

# Spinning the Supercooled PET to Obtain Highly Oriented and Crystallized PET Fibers at Low Speeds

Jinan Cao

Faculty of Engineering and Industrial Sciences, Swinburne University of Technology, Hawthorn, Victoria 3122, Australia

Received 15 December 2005; accepted 14 February 2006

DOI 10.1002/app.24449

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** An attempt has been made to investigate the feasibility for a novel concept of supercooled spinning to obtain orientation-induced crystallization at speeds lower than that for the high-speed spinning technology. This is achieved by setting the nozzle temperature lower than the melting point for PET, making the polymer a supercooled fluidic liquid, and then spinning the supercooled. The experimental results show that high orientation and high crystallinity can be achieved at a spinning speed of 2500 m/min, which is in good comparison with a

speed of 5000–6000 m/min to obtain similar degree of orientation and crystallinity in the high-speed spinning. The properties of the as-spun fibers obtained by supercooled spinning were analyzed, and a rational theoretical account for the supercooled spinning is explored. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3078–3082, 2006

**Key words:** high-speed spinning; supercooled spinning; orientation-induced crystallization; poly(ethylene terephthalate)

## INTRODUCTION

Several decades ago, a technology named high-speed spinning emerged to draw attention from researchers in polymer science and engineering. Unlike conventional melt spinning, by which unoriented yarns is obtained, followed up by a drawing and annealing process to obtain fully oriented yarns (FOY), the high-speed spinning aims to obtain FOY by a single spinning process, to make the following up drawing and annealing process redundant.<sup>1–3</sup> The idea of high-speed spinning was revolutionary, and it demonstrates a great success in polymer science and engineering. Indeed, the mechanism of structure formation of macromolecules on spinline remains a subject of research, and a high speed of up to 10,000 m/min has been reached to explore new opportunities for developing novel fiber manufacturing technology.<sup>4–9</sup> However, there are two fundamental problems associated with the high-speed spinning. The first lies in engineering aspect. The high-speed spinning requires a take-up speed of up to 8000–9000 m/min to obtain FOY poly(ethylene terephthalate) (PET) fibers, bringing up considerable energy consumption, high cost for manufacturing the take-up bobbin, and high cost for operation safety. The second is the fundamental mechanism of the high-speed spinning. Why and how does orientation-induced crystallization occur on spinline? Why is the spinning speed

instead of the draw ratio working? Namely, if PET achieves orientation-induced crystallization at 6000 m/min under a given set of spinning conditions, so should PET crystallize at 3000 m/min if the extruding rate is reduced by half under the draw ratio consideration. However, the laboratory experimental results show that this account does not work; it is the take-up speed that correlates to the orientation-induced crystallization on spinline.

Based on our analysis of the principles of structure formation of polymer molecules, we believe that it would be possible for orientation-induced crystallization to occur at lower speeds that are practical to the fiber making industry. It is the aim of this article to introduce a new concept of spinning the supercooled PET to obtain FOY at lower spinning speeds. Theoretical basis of the concept will be explained, and the experiments were carried out to verify the idea. It will be shown that the orientation-induced crystallization can occur at much lower speeds than those specified for the high-speed spinning technology. The properties of as-spun fibers of the supercooling spinning were also investigated.

## EXPERIMENTAL

### Sample specifications and supercooled spinning of PET

PET chips (Teijin Co.) were placed in an oven at 110°C for 2 h, followed by a crystallization process at 180°C for another 2 h. The PET chips were then heated to

Correspondence to: J. Cao (jcao@swin.edu.au).

**TABLE I**  
**Main PET Specification and Spinning Conditions**

Polymer	PET
Molecular weight	30,000
Mass flow rate	2.50 g/min
Melting temperature	275°C
Spinneret temperature	265°C
Spinneret diameter	1.0 mm
Spinline length	3.30 m

285°C for melting. Different from conventional melt spinning, the supercooled spinning sets the nozzle temperature to 265°C, which is lower than the melting temperature. Because of the low extruding rate and the broad distribution of the melting temperature for PET, it is reasonable to believe that part or all the PET passing through the nozzle have reached the supercooled fluidic liquid state. Owing to crystallization kinetics, the PET can be in a state of supercooled fluidic liquid for a certain time period. The supercooled fluidic liquid shall be extruded out from the nozzle before solidification, by crystallization. This setting aimed at permitting the PET to have more chances to crystallize on the spinline. The main spinning conditions are listed in Table I.

**Measurements of the properties of as-spun fibers**

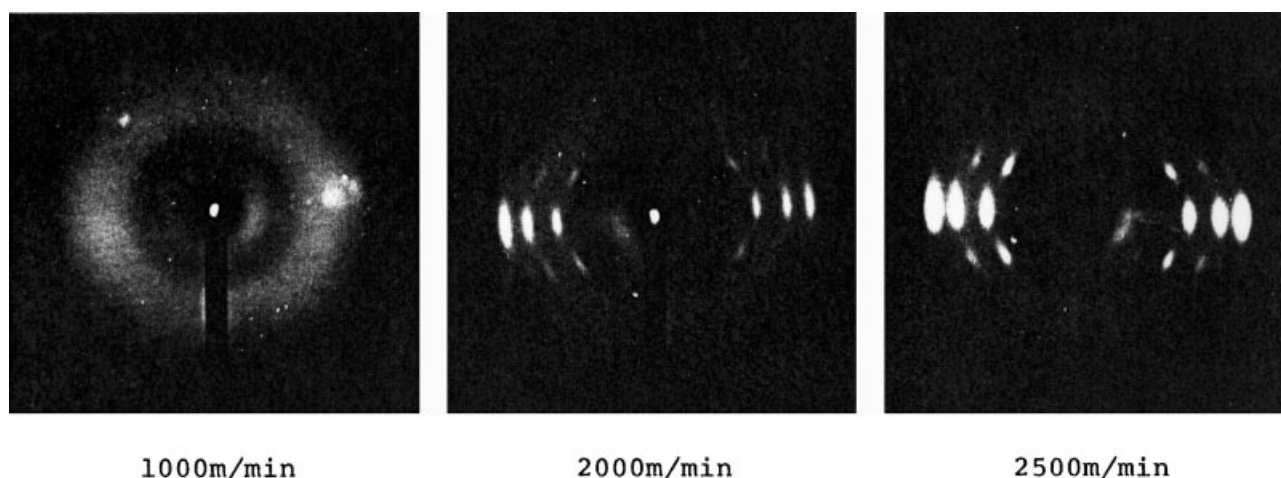
X-ray diffraction was carried out using a nickel-filtered Cu K $\alpha$  radiation source at 35 kV  $\times$  50 mA (Rigaku Denki) at a sample-detector distance of 40 mm. Density was measured using a density gradient column containing *n*-heptane and tetrachloromethane at 25°C. Birefringence was obtained by subtracting the reflective index for the perpendicular,  $n_{\perp}$ , from that for the parallel,  $n_{\parallel}$ , of the fibers, using an interference microscope. Mechanical testing was carried out on a tensile testing device (Tensilon UTM-4L, Toyo Sokki) to obtain the stress-strain curve, with the specimen length being

20 mm and elongation rate being 20 mm/min. Young’s modulus, yield stress, tenacity, and elongation at break were then determined from the stress-strain curves.

**RESULTS AND DISCUSSION**

Displayed in Figure 1 are the wide-angle X-ray diffraction (WAXD) patterns of the as-spun PET fibers. The fiber spun at 1000 m/min showed low orientation and was basically an amorphism. As the spinning speed increased to 2000 m/min, however, an oriented and crystallized pattern is observed, and the WAXS pattern becomes even sharper and clearer as the spinning speed approached 2500 m/min, indicating that the idea to spin the supercooled is working. This sort of high orientation and high crystalline WAXD patterns can only be observed for the fibers spun at 5000–6000 m/min and above in the high-speed spinning. The supercooled spinning placed the melt PET’s incubation period for crystallization inside the nozzle, so that the orientation-induced crystallization can occur on the spinline. The merit of the supercooled spinning is obvious; it produces FOY fibers in a single spinning process, and yet the required spinning speed is within the practical range to the fiber making industry. The supercooled spinning may become an alternative methodology to the high-speed spinning.

The *c*-axis crystalline orientation factor, birefringence, and crystallinity calculated from density as well as the mechanical properties of the as-spun fibers are shown in Table II, and Figures 2 and 3 show the density and birefringence plots in comparison with that obtained in the high-speed spinning.<sup>1-9</sup> The stress-strain curves are displayed in Figure 4. It is seen that the *c*-axis crystalline orientation factor,  $f_c$ , for the fibers spun at 2000 m/min and above was extremely high, and reached a figure that could only be obtained at the high-speed spinning rate of 8000–9000 m/min. On the



**Figure 1** WAXD patterns of the as-spun PET fibers obtained by supercooled spinning.

TABLE II  
Main Physical Properties of the As-Spun PET Fibers

Spinning velocity (m/min)	$f_c$	$\Delta n$	$X_c$ (%)	Young's modulus (kg/mm <sup>2</sup> )	Yield stress (kg/mm <sup>2</sup> )	Tenacity (kg/mm <sup>2</sup> )	Elongation at break (%)
1000	—	—	—	226	6.8	28.0	186
2000	0.948	0.066	28	362	8.8	21.4	119
2500	0.946	0.079	33	399	9.6	29.3	125

other hand, the density and birefringence were a little bit lower than that for the high-speed spinning. The Young's modulus and tenacity were slightly lower than that for high-speed spinning as well, but were in a comparable range. The  $c$ -axis crystallite orientation factor was calculated according to Wilchinsky's method by measuring the azimuthal profiles of diffraction intensities for the (010), ( $\bar{1}$ 10) and (100) lattices,<sup>10</sup> namely,

$$f_{c,z} = \frac{3\langle \cos^2 \phi_{c,z} \rangle - 1}{2} \quad (1)$$

$$\langle \cos^2 \phi_{c,z} \rangle = 1.0 - 0.735\langle \cos^2 \phi_{010,z} \rangle - 0.689\langle \cos^2 \phi_{\bar{1}10,z} \rangle - 0.576\langle \cos^2 \phi_{100,z} \rangle \quad (2)$$

$$\langle \cos^2 \phi_{hkl,z} \rangle = \frac{\int_0^{\pi/2} I_{hkl}(\phi) \sin \phi \cos^2 \phi d\phi}{\int_0^{\pi/2} I_{hkl}(\phi) \sin \phi d\phi} \quad (3)$$

and crystallinity,  $X_c$  was calculated from density according to

$$X_c(\%) = \frac{\rho - \rho_a}{\rho_c - \rho_a} \times 100\% \quad (4)$$

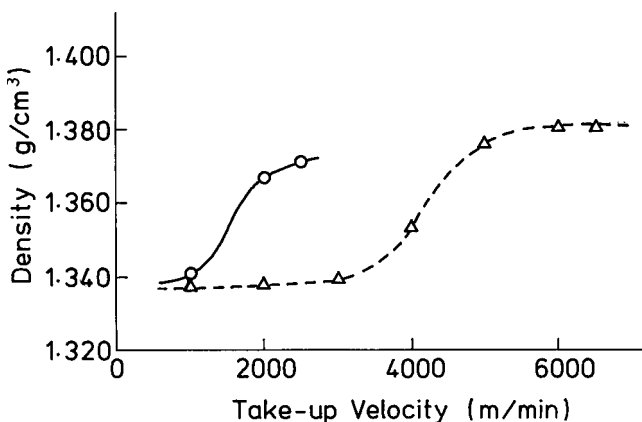


Figure 2 Density of the as-spun PET fiber increases with increasing the spinning speed. The solid line is the result for supercooled spinning as compared with the dotted line for high-speed spinning.

where  $\rho_a$  and  $\rho_c$  are the densities for the amorphous PET and full crystalline PET, being 1.335 and 1.455 g/cm<sup>3</sup>, respectively, and  $\rho$  being the measured value for the as-spun fibers.

These results demonstrate that the concept of the supercooled spinning is valid, and therefore worthy of further investigations.

Basically, melt spinning is a shape-forming process that plays dual functions: stretching by spinning quenches the polymer melt through a tremendous increase of the surface area per unit volume, which tends to reduce the chance of crystallization on one hand; stretching by spinning results in a molecular orientation, and therefore an accelerated crystallization on the other. It is this role of the unity of the opposites that dominates melt spinning.<sup>11,12</sup>

Stretching of molecular chains is the driving force for orientation-induced crystallization. However, there is a distinction between the macroscopical draw ratio that we calculate from the change in filament diameter and microscopical stretching of macromolecular chains.

Macromolecular chains exist in polymer melt as clusters rather than fully randomized coils that are described by the Gaussian distribution.<sup>13</sup> The deformation

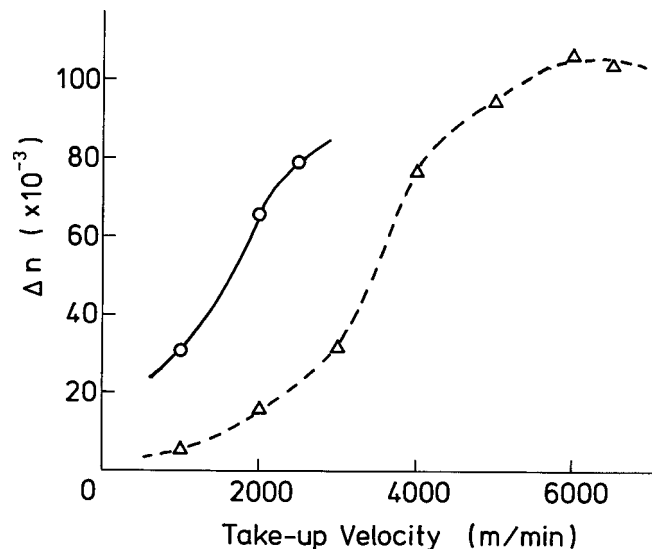


Figure 3 Birefringence of the as-spun PET fiber increases with increasing the spinning speed. The solid line is the result for supercooled spinning as compared with the dotted line for high-speed spinning.

required for the macroscopical draw ratio of a spinning process is met by the sum of the displacement between clusters and the stretching deformation of the clusters that is the cause of orientation-induced crystallization, as illustrated in Figure 5. Indeed, non-Gaussian distribution is a subject of research.<sup>14-16</sup>

The earlier explanation can be further evidenced by taking polypropylene as an example. When a polypropylene with its molecular weight 180,000 is spun at 3000 m/min, the macroscopical draw ratio of the fiber reaches 1500.<sup>11</sup> However, the end to end distance,  $\langle R \rangle = \sqrt{nl}$ , where  $n$  is the number of chain number,  $l$  the length of free joint of the chain. This is compared with the fully stretched length of the chain,  $nl$ , indicating that the microscopical maximum stretching ratio before breakage of the covalent bonding is only 40.

Given this account is true, we need to devise an effective method to stretch molecular chains to make orientation-induced crystallization to occur. While the high-speed spinning relies on high speeds that increase the draw ratio, resulting in a proportional increase in the microscopical stretch of molecular chains, the supercooled spinning relies on temperature control; at supercooling temperature, the displacement between clusters becomes lower, in turn a high degree of deformation of the clusters. i.e., stretching of the molecular chains is realized for a given macroscopic draw ratio of melt spinning. This may account for the reason why orientation-induced crystallization occurs at much lower speeds than that for the high-speed spinning.

We can also interpret the mechanism of the supercooled spinning by taking into account the crystallization kinetics. The crystallization half-time is very long at temperatures close to the melting point, because of the low crystallization rate of PET. The supercooled

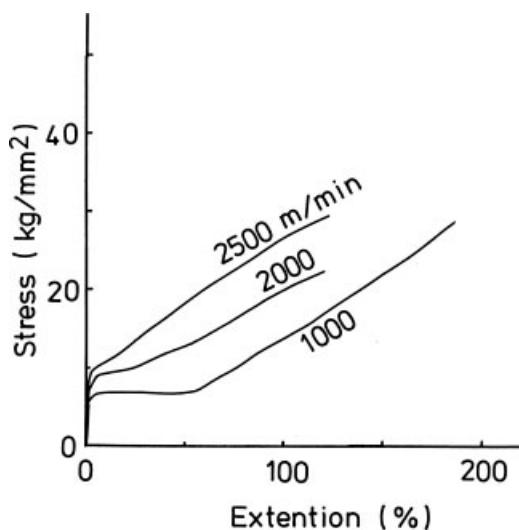


Figure 4 Stress-strain curves of the as-spun PET fibers obtained by supercooled spinning.

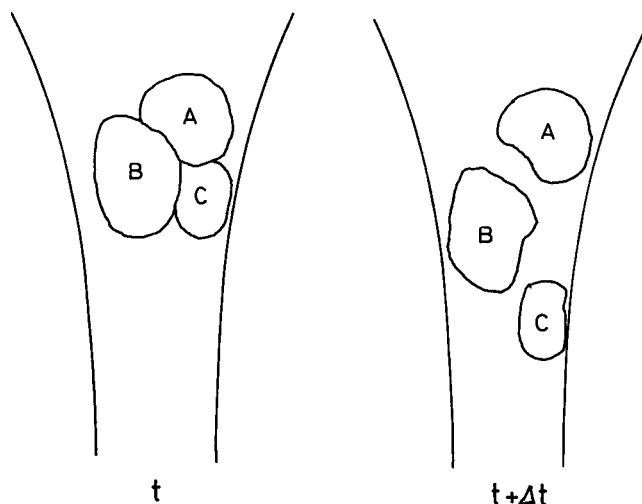


Figure 5 Illustration showing how the displacement between clusters makes its contribution to the deformation required by macroscopical draw ratio in melt spinning.

spinning keeps the initial incubation period in the nozzle, so that the supercooled PET liquid can have high crystallization rate on the spinline.

### CONCLUSIONS

The property investigation for the as-spun fibers obtained by supercooled spinning has shown that highly oriented and crystallized PET fibers can be obtained at spinning speeds of 2000–2500 m/min, as compared with 5000–6000 m/min in the high-speed spinning to achieve the similar degree of orientation and crystallization, indicating a possible alternative technology to obtain FOY in a single spinning process without a drawing and annealing process followed up. The *c*-axis orientation of the as-spun fibers was particularly high; however, other properties showed slightly lower values than that for the high-speed spinning. It is considered that the concept of supercooled spinning is valid not only for melt spinning, but also true to other polymer processes, where there is a need to control the structure formation during processing.

The author is grateful to Professor Takeshi Kikutani of the Tokyo Institute of Technology for providing helpful advices and discussions, as well as encouragements during the course of this work.

### References

1. Shimizu, J.; Okui, N.; Kikutani, T. In High Speed Fibre Spinning: Science and Engineering Aspects; Ziabicki, A., Kawai, H., Eds.; Wiley: New York 1985, p 429.
2. Shimizu, J. Sen'i Gakkaishi 1982, 38, P499.
3. Shimizu, J.; Kikutani, T.; Takaku, A.; Okui, N. Sen'i Gakkaishi 1984, 40, T63.

4. Kikutani, T.; Arikawa, S.; Takaku, A.; Okui, N. *Sen'i Gakkaishi* 1995, 51, 408.
5. Kikutani, T.; Radhakrishnan, J.; Arikawa, S.; Takaku, A.; Okui, N.; Jin, X. *J Appl Polym Sci* 1996, 62, 1913.
6. Furuta, T.; Radhakrishnan, J.; Ito, H.; Kikutani, T.; Okui, N. *Compos Interface* 1999, 6, 451.
7. Yoshioka, T.; Tsuji, M.; Kawahara, Y.; Kikutani, T.; Kohjiya, S. *Polymer* 2005, 46, 1886.
8. Shi, X. Q.; Ito, H.; Kikutani, T. *Polymer* 2005, 46, 11442.
9. Shi, X. Q.; Ito, H.; Kikutani, T. *Polymer* 2006, 47, 611.
10. Wilchinsky, Z. W.; *Advances in X-ray Analysis*, Vol. 6; Plenum: New York, 1961.
11. Cao, J.; Kikutani, T.; Takaku, A.; Takaku, A.; Shimizu, J. *J Appl Polym Sci* 1989, 37, 2683.
12. Bhuvanesh, Y. C.; Gupta, V. B.; *J Appl Polym Sci* 1995, 58, 663.
13. Yeh, C. S. Y. *J Macromol Sci Phys* 1972, 6, 451.
14. Sarac, Z.; Erman, B.; Bahar, I. *Macromolecules* 1995, 28, 582.
15. Jarecki, L.; Ziabicki, A. *Polymer* 2002, 43, 2529.
16. Jarecki, L.; Ziabicki, A. *Polymer* 2002, 43, 4063.