

Isotactic Polypropylene Microfiber Prepared by Continuous Laser-Thinning Method

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ABSTRACT: An isotactic polypropylene (i-PP) microfiber was continuously produced by using a carbon dioxide (CO₂) laser-thinning apparatus developed in our laboratory. The CO₂ laser-thinning apparatus could wind up the obtained microfiber in the range of 100 m min⁻¹ to 2500 m min⁻¹. The diameter of the microfiber decreased and its birefringence increased with increasing winding speed. When the microfiber obtained by irradiating the CO₂ laser operated at a power density of 31.8 W cm⁻² to the original fiber supplied at 0.30 m min⁻¹ was wound at 1,387 m min⁻¹, the obtained microfiber had a diameter of 3.5 μm and a birefringence of

25×10^{-3} . The draw ratio calculated from the supplying and the winding speeds was 4,623-fold. The SEM photographs showed that the obtained microfibers had a smooth surface without a surface roughened by a laser-ablation and were uniform in diameter. The wide-angle X-ray diffraction photographs of the microfibers wound at 848 and 1,387 m min⁻¹ showed the existence of the oriented crystallites. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 27–31, 2006

Key words: poly(propylene); fibers; DSC; WAXS

INTRODUCTION

It was found that microfibers were prepared by a carbon dioxide (CO₂) laser-heating carried out under a very low applied tension at the high laser power density. The applied tension in the CO₂ laser-thinning was in the range of 1/100 to 1/1000 of the applied tension in a laser-heating zone-drawing, and the power density in the CO₂ laser-thinning was about five times larger than that in the CO₂ laser-heating zone-drawing.^{1,2} The CO₂ laser-thinning method was already applied to a poly(ethylene terephthalate) (PET),^{3,4} a nylon 6,⁵ and an isotactic polypropylene (i-PP)⁶ fibers. The PET microfiber with a diameter of 1.5 μm, the nylon 6 microfiber with a diameter of 1.9 μm, and the i-PP microfiber with a diameter of 1.8 μm were obtained. The CO₂ laser-thinning method easily provides the microfiber without especially highly skilled techniques and is remarkable as a method to produce the microfiber. However, only the microfiber with a slight 1.5 m length was obtained by using the present CO₂ laser-thinning apparatus. This result is not very valuable from an industrial point of view, even if it has an interest academically.

We tried to develop the method to continuously prepare the microfiber by using the CO₂ laser-heating

and then succeeded in assembling the apparatus that can prepare microfiber continuously. The developed apparatus can wind up the microfiber as a monofilament in the winding speed range of 100 to 2,500 m min⁻¹. The new apparatus was already applied to the nylon 6 fiber,⁷ and the nylon 6 microfiber with a diameter of 3.2 μm was continuously obtained by winding the microfiber at a speed of 848 m min⁻¹.

The microfibers are now manufactured with especially highly skilled techniques such as a conjugate spinning requiring a highly complex spinneret, an islands-in-a-sea type fiber spinning, a melt blowing, and a flash spinning. Heretofore, it was impossible to prepare microfibers by any other method. The polymer that is possible to produce the microfiber by these methods is limited to PET, nylon, and polyethylene. On the other hand, it is possible to produce all thin thermoplastic polymers by using the developed apparatus because the thinning by the laser-heating can be regarded as a die-less spinning.^{1–6}

In this study, the continuous laser-thinning method was applied to the i-PP fiber to prepare the i-PP microfiber. We present here the results pertaining to the properties of the i-PP microfiber obtained by using the developed apparatus to continuously thin the fiber.

EXPERIMENTAL

Materials

Original i-PP fibers were produced from commercial grade i-PP pellets by using a laboratory-scale melt

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extruder and take-up unit. The used pellets had $\bar{M}_w = 30,000$ and $\bar{M}_n = 50,000$. Its tacticity was highly isotactic, approximately 96% was determined by using nuclear magnetic resonance techniques. The original fibers were spun into monofilaments at a spinning temperature of 230°C. The original fiber had a diameter of 409 μm , degree of crystallinity of 44%, and birefringence of 0.3×10^{-3} . An as-spun fiber were found to be isotropic from a wide-angle X-ray diffraction photograph as shown in Figure 1.

Measurements

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

Draw ratio can be calculated easily using the following equation:

$$\text{Draw ratio} = (\text{winding speed}/\text{supplying speed}) \quad (1)$$

SEM micrographs of the fibers were observed on a JEOL JSM-T20 with an acceleration voltage of 19 kV.

Wide-angle X-ray diffraction photographs of the fibers were taken using a flat-film camera. The camera was attached to a Rigaku X-ray generator (Rigaku Co., Japan) that was operated at 36 kV and 18 mA. The radiation used was Ni-filtered $\text{CuK}\alpha$. 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.

Differential scanning calorimetry (DSC) measurements were carried out using a Rigaku DSC 8230C calorimeter. The DSC scans were performed within



Original fiber

Figure 1 Wide-angle X-ray diffraction photograph of original fiber.

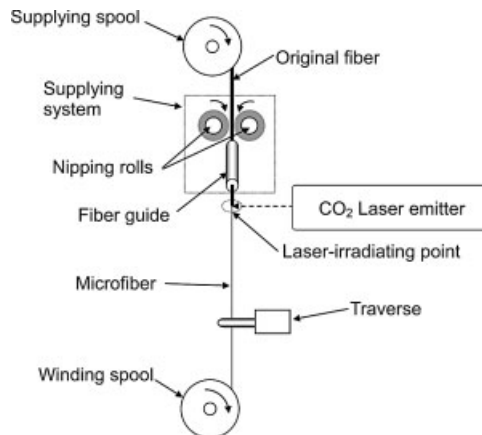


Figure 2 CO₂ laser-thinning apparatus used for producing the microfiber.

the temperature range of 25 to 200°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.

CO₂ laser-thinning apparatus

The CO₂ laser-thinning apparatus to continuously produce the microfiber consists of supplying and winding motors with spools, a continuous wave CO₂ laser emitter (PIN10S, ONIZCA Glass Ltd., Japan), a supplying system composed of a fiber guide and nipping rolls, and a traverse as shown in Figure 2. The continuous wave CO₂ laser emitted light at 10.6 μm , and the laser beam was a 4.0-mm diameter spot. A laser power was measured by the power meter during the laser irradiating. The laser power density (PD) was estimated by dividing the measured laser power in the area of the laser spot. Laser power of more than 90% is obtained in the area of the laser spot. It is necessary to supply the fiber to a laser irradiating point at a constant speed to stably prepare the microfiber. The supplying system pulls out the original fiber of the supplying spool and supplies it to the laser irradiating point at a constant speed. The supplying system plays an important role in the CO₂ laser-thinning apparatus. The fiber thinned at the laser irradiating point is wound on the spool in the winding speed range of 100 m to 2,500 m min^{-1} .

RESULTS AND DISCUSSION

Thinning condition and properties of microfiber

Figure 3 shows the winding speed dependence of the diameter for the i-PP microfibers obtained at various supplying speeds. The diameter of the microfiber obtained at each supplying speed decreases with an increase in the winding speed. The diameter of the fiber thinned at each winding speed tends to decrease

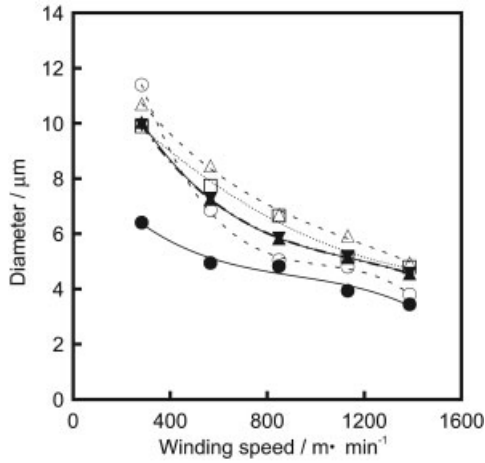


Figure 3 Winding speed dependence of the diameter of the i-PP microfibers obtained at various supplying speeds (in $m \cdot min^{-1}$): ● 0.30, ○ 0.38, ▲ 0.45, □ 0.53, ▼ 0.60, △ 0.68.

with a decrease in the supplying speed. When the microfiber prepared by irradiating the laser to the original fiber supplied at a supplying speed of $0.30 m \cdot min^{-1}$ was wound at a winding speed of $1,387 m \cdot min^{-1}$, the thinnest microfiber with a diameter of $3.5 \mu m$ was obtained, and its draw ratio reached 4,623-fold. The PD that can be irradiated to the original fiber without cutting the fiber is closely related to the supplying speed as shown in Figure 4. The PD value increases in proportion to the supplying speed. The PD at the supplying speed ($0.3 m \cdot min^{-1}$) that gives the thinnest microfiber is $31.8 W \cdot cm^{-2}$.

Figure 5 shows the SEM photographs of $5,000\times$ magnification for the microfibers wound at three different winding speeds. The SEM photographs show that the microfibers have a smooth surface without a surface roughened by laser ablation and are uniform in diameter.

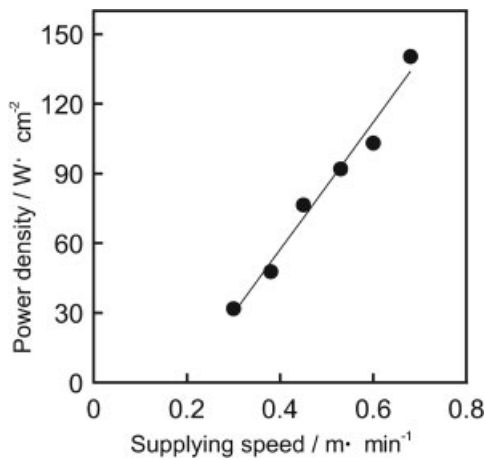


Figure 4 Relation between the supplying speed and laser power density (PD).

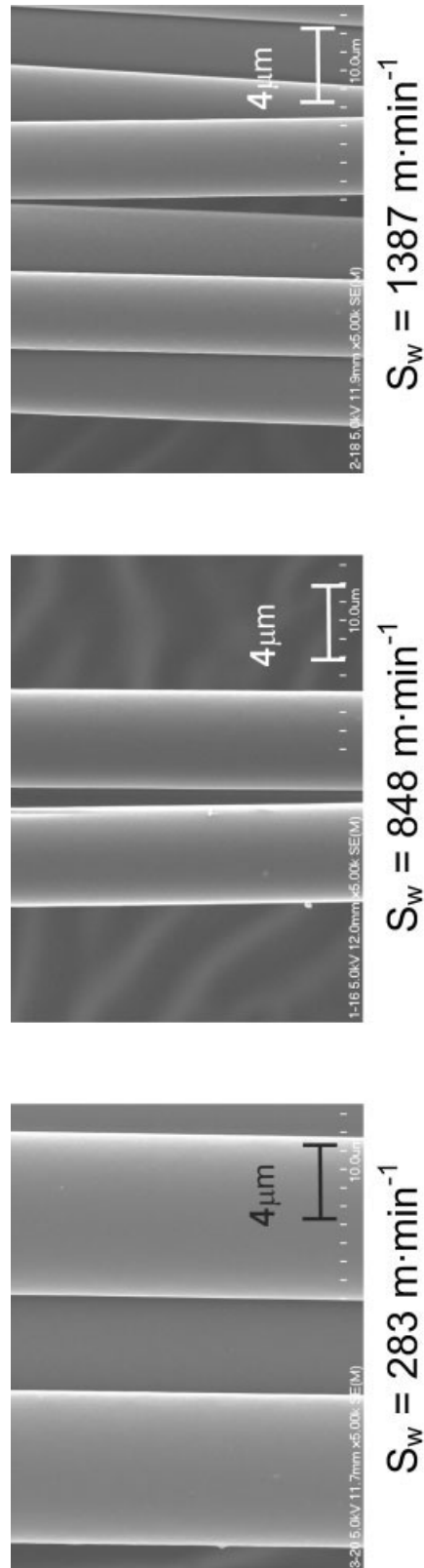


Figure 5 SEM photographs of $5,000\times$ magnification for the microfibers wound at three different winding speeds (S_w).

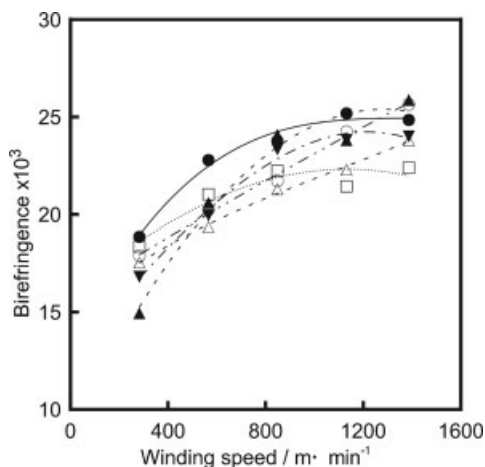


Figure 6 Winding speed dependence of birefringence of the i-PP microfibers obtained at various supplying speeds (in m min^{-1}): ● 0.30, ○ 0.38, ▲ 0.45, □ 0.53, ▼ 0.60, △ 0.68.

Figure 6 shows the winding speed dependence of the birefringence for the i-PP microfibers obtained at various supplying speeds. The birefringence increases with an increase in the winding speed. The birefringence of the microfibers obtained at a supplying speed of 0.3 m min^{-1} and a PD of 31.8 W cm^{-2} depends strongly on the winding speed. The microfiber with the highest birefringence of 25×10^{-3} was obtained when the microfiber was wound at a winding speed of $1,387 \text{ m min}^{-1}$. The increase of the birefringence is caused by the increases in the degrees of the molecular chain orientation, crystallinity, and orientation of crystallites because the total birefringence is the sum of the crystalline and the amorphous birefringence.

Wide-angle X-ray diffraction of the microfiber

Figure 7 shows the wide-angle X-ray diffraction photographs of the microfibers wound at three different winding speeds. The sharpening of the diffraction spot indicates an improvement in crystal perfection and an increase in the degree of crystal orientation and crystal size. The microfibers wound at 848 and $1,387 \text{ m min}^{-1}$

min^{-1} have three strong equatorial reflections [(110), (040), and (130)] and two reflections [(041) and ($1\bar{3}\bar{1}$)]. The windings at 848 and $1,387 \text{ m min}^{-1}$ are further improved in degrees of crystallinity and orientation compared with the winding at 284 m min^{-1} , and the microfibers obtained at high winding speeds have highly oriented crystallites. This fact indicates that not only the molecular flow but also the molecular orientation and crystallization are induced by the higher strain rate during the thinning process and that agrees approximately with the birefringence result mentioned above.

The i-PP crystallizes in three polymorphic forms: α -monoclinic, β -hexagonal,^{8–10} and γ -orthorhombic crystal forms.^{11,12} The α form is the most stable crystalline phase and can be easily obtained by crystallization from the melt or from solution.¹³ The α form is further classified in two limiting modifications, i.e., α_1 and α_2 .^{14,15} The α_1 form is characterized by a statistical disorder like that described for the space group C2/c. The α_2 form is characterized by regularity of up and down positioning of the chains, as in the space group P2₁/c.

Both the α_1 and α_2 forms have substantially identical X-ray spectra. However, while only reflections with $(h + k)$ even are allowed in the α_1 form, reflections with $(h + k)$ odd may be present in the α_2 form.¹⁶ All reflections observed are reflections with $(h + k)$ even. It is known that the β form exhibits a strong equatorial reflection (300) at $2\theta = 16.10^\circ$ and that the γ form¹⁷ is observed (113) at $2\theta = 14.98^\circ$ and (117) at 20.06° . However, no reflections due to the β and γ form are observed in Figure 7. Therefore, these wide-angle X-ray diffraction photographs show that only the α_1 form exists in the microfibers. These results are very much in agreement with the results of the DSC measurements that will be described below.

Melting behavior of the microfiber

Figure 8 shows DSC curves for the original fiber and the microfibers wound at three different winding speeds. The original fiber had a single melting endotherm peak at 162°C ; the microfiber wound at 283 m min^{-1}

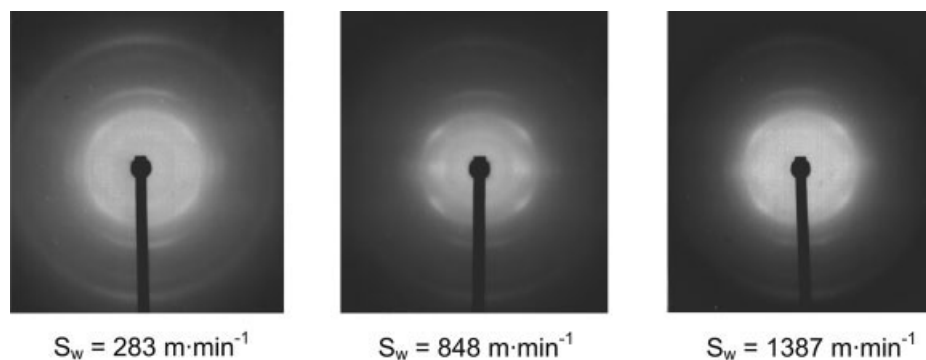


Figure 7 Wide-angle X-ray diffraction photographs of the i-PP microfibers wound at three different winding speeds (S_w).

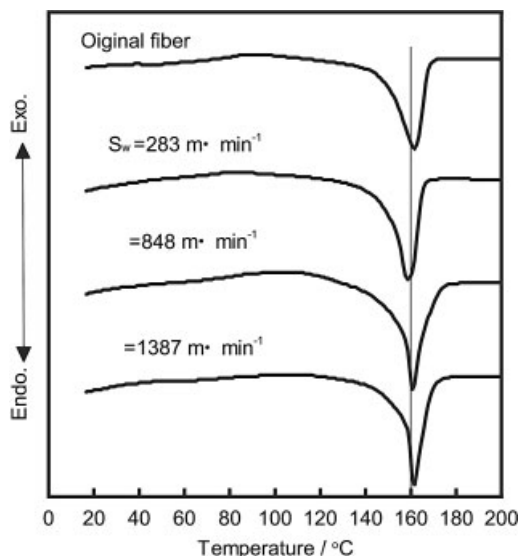


Figure 8 DSC curves of the original fiber and the i-PP microfibers wound at three different winding speeds.

min^{-1} had a single melting endotherm peak at 160°C , and the microfibers wound at 848 and $1,387 \text{ m min}^{-1}$ had a single melting endotherm peak at 163°C . The melting peaks of the microfibers wound at 848 and $1,387 \text{ m min}^{-1}$ are sharper than that of the microfiber obtained at 283 m min^{-1} . The higher winding speed is, the higher the melting point. A sharpening of the melting peak is caused by an increase in the degree of perfection of the crystallites.^{18,19}

The melting behavior of i-PP crystallized in different ways has been studied by several workers.^{20–26} An endotherm peaking at 161°C is due to the melting of the α_1 form, and a high endotherm peaking above 170°C is due to the melting of α_2 form.²³ Jacoby et al.¹⁵ reported that a melting endotherm due to the melting of the β form was observed at about 150°C .

These DSC curves obtained have only a single melting endotherm peak around 160°C , but no melting endotherm peaks at 150 and 170°C are observed. This means, therefore, that all melting peaks are due to the melting of the α_1 form and that no melting endotherm peaks due to the β and α_2 forms are observed. The results obtained agree well with the results of the wide-angle X-ray diffraction as mentioned above.

CONCLUSIONS

The CO_2 laser-thinning method using the apparatus developed by us was applied to the i-PP fiber to continuously prepare the i-PP microfiber. The apparatus made it possible to continuously wind the microfiber on the spool at the high winding speed. In the winding speed dependence of the diameter and the birefringence, the diameter of the microfiber decreased with increased winding speed, and its bire-

fringence increased with increased winding speed. The thinner the microfiber was, the higher the birefringence. When the microfiber obtained by irradiating the laser to the original fiber supplied at 0.30 m min^{-1} was wound on the spool at a winding speed of $1,387 \text{ m min}^{-1}$, the thinnest microfiber with a diameter of $3.5 \mu\text{m}$ was obtained, and its birefringence was 25×10^{-3} . The degrees of the crystallinity and the crystalline orientation increased with increased winding speed. The laser-thinning at the high winding speed caused the strain-induced crystallization and gave thinner microfiber having highly oriented crystallites.

The mechanism of the CO_2 laser-thinning is conceivable as follows. First, the original fiber supplied to the laser-irradiating point at a constant speed is heated by the high output power laser up to the nearly molten state, and the plastic flow from the nearly molten state immediately induces the thinning, the molecular orientation, and the strain-induced crystallization.

The CO_2 laser-thinning method can prepare the microfiber easily without requiring large-scale equipment unlike conventional techniques such as conjugate spinning, islands-in-a-sea type fiber spinning, melt blowing, and flash spinning. All of the thermoplastic polymers can be thinned by the CO_2 laser-thinning method. We are applying the CO_2 laser-thinning method by using the developed apparatus to other thermoplastic polymers.

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