Effect of Zone Drawing Accompanied with Crosslinking on the Structure and Properties of Ultrahigh Molecular Weight Polyethylene Gel Film

SUNG SOO HAN,[1] WON SIK YOON,[1] JIN HYUN CHOI,[2] SANG YONG KIM,[2] BYUNG CHUL JI,[3] WON SEOK LYOO[4]

[1] School of Textiles, Yeungnam University, Kyongsan 712-749, Korea

[2] Department of Fiber and Polymer Science, Seoul National University, Seoul 151-742, Korea

[3] Department of Dyeing and Finishing, Kyungpook National University, Taegu 702-701, Korea

[4] Division of Polymer Researches, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul, Korea

Received 17 May 1996; accepted 8 March 1997

ABSTRACT: To enhance the thermal properties of ultrahigh molecular weight (UHMW) (viscosity-average molecular weight of 6×10^6) polyethylene (PE) gel film, this was crosslinked by dicumyl peroxide (DCP) during a high-temperature zone drawing, which is effective to orient film. Through a series of experiments, it turned out that crosslinking actualized by an optimum amount of DCP and high-temperature zone drawing technique caused significant changes in the structure and properties of UHMW PE gel film. That is, crosslinking increased storage modulus of UHMW PE gel film at 25°C, resulting in improving thermal properties of the film. On the contrary, the crosslinking effect played a hindering role in raising the draw ratio of UHMW PE gel film. Maximum storage modulus of 165 GPa at 25°C could be obtained at the draw ratio of 324 of uncrosslinked homo-PE gel film. In the case of crosslinked PE gel film, the highest storage modulus at 25°C reached 65 GPa at maximum draw ratio of 150. Crosslinked film exhibited high modulus, even at 190°C, to some extent, while uncrosslinked homo-PE gel film was molten completely at 150°C. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1583–1590, 1997

Key words: thermal property; UHMW PE gel film; DCP; zone drawing; crosslinking; storage modulus

INTRODUCTION

Preparative methods for fibers having various functionalities have been highly developed according to the increased requirement for new materials. Among them, manufacturing methods of high strength and high modulus fibers can be classified as follows.[1] (1) synthesis and spinning of new polymers having a rigid rod structure, i.e., liquid crystalline polymer;[1] (2) modification of molecular structure of polymeric fiber, i.e., carbon fiber from polyacrylonitrile or pitch precusor;[2] (3) orientation of a flexible chain polymer like polyethylene (PE) or poly(vinyl alcohol) along the fiber axis, i.e., ultra drawing of gel-spun fiber,[3] ultra drawing of crystal mat,[4,5] surface-growing method,[6] solid-extrusion method,[7] and zone drawing.[8–12]

Up until now, in the case of PE, by utilizing

Correspondence to: W. S. Lyoo.

Journal of Applied Polymer Science, Vol. 66, 1583–1590 (1997)
 CCC 0021-8995/97/081583-08

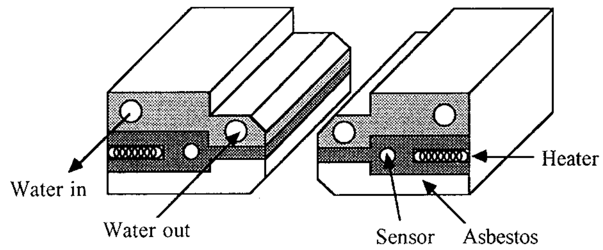

Figure 1 Schematic representation of the band heater assembly.

these methods described above, a tensile modulus of over 200 GPa could be obtained, which was a higher value than that of steel (72 GPa) at a bulk state. However, thermal stability of high-strength fiber from a flexible chain polymer like PE was inferior to those fibers from liquid crystalline polymer and carbon fiber. Thus, improving thermal stability of PE, the crosslinking method has been tried, and it includes crosslinking by radiation[13,14] and crosslinking by peroxide.[15,16] Radiation method caused not only crosslinking but chain scission in polymer backbone to decrease tensile strength and tensile modulus. Crosslinking by peroxide was achieved by introducing a crosslinking agent in PE on drawing in the hot atmosphere. In this method, the crosslinking agent should be introduced before the PE chains orient. The reason is because crosslinking reactions do not occur after the orientation accompanied with crystallization.

The zone drawing technique, a method inducing a necking on one point of a film by heat, have many advantages compared to a hot drawing, such as fewer probabilities of microcrystallites formation, back folding of molecular chains, and thermal degradation of the sample.[8–12]

In this study, to improve the thermal stability of UHMW PE gel film, this was crosslinked by dicumyl peroxide (DCP) in decaline. In addition, for effective orientation of PE chain, the gel film prepared was drawn using a high-temperature zone drawing technique, which is superior to hot drawing in many aspects. That is, this method makes up for the weak points of insufficient crosslinking after drawing, lowered draw ratio after crosslinking, and excessive chain scission due to longer crosslinking reaction time generated in the hot drawing and crosslinking methods reported previously.[15,16] Also, the morphology and thermal properties of crosslinked-undrawn and zone-drawn PE gel films were investigated from the viewpoint of comparison with the cases of uncrosslinked homo-PE gel film.

EXPERIMENTAL

Preparation of UHMW PE Gel Film

The concentration of PE (viscosity-average molecular weight of 6×10^6 g/mol and density of 0.93 g cm^3, Hoechst, Hostalen GUR415) solution in decalin was 0.5 g dL. The polymer–solvent mixture with anti-oxidant [di-*t*-butyl-*p*-cresol, 0.1% (*w*/*w*)] was heated with stirring at 85°C for 10 min, followed by 115°C for 70 min, and finally 135°C for 40 min under a nitrogen atmosphere to form uniform solution. The homogenized solution was poured into aluminium tray and cooled in the air to form a gel. Gel film whose thickness was 200μm was prepared after decalin was removed by drying film in the air for 15–60 days.

Introduction of Crosslinking Agent in UHMW PE Gel

UHMW PE gel cooled in the air to have volume of about 25% to initial volume was kept in DCP–decalin solution at 60°C for 6 h. (The absorbed amount of DCP was calculated by the difference between the initial weight of PE powder and the increased weight of crosslinked UHMW PE gel film.

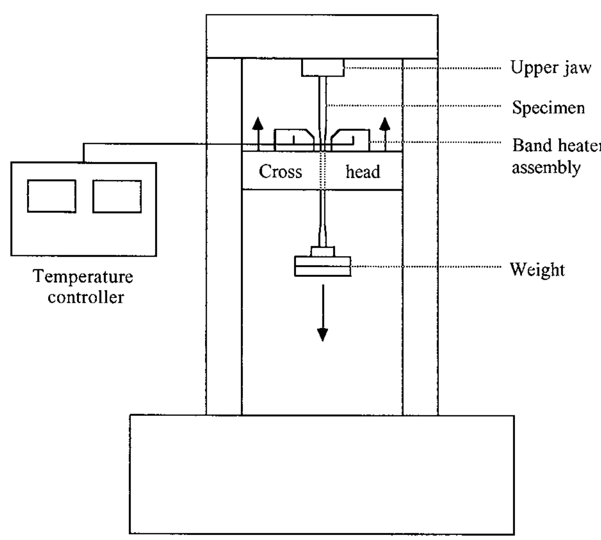

Figure 2 Schematic representation of the zone drawing apparatus.

Table I Relation Between Zone Drawing Conditions and Draw Ratio

Drawing Step	Drawing Temperature (°C)	Drawing Stress (kgf/mm^2)	Crosshead Speed (mm/min)	Draw Ratio
1	127	0.4	10	35
2	127	5.6	10	154
3	127	19	10	205
4	127	34	20	262
5	127	42	20	286
6	127	53	20	301
7	127	60	50	324

Zone Drawing of Gel Film

Zone drawing was carried out at 127°C by moving a pair of narrow band heaters with dimensions in the length of 7 cm, in the width of 2.5 cm, and in the thickness of 1 mm along the film (Fig. 1). The film of 200μm thickness, 5 mm width, and 10 cm length was drawn under tensions controlled by different dead weights, respectively, on an Instron model 4201 (Fig. 2). Crosshead speed was controlled as 10, 20, and 50 mm/min according to the number of drawing steps. The relation between the number of drawing steps and resulting draw ratio of uncrosslinked PE gel film is shown in Table I. In the case of zone drawing of PE gel film containing DCP, crosshead speed was controlled from 1 to 10 mm/min with the same method adopted in the drawing method of homo-PE gel film.

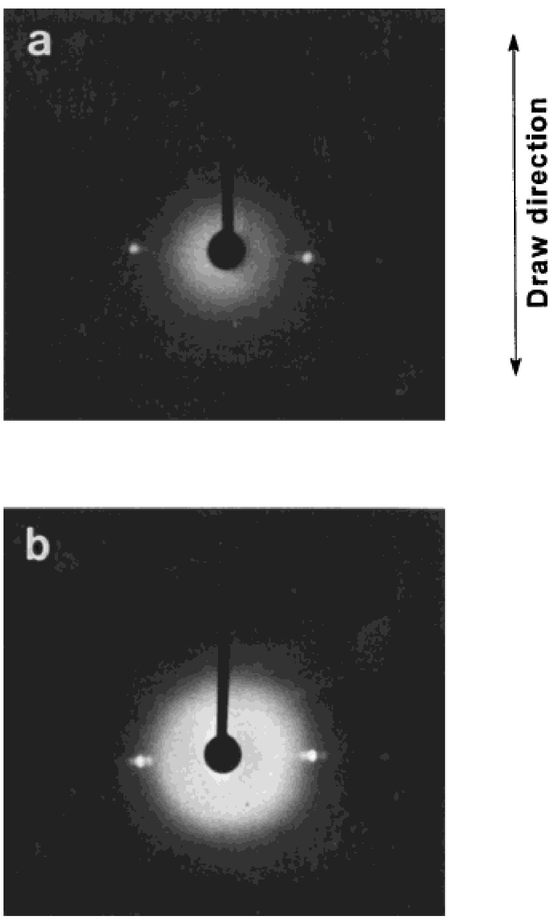

Figure 3 X-ray fiber patterns of uncrosslinked homo-PE gel films zone-drawn at 127°C: (a) draw ratio of 90, (b) draw ratio of 205.

Characterization of Gel Film

Viscoelastic properties of sample were characterized by measuring the storage modulus (E') using Rheo-

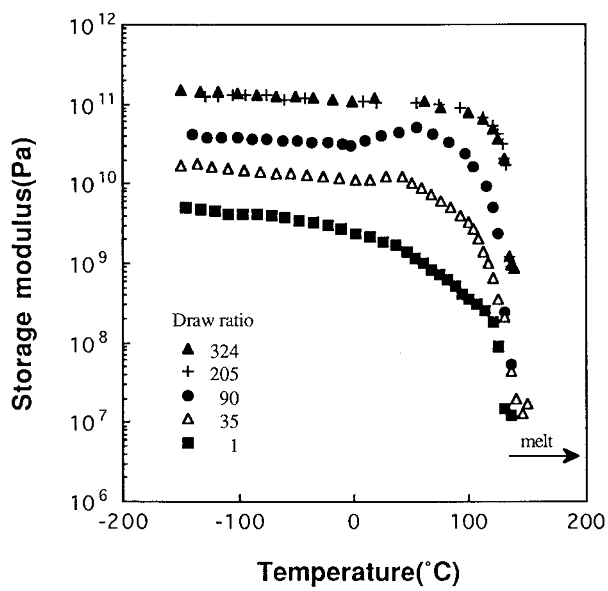

Figure 4 Storage modulus (E') of uncrosslinked homo-PE gel film zone-drawn at 127°C.

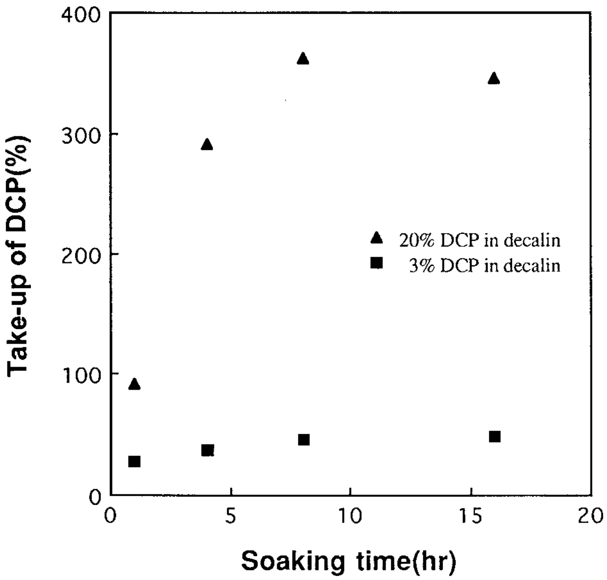

Figure 5 Effect of soaking time on the take-up percent of DCP in PE gel.

vibron DDV-II-EA. Temperature range, measuring frequency, and heating rate was 150–200°C, 110 Hz, and 3°C/min, respectively. Wide-angle X-ray diffraction (XRD) patterns were photographed using a nickel-filtered CuKα radiation (40 kV, 200 mA) and Laue camera (Mac Science, MXP-18). The cross sections and surfaces of UHMW PE gel films were observed by a scanning electron microscope (JEOL JSM-35). Differential scanning calorimetry (DSC; Du Pont 1090) was carried out under nitrogen at the scanning rate of 10°C/min.

RESULTS AND DISCUSSION

Zone-Drawing Behavior and Characterization of Uncrosslinked PE Gel Film

Table I shows changes of draw ratio with drawing steps in zone-drawing of uncrosslinked homo-PE gel film. Maximum draw ratio up to 324 could be achieved through seven drawing steps. The thickness of drawn film was below 1 μm. The zone-drawing parameters affecting draw ratio, structure, and physical properties of sample are the processing conditions, such as crosshead speed, drawing stress, heat band thickness, and temperature and humidity of surroundings; and the sample conditions such, as thickness, coefficient of heat conduction, viscosity, modulus, coefficient of change of modulus with temperature, and coefficient of change of viscosity with temperature of samples used. In this study, sample conditions were fixed. Drawing temperature was fixed to 127°C. Crosshead speed was controlled to 10, 20, and 50 mm/min according to the drawing step for the sufficient heat conduction to the normal direction to drawing direction. Drawing stress was varied considering cross-sectional area and physical properties changed in drawing of samples. Through a procedure described above, the draw ratio–drawing stress relationship in Table I was obtained.

The wide-angle X-ray diffractograms of two noncrosslinked PE gel films zone-drawn at 127°C show typical fiber patterns (Fig. 3). The two samples differ in their draw ratios. Strong equatorial reflections (110) and (200) indicate well-oriented crystallites with orthorombic unit cells[17,18] for both samples. Additional reflections at lower diffraction angles indicate the presence of unstable triclinic (gamma) modification. These reflections seem to be more pronounced with the sample drawn to higher degree [Fig. 3(b)]. This behavior was also observed by Matsuo and Maley.[19]

Storage modulus of uncrosslinked homo-PE gel film as a function of draw ratio is shown in Figure 4. Storage modulus increased drastically up to the draw ratio of 205 and reached almost constant in further drawing owing to ineffective molecular orientation of PE over the draw ratio of 200. Maximum storage modulus reached 215 GPa at −150°C and 165 GPa at 25°C nearly approaching the theoretical value of PE. Steep decrease of storage modulus was revealed over 50°C, and no more

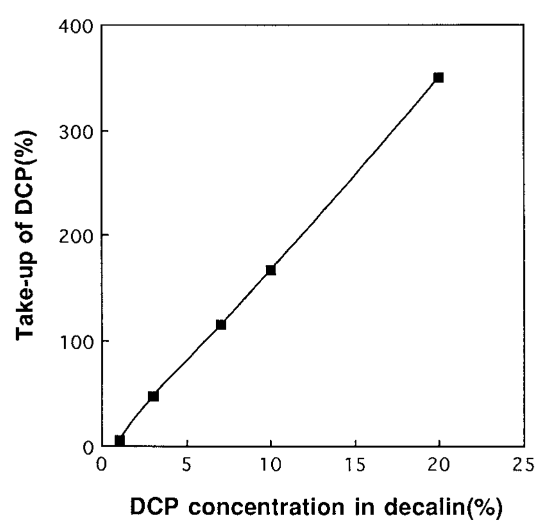

Figure 6 Take-up percent of DCP in PE gel with DCP concentration in decalin.

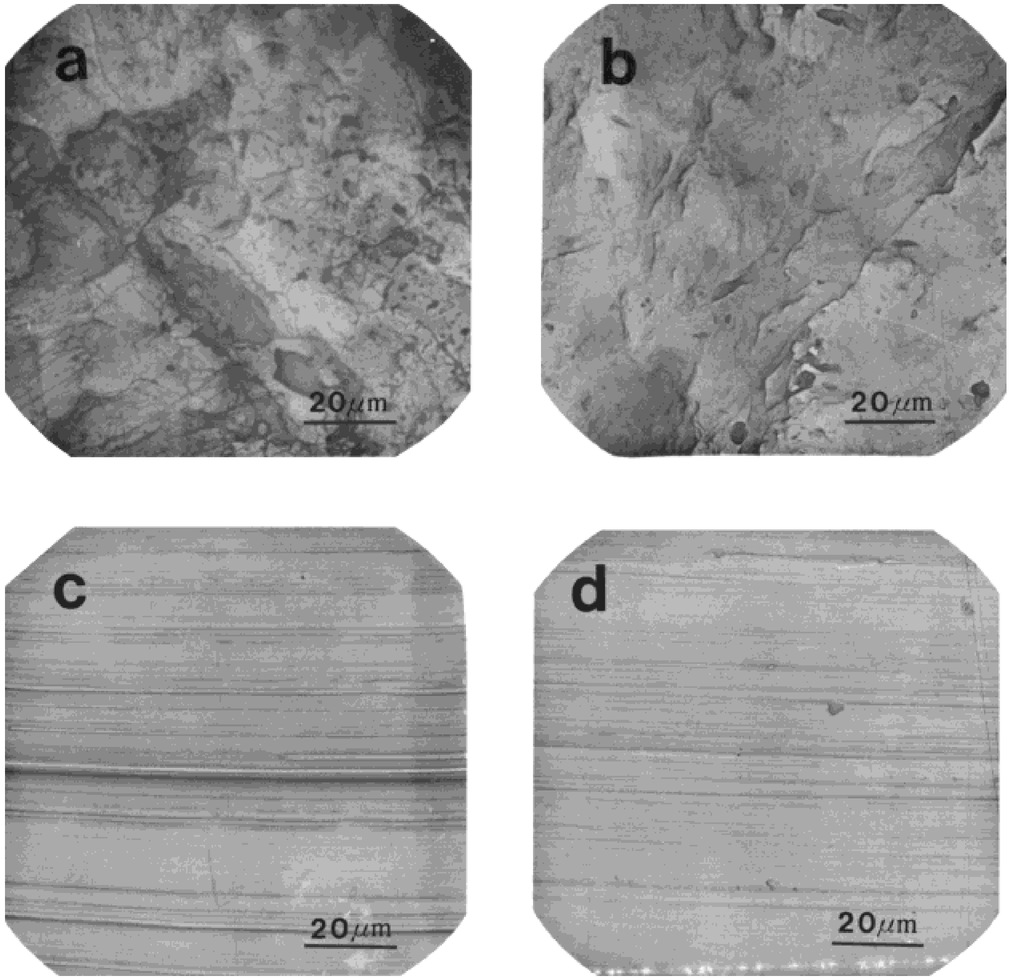

Figure 7 Scanning electron micrographs of UHMW PE gel films (×500): (a) DCP of 50%, unannealed and undrawn; (b) DCP of 50%, annealed at 150°C for 90 min and undrawn; (c) homo-PE and a draw ratio of 180; (d) DCP of 50% and a draw ratio of 90.

storage modulus was detected around 150°C, the melting temperature of PE measured by DSC.

Crosslinking of UHMW PE Gel

In this study, crosslinking was conducted to improve lowering of modulus at high temperature, even if PE gel film had a high modulus at room temperature. Figure 5 shows the take-up percent of DCP (DCP–PE, w/w) in PE gel as a function of the soaking time. After 6 h, absorption of DCP to PE gel reached equilibrium at both 3% and 20% DCPs in the decalin solutions. Consequently, soaking time was fixed at 6 h in the following experiments. Dependence of the take-up percent of DCP in a PE gel on DCP concentration in decalin is shown in Figure 6. An almost linear relationship was observed between DCP concentration in decalin and the take-up of DCP. A maximum take-up concentration of DCP of 350% to the weight of PE was achieved in the case of 20% DCP in decalin solution. Film containing DCP content of over 100% was coagulum of DCP rather than PE film. Actually, a DCP content of over 100% is meaningless in preparation of crosslinked PE gel film. Therefore, further experiments were carried on UHMW PE gel film containing DCP of 50%.

Structure and Properties of Crosslinked UHMW PE Film

Figure 7 shows scanning electron micrographs of surfaces of gel films containing DCP of (a) 50% unannealed and (b) annealed at 150°C for 90 min,

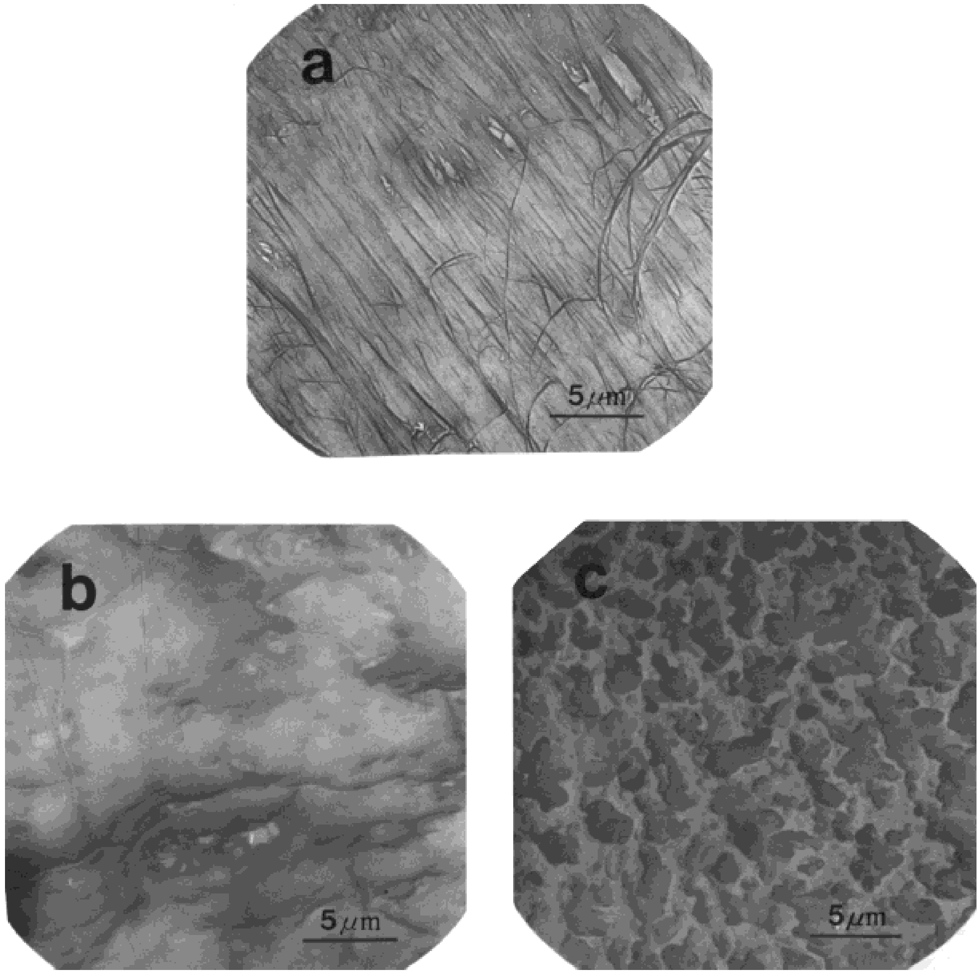

Figure 8 Scanning electron micrographs of fracture surfaces of UHMW PE gel films fractured under liquid nitrogen (×2000): (a) undrawn homo PE; (b) DCP of 50%, unannealed and undrawn; (c) DCP of 50%, annealed at 150°C for 90 min and undrawn.

(c) uncrosslinked homo-PE gel film drawn to 180 times, and (d) gel films containing 50% of DCP drawn to 90 times. A sponge-like fibril structure was found in unannealed film surface [Fig. 7(a)], whereas a flat surface was observed in annealed gel film resulting from slight melting of film surface by annealing accompanied with crosslinking by DCP [Fig. 7(b)]. A sponge-like structure changed to a well-oriented filament structure when zone-drawn at 127°C, and its surface was similar to that of uncrosslinked homo-PE gel film zone-drawn at 127°C [Figs. 7(c) and (d)].

Scanning electron micrographs of the fractured surfaces of (a) undrawn UHMW PE gel film, (b) gel films containing DCP of 50% unannealed, and (c) annealed at 150°C for 90 min are shown in Figure 8. A micrograph of zone-drawn homo-PE film could not be obtained because fracturing highly oriented PE gel film under liquid nitrogen was very difficult. Uncrosslinked–undrawn homo-PE gel film exhibited well-developed fibrillar structure, whereas gel film containing DCP of 50% did not, due to interruption of crystallization by DCP. Also, annealed gel film containing DCP of 50% revealed uniform distribution of irregular PE grains. In the case of this film, a brittle failure occurred without fibrillation when it was fractured, which was different from that of uncrosslinked PE film. The reason might be that crosslinking in film occurred by annealing.

DSC thermograms of UHMW PE gel films are shown in Figure 9. Uncrosslinked–undrawn homo film shows only a one melting peak at 132°C [Fig. 9(a)]. Small melting peaks at 130, 140, and 147°C exist in DSC thermogram of crosslinked gel film drawn to 90 times [Fig. 9(c)], whereas a large endotherm at 142°C and its shoulder at 150°C are found in that of uncrosslinked homo gel film obtained at the same draw ratio [Fig. 9(b)]. Sakami et al.[20] reported that three endothermic peaks at about 130, 140, and 150°C in DSC thermogram of PE were assigned to meltings of finely micro crystal, well-oriented crystal, and extended chain crystal, respectively. Therefore, the finely micro crystal existing in crosslinked–undrawn film still existed in crosslinked film drawn to 90 times. On the other hand, the peak at 130°C disappeared in the case of uncrosslinked homo gel film with same draw ratio. This strongly suggests that crosslinking of chain end or side chain that could change to fine crystal occurred prior to that of chain center, resulting in a lowered maximum draw ratio of 150, unreachable to the half-value of uncrosslinked film. Moreover, the melting temperature and heat of fusion of crosslinked film were lower than those of uncrosslinked homo one. The reason is because crosslinking impeded crystallization. This is consistent with previous results in Figure 8.

Figure 10 shows storage modulus of crosslinked UHMW PE gel film as a function of temperature at three different draw ratios. A maximum storage modulus of crosslinked UHMW PE gel film reached 56 GPa at 25°C. In addition, a storage modulus of 0.77 GPa was obtained even at 190°C. As discussed previously, in the case of the uncrosslinked homo-PE gel film, melting occurred around 150°C. From the facts described above, it was identified that zone drawing accompanied with crosslinking is a profitable method of enhancing physical properties, especially the thermal resistance of UHMW PE fibrous material.

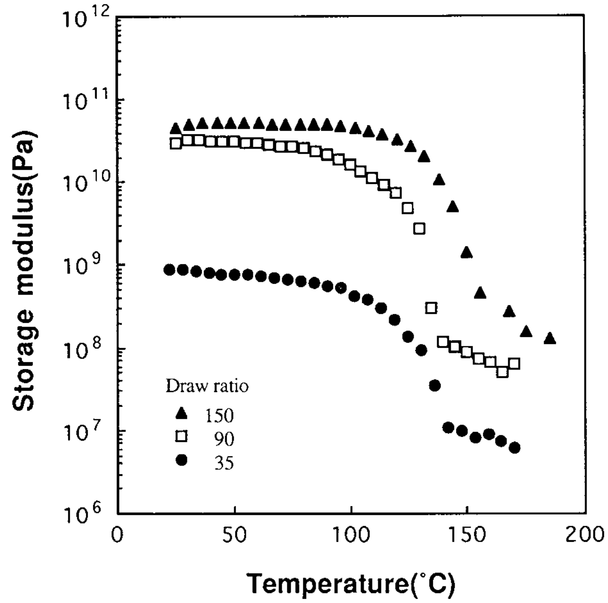

Figure 10 Storage modulus (E') of crosslinked UHMW PE gel film zone-drawn at 127°C.

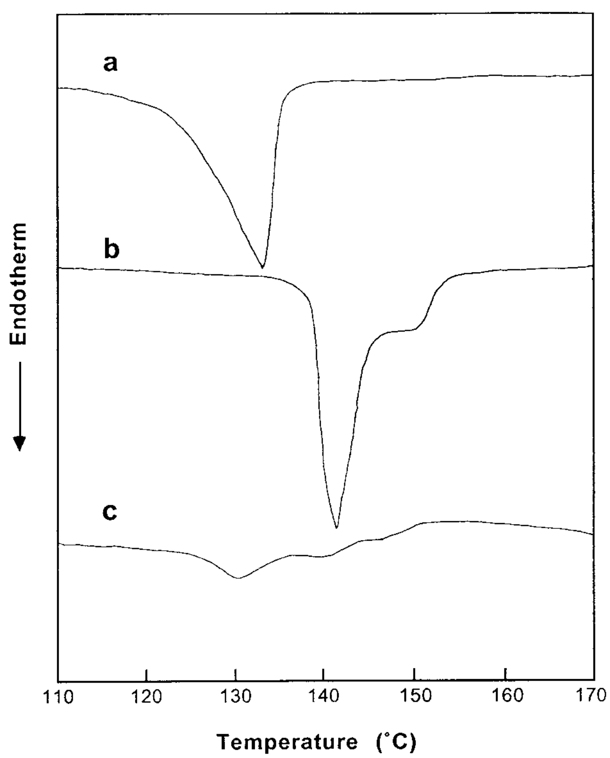

Figure 9 DSC thermograms of UHMW PE gel films: (a) undrawn homo PE; (b) drawn (×90) homo PE; (c) crosslinked PE (×90).

CONCLUSION

Considering the crosslinking effects of DCP on the structure and properties of zone-drawn UHMW PE gel film, we may conclude the following. UHMW PE gel film was crosslinked by DCP through a high-temperature zone drawing experiments. Crosslinking increased storage modulus of UHMW PE gel film at higher temperature, resulting in improving the thermal resistance of the film. On the other hand, the crosslinking effect played a hindering role in raising the draw ratio of UHMW PE gel film. Maximum storage modulus of 165 GPa at 25°C could be obtained at the draw ratio of 324 of uncrosslinked homo PE gel film. In the case of crosslinked PE gel film, the highest storage modulus at 25°C reached 65 GPa at a maximum draw ratio of 150. Crosslinked film exhibited high modulus, even at 190°C, to some extent, while uncrosslinked homo film was molten completely at 150°C.

REFERENCES

1. A. Ciferri and B. Valenti, in *Ultra-High Modulus Polymers,* A. Ciferri and I. M. Ward, Eds., Applied Science, London, 1984.
2. J. B. Donnet and R. C. Bansal, in *Carbon Fibers,* M. Lewin, Ed., Marcel Dekker, New York, 1984.
3. P. Smith and P. J. Lemstra, *Colloid Polym. Sci.,* **258,** 89 (1980).
4. D. J. Bundell and A. Keller, *J. Macromol. Sci., Phys.,* **B(2),** 301 (1968).
5. T. Kanamoto, S. Kiyooka, Y. Tovmasyan, H. Sano, and H. Narukawa, *Polymer,* **31,** 2039 (1990).
6. A. Zwijnenburg and A. J. Pennings, *Colloid Polym. Sci.,* **254,** 868 (1976).
7. W. T. Mead and R. S. Porter, *J. Polym. Sci., Polym. Symp. Ed.,* **63,** 289 (1978).
8. S. S. Han, W. S. Yoon, W. S. Lyoo, C. J. Lee, B. C. Ji, and E. K. Kim, *J. Macromol. Sci., Phys.,* **B36,** 1 (1997).
9. W. S. Lyoo, S. S. Han, J. H. Choi, Y. W. Cho, and W. S. Ha, *J. Korean Fib. Soc.,* **32,** 1023 (1995).
10. T. Kunugi and I. Akiyama, *Polymer,* **23,** 1199 (1982).
11. P. D. Garrett and D. T. Grubb, *Polym. Commun.,* **29,** 60 (1988).
12. T. Kunugi, T. Kawasumi, and T. Ito, *J. Appl. Polym. Sci.,* **40,** 2101 (1990).
13. R. Basheer and M. Dole, *J. Polym. Sci., Polym. Phys. Ed.,* **21,** 949 (1983).
14. B. J. Qu, W. F. Shi, R. Y. Liang, S. Z. Jin, Y. H. Xu, Z. H. Wang, and B. Ranby, *Polym. Eng. Sci.,* **35,** 1005 (1995).
15. M. Matsuo and C. Sawatari, *Macromolecules,* **20,** 1745 (1987).
16. J. Bongardt, G. H. Michler, I. Naumann, and G. Schulze, *Angew. Makromol. Chem.,* **153,** 55 (1987).
17. P. Smith, P. J. Lemstra, J. P. L. Pijpers, and A. M. Kiel, *Colloid Polym. Sci.,* **259,** 1070 (1980).
18. P. Smith, P. J. Lemstra, and H. C. Booij, *J. Polym. Sci., Polym. Phys. Ed.,* **19,** 877 (1981).
19. M. Matsuo and R. S. J. Maley, *Macromolecules,* **16,** 1500 (1983).
20. H. Sakami, T. Izushi, and S. Iida, *Kobunshi Robunshu,* **38,** 103 (1981).