

Morphology and Mechanical Properties of Biaxially Oriented Films of Polypropylene and HDPE Blends

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SYNOPSIS

Biaxially oriented films of blends of high-density polyethylene (HDPE) with polypropylene (PP) homopolymer and PP copolymers prepared by twin-screw extrusion and lab-stretcher have been investigated by scanning electron microscopy (SEM), polarized microscopy, differential-scanning calorimeter, and universal testing machine. Three different kinds of PP copolymers were used: (i) ethylene-propylene (EP) random copolymer; (ii) ethylene-propylene (EP) block copolymer; (iii) ethylene-propylene-butylene (EPB) terpolymer. In the SEM study of the morphology of films of HDPE with various PP blends, phase separation is observed between the PP phase and the HDPE phase for all blends and compositions. In all blends, HDPE serves to reduce the average spherulites size, probably acting as a nucleating agent for PP. The reduction of spherulite size appeared most significantly in the blend of EPB terpolymer and HDPE. A large increase of crystallization temperature was found in the blend of EPB terpolymer and HDPE compared with the unblended EPB terpolymer. For the blend of EPB terpolymer and HDPE, the improvement of tensile strength and modulus is observed with an increase of HDPE content, and this can be considered as a result of the role of HDPE in reducing average spherulite size. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The blending of isotactic polypropylene (PP) and high-density polyethylene (HDPE) has been studied extensively in recent years.¹⁻¹⁰ Blends of PP and HDPE are now used commercially because of their high-impact strength and low-temperature toughness by addition of HDPE to PP.¹ Lovinger and Williams² have studied PP-HDPE blends by mechanical testing and morphological analysis. Greco et al.³ have studied blends of HDPE and ethylene-propylene copolymer by morphological and thermal analysis. Choudhary et al.⁴ and Lee et al.⁹ have studied PP-HDPE blends by rheological and mechanical testing, and have shown that the impact

strength of the PP-HDPE blends was strongly improved by the addition of the ethylene-propylene diene terpolymer (EPDM).

In the work of PP and polyethylene (PE) blends, some investigators^{9,11} found a monotonic increase in tensile strength with PP content, while other investigators^{2,12} observed a maximum in tensile strength and modulus at a certain composition, and they reported that there may be a relation between tensile properties and morphologies such as spherulite sizes. In this study, we examine the morphology and tensile properties of the blends of HDPE with PP homopolymer, ethylene-propylene (EP) random copolymer, EP block copolymer, and ethylene-propylene-butylene (EPB) terpolymer by scanning electron microscopy, polarized microscopy, and universal testing machine. The interrelationships between morphology and tensile properties in the blends of HDPE with PP homopolymer and various PP copolymers are presented.

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Table I Characteristics of Polymer Samples Used

Sample	Melt Index ^a	Density (g cm ⁻³)	<i>T_m</i> (°C) ^b	<i>T_c</i> (°C) ^b
PP ^c	1.68	0.903	164.0	109.1
EP random copolymer ^d	6.82	0.890	145.1	111.4
EP block copolymer ^e	1.43	0.915	164.0	109.8
EPB terpolymer ^f	4.87	0.889	131.2	87.8
HDPE ^g	0.46	0.958	130.0	115.0

^a Measured in our laboratory at 230°C.

^b Measured in our laboratory by DSC.

^c Supplied by Honam Oil Refinery Co.

^d 3.5% ethylene, 96.5% propylene, supplied by Honam Petrochemical Co.

^e 5% ethylene, 95% propylene, supplied by Sumitomo Co.

^f 3% ethylene, 92% propylene, 5% butylene, supplied by Honam Petrochemical Co.

^g Supplied by Korea Petrochemical Co.

EXPERIMENTAL

Polymers

The polymers used in this study were obtained from commercial sources. The characteristics and sources of the polymers are shown in Table I. The PP was supplied by Honam Oil Refinery Co. The EP random copolymer and EPB terpolymer were supplied by Honam Petrochemical Co. The EP block copolymer was supplied by Sumitomo Co., and the HDPE was supplied by Korea Petrochemical Co.

Blend and Film Preparations

Blends with weight fractions of PP of 0.90, 0.75, 0.50, and 0.25 were prepared by screw extrusion. Blends were prepared using a twin-screw extruder in a model LSM 30.34/GL34-D of Leistritz Co. at 220°C and 150 rpm. The extrudates were cooled through the water bath and then pelletized. To prepare oriented film of the blends, a sample of 100 mm × 100 mm × 1 mm was prepared by hot press at 220°C and then the biaxially oriented film was prepared by stretching the above sample into 4 (width) × 6 (length) times at 200°C with a lab-stretcher, model B-10 heavy-duty type, Toyoseki Co. The film thickness was 30 ± 3 μm.

Measurements

The morphology of the cross-section of biaxially oriented films for all the blends was examined by scanning electron microscopy in a Hitachi model S-2500C microscope at 20 kV accelerating voltage after gold sputter coating. The fractured surface of the films was prepared by cryogenic fracturing.¹³ The

melting point (*T_m*) of all samples was measured with a Perkin-Elmer differential-scanning calorimeter, model DSC-7. Blend samples of 6–7 mg were initially heated in a nitrogen atmosphere from 40 to 200°C at a heating rate of 10 K/min, following by 10 K/min cooling. The samples were then reheated from 40 to 200°C at a heating rate of 10 K/min. Crystallization temperature (*T_c*) of the blends was obtained when the sample was cooled from the melt at 200°C. The *T_m* and *T_c* were the maximum peak temperatures. For the growth of spherulite, the films were melted on a hot stage of polarized-light microscopy at 230°C and then cooled slowly until 100–120°C. The gloss of film surfaces was measured by gloss meter according to ASTM D2547. Tensile properties were measured by Instron universal testing machine according to ASTM D882. The dimensions of the test specimens were 100 mm × 15 mm × 30 μm. The test speed was 300 mm/min.

RESULTS AND DISCUSSION

Morphology

Polypropylene and polyethylene are known to be immiscible.^{1–10} The morphology of the various PP-HDPE blends was studied using scanning electron microscopy (SEM). Figure 1(a–d) shows micrographs of cryogenically fractured cross-sections of biaxially oriented films of blends of 0.25 weight fraction HDPE with PP homopolymer, EP random copolymer, EP block copolymer, and EPB terpolymer, respectively. Two phases are observed in all blend samples. However, there are indications in all blends of adhesion between the two phases. The morphology of EPB terpolymer and HDPE blend

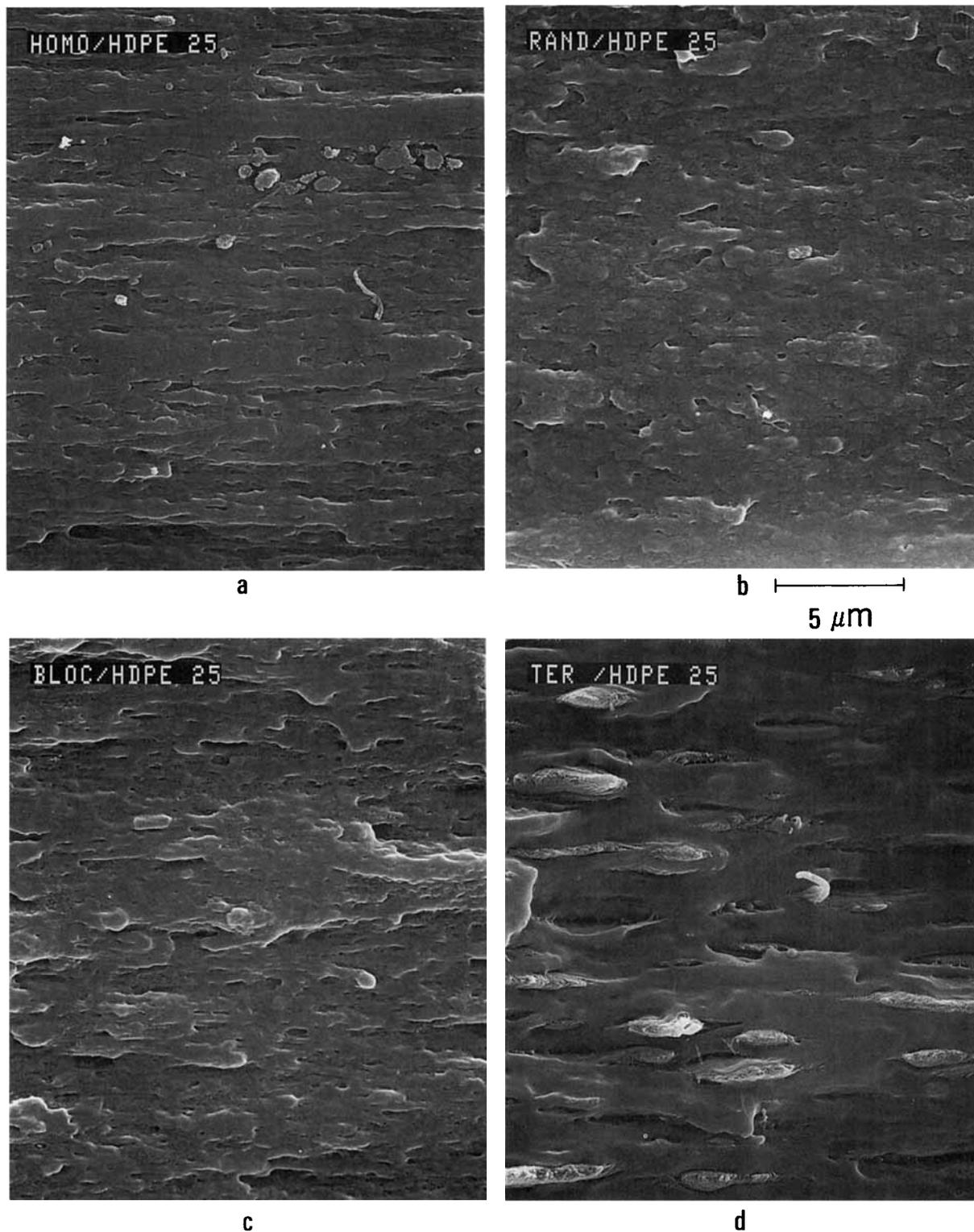


Figure 1 Scanning electron micrographs of cryogenically fractured cross-sectional surfaces of the biaxially oriented films of various blends: (a) PP homopolymer/HDPE (75 : 25); (b) EP random copolymer/HDPE (75 : 25); (c) EP block copolymer/HDPE (75 : 25); (d) EPB terpolymer/HDPE (75 : 25).

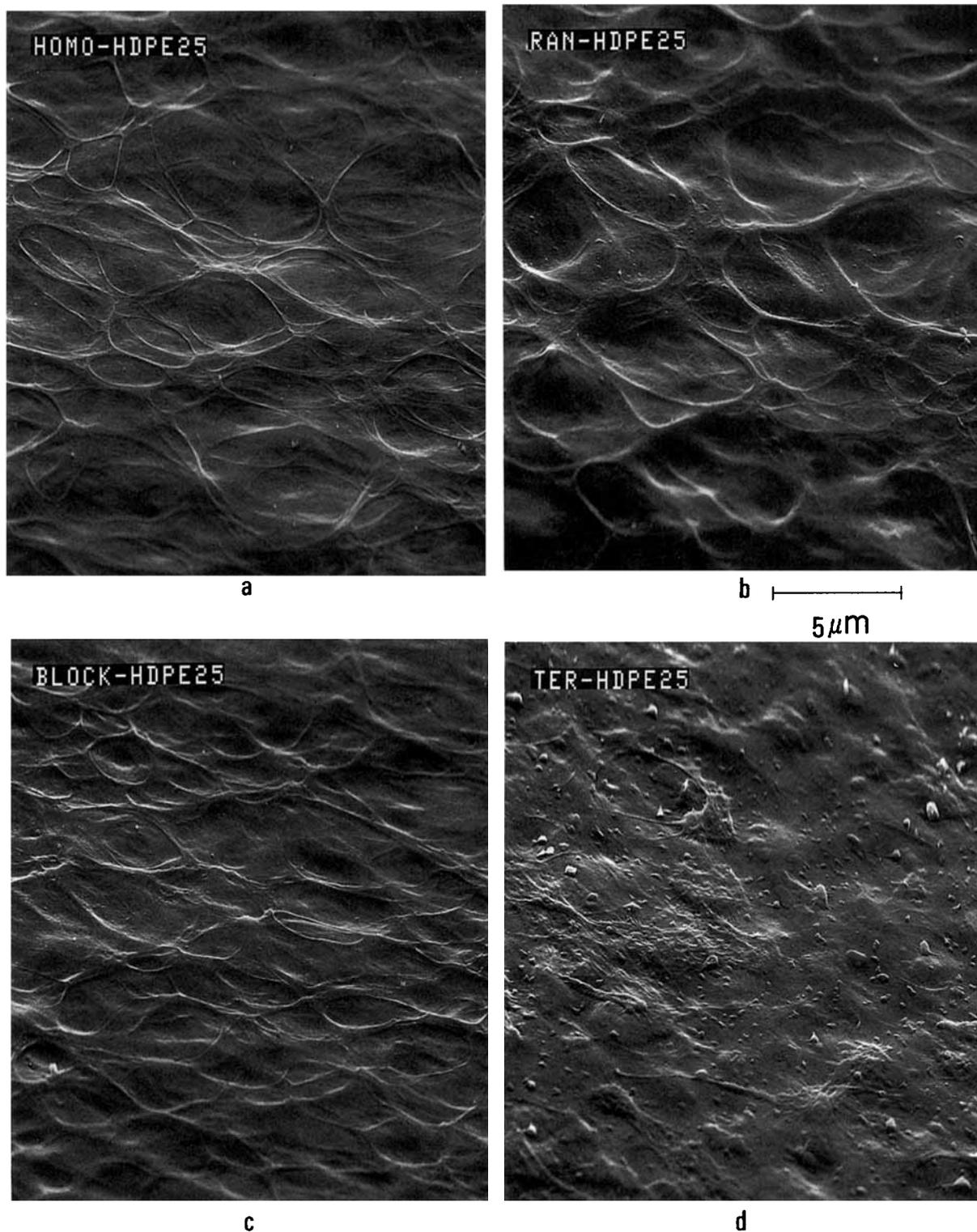


Figure 2 Scanning electron micrographs of biaxially oriented film surfaces of various blends: (a) PP homopolymer/HDPE (75 : 25); (b) EP random copolymer/HDPE (75 : 25); (c) EP block copolymer/HDPE (75 : 25); (d) EPB terpolymer/HDPE (75 : 25).

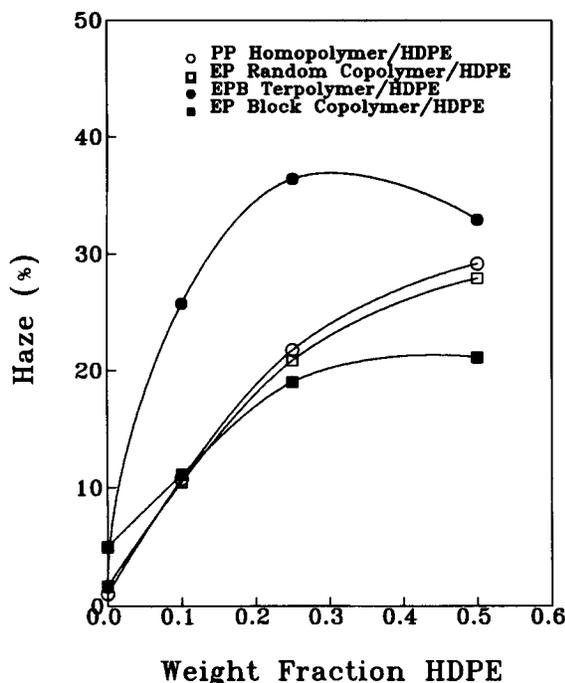


Figure 3 Effect of blend composition on the haze of biaxially oriented films of various blends: (a) PP homopolymer/HDPE (75 : 25); (b) EP random copolymer/HDPE (75 : 25); (c) EP block copolymer/HDPE (75 : 25); (d) EPB terpolymer/HDPE (75 : 25).

[Fig. 1(d)] is somewhat different from that of Figure 1(a-c). Structurally, the difference among the three PP copolymers is that EPB terpolymer has some rubber characteristics compared with other PP copolymers, and the morphology differences in the blend of HDPE and EPB terpolymer may be caused by these rubber characteristics.

The film surfaces of the four different types of PP-HDPE blends were studied using SEM. Figure 2(a-d) shows micrographs of biaxially oriented film surfaces of the blends of PP homopolymer, EP random copolymer, EP block copolymer, and EPB terpolymer with 0.25 weight fraction HDPE, respectively. From Figure 2, we can see that the film surface is not smooth. The surface roughness of the blend film is increased for 0.5 weight fraction HDPE in all blends. The haze of film surface of the various PP-HDPE blends is shown in Figure 3. From Figure 3, we can see that the haze increases with an increase of HDPE content. For the blend of EPB terpolymer and HDPE, the haze increases most significantly with HDPE content; this indicates that the film has lower transparency compared with the other blend films.

The spherulites of the unblended polymers are shown in Figure 4. The average diameter of the

spherulite of the PP and PP copolymers is 50–100 μm or larger. On the other hand, PE spherulites are generally very small (less than 10 μm) as a result of high nucleation and growth rates. The spherulites of the blends of PP homopolymer, EP random copolymer, EP block copolymer, and EPB terpolymer with 0.25 weight fraction HDPE are shown in Figure 5(a-d), respectively. The micrographs of Figure 5 show a very strong influence of HDPE on the average spherulite size in all blends. That is, PE serves to reduce the average spherulite size, probably acting as a nucleating agent for PP. Especially for the blend of EPB terpolymer and HDPE [Fig. 5(d)], the spherulite size is decreased most significantly compared with other blends. The reason that the appearance of small spherulite in EPB terpolymer-HDPE (75 : 25) blend is not known yet, however. The morphology of blends of 0.5 and 0.75 weight fractions of HDPE is similar, with the average diameter of the spherulites decreasing to less than 10 μm . The relation between spherulite size and mechanical properties is discussed in next section.

It is well-known that the morphology of the blends is greatly affected by the difference in the melt index. Figure 6 shows the melt index of the various PP-HDPE blends; we can see that the melt index is decreased almost linearly with HDPE content. The melt index of the blends of HDPE with EP random copolymer and EPB terpolymer is similar with blend compositions. Also, the melt index of the blends of HDPE with PP homopolymer and EP block copolymer is similar with compositions. In the present study, the morphology difference in the blend of HDPE and EPB terpolymer may be more influenced by the rubber characteristics of the EPB terpolymer than by the melt index difference of the blends.

It is important to note that the blended films were stretched at 200°C, which is above the melting temperature of the blends. However, in this case, unisotropic structure is not always expected in the stretched films.

Thermal Behavior

The melting behavior of PP homopolymer, EP random copolymer, EP block copolymer, and EPB terpolymer of the blends with 0.25 weight fraction HDPE are shown in Figure 7(a-d), respectively. Figure 7(e) shows the melting peak of the pure HDPE. From Figure 7(a-c), we can see that double melting peaks are observed in the blends of HDPE with PP homopolymer, EP random polymer, and EP block copolymer, respectively. The first melting peak is the HDPE and the second melting peak is

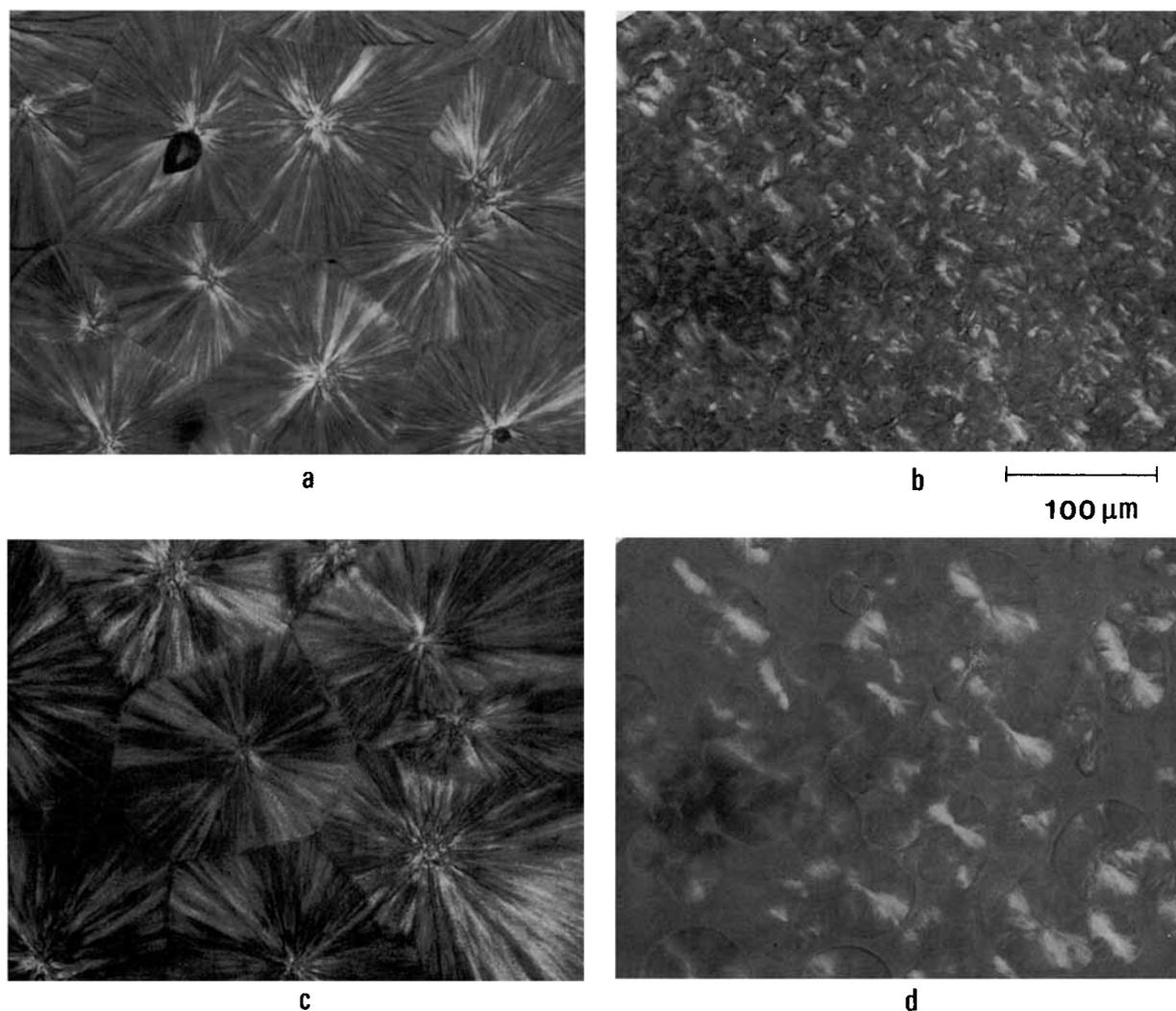


Figure 4 Morphologies of biaxially oriented films of various unblended polymers, as seen in the polarizing microscope: (a) PP homopolymer; (b) EP random copolymer; (c) EP block copolymer; (d) EPB terpolymer.

the various PP. For the blend of HDPE and EPB terpolymer, we can see the single melting peak in Figure 7(d). In this case, the two melting peaks are overlapped at about 130°C; it is difficult to measure the degree of crystallinity of the blends.

The effect of blend composition on the melting point of various PP are shown in Figure 8. We can see that no significant melting point depression of the various PP is observed. For the melting point of HDPE in the blends, no depression was observed, which indicates that PP phase and HDPE phase are immiscible in all blend compositions.

The crystallization behavior of PP homopolymer, EP random copolymer, EP block copolymer, and EPB terpolymer of the blends with 0.25 weight fraction HDPE are shown in Figure 9(a–d), respectively. Figure 9(e) shows the crystallization peak of the pure

HDPE. From Figure 9(b, d), we can see that double crystallization peaks are observed in the blends of HDPE with EP random polymer and EPB terpolymer, respectively. The first crystallization peak is the PP copolymer and the second peak is the HDPE. For the blend of HDPE with PP homopolymer and EPB terpolymer, we can see the single crystallization peak in Figure 9(a, c), respectively. In this case, the two crystallization peaks are overlapped at about 115°C.

The effect of blend composition on the crystallization temperature (T_c) of various PP are shown in Figure 10. We can see that the T_c is increased about 2–4 degrees for the blends of 0.25 weight fraction HDPE with PP homopolymer, EP random polymer, and EP block copolymer. For the blend of HDPE and EPB terpolymer, the T_c is increased

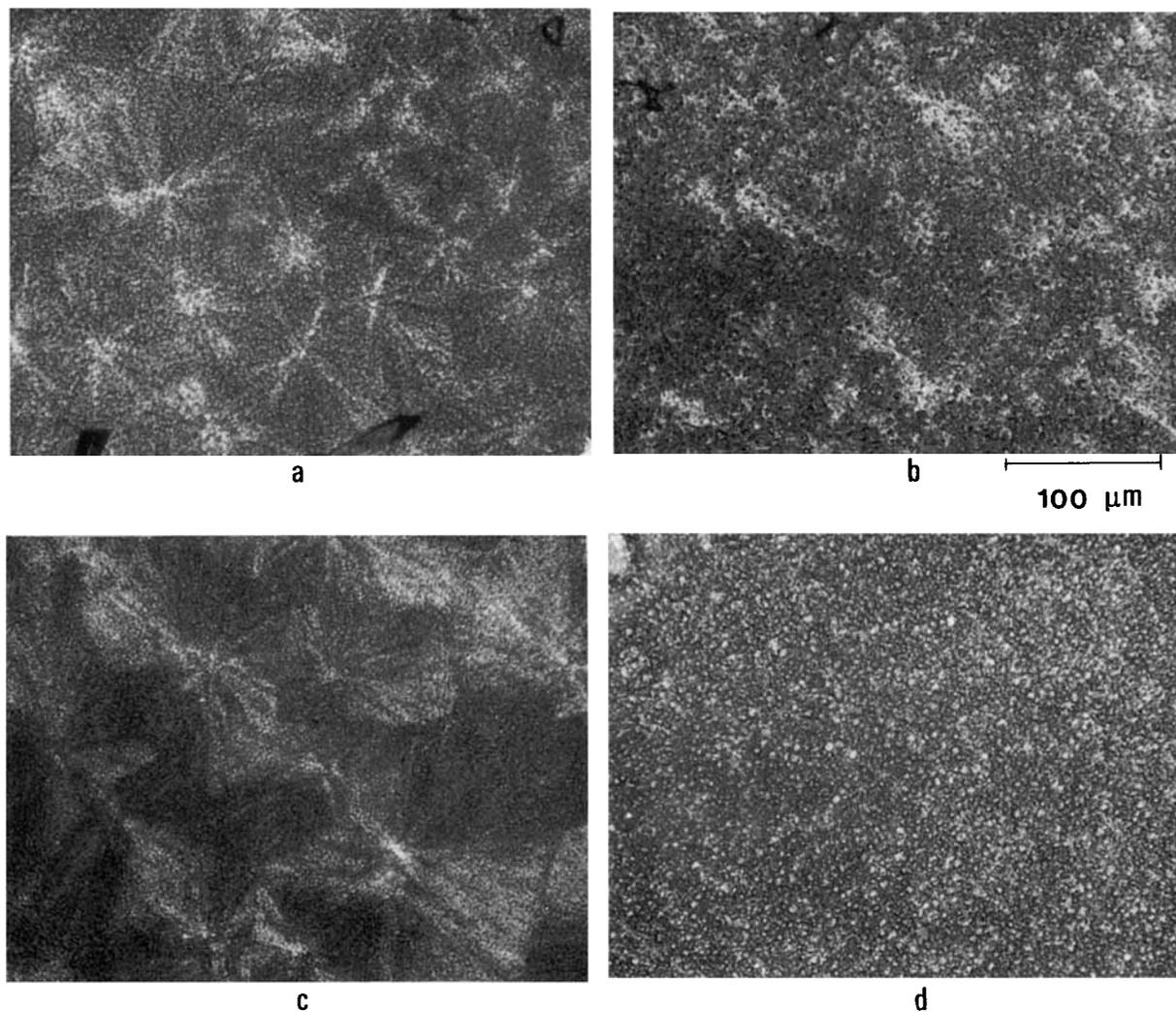


Figure 5 Morphologies of biaxially oriented films of various blends, as seen in the polarizing microscope: (a) PP homopolymer/HDPE (75 : 25); (b) EP random copolymer/HDPE (75 : 25); (c) EP block copolymer/HDPE (75 : 25); (d) EPB terpolymer/HDPE (75 : 25).

about 9 degrees. By the addition of HDPE into the EPB terpolymer, a fast crystallization occurred, compared with the unblended EPB terpolymer. The increase of T_c was found to be most significant in the blend of EPB terpolymer and HDPE, compared with the other blends.

Mechanical Properties

Tensile strength and modulus of biaxially oriented films of blends of PP homopolymer and PP copolymers with HDPE are shown in Figures 11 and 12, respectively. We can see that the tensile strength at break and tensile modulus (measured at 1% elongation) of blends of HDPE with PP homopolymer, EP random copolymer, and EP block copolymer are seen to decrease monotonically with increase of

HDPE content up to 0.5 weight fraction HDPE. For the blend of EPB terpolymer and HDPE, tensile strength and modulus are seen to increase almost linearly with increase of HDPE content up to 0.5 weight fraction HDPE.

We compared these tensile results with the morphology of blend samples. As we saw in Figure 5, the spherulite size of blend of EPB terpolymer and HDPE is smaller than that of blends of PP homopolymer, EP random copolymer, and EP block copolymer with HDPE. At this point, we should examine how this morphology might account for the mechanical behavior of blends of PP homopolymer and PP copolymers with HDPE.

Several investigators have shown that ultimate strength is improved with decreasing spherulite size, primarily because yielding and failure are commonly

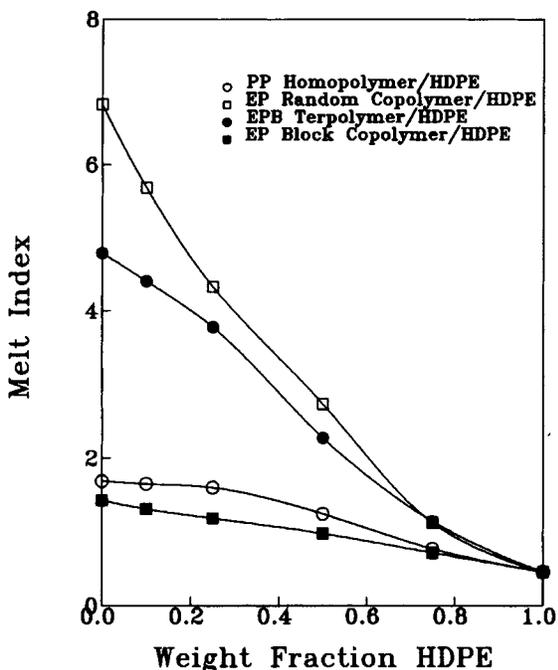


Figure 6 Effect of blend composition on the melt index of the blends of HDPE with PP homopolymer, EP random copolymer, EP block copolymer, and EPB terpolymer.

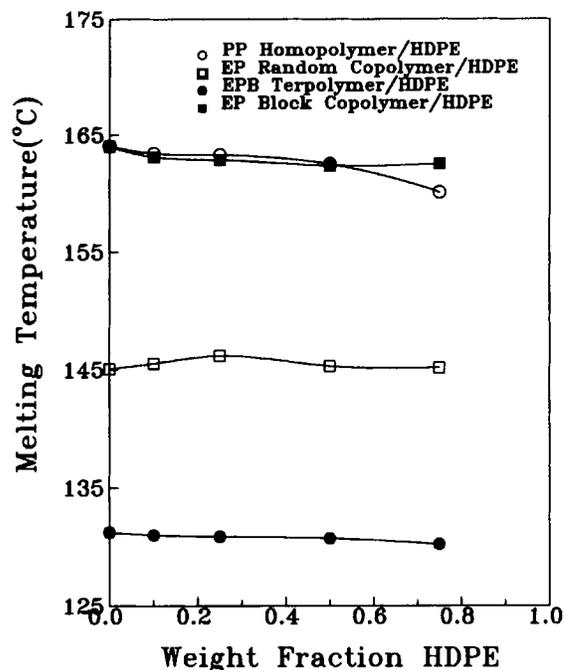


Figure 8 Effect of blend composition on the melting point of the PP homopolymer and PP copolymers blended with HDPE.

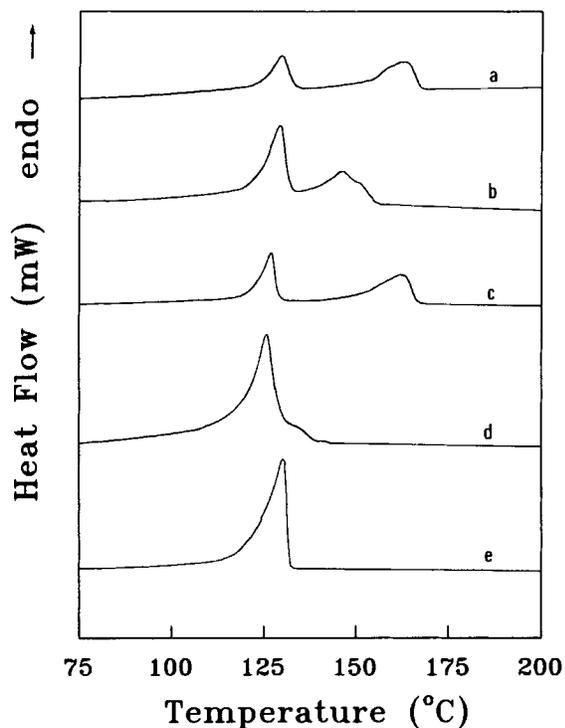


Figure 7 Thermograms showing the melting point of the PP homopolymer and PP copolymers blended with HDPE: (a) PP homopolymer; (b) EP random copolymer; (c) EP block copolymer; (d) EPB terpolymer; (e) HDPE homopolymer.

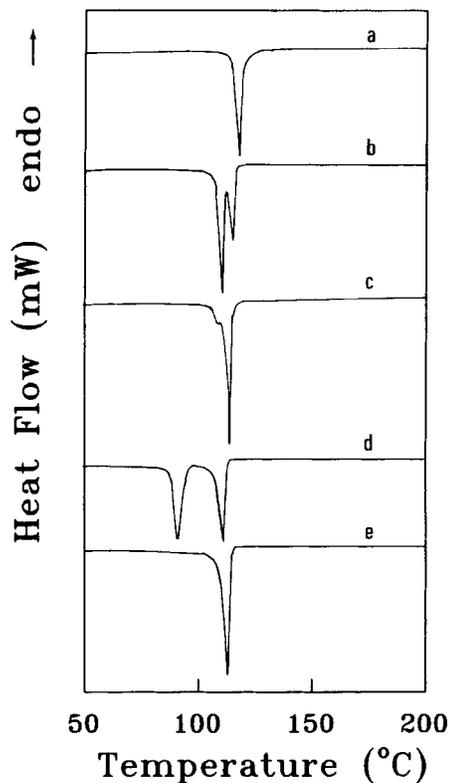


Figure 9 Thermograms showing the crystallization temperature of the PP homopolymer and PP copolymers blended with HDPE: (a) PP homopolymer; (b) EP random copolymer; (c) EP block copolymer; (d) EPB terpolymer; (e) HDPE homopolymer.

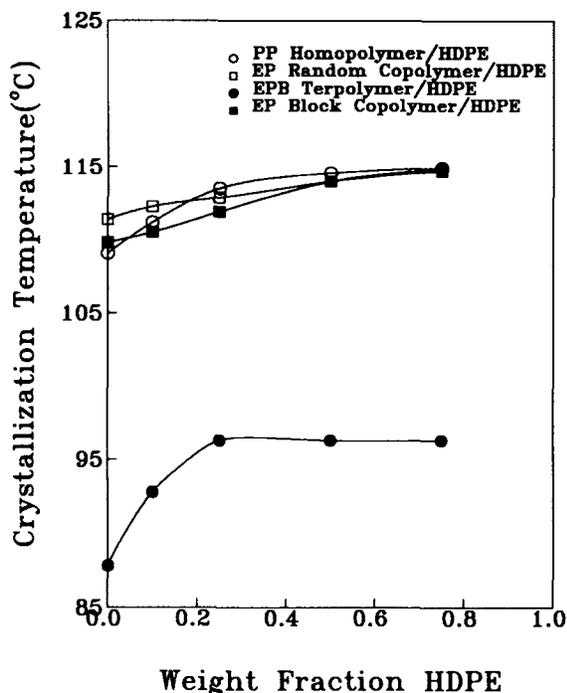


Figure 10 Effect of blend composition on the crystallization temperature of the PP homopolymer and PP copolymers blended with HDPE.

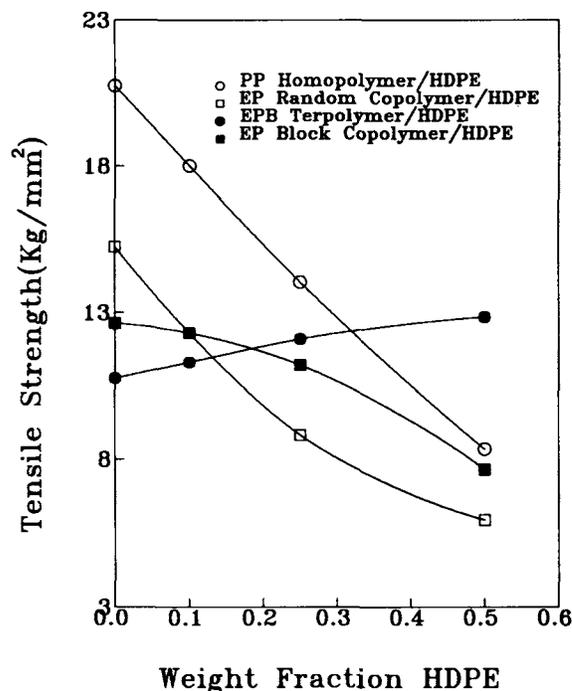


Figure 11 Effect of blend composition on the tensile strength of biaxially oriented films of the blends of HDPE with homopolymer, EP random copolymer, EP block copolymer, and EPB terpolymer.

initiated at interspherulitic boundaries.^{14,15} Some investigators have also shown that increases in overall crystallinity, by the addition of PE to PP, result in enhancement of modulus and possibly of strength.^{15,16} As regards tie molecules and inter-crystalline links, their role in transmitting stresses between lamellae, and thus increasing strength, has been described by Vadimsky and co-workers.¹⁷ Recently Heino and Seppala¹⁸ have studied the blends of thermotropic liquid crystalline polymer with several PP copolymers and have shown that a notable improvement in impact strength was achieved when a small amount of ethylene-based terpolymer was added as compatibilizer.

In this study, the average diameter of the spherulite of the unblended EPB terpolymer was 60–70 μm [Fig. 4(d)]. For the blend of EPB terpolymer and 0.25 weight fraction HDPE, the average diameter of the spherulite of the mixture is 5–10 μm [Fig. 5(d)]. For the blends of EPB terpolymer with 0.50 and 0.75 weight fractions HDPE, the average diameter of the spherulite was similar with the blends of EPB terpolymer and 0.25 weight fraction HDPE.

For the blends of PP homopolymer, EP random copolymer, and EP block copolymer with 0.25 weight fraction HDPE, the average diameter of the spherulite of the mixture [Fig. 5(a–c)] is about 50–100 μm and not greatly changed compared with the un-

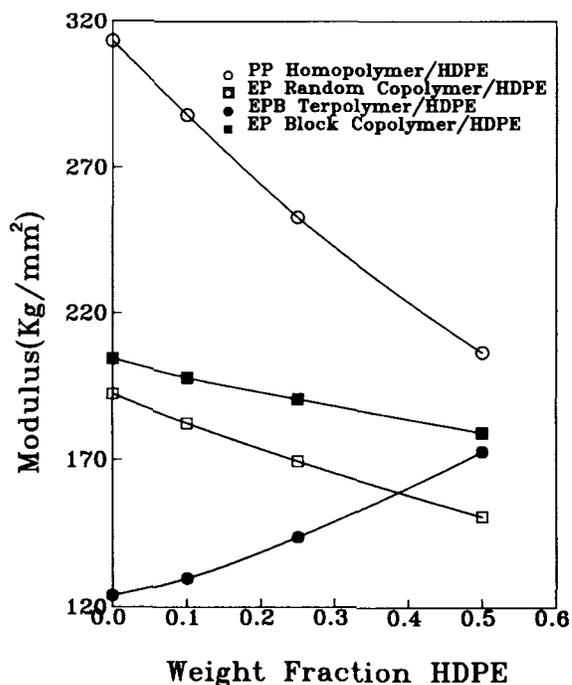


Figure 12 Effect of blend composition on the tensile modulus of biaxially oriented films of the blends of HDPE with homopolymer, EP random copolymer, EP block copolymer, and EPB terpolymer.

blended various PP [Fig. 4(a-c)]. In the present study of tensile strength and modulus and the result of spherulite size with blends of HDPE with PP homopolymers, EP random copolymer, EP block copolymer, and EPB terpolymer, it is observed that the morphological effect, such as spherulite size, may be correlated with the tensile properties.

CONCLUSIONS

In the SEM study of blends of HDPE with PP homopolymer, EP random polymer, EP block polymer, and EPB terpolymer, phase separation was observed between the PP-rich phase and the HDPE-rich phase for all blends and compositions. There are indications in all blends of adhesion between the two phases, however.

In the study of morphology by polarized microscopy, HDPE serves to reduce the average spherulite size in the blends of HDPE with PP homopolymer and various PP copolymers. The reduction of spherulite size was observed to be most significant in the blend of EPB terpolymer and HDPE.

In the study of the crystallization temperature of the various blends with composition, a fast crystallization of EPB terpolymer occurred in the blend of EPB terpolymer and HDPE, compared with the unblended EPB terpolymer. The increase of T_c was found to be most significant in the blend of EPB terpolymer and HDPE.

For the blends of HDPE with PP homopolymer, EP random polymer, and EP block copolymer, the mechanical properties (such as tensile strength and modulus) were decreased with increase of HDPE content. For the blend of HDPE and EPB terpolymer, the tensile strength and modulus were increased with increase of HDPE content up to 0.5 weight fraction. In the study of tensile strength and modulus and the result of spherulite size with blends of HDPE with PP homopolymer, EP random copolymer, EP block copolymer, and EPB terpolymer,

the morphological effect (such as spherulite size) may be correlated with the tensile properties.

REFERENCES

1. A. P. Plochocki, in *Polymer Blends*, Chap. 21, D. R. Paul and S. Newman, Eds., Academic Press, New York, 1978.
2. A. J. Lovinger and M. L. Williams, *J. Appl. Polym. Sci.*, **25**, 1703 (1980).
3. R. Greco, C. Mancarella, E. Martuscelli, G. Ragosta, and Y. Jinghua, *Polymer*, **28**, 1922 (1987).
4. V. Choudhary, H. S. Varma, and I. K. Varma, *Polymer*, **32**, 2541 (1991).
5. G. A. Gallagher, R. Jakeways, and I. M. Ward, *J. Appl. Polym. Sci.*, **43**, 1399 (1991).
6. R. A. Varin and D. Djokovic, *Polym. Eng. Sci.*, **28**, 1477 (1988).
7. V. Flaris and Z. H. Stachurski, *J. Appl. Polym. Sci.*, **45**, 1789 (1992).
8. C. S. Ha and S. C. Kim, *J. Appl. Polym. Sci.*, **37**, 317 (1989).
9. J.-O. Lee, B.-K. Kim, C.-S. Ha, K.-W. Song, J.-K. Lee, and W.-J. Cho, *Polymer (Korea)*, **18**, 68 (1994).
10. Q. Du and L. Wang, *J. Polym. Sci., Polym. Phys. Ed.*, **27**, 581 (1989).
11. G. L. Slonimskii, I. N. Mysayelyan, V. V. Kazantseva, and B. M. Ozerov, *Polym. Sci. USSR*, **6**, 900 (1964).
12. O. F. Noel and J. F. Carley, *Polym. Eng. Sci.*, **15**, 117 (1975).
13. W. N. Kim, C. E. Park, and C. M. Burns, *J. Appl. Polym. Sci.*, **49**, 1003 (1993).
14. C. J. Kuhre, M. Wales, and M. E. Doyle, *SPE J.*, **20**, 1113 (1964).
15. J. L. Way and J. R. Atkinson, *J. Mater. Sci.*, **7**, 1345 (1972).
16. P. J. Phillips and J. Patel, *Polym. Eng. Sci.*, **18**, 943 (1978).
17. R. G. Vadimsky, H. D. Keith, and F. J. Padden, Jr., *J. Polym. Sci.*, **7**, 1367 (1969).
18. M. T. Heino and J. V. Seppala, *J. Appl. Polym. Sci.*, **48**, 1677 (1993).

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