Zone Drawing and Zone Annealing of Poly(ethylene terephthalate) Microfiber Prepared by CO_2 Laser Thinning

Akihiro Suzuki, Takahiro Okano

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

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ABSTRACT: A zone-drawing and zone-annealing method was applied to a poly(ethylene terephthalate) microfiber, obtained by using CO_2 laser thinning, to develop its mechanical properties. The microfiber used for the zone drawing and zone annealing was prepared by winding at 1386 m/min the microfiber obtained by irradiating the laser at 18.1 W/cm^2 and had a diameter of 2.8 μm and a birefringence of 0.097. Zone drawing was carried out at a drawing temperature of 105°C under an applied tension of 53 MPa, and zone annealing at an annealing temperature of 155°C under 195 MPa applied tension. Zone drawing and zone annealing were carried out at a treatment speed of 0.21 m/min. The diameter of the microfiber decreased, and its birefringence increased, with zone drawing and zone annealing. The zone-annealed microfiber finally obtained had a diameter of 2 μm, a birefringence of 0.234, a tensile modulus of 17.9 GPa, and a tensile strength of 1.1 GPa. The wide-angle X-ray diffraction photograph of the zone-annealed microfiber showed the existence of highly oriented crystallites. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2989–2994, 2004

Key words: poly(ethylene terephthalate) (PET); fibers; mechanical properties; modulus; WAXD

INTRODUCTION

In preliminary experiments to optimize the condition of a laser-heating zone drawing[1] for a poly(ethylene terephthalate) (PET) fiber, it was determined that PET microfiber could be prepared by laser heating carried out under very low applied tension at higher power density compared with the condition of the laser-heating zone drawing for the as-spun PET fiber.[2,3] Further, to prepare continuous microfibers by carbon dioxide (CO_2) laser thinning, the new apparatus for the CO_2 laser thinning was assembled in our laboratory. The developed apparatus is able to wind the microfiber as a monofilament, at winding speeds ranging from 100 to 2500 m/min, and has already been applied to nylon 6[4] and isotactic polypropylene (i-PP)[5] fibers. The nylon 6 and i-PP microfibers (diameter: 3.2 and 3.5 μm, respectively) were obtained by winding the microfibers at 848 and 1387 m/min, respectively.

The microfibers are now manufactured by highly skilled techniques such as conjugate spinning, islands-in-a-sea–type fiber spinning, melt blowing, and flash spinning. The methods are not easily adapted to any but quite small scale preparations. On the other hand, the CO_2 laser-thinning method easily yields microfibers without the use of highly skilled techniques, and it is suitable for producing microfibers of various polymers at a small scale.

Although the laser thinning of fibers was characterized by the plastic flow accompanied by a molecular orientation and a strain-induced crystallization, the mechanical properties of the obtained microfiber were insufficient because of the lack of the highly oriented amorphous chains and crystallites. Therefore, it was necessary to draw and anneal the microfiber obtained to improve its mechanical properties.

A zone-drawing and zone-annealing method was previously applied to various polymers, such as PET and nylon 6 fibers and films, to develop their mechanical properties.[6–10] This method is suitable for improving the mechanical properties of fibers and films. To obtain a high-modulus and high-strength microfiber, the zone-drawing and zone-annealing method was applied to the microfiber obtained by CO_2 laser thinning.

In this study, the zone-drawing and zone-annealing method was applied to the PET microfiber prepared by CO_2 laser thinning to prepare high-modulus and high-strength microfibers. We present here the results pertaining to the zone-drawn and zone-annealed PET microfibers.

EXPERIMENTAL

Materials

The original PET fiber used in the present study was a commercial-grade fiber (Kanebo Gohsen Ltd., Osaka,

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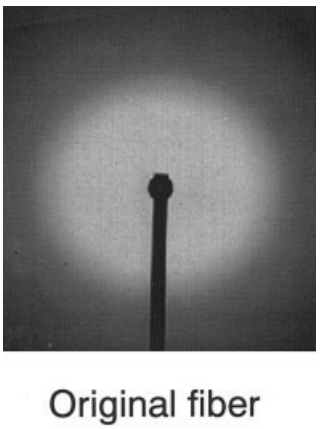

Figure 1 WAXD photograph of original fiber.

Japan) ($\overline{M}_w$= 55,000, $\overline{M}_n$ = 30,000) and had a diameter of 143.6 μm, degree of crystallinity of 4.5%, and birefringence of 0.070. The original fiber was amorphous and isotropic, as shown in Figure 1.

Measurements

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

Wide-angle X-ray diffraction (WAXD) photographs of the fibers were taken using a flat-film camera. The camera was attached to a Rigaku X-ray generator (Rigaku Co., Akishima, Japan) that 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.

SEM micrographs of the fibers were observed on a JEOL JSM-T20 apparatus (JEOL, Tokyo, Japan) with an acceleration voltage of 19 kV.

The fiber was exposed for 4 h to the X-ray beam from a pinhole collimator with a diameter of 0.4 mm.

A tensile testing machine (Tensilon; Orientec Co., Tokyo, Japan) was used to determine tensile modulus, tensile strength, and elongation at break. The tensile testing machine was modified to measure the mechanical properties of the microfiber. A gauge length of 5 cm and elongation rate of 10 mm/min were used. The experimental results are the average of 10 measurements.

CO_2 laser-thinning apparatus

The CO_2 laser-thinning apparatus, for continuous production of the microfiber, consisted of supplying and winding motors with spools of 90 mm diameter, a continuous-wave CO_2 laser emitter (PIN10S, Onizca Glass, Oume, Japan), a supplying system composed of a fiber guide and nipping rolls, and a traverse, as shown in Figure 2. The continuous-wave CO_2 laser emitted light at 10.6 μm, and the laser beam was a 4.0-mm diameter spot. Laser power was measured by a power meter (Nova Ophir Optronics, Ltd., Wilmington, DE) during laser irradiation. The laser power density was estimated by dividing the measured laser power in the area of the laser spot. Laser power of more than 90% was obtained in the area of the laser spot. To prepare a stable microfiber it is necessary to supply the fiber to a laser-irradiating point at a constant speed. The supplying system pulls out the original fiber of the supplying spool and feeds it to the laser-irradiating point at a constant speed. The supplying system plays an important role in the CO_2 laser-thinning apparatus. The fiber thinned at the laser-irradiating point is wound onto the spool at winding speeds ranging from 100 to 2500 m/min.

Zone-drawing and zone-annealing method of the microfiber wound onto the spool

It is difficult to draw and anneal only a single microfiber because its diameter and tensile strength are too small. To make possible zone drawing and zone annealing of bundled microfibers we constructed an apparatus to zone-draw and zone-anneal microfibers that could be wound onto a spool, as shown in Figure 3(c). A microfiber wound onto the winding spool was cut along a cutting line, as shown in Figure 3(a). One end of the microfiber bundle was attached to the winding spool with adhesive tape [see Fig. 3(b)], whereas the other end was attached to a weight after being passed through the zone heater that was set up at an arbitrary temperature [see Fig. 3(c)]. First, the microfibers were zone-drawn at a drawing speed of 0.21 m/min by using a speed-control motor. The drawn microfibers were wound onto the winding spool again using the speed-control motor to zone-

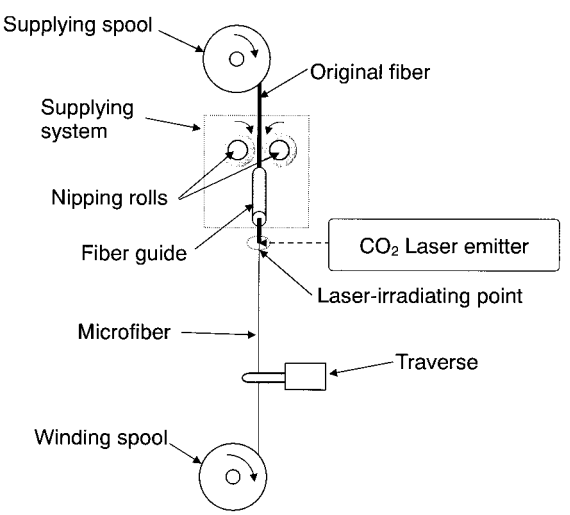

Figure 2 CO_2 laser-thinning apparatus used for producing the microfiber.

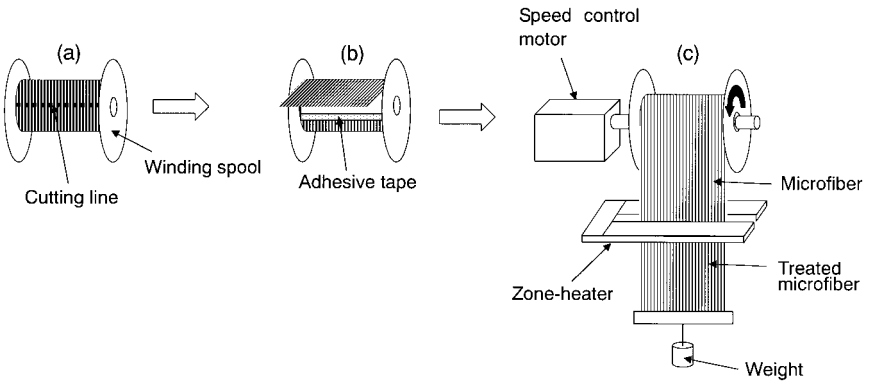

Figure 3 Schematic of apparatus used for zone-drawing and zone-annealing of the microfiber wound onto the spool.

anneal them. The zone-drawn microfibers wound onto the spool were annealed at a higher temperature under higher applied tension compared with conditions of the zone drawing.

RESULTS AND DISCUSSION

Figure 4 shows the winding speed dependency of the diameter for PET microfibers obtained at three different supplying speeds. The diameter of the microfiber obtained at each supplying speed decreases with increasing winding speed. The diameter of the fiber thinned at each winding speed tends to decrease with decreasing supplying speed. When the microfiber prepared by irradiating the laser to the original fiber, supplied at a supplying speed of 0.30 m/min, was wound at a winding speed of 2100 m/min, the thinnest microfiber with a diameter of 2.8 μm was obtained, and its draw ratio approached 7000-fold. The power density (PD) that can be irradiated to the original fiber without cutting the fiber is closely related to the supplying speed, as shown in Figure 5. The PD value and the supplying speed are proportional to each other. The PD at the supplying speed (0.3 m/min) that produces the thinnest microfiber is 17.8 W/cm^2.

Figure 6 shows SEM micrographs (at magnifications of $\times$5000) of microfibers wound at four different winding speeds. From the SEM micrographs we were able to confirm visually that the diameter decreases with increasing winding speed. Observation of the SEM micrographs shows that the microfibers have a smooth surface, without a surface roughened by laser ablation, and are uniform in diameter.

Figure 7 shows the winding speed dependency of the birefringence for the PET microfibers obtained at three different supplying speeds. The birefringence depends strongly on the winding speed at above 1000 m/min. The highest birefringence of 0.097 was obtained when the microfiber, obtained by irradiating the laser to the original fiber supplied at 0.3 m/min, was wound at 2100 m/min. In general, when the birefringence of PET was $\geq$0.070, the strain-induced crystallization is assumed to occur.[11] When the microfibers, obtained by irradiating the laser to the original

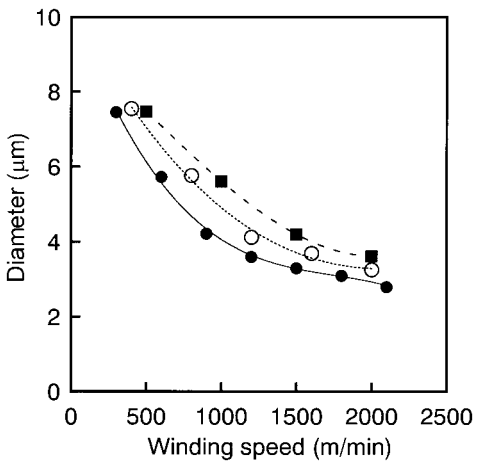

Figure 4 Winding speed dependency of the diameter of the PET microfibers obtained at three different supplying speeds (in m/min): ● 0.3, ○ 0.4, ■ 0.5.

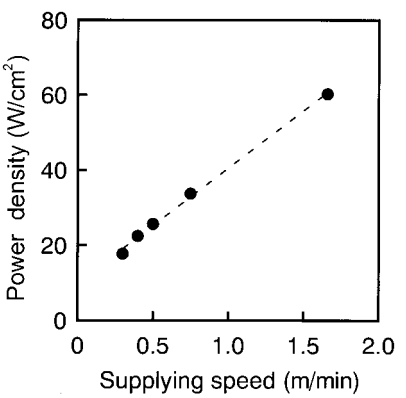

Figure 5 Relation between the supplying speed and laser power density (PD).

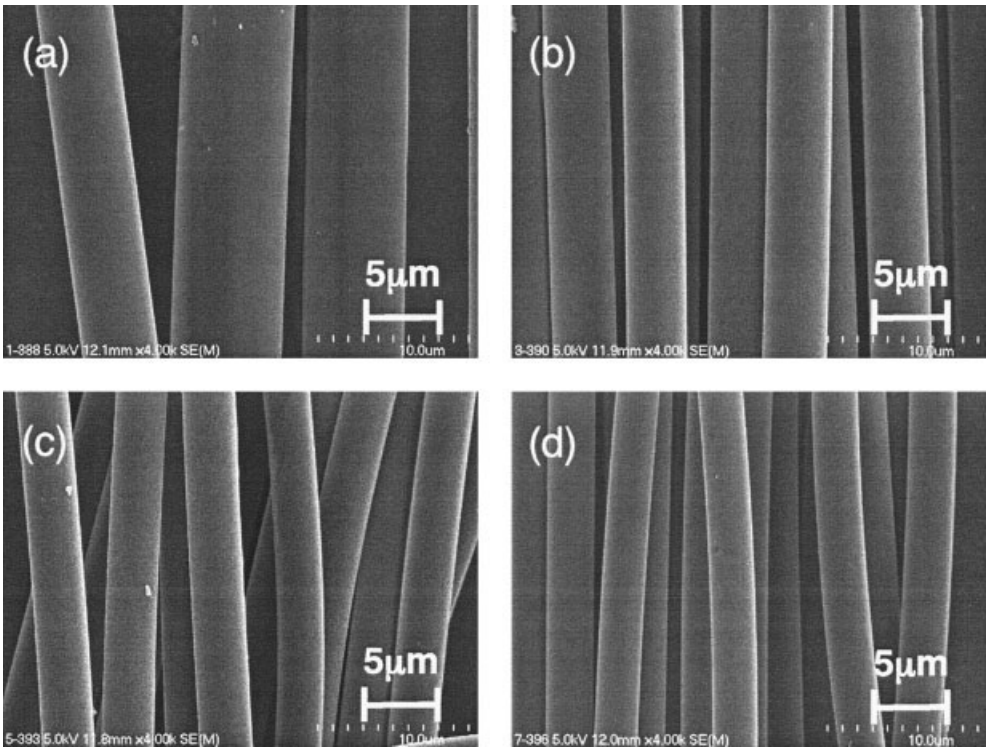

Figure 6 SEM micrographs (magnification ×5000) for microfibers wound at four different winding speeds (in m/min): (a) 300, (b) 900, (c) 1500, (d) 2100 (supplying speed: 0.3 m/min).

fiber supplied at 0.3 m/min, were wound at speeds $>$ 1500 m/min, its birefringence was $\geq$0.070. The increase of birefringence with the winding speed is attributed to 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 amorphous birefringence values.[12]

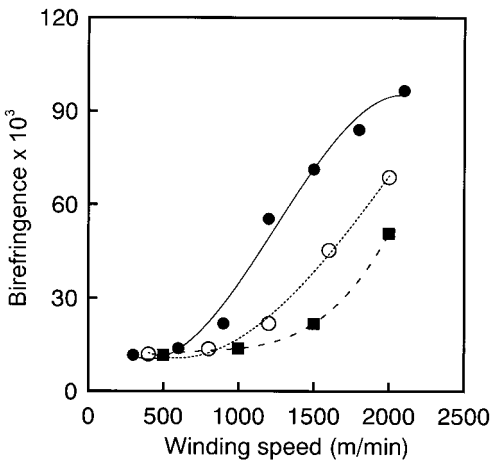

Figure 7 Winding speed dependency of the birefringence of the PET microfibers obtained at three different supplying speeds (in m/min): ● 0.3, ○ 0.4, ■ 0.5.

To prepare the thinnest microfiber with high modulus and high strength, the microfiber used for the zone drawing and zone annealing had a diameter of 2.8 μm and birefringence of 0.097.

The purpose of the zone drawing is to fully orient amorphous chains in the drawing direction without a thermal crystallization. Zone drawing was carried out near the glass-transition temperature (T_g) to avoid any thermal crystallization because the crystallites inhibit the molecular chains from highly orienting along the drawing direction. To uniformly zone-draw the microfiber near T_g, the zone drawing carried out at a treating speed of 0.21 m/min was found to be optimum. This treating speed was used throughout the zone drawing and zone annealing procedures. The optimum condition for zone drawing was determined by measuring the birefringence of fibers drawn under various conditions. Preliminary experiments were car-

TABLE I
Optimum Conditions for Zone Drawing and Zone Annealing

Treatment	Applied tension (MPa)	Treatment temperature (°C)	Treatment speed (m/min)
Zone drawing	53.1	105	0.21
Zone annealing	194.9	155	0.21

TABLE II
Total Draw Ratio, Diameter, and Birefringence for the Original Fiber, Microfiber, Zone-Drawn (ZD) Microfiber, and Zone-Annealed (ZA) Microfiber

Fiber	Total draw ratio	Diameter (μm)	Birefringence
Original fiber	—	241.2	0.25×10^{-3}
Microfiber	7,000	2.8	0.097
ZD microfiber	11,200	2.2	0.168
ZA microfiber	16,800	2.0	0.234

TABLE III
Mechanical Properties for the Microfiber, Zone-Drawn (ZD) Microfiber, and Zone-Annealed (ZA) Microfiber

Fiber	Tensile modulus (GPa)	Tensile strength (GPa)	Elongation at break (%)
Microfiber	2.5	0.24	208
ZD microfiber	12.3	0.78	57
ZA microfiber	17.9	1.12	18

ried out to decide an optimum zone-drawing condition, and then the zone drawing carried out at 105°C under 53 MPa was found to be optimum. The microfiber obtained by zone drawing carried out under optimum conditions was designated as a ZD microfiber.

The purpose of zone annealing is to crystallize the ZD microfiber with highly oriented amorphous chains. Consequently, the condition inducing the highest birefringence was chosen as the optimum one for zone annealing. The microfiber zone-annealed under optimum conditions was designated as a ZA microfiber.

The optimum conditions for zone drawing and zone annealing are summarized in Table I. The microstructure and mechanical properties of the microfiber obtained under each optimum condition are discussed below.

Table II lists the total draw ratio (λ_t), diameter, and birefringence (Δn) for the microfiber, ZD microfiber, and ZA microfiber. The λ_t and the Δn values increase stepwise with the processing, and then the obtained ZA microfiber finally has λ_t = 16,800 and Δn = 0.234. The Δn value of the ZA microfiber is slightly lower than that of the laser-heated zone-annealed fiber reported previously,[1] and it is almost the same value as the intrinsic crystallite birefringences (Δn_c° = 0.22–0.251) that were reported by a number of investigators.[13–17]

Figure 8 shows the WAXD photographs of the microfiber, the ZD microfiber, and ZA microfiber. The microfiber does not have reflections because of crystallites identical to those of the original fiber, as shown in Figure 1. However, there is a significant difference in the birefringences of the original fiber and the microfiber, as shown in Table II. The results show that the microfiber has highly oriented amorphous chains, although it does not have crystallites.

In the ZD microfiber, three principal indistinct reflections (010, $\bar{1}10$, and 100), attributed to the crystallites formed by the strain-induced crystallization that occurred during the zone drawing, are observed on the equator. Their reflections become more conspicuous at the ZA microfiber. The sharpening of the diffraction spots indicates enhancements in crystallinity, crystalline orientation, and crystal perfection. The WAXD photograph of the ZA microfiber shows that the ZA microfiber has high levels of crystallinity and crystalline orientation.

Table III lists the mechanical properties of the microfiber, ZD microfiber, and ZA microfiber. The tensile modulus and the tensile strength increase stepwise with increasing processing. The tensile modulus and the tensile strength of the ZA microfiber are 17.9 and 1.12 GPa, respectively. These values are almost identical to those of the laser-heated zone-annealed PET fiber[1] and that of the high-performance PET fiber produced by a combination of threadline modification and postdrawing techniques.[18]

CONCLUSIONS

Using the apparatus developed in our laboratory, CO_2 laser thinning was applied to the original PET

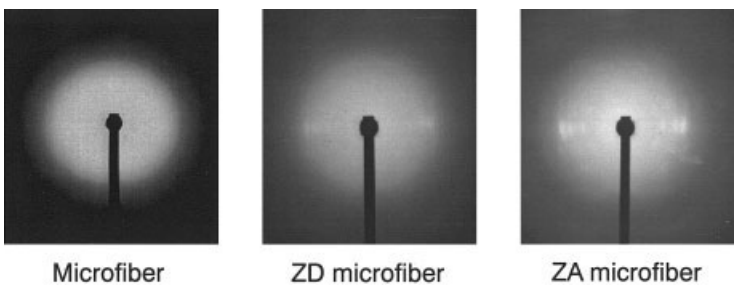

Figure 8 WAXD photographs of the microfiber, zone-drawn microfiber, and zone-annealed microfiber.

fiber for continuous preparation of a PET microfiber. The PET microfiber obtained was zone-drawn and zone-annealed to improve its mechanical properties. The microfiber used for the zone drawing and zone annealing had a diameter of 2.8 μm and a birefringence of 0.097. Zone drawing was carried out at a drawing temperature of 105°C under an applied tension of 53 MPa, and zone annealing at an annealing temperature of 155°C under an applied tension of 195 MPa. The annealed microfiber finally obtained had a diameter of 2 μm, a birefringence of 0.234, a tensile modulus of 17.9 GPa, and a tensile strength of 1.1 GPa. The WAXD micrograph showed that the obtained ZA microfiber had high levels of crystallinity and crystalline orientation. The zone-drawing and zone-annealing method was found to be effective in producing PET microfibers with high modulus and high strength.

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References

1. Suzuki, A.; Mochizuki, N. J Appl Polym Sci 2001, 82, 2775.
2. Suzuki, A.; Mochizuki, N. J Appl Polym Sci 2003, 88, 3279.
3. Suzuki, A.; Mochizuki, N. J Appl Polym Sci 2003, 90, 1955.
4. Suzuki, A.; Kamata, K. J Appl Polym Sci, to appear.
5. Suzuki, A.; Narisue, S. J Appl Polym Sci, to appear.
6. Kunugi, T.; Suzuki, A.; Hashimoto, M. J Appl Polym Sci 1981, 26 1951.
7. Suzuki, A.; Kuwabara, T.; Kunugi, T. Polymer 1998, 39, 4235.
8. Suzuki, A.; Kohno, T.; Kunugi, T. J Polym Sci Part B: Polym Phys 1998, 36, 1731.
9. Suzuki, A.; Chen, Y.; Kunugi, T. Polymer 1998, 39, 5335.
10. Suzuki, A.; Toda, K.; Kunugi, T. Polymer 2000, 41, 6061.
11. Yamada, H.; Kikutani, U.; Takaku, A.; Shimizu, J. Sen-i Gakkaishi 1988, 44, 177.
12. Stain, R. S.; Norris, F. N. J Polym Sci Part A: Polym Chem 2001, 82, 2775.
13. Patterson, D.; Ward, I. M. Trans Faraday Soc 1957, 53, 1516.
14. Dumbleton, J. H. J Polym Sci A-2 1968, 6, 795.
15. Konda, A.; Nose, K.; Ishikawa, H. J Polym Sci A-2 1976, 14, 1495.
16. Kunugi, T.; Shiratori, K.; Uematu, K.; Hashimoto, M. Polymer 1979, 20, 171.
17. Garg, S. K. J Appl Polym Sci 1982, 27, 2857.
18. Wu, G.; Tucker, P. A.; Cuculo, J. A. Polymer 1997, 38, 1091.