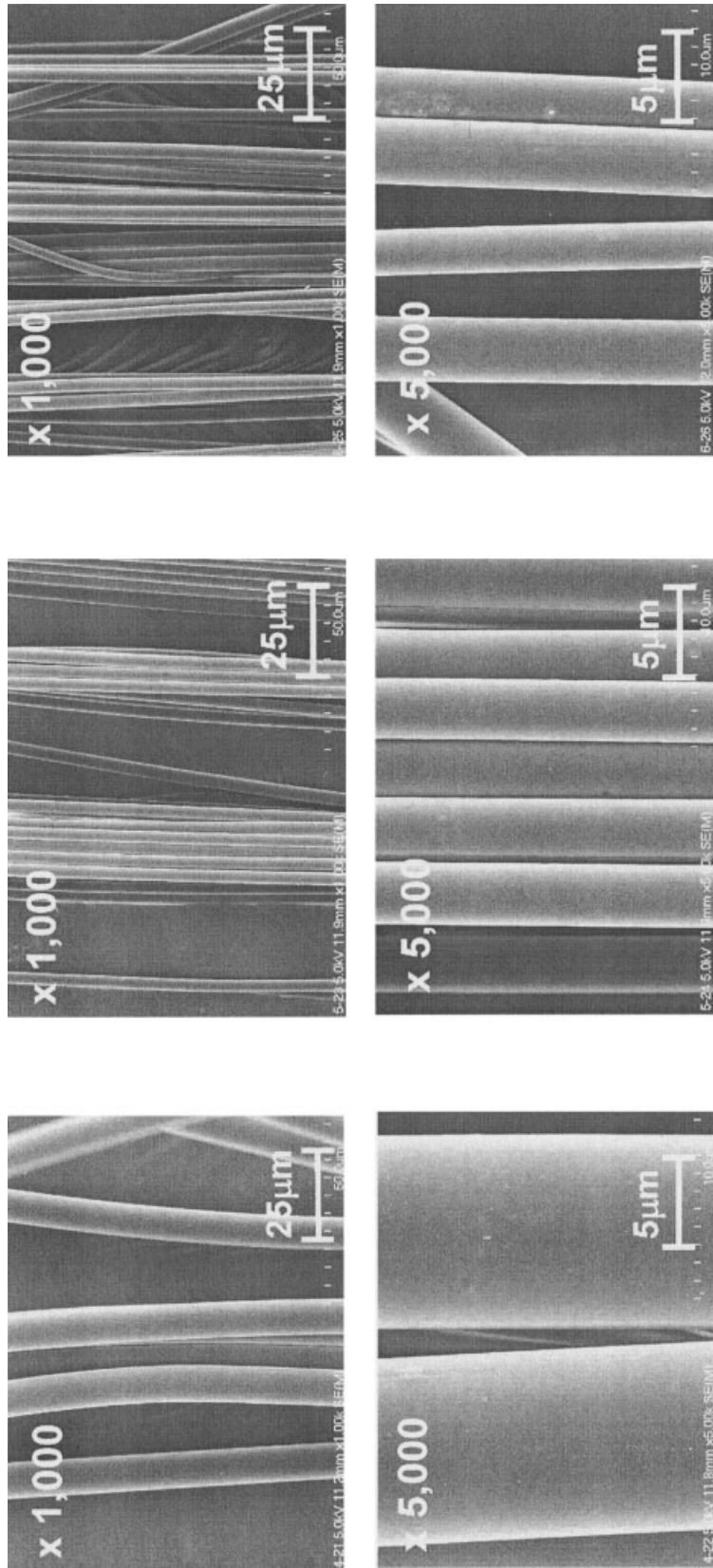
Figure 5 SEM micrographs of microfibers wound at 142, 566, and 848 m min^{-1} (from left to right).
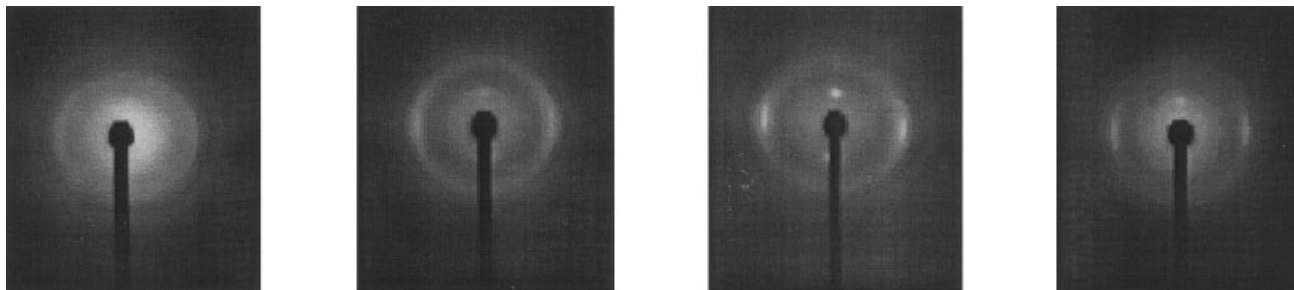
Figure 6   WAXD photographs of microfibers wound at 142, 283, 566, and 848 m min^{-1} (from left to right).

Figure 6 shows WAXD photographs of microfibers wound at a series of winding speeds. Nylon 6 has two known crystal modifications: an α form[8] and a γ form.[9] These forms have monoclinic unit cell structures with a difference in the direction of the hydrogen bonds between adjacent chains. The α form has hydrogen bonds between antiparallel chains, and the γ form has hydrogen bonds between parallel chains.[8,10] The α form gives two strong equatorial reflections from the (200) and (002/202) planes, and the γ form gives a single equatorial reflection and a strong meridional reflection from the (020) plane.

The WAXD photographs of microfibers wound at 142 and 283 m min^{-1} show indistinct reflections due to the α and γ forms. However, the WAXD photographs of microfibers wound at 566 and 848 m min^{-1} show strong equatorial and meridional reflections due to the γ form. These reflections due to the γ form gradually became clear as the winding speed increased. The increase in the winding speed induced crystallization and molecular orientation.

In the hot-air drawing[11] and laser-heating zone drawing[6] of nylon 6 fibers, the drawn fibers had two strong reflections due to the α form on the equator, but no reflection due to the γ form was observed. The morphology of the crystallites existing in the hot-air-drawn fiber and the laser-heated zone-drawn fiber was only the α form.

The γ-form content in the original fiber was 8% or less, decreased with drawing, and was almost zero at a draw ratio of 3.5×. The γ form converted easily into the α form by drawing.[12] These WAXD photographs suggest that the microfiber was different from the drawn fibers in the morphology of the crystallites. The appearance of the γ form in the microfiber was due to the crystallization of molecular chains not sufficiently extended. The γ form in the obtained microfiber was converted into the α form by cold drawing.

CONCLUSIONS

A CO_2-laser-thinning apparatus to continuously produce microfibers was developed in our laboratory and applied to nylon 6 fibers. The apparatus made it possible to wind microfibers on a spool at a higher winding speed. The diameter decreased and the birefringence increased as the winding speed increased. When a microfiber, obtained through laser irradiation of the original fiber supplied at 0.32 m min^{-1}, was wound on a spool at 848 m min^{-1}, the thinnest microfiber obtained had a diameter of 3.2 μm and a birefringence of 47 × 10^{-3}.

The continuous-laser-thinning apparatus can produce microfibers more easily than conventional technologies, such as conjugate spinning, melt blowing, and flash spinning. It is possible to thin all thermoplastic polymers with this laser-thinning apparatus without a large-scale instrument or highly skilled techniques.

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