

Cross-Linking Effect of Polyethylene–Polypropylene Blend Films Prepared by Gelation/Crystallization from Solution

Chie SAWATARI[†] and Masaru MATSUO*

*Department of Clothing Science, Faculty of Home Economics,
Nara Women's University, Nara 630, Japan*

(Received June 18, 1987)

ABSTRACT: Cross-linking of polyethylene–polypropylene blend films, prepared by gelation/crystallization from solutions, was done according to the following two methods. One was carried out under elongation of the blend gel films containing dicumyl-peroxide. The other was with electron-beam irradiation of the undrawn specimens and subsequently the specimens were elongated. The mechanical properties of the resultant specimens in undrawn and drawn states were found to become much weaker with increasing polypropylene content. This phenomenon was attributed to the considerable scission of main-chains of polypropylene. Consequently it turned out that both methods are appropriate for producing a net cross-linking effect of polyethylene occurring preferentially in the amorphous regions.

KEY WORDS Cross-Linking / Polyethylene–Polypropylene Blend / Gelation/Crystallization / Electron Beam Irradiation / Scission of Main-Chains /

In recent year, the preparation of polymeric fibers and films with high modulus has been extensively investigated and good results have been obtained for polyethylene.^{1–10} However, the range of application of polyethylene is limited by its low melting point, although the theoretical Young's modulus is one of the highest among crystalline polymers. Attempts have been made to remove this defect by cross-linking. The studies are mainly classified into two methods. One is γ - and electron beam irradiations and the other chemical reaction.

The cross-linking by γ - and electron-beam irradiations has been applied to an oriented system by Pennings *et al.* in order to produce polyethylene fibers and films with improved mechanical and thermal properties.^{11,12} They pointed out that apart from cross-linking, γ -irradiation also unfortunately causes main-chain scission, thus reducing the tenacity of the

filaments.^{11,12} A similar method was carried out by Sawatari and Matsuo using electron beam irradiation.¹³ They exposed an electric beam to ultradrawn films, the draw ratios being greater than 50, under nitrogen. Unfortunately, the mechanical properties of the resultant specimens became much weaker with increasing radiation dose and the specimens with a dose of 200 Mrad were easily torn by hand. This result was attributed to the considerable radiation-induced scission of extended chains forming the crystals. These results^{11–13} indicate that cross-linking of ultradrawn polyethylene films by the irradiation is not appropriate for producing a net cross-linking effect occurring preferentially in the amorphous regions. This unfavorable finding is due to the high crystallinity of ultradrawn films. Recently, Matsuo *et al.* tried to draw polyethylene cross-linked by electron beam

[†] Present address: Faculty of Education, Shizuoka University, Shizuoka 422, Japan.

* To whom all correspondence should be addressed.

with radiation doses in the range from 12 to 96 Mrad using ultra-high molecular weight polyethylene.¹⁴ As the result, it turned out that the undrawn specimens at a fixed dimension can be kept at 200°C for a prolonged time, being independent of the radiation dose but the elongation hampers the heat-resistant effect and the specimens were broken at temperatures lower than 175°C.

The cross-linking by chemical reaction was first carried out to cross-link ultra-high molecular weight polyethylene without rupture of chains by Pennings *et al.*¹⁵ As-spun fibers were highly porous in a solution of dicumyl peroxide (DCP) in hexane and DCP could be introduced easily into the filaments before attaining a high degree of crystallinity due to hot drawing. They reported that cross-linked filaments can be kept at 195°C for prolonged time without significantly influencing the tenacity of the fiber at 20°C, when a tension was applied during the heat treatment. Another method was proposed by Matsuo and Sawatari^{16,17} on the basis of the approach of Pennings *et al.*¹⁵ According to their reports,^{16,17} DCP introduced into ultra-high molecular weight polyethylene gel films prepared by gelation/crystallization from a dilute solution according to Smith and Lemstra.^{5,6} The introduction of DCP was carried out in the swollen state of gel films containing decalin. After evaporating the solvent, dry gel films can be readily elongated to the desired draw ratios at 150°C under nitrogen and sulfur trioxide and sulfuric acid vapor. The optimum elongation condition for each specimen was determined by trial and error. Thus, it was found that for samples drawn to 50-fold the cross-linking reaction occurred readily in the absence of sulfur trioxide and sulfuric acid¹⁶ but for samples with 100-fold, sulfur trioxide and sulfuric acid vapor was essential for successful cross-linking.¹⁷ The storage modulus of the specimen drawn up to 50-fold was 46 GPa at room temperature and 0.5 GPa at 230°C, while the modulus of the specimen with 100-fold was

114 GPa at room temperature and 2.0 GPa at 200°C. However, the latter specimens could not be maintained beyond 200°C.

On the basis of the experimental results for cross-linking of polyethylene by the introduction of DCP as well as by electron-beam irradiation, our focus in the present paper is on the cross-linking of blend films of polyethylene (PE) and polypropylene (PP) prepared by gelation/crystallization from semidilute solutions. The PE-PP blend films could be prepared by the gelation/crystallization in previous work.¹⁸ The PE/PP compositions were chosen as 75/25, 50/50, 25/75. The critical concentration to ensure optimum draw characteristics for each composition was determined by preparing gel films at various concentrations and studying their drawability in order to ascertain which concentration would give the best results. For all compositions a concentration of about 0.45 g/100 ml proved most suitable. The resultant blend film after evaporating the solvent could be readily elongated to a high draw ratio in a poly(ethylene glycol) bath at 140°C. The morphological properties of the blend film were dependent upon the compositions. The texture was generally fibrillar with no indication of separate polyethylene and polypropylene domains, indicating mixing of the two components despite their known incompatibility in solution. This effect was concluded to be due to the existence of a suitable level of entanglements between polyethylene and polypropylene chains, which hampers the growth of separate phases of the two polymers in the gelation/crystallization process. The melting point of the polyethylene component became higher than the equilibrium melting point because of superheating effects which have previously been observed for highly oriented polyethylene films.¹⁹ The melting point of polypropylene increased with increasing draw ratio and approached the theoretical value.²⁰ The 25/75 blend film with a draw ratio of 60 could be kept at 160°C at a fixed dimension, which is higher than the

apparent melting point (155°C) of polyethylene with a draw ratio of 300,¹³ associated with the superheating effect. In order to pursue further improvement in high temperature resistance, the cross-linking of the blend films was performed with electron beam as well as with reaction of DCP. The resultant specimens were analyzed in terms of morphological and mechanical aspects.

EXPERIMENTAL

The samples used in this paper were linear polyethylene and isotactic polypropylene with molecular weights of 6×10^6 and 4.4×10^6 , respectively. The solvent was decalin. The PE/PP compositions chosen were 75/25, 50/50, and 25/75. Decalin solutions (1500 ml) were prepared by heating the well-blended polymer/solvent mixture at 150°C for 20 min under nitrogen and mixed vapor of sulfur trioxide and sulfuric acid. The hot homogenized solution was quenched by pouring it into an aluminum tray, thus generating a gel. The decalin was allowed to evaporate from the gel under ambient conditions. When the volume of the gel approached a 70% decrease, 300 ml of a decalin solution containing appropriate quantities of i) DCP or ii) DCP and tri-allyl-isocyanurate (TAIC) or iii) DCP and diallyl-phthalate (DAP) at 50°C were poured into the aluminum tray. The quantities shall be discussed later. The decalin was again evaporated at 50°C. The nearly dry gel film was vacuum-dried for 1 day to remove residual traces of decalin.

Furthermore, dry gel films without containing DCP and TAIC (or DAP) were prepared according to the same method discussed already.^{16,17} The films were exposed to an electron beam under nitrogen flow in order to avoid oxygenation as well as the heating effect of irradiation. The electron-beam was irradiated at Sumitomo Electric Co., Ltd. Radiation doses 12 and 96 Mrad were employed.

The dry gel film was cut into strips 24 mm long and 15 mm wide. The strips were clamped in a manual stretching device in such a way that the length to be drawn was 4 mm. The specimen was placed in an oven at 150°C under nitrogen and mixed vapor of sulfur trioxide and sulfuric acid and then was immediately elongated manually to the desired draw ratio. The manual stretching was warmed prior to clamping the specimen in order to avoid as much as possible a decrease of temperature when placing the device in the oven. The temperature 150°C was chosen to be similar to the cross-linking of polyethylene dry gel film.¹⁶ As discussed in the previous work,¹⁶ the reaction of DCP at 150°C is almost completed during elongation, and the maximum draw ratio of 50 was attained. In contrast, the cross-linking at 140°C was insufficient to prepare films with high temperature resistance, although the maximum draw ratio was close to 100.¹⁷ Furthermore it was confirmed that the drawing of polypropylene was impossible at temperatures lower than 140°C in an hot oven. At temperatures higher than 150°C, too many cross-links were introduced into the amorphous phase of polyethylene in a rather short period of time, resulting in a random connectedness of the polyethylene chains and thus inhibiting chain alignment in the direction of stretching during the drawing process.

The drawn films were annealed at a fixed dimension in the stretching direction for 90 min in an hot oven at 150°C under nitrogen in order to promote cross-linking in the amorphous regions. Subsequently the annealed films were immersed in an excess of ethanol at 50°C for 6 h.

The temperature-dependence of the complex dynamic tensile modulus was measured by a viscoelastic spectrometer (VES-F) of the Iwamoto Machine Co., Ltd. The specimens used in this experiment were cut to a length of 60 mm and the width of 1.5 mm and were clamped over a length of 10 mm at the ends. The measurements were carried out over a

temperature range from -50°C to the melting temperature of the specimen at a fixed frequency of 10 Hz. In the measurement, the film was subjected to a static strain due to a suitable stress in order to apply a suitable dynamic displacement in the range 0.025–0.125% smoothly.

The X-ray measurements were carried out by 12 kW rotating anode X-ray generator (RDA-rA). Wide angle X-ray diffraction (WAXD) patterns were obtained with a flat film camera using $\text{CuK}\alpha$ radiation at 200 mA and 40 kV. The X-ray beam was monochromatized by a curved graphite monochromator. The exposure time for all specimens was 20 min.

The fusion behavior of specimens was studied by differential scanning calorimetry (DSC) using Rigaku Denki calorimeter (8089 TG-DSC). Each film was cut into square pieces weighting about 5 mg and the pieces were placed in a standard aluminum sample pan. The pieces were heated at a constant rate of 10 K min^{-1} . Since the shape of the DSC curves and the location of the peak for a given heating rate are very dependent on the packing and the size of the pieces, these parameters were kept as constant as possible.

RESULTS AND DISCUSSION

Figure 1 shows WAXD patterns endview from undrawn blend films annealed for 200 min at 150°C under nitrogen, when the incident X-ray beam was directed parallel to the film surface. The patterns on line A show the diffraction from original blend films and the individual homopolymers without containing DCP. The patterns on line B show the diffraction from the specimens containing 17% DCP and the patterns on line C the diffraction from the specimens containing 17% DCP and 1.7% TAIC. The patterns on line A displays the random orientation of the *c*-axes of polyethylene and the preferential orientation of the *c*-axes of polypropylene perpendicular to

the film surface. This result is attributed to the deserved fact that polyethylene crystals, the *c*-axes being oriented perpendicular to the film surface, were melt and recrystallized, while polypropylene crystals retained the original orientation. The patterns on line B show an indistinct broad ring from the amorphous regions of polyethylene and polypropylene in addition to weak diffraction arcs from polypropylene crystals. Here the question may be arisen whether an increase in the amorphous content is due to the cross-linking owing to the occurrence of vulcanization or due to the considerable main-chain scission. In order to solve this question, the temperature-dependence of the complex dynamic tensile modulus was measured at a fixed frequency of 10 Hz, since the mechanical properties are affected by rupture of main-chains, sensitively.

Figures 2 and 3 exhibit the behavior of the storage and loss moduli, respectively, for the blend films treated by 17% DCP and Figures 4 and 5 also show the behavior of the specimens treated by 17% DCP and 1.7% TAIC. A series of the results indicates that the polypropylene films were melt around 150°C being lower than the equilibrium melting point ($186 \pm 2^{\circ}\text{C}$),²¹ while the polyethylene films were maintained beyond 200°C . Such behavior suggests a considerable main-chain scission of polypropylene and the cross-linking of polyethylene. Accordingly, the improvement in high temperature resistance of the 75/25 and 50/50 blend films depends on the heat resistance of polyethylene. Comparing the results in Figure 2 with those in Figure 4, it is evident that TAIC plays an important role for improvement in high temperature resistance and especially the 75/25 blend film was maintained up to 280°C .

Based on the above results, the elongation was carried out using the specimens containing 17% DCP and 1.7% TAIC. However, all the blend films drawn up to 50-fold were broken at temperatures lower than 160°C . From this preliminary experiment, it may be expected

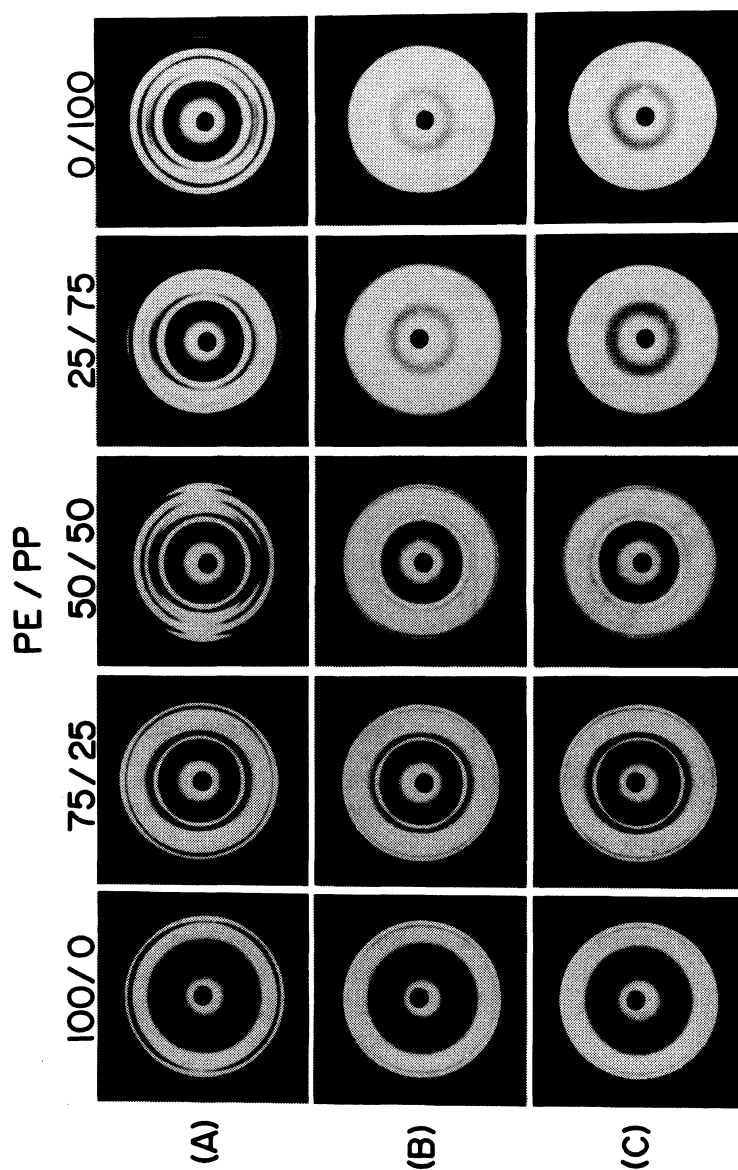


Figure 1. WAXD patterns (end view) from undrawn blend films annealed for 200 min at 150°C under nitrogen (a) line A, diffraction from the original films; (b) line B, diffraction from the films treated with 17% DCP; (c) line C, diffraction from the films treated with 1.7% TAIC.

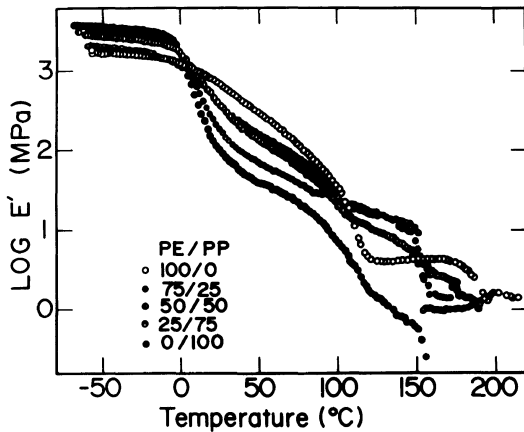


Figure 2. Temperature-dependence of the storage modulus for the undrawn blend films treated with 17% DCP.

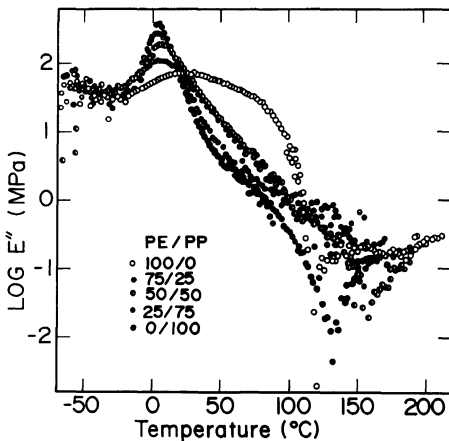


Figure 3. Temperature-dependence of the loss modulus for the undrawn blend films treated with 17% DCP.

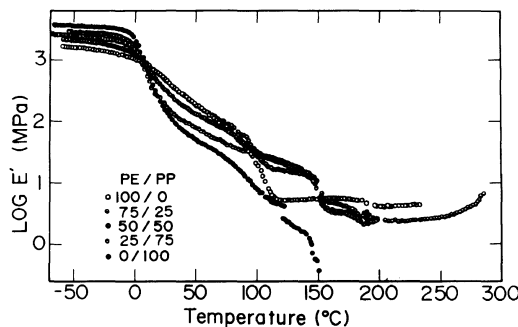


Figure 4. Temperature-dependence of the storage modulus for the undrawn blend films treated with 17% DCP and 1.7% TAIC.

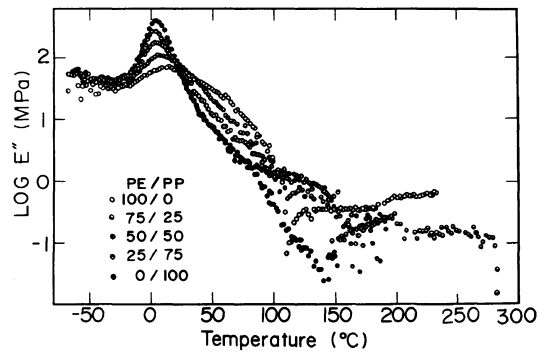


Figure 5. Temperature-dependence of the loss modulus for the undrawn blend films treated with 17% DCP and 1.7% TAIC.

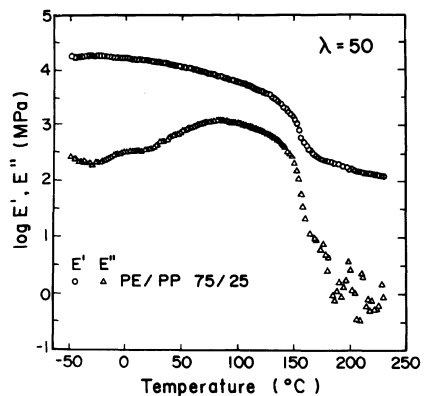


Figure 6. Temperature-dependence of the storage modulus and loss modulus of the 75/25 blend film with $\lambda=50$, where the elongation was carried out for the specimen containing 200% DCP and 20% TAIC.

that the amount of 17% DCP and 1.7% TAIC are too small to perform the cross-linking under the elongation. Therefore the specimens containing a large amount of DCP (200%) and TAIC (20%) were elongated up to a draw ratio of 50 as a trial.

Figure 6 shows the temperature-dependence of the storage and loss moduli of the 75/25 blend film with $\lambda=50$, when a tension was applied during the heat-resistant. The profiles of the storage modulus E' and the loss modulus E'' are similar to those of polyethylene, as has been reported in the previous work.^{16,17} The film was maintained at 230°C. The modulus at 20°C is about 16 GPa and that at

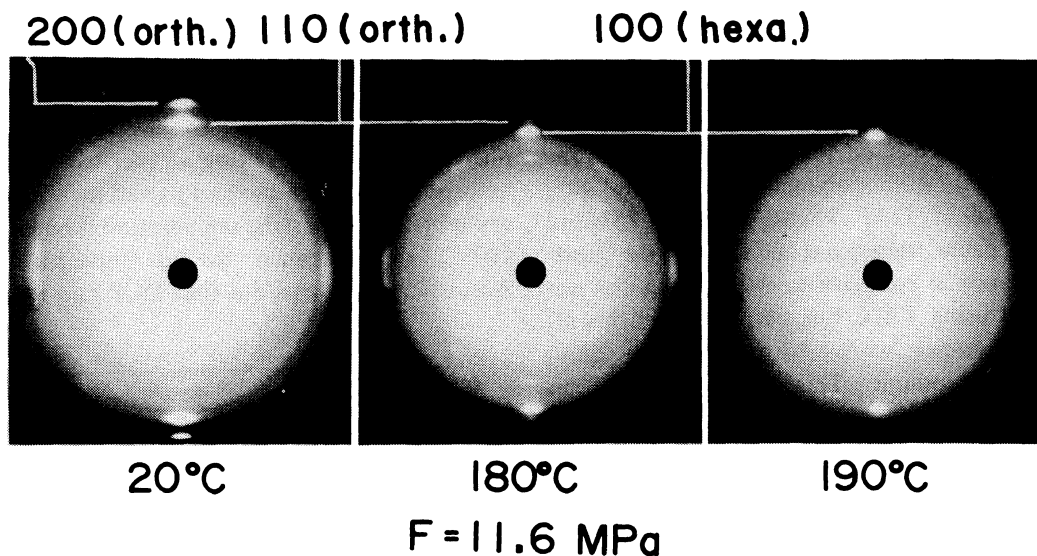


Figure 7. Temperature-dependence of WAXD patterns (through view) of the 75/25 blend film with $\lambda = 50$, where the elongation was carried out for the specimen containing 200% DCP and 20% TAIC.

230°C is about 0.1 GPa. Both the values are lower than those of cross-linked polyethylene reported elsewhere.¹⁶ This is due to the unfavorable fact that the crystal lattice modulus of polypropylene²² is essentially much lower than that of polyethylene¹⁰ and the amorphous regions of polypropylene do not contribute to cross-linking due to the chemical reaction by the introduction of DCP and TAIC. Incidentally, the heat-resistant effect becomes worse as the content of polypropylene increases, although the result is not represented in this paper.

Figure 7 shows the temperature-dependence of the X-ray patterns (through view) of the 75/25 blend film with $\lambda = 50$, when the incident beam was directed perpendicular to the film surface. In this system, the specimen was mounted horizontally in the stretching direction with the fixed dimensions at a constant stress of 11.6 MPa in order to avoid shrinkage of the specimen. The specimen was annealed for 20 min at the indicated temperatures prior to taking a picture.

As can be seen in the patterns, the strong

reflections of the (110) and (200) planes of polyethylene as well as the weak reflections from polypropylene crystals were observed in the pattern at 20°C. The pattern at 180°C shows the (100) reflection from the hexagonal phase of polyethylene in stead of the (110) and (200) planes of the orthorhombic phase, indicating a transformation to the hexagonal rotator phase. Although the weak reflection spots from polypropylene crystals retained at 180°C but the spots ceased to exist at 190°C, indicating the melting of polypropylene crystals. Accordingly, it is evident that the thermal behavior of polypropylene is quite different from that of polyethylene, where a transformation to the hexagonal phase is observed.

As discussed before, additional experiments about the temperature-dependence of the storage modulus of the blend films with different PE/PP compositions indicate that the heat-resistant effect becomes worse with increasing the content of polypropylene. Especially, the melting point of polypropylene shifted to about 150°C, indicating considerable chain-scission of polypropylene. Hence, as a trial, the

following experiments were carried out using DAP instead of TAIC in order to avoid the rupture of main-chains as much as possible.

Figure 8 shows the temperature-dependence of E' and E'' for the blend films and the individual homopolymers containing 40% DCP and 5% DAP. The 50/50 and 25/75 blend films cause significant effect on the heat-resistance in comparison with the results obtained using TAIC but unfortunately this effect becomes worse with increasing polyethylene content. This phenomenon is in contradict with that obtained using TAIC and this means rupture of main-chains of polyethylene.

Here it is of interest to ascertain whether polypropylene chains, more or less, are cross-linked by chemical reaction of DCP and DAP, since the 50/50 blend, the 25/75 blend, and the polypropylene homopolymer were maintained around 190°C. In order to check this problem, the WAXD patterns of polypropylene with $\lambda=50$ were obtained with increasing temperature. Figure 9 shows the temperature-dependence of the WAXD patterns (through view) at the indicated temperatures. As in the case of Figure 7, the specimen was fixed at a constant stress of 11.4 GPa to suppress

shrinkage due to melting of the specimen. The patterns at 20 and 185°C display strong diffraction spots indicating the stable crystal phase, whereas the pattern at 190°C weak diffraction spots indicating an increase in the amorphous content due to a partial melting of crystal phase. When the temperature is beyond 190°C, the specimen melted immediately. Accordingly, it turns out that DCP and DAP

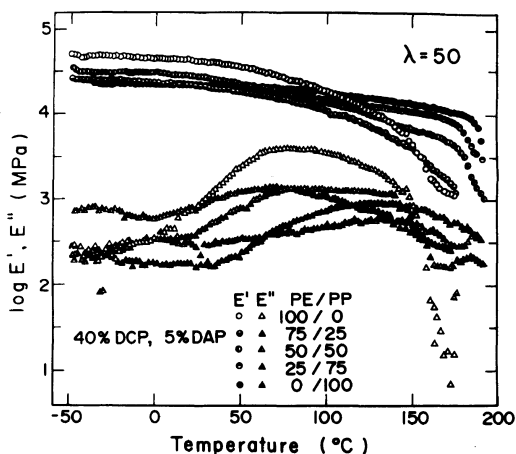


Figure 8. Temperature-dependence of the storage and loss moduli of the blend films and the individual homopolymers with $\lambda=50$, where the elongation was carried out for the films containing 40% DCP and 5% DAP.

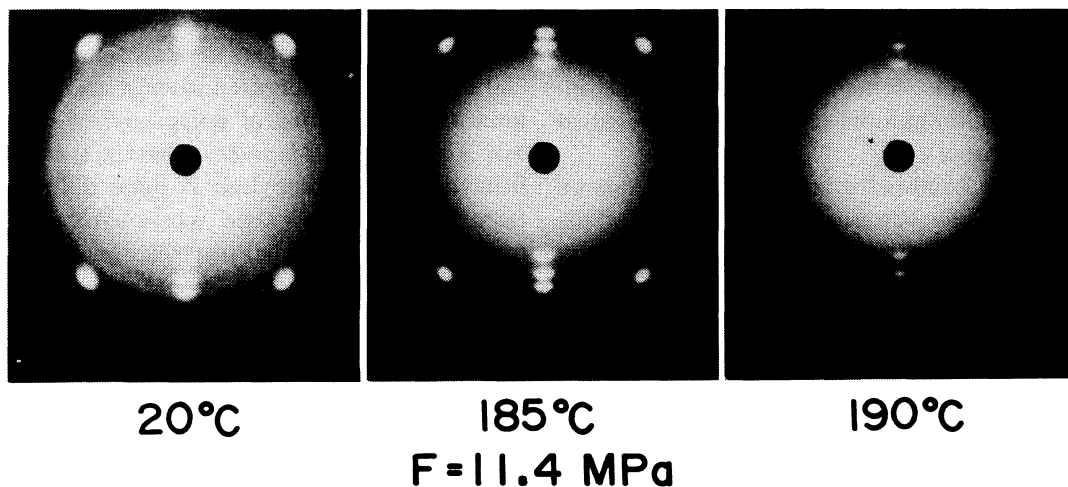


Figure 9. Temperature-dependence of the WAXD patterns of polypropylene with $\lambda=50$, where the elongation was carried out for the specimen containing 40% DCP and 5% DAP.

are insufficient to bring about the cross-linking of polypropylene chains but are independent of the rupture of the main-chains.

Through a series of the experimental results, it may be concluded that the cross-linking of polypropylene cannot be performed with the chemical reaction of DCP and the chemical reaction is useless for improvement of polypropylene and the blends at high resistant temperatures.

As another method, cross-linking of the PE-PP blend films was attempted with electron-beam irradiation. Figure 10 shows WAXD patterns (end view) of the 75/25, 50/50, and 25/75 blend films which were irradiated with an electron-beam with doses of 12 and 96 Mrad. Observation revealed the preferential orientation of the *c*-axes of polyethylene and polypropylene crystals like single crystal mats, as has been reported for non-cross-linked blend films already.¹⁸ On the basis of a series of the patterns, it may be inferred that the orientational fluctuation of crystallites as well as the considerable radiation-induced scission of extended chains within crystallites cannot be easily observed as long as the irradiation dose is lower than 96 Mrad.

Figure 11 shows DSC curves for the effect of radiation dose on the melting of the blend films and polyethylene homopolymer in an undeformed state. The melting peak shifts to a lower temperature with increasing radiation dose. The undrawn films reveals an increase in the melting temperature of polyethylene occurring mainly over the first 12 Mrad radiation dose. The melting point falls away at the radiation dose of 96 Mrad. In contrast, the melting peak of polypropylene shifts to a lower temperature considerably with increasing radiation dose and the heat of fusion becomes lower. The increase in radiation dose causes considerable decreases in the melting point as well as in the crystallinity. Such a phenomenon is attributed to chain scission within crystallites.

Figure 12 shows the temperature-dependence of E' and E'' for undrawn polyethylene films as a function of radiation dose. The storage modulus for the specimens decreases over the first 12 Mrad up to 100°C. The decrease of the storage modulus of polyethylene gel film is considerable and this tendency is pronounced especially for the specimen irradiated with high radiation dose of 96 Mrad. The extremely considerable decrease around 130°C for all the specimens is due to the melting of crystallites which can be observed by DSC measurements in Figure 11(a). The specimen has the storage moduli of about 2.1 GPa at 20°C and of about 1 MPa at 200°C, indicating an improvement in high temperature resistance for the specimens irradiated with 12 and 96 Mrad. Such an improvement can be observed only at a fixed dimension of the specimen. The loss modulus E'' shows a maximum peak in the range 60–80°C. The peak has been reported to correspond to the α -mechanism associated with grain boundary phenomena due to the rotation of crystal grains as well as associated with smearing-out effect of the crystal lattice potential due to onset of rotational oscillation of polymer chains within the crystal grains.^{23–25}

Figure 13 shows the temperature-dependence of E' and E'' for the 75/25 blend films in an undrawn state, as a function of radiation dose. The storage modulus decreases over the first 12 Mrad as in the case of polyethylene gel films shown in Figure 12. Even the specimens irradiated with 12 and 96 Mrad were melted around 130°C. Such an unfavorable phenomenon is probably due to the fact that apart from cross-linking, electron-beam radiation unfortunately causes scission of the main-chains of polypropylene. Actually, it was confirmed that the temperature-dependence of the storage modulus of the blend films becomes greater as the polypropylene content increases and especially polypropylene homopolymer film could be easily torn by hand.

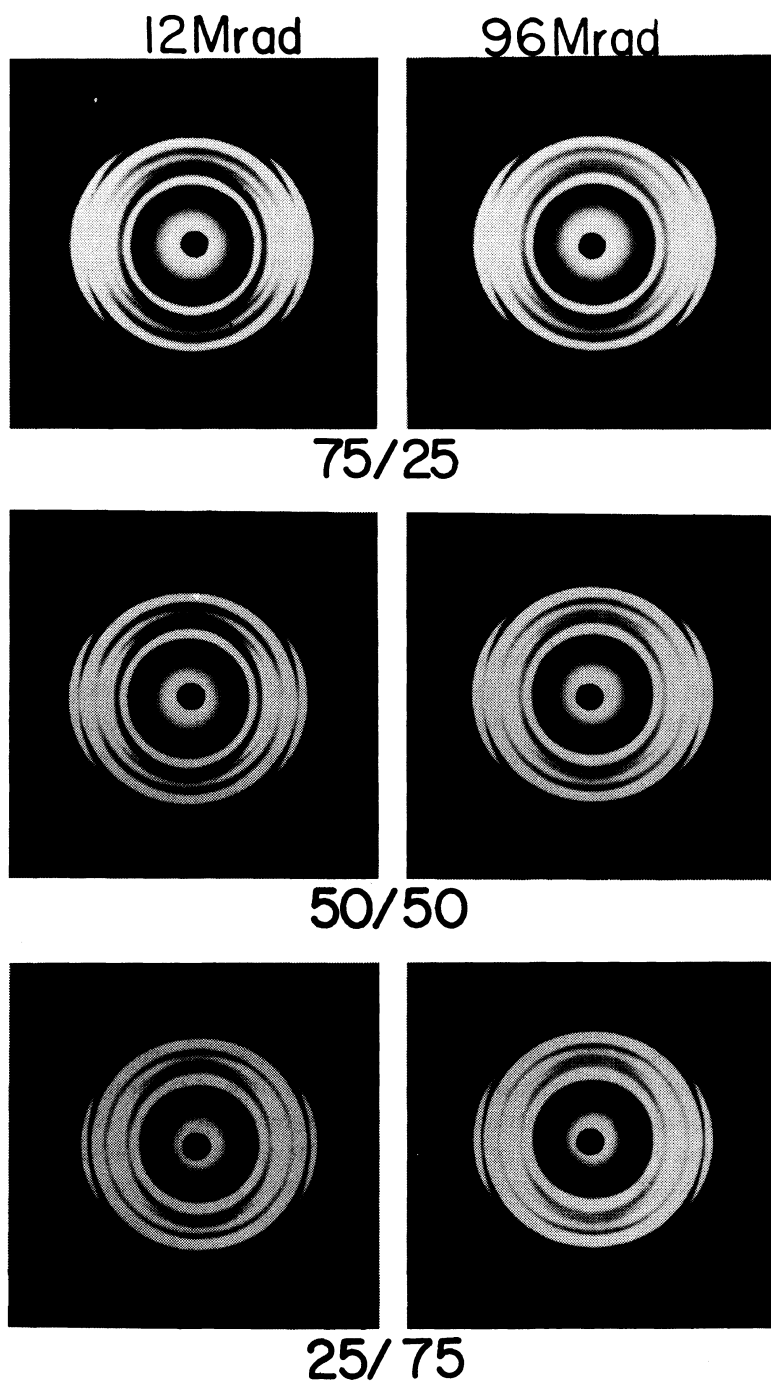


Figure 10. WAXD patterns (end view) of the undrawn blend films with 75/25, 50/50, and 25/75, irradiated with electron-beam with the doses of 12 and 96 Mrad.

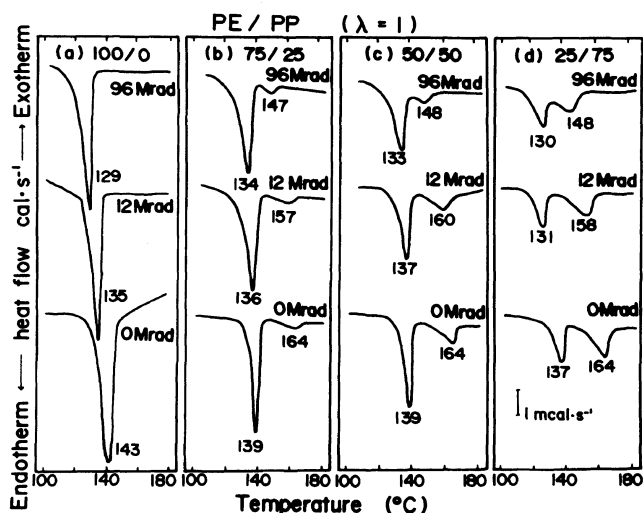


Figure 11. DSC curves of the undrawn blend films and polyethylene films as a function of radiation dose.

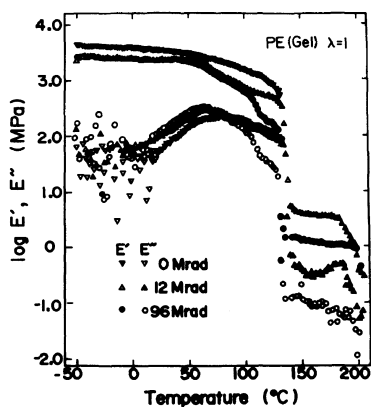


Figure 12. Temperature-dependence of the storage and loss moduli for undrawn polyethylene films as a function of radiation dose.

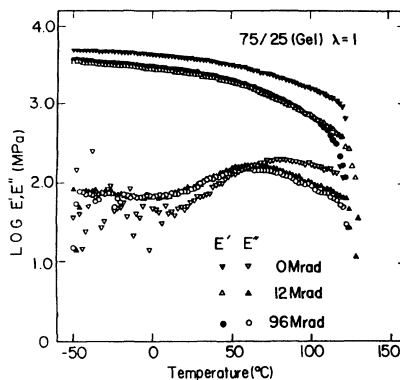


Figure 13. Temperature-dependence of the storage and loss moduli for the undrawn 75/25 blend films as a function of radiation dose.

CONCLUSION

Cross-linking of blend gel films was done by chemical reactions of DCP and electron-beam irradiation by using ultra-high molecular weight polyethylene (6×10^6) and polypropylene (4.4×10^6). As a result, the cross-linking was performed in the polyethylene regions and was found to improve in high temperature resistance, while that of cross-linking could not be realized in the polypro-

pylene regions. Accordingly it turned out that the heat resistance becomes worse as polypropylene content increases.

Acknowledgement. We are indebted to Messrs Ueno, Inui, and Besho, Sumitomo Electric Co., Ltd., for irradiation of the specimens at their laboratory.

REFERENCES

1. A. Zwijnenburg and A. J. Pennings, *Colloid. Polym.*

1. *Sci.*, **253**, 452 (1975).
2. J. Clements, G. Cappaccio, I. M. Ward, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 693 (1979).
3. P. J. Barham and A. Keller, *J. Mater. Sci.*, **15**, 2229 (1980).
4. J. Smook, J. C. Torfs, P. F. van Hulsten, and A. J. Pennings, *Polym. Bull.*, **2**, 293 (1980).
5. P. Smith and P. J. Lemstra, *J. Mater. Sci.*, **15**, 505 (1980).
6. P. Smith, P. J. Lemstra, H. C. Booij, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 877 (1981).
7. T. Kanamoto, E. S. Sherman, and R. S. Porter, *Polym. J.*, **11**, 497 (1979).
8. T. Kanamoto, A. Tsuruta, K. Tanaka, and M. Takeda, *Polym. J.*, **15**, 327 (1983).
9. K. Furuhashi, T. Yokokawa, and K. Miyasaka, *J. Polym. Sci., Polym. Phys. Ed.*, **22**, 133 (1984).
10. M. Matsuo and C. Sawatari, *Macromolecules*, **19**, 2036 (1986).
11. J. deBoer and A. J. Pennings, *Polym. Bull.*, **5**, 317 (1981).
12. J. deBoer and A. J. Pennings, *Polym. Bull.*, **7**, 309 (1982).
13. C. Sawatari and M. Matsuo, *Colloid. Polym. Sci.*, **263**, 783 (1985).
14. C. Sawatari, H. Nishikido, and M. Matsuo, in preparation.
15. J. deBoer, H.-J. van den Berg, and A. J. Pennings, *Polymer* **25**, 513 (1984).
16. M. Matsuo and C. Sawatari, *Macromolecules*, **19**, 2028 (1986).
17. M. Matsuo and C. Sawatari, *Macromolecules*, **20**, 1745 (1987).
18. C. Sawatari, S. Shimogiri, and M. Matsuo, *Macromolecules*, **20**, 1033 (1987).
19. M. Matsuo, K. Inoue, and N. Abumiya, *Sen-i-Gakkaishi*, **40**, 275 (1984).
20. P. J. Flory and A. J. Vrij, *J. Am. Chem. Soc.*, **85**, 3548 (1963).
21. W. R. Krigbaum and I. Uematsu, *J. Polym. Sci., A*, **3**, 767 (1965).
22. C. Sawatari and M. Matsuo, *Macromolecules*, **19**, 2653 (1986).
23. S. Suehiro, T. Yamada, H. Inagaki, T. Kyu, S. Nomura, and H. Kawai, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 763 (1979).
24. H. Kawai, S. Suehiro, T. Kyu, and A. Shimomura, *Polym. Eng. Rev.*, **3**, 109 (1983).
25. M. Matsuo, C. Sawatari, and T. Ohhata, *Macromolecules*, submitted.