

Cocrystallization and Miscibility Studies of Blends of Ultrahigh Molecular Weight Polyethylene with Conventional Polyethylenes

THEIN KYU and PARIMAL VADHAR*, *Center for Polymer Engineering, University of Akron, Akron, Ohio 44325*

Synopsis

Ultrahigh molecular weight polyethylene (UHMWPE) was mechanically mixed with conventional polyethylenes (LLDPE, HDPE, and LDPE) using an internal mixer. Rheological studies of these blends suggest that UHMWPE seems to be miscible with LLDPE, HDPE, and LDPE in the melt state. Yield characteristics are observed in all blend systems, particularly in high UHMWPE blend compositions. Differential scanning calorimetry and small-angle light scattering studies show that cocrystallization takes place in the blends of UHMWPE/LLDPE and UHMWPE/HDPE blends. However, separate crystals are formed in UHMWPE/LDPE. The formation of separate crystals may be attributed to long chain branching of conventional low-density polyethylene. Tensile properties of the former two blends vary almost linearly with blend compositions, while deviations are seen in the latter UHMWPE/LDPE blends.

INTRODUCTION

In recent years, ultrahigh molecular weight polyethylene (UHMWPE) has received considerable attention in both academia and industries for its potential industrial applications.^{1,2} It has been possible to prepare ultrahigh strength and ultrahigh modulus fibers with this material. This achievement can largely be attributed to the development of gel-spinning technique in which UHMWPE fibers are spun in the presence of selective solvents³⁻⁵ or paraffin oils.⁶ A similar achievement has been obtained by drawing gel films or single crystal mats.⁸⁻¹¹ The low molecular weight species perhaps separate macromolecules and reduce the complex chain entanglements during gel-spinning, eventually leading to ultrahigh molecular orientation in the fibers. The ultrahigh orientation and extremely high crystallinity yield the highest number of covalent bonds per unit volume with minimal defects.⁵ This situation, as has been predicted by Flory,¹² naturally gives ultrahigh strength and ultrahigh modulus approaching the theoretical values.

Because of its extremely high molecular weight (normally a few millions average molecular weight), the melt viscosity of UHMWPE is extremely high.¹³ This factor imposes a considerable hindrance on polymer processings; thus its application is limited to compression molding. Recently the blending of crystallizable polymers, in particular polyolefin blends, has gained considerable technological significance.¹⁴ According to Speed,¹⁵ the addition of conven-

*Present address: Signode Corp., Engineering Research, 3650 W. Lake Ave., Glenview, Illinois 60025.

tional low-density polyethylene (LDPE) to linear low-density polyethylene (LLDPE) has improved the bubble stability of tubular extrusion blowing and optical clarity. The toughness of LDPE can be enhanced by an addition of LLDPE. There are numerous articles in the literature and patents in polyolefin blends as reviewed by Plochocki.¹⁴ The extent to which such blends have been commercially implemented is difficult to document. Examples of some of the claimed benefits include improved impact strength, optical clarity, environmental stress-cracking resistance, resistance to thermal embrittlement, and enhanced crystallization rate.

As for the UHMWPE blends with conventional polyethylenes, there are a limited number of publications available in the literature.^{16,17} A study of this kind is due to Dumoulin et al.,¹⁶ who investigated the properties of UHMWPE blends at the UHMWPE content less than 6%. The primary reason for this is associated with the ultrahigh melt viscosity of the material, which restricts polymer processibility by conventional techniques.

In this study, various blends of UHMWPE with conventional polyethylenes, including linear low-density, conventional low-density, and high-density polyethylenes, are prepared by solvent and mechanical mixing techniques. As has been reported in a previous article,¹⁷ the mixing condition exerts profound effects on the properties of the well-mixed UHMWPE/LLDPE blends, based on rheology, mechanical, and morphological characterization methods. Hence, we only compare the properties of the well-mixed UHMWPE/LLDPE, UHMWPE/HDPE, and UHMWPE/LDPE blends.

EXPERIMENTAL

The UHMWPE material used in this study is UHMWPE 1900 supplied by Hercules Inc. The average molecular weight is estimated to be approximately 5×10^6 . The degree of chain branching as suggested by nuclear magnetic resonance study is less than 0.1 methylene unit per 1000 carbons. There is no other detectable long or short chain branching. Conventional polyethylenes are supplied by various companies. LLDPE (Union Carbide, GRSN-7047) having an average molecular weight $M_w = 135,000$ and $M_w/M_n \cong 4.0$, HDPE (Chemplex 6186) with $M_w = 134,800$ and $M_w/M_n \cong 7.4$, and LDPE (BP Chemicals) with $M_w = 114,000$ and $M_w/M_n \cong 5.2$ were used. The LLDPE is a copolymer of ethylene and butene-1 with no detectable long chain branching. The density of LLDPE is somewhat close to that of branched LDPE, but it has a comparable molecular weight with that of HDPE. However, there are 18 $\text{CH}_3/1000\text{C}$ short chain branches in LLDPE.

Various blends of UHMWPE with conventional polyethylenes (LLDPE, HDPE, and LDPE) were prepared in an internal mixer (Haake Rheocord). In a previous study¹⁷ we realized that a sequential loading technique gave better mixes. In that preparation method, UHMWPE was first loaded and nicely fused at 250°C for 4 min in the rotating mixer, and then quickly cooled down to 180°C by passing nitrogen gas. The second desired component was charged subsequently and mixed for about 10 min. The rotor speed was operated initially at 5 rpm, but was gradually raised to 50 rpm. The mixing was carried out under nitrogen gas environment. Other mixing conditions and mixing techniques, including solvent mixing and mechanical mixing with a static

mixer, were also conducted. However, we report only on the well-mixed polyethylene blends described above.

For rheological measurements, tiny crushed blend samples were used. These crushed samples were further compression-modeled into sheet forms in a laboratory hot press at 180°C and at elevated pressure for 10 min. The specimens were quenched in ice water. These sheet samples were cut into dumbbell shape for mechanical testing. Thin sheet samples were prepared for morphological characterization studies.

Rheological experiments were carried out on an Instron Capillary Rheometer using three dies of diameter $D = 0.058$ in. (1.47 mm) and length-to-diameter (L/D) ratios of 29.4, 18.6, and 9.6. These dies were of flat entrance type. The viscosity was measured at various temperatures and shear rates. However, the viscosity results are compared at 225°C as a function of various blend compositions. Tensile properties were measured on a Monsanto tensile tester (Tensometer 500) at room temperature with a crosshead speed of 5 cm/min.

Small-angle light scattering studies were carried out by a photographic method under cross-polarization (H_v scattering, i.e., polarization direction is vertical with an analyzer in horizontal direction) and parallel polarization V_v (both polarization and analyzer are vertical). A 2 mW He-Ne laser of wavelength 6328 Å was used. DSC scans were performed on a DSC apparatus (DuPont 9900) at a rate of 10°C/min, unless otherwise indicated.

RESULTS

In Figure 1 are shown the variations of the true shear viscosity as a function of the true shear rate for various compositions of the three blend systems UHMWPE/LLDPE, UHMWPE/HDPE, and UHMWPE/LDPE. The viscosity of pure conventional polyethylene increases monotonically with decreasing shear rate. The rate of viscosity increase becomes more pronounced with increasing UHMWPE component. The viscosity of pure UHMWPE cannot be determined because the extrusion is extremely unstable and melt fracture often takes place. The true shear viscosity is plotted against the true shear stress in Figure 2. The viscosity increases dramatically with decreasing

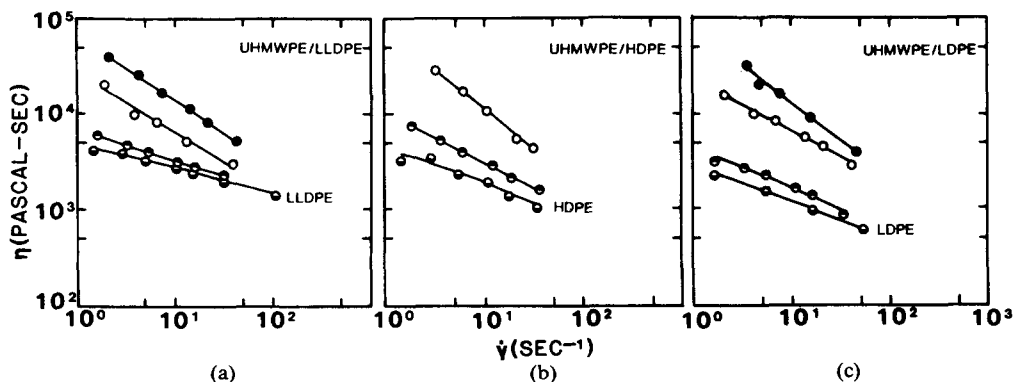


Fig. 1. The true shear viscosity as a function of shear rate for various blends of ultrahigh molecular weight polyethylene with (a) linear low-density, (b) high-density, and (c) conventional low-density polyethylenes: (●) 80/20; (○) 50/50; (◐) 20/80.

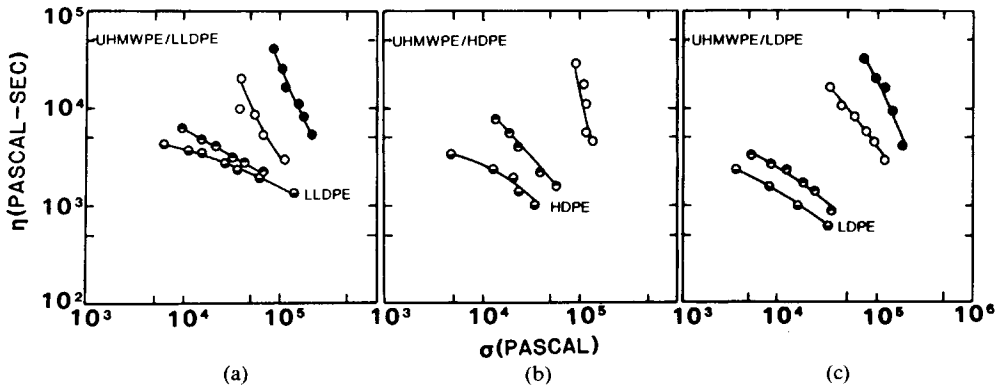


Fig. 2. The true shear viscosity as a function of shear stress for the blends of ultrahigh molecular weight polyethylene with (a) linear low-density, (b) high-density, and (c) conventional low-density polyethylenes: (●) 80/20; (○) 50/50; (◐) 20/80.

shear stress, in particular with the higher UHMWPE compositions, showing yield phenomenon. This phenomenon is often observed in particle-filled plastics,¹⁸ thermotropic liquid crystals,^{19,20} and other thermoplastic blends.^{21,22}

Figure 3 shows the plots of the true shear viscosity as a function of blend compositions for the three blends. The shear viscosity increases more or less linearly with the compositions. The additivity rule of logarithmic viscosity vs. compositions has been frequently observed in the compatible polymer blends.^{23,24} However, it is generally difficult to predict the polymer compatibility from the viscosity results alone. The similarity of the viscosity composition for the three blend systems is perhaps very interesting, suggesting that UHMWPE may be compatible with the conventional polyethylene in the melt state.

Figure 4 illustrates the fusion endotherms of various blend compositions. In both UHMWPE/LLDPE and UHMWPE/HDPE systems, only a single peak

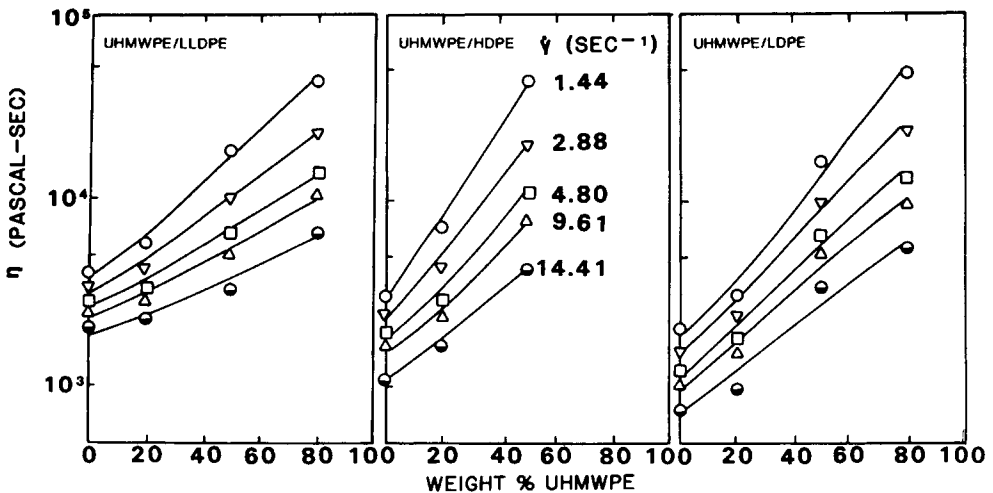


Fig. 3. The true shear viscosity versus the percent weight fraction of ultrahigh molecular weight polyethylenes at various true shear rates for the blends of: (a) UHMWPE/LLDPE; (b) UHMWPE/HDPE; (c) UHMWPE/LDPE.

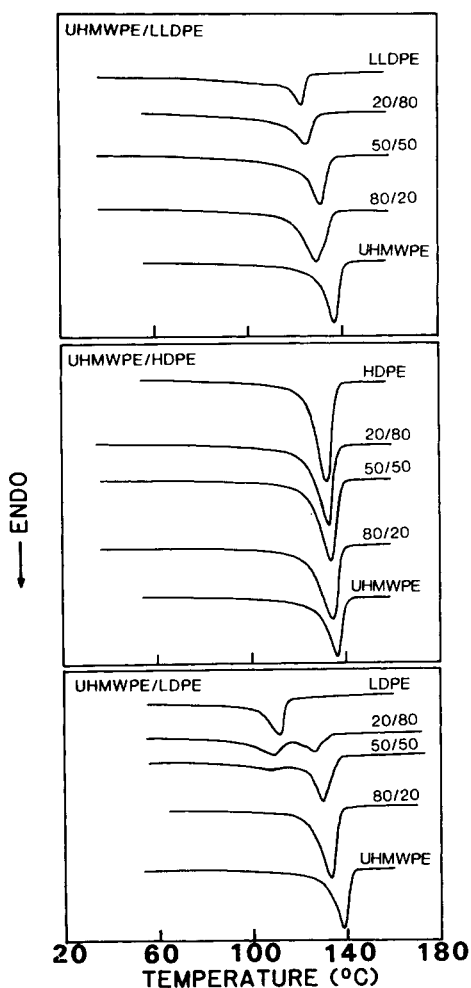


Fig. 4. The fusion endotherms of various blends of: (a) UHMWPE/LLDPE; (b) UHMWPE/HDPE; (c) UHMWPE/LDPE. The heating rate is 10°C.

appears in the intermediate blends, which moves systematically with the composition. While the endothermic peaks of UHMWPE and LLDPE are separated by about 10°C, the peaks are in close proximity in the UHMWPE/HDPE system. In such cases, the analysis on the melting temperature is inadequate. Another parameter which may be sensitive to such situations is the half-width. One can expect to have a larger half-width if the two components form separate crystals, although the peaks may be located in close proximity. However, the half-width of intermediate blends is not necessarily greater than the pure components. This implies that separate crystals are not formed in UHMWPE/LLDPE and UHMWPE/HDPE.

On the contrary, two endothermic peaks are discernible in the UHMWPE/LDPE blends. The peak position of the LDPE appears to remain invariant while the magnitude decreases significantly with decreasing LDPE compositions. The melting endotherm of UHMWPE is dominant over that of

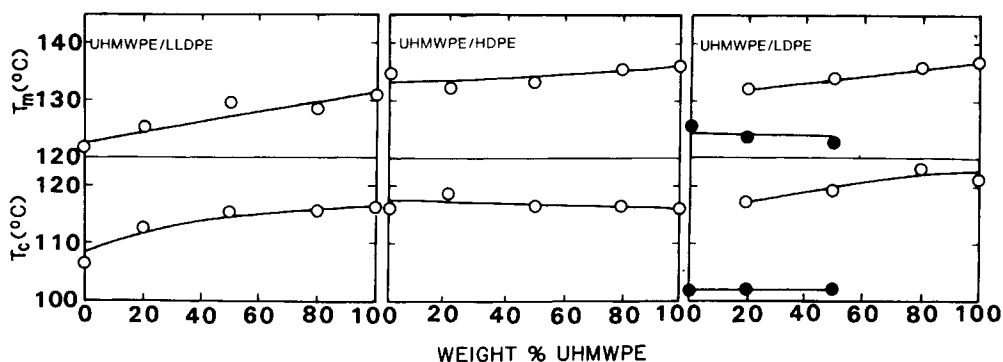


Fig. 5. The melting (T_m) and crystallization temperature (T_c) as a function of blend compositions of: (a) UHMWPE/LLDPE; (b) UHMWPE/HDPE; (c) UHMWPE/LDPE. The heating and cooling rates are 10°C .

LDPE in the 50/50 blend so that the endotherm of LDPE is barely detectible and virtually diminishes in the 80/20 compositions. The peak position of UHMWPE, however, shifts to lower temperature with increasing LDPE components. These melting results are in close agreement with those obtained by Smith and Manley²⁵ for mixtures of polyethylenes fractions, Donatelli's results²⁶ of LDPE/HDPE, and Kyu et al.'s results²⁷ of LLDPE/LDPE blends, where separate crystals are formed between the components during crystallization.

In the cooling runs, a single exotherm is observed in the former two blend systems whereas two exotherms are evident in the latter blend systems. These results are consistent with the heating runs. The melting and crystallization temperatures are plotted as a function of blend compositions in Figure 5. The linear variations of the T_m and T_c with composition can be seen clearly in UHMWPE/LLDPE and UHMWPE/HDPE. In the case of UHMWPE/LDPE blends, both the T_m and T_c of LDPE component are fairly invariant with the composition. However, the melting as well as crystallization temperatures of the UHMWPE decrease with the addition of LDPE component.

In Figure 6 are shown the depolarized light scattering Hv patterns of the three-blend system obtained under cross-polarization conditions. Typical four-lobe scattering patterns²⁸ characteristics of spherulite structures are observed in the UHMWPE/LLDPE and UHMWPE/HDPE blend systems. However, the dual scattering patterns are seen in the case of UHMWPE/LDPE blends. When the UHMWPE/LDPE 20/80 blend is heated, the outer lobe disappears at the melting temperature of LDPE crystals, and the inner cross pattern fades away when the temperature approaches the T_m of UHMWPE. These dual scattering patterns suggest that separate spherulites are formed between the UHMWPE and LDPE components. Strictly speaking, the inner scattering pattern is not a typical spherulitic scattering; it is rather reminiscent of those of incomplete spherulitic scattering (such as rods or sheaf) or highly disordered spherulites.^{29,30} Nevertheless, the important conclusion is that separate crystals or separate superstructures are formed between the UHMWPE and LDPE components.

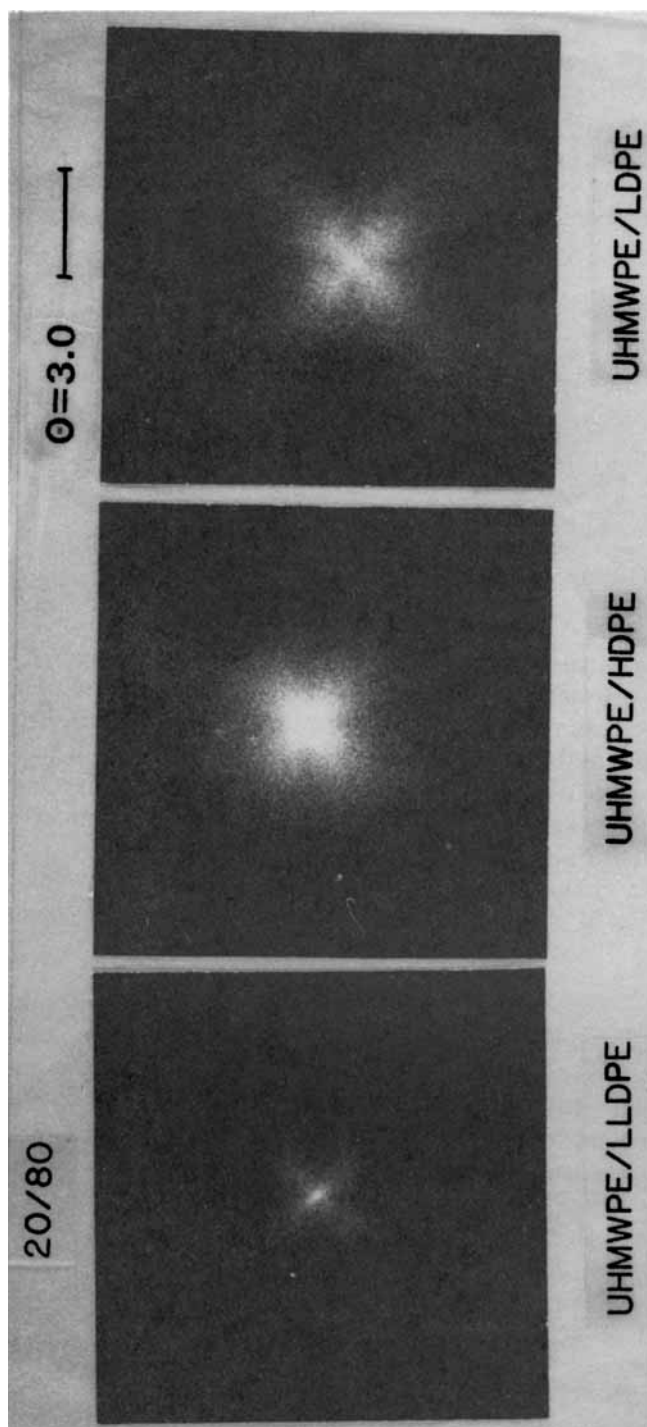


Fig. 6. The depolarized light scattering patterns under Hv crosspolarization conditions for 20/80 blend compositions of UHMWPE/LLDPE, UHMWPE/HDPE, and UHMWPE/LDPE.

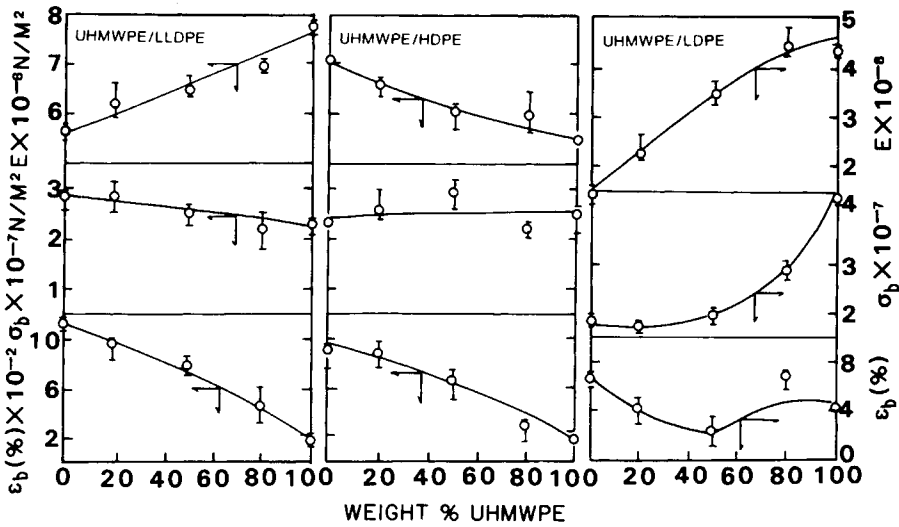


Fig. 7. The tensile modulus, strength at break and elongation at break as a function of blend compositions of: (a) UHMWPE/LLDPE; (b) UHMWPE/HDPE; (c) UHMWPE/LDPE.

The tensile properties of the three blends are compared in Figure 7 in which the moduli, the strength at break, and the elongation at break are plotted as a function of blend compositions. The moduli-composition curves are fairly linear for all blend systems. It suggests that the tensile modulus may not be a sensitive parameter to predict the compatibility of the blends. The strength and elongation at break vary more or less linearly with the composition of the UHMWPE/LLDPE and UHMWPE/HDPE systems. However, negative deviations are seen in the case of UHMWPE/LDPE which are reminiscent of the characteristics of incompatible polyethylene/polypropylene blends.³¹

DISCUSSION

Polymer miscibility³² is generally referred to the amorphous states as opposed to that of metal alloys where the miscibility is applied to mix atomic crystals. Crystalline polymer blends consist of both amorphous and crystalline regions in pure components. Therefore, the miscibility studies of crystalline polymer blends are generally very complex and require analysis in both melt and solid states. Miscibility may be used in the melt state while cocrystallization (mix crystal formation) may be applied in the solid state.

The investigation of melt viscosity has been widely used to predict the miscibility of polymer blends. In the miscible polymer blends, the additivity scheme of $\log \eta$ vs. composition has been frequently used.^{23,24} Both positive and/or negative deviations are seen in most blends; thus it is often difficult to determine the miscibility between the components. The present rheological results are not an exception; the conclusion may be tentative. Due to the great similarity of rheological results among the three blend systems (as shown in Figs. 1-3) and little or no deviation from the log-linear additivity rule, it is reasonable to conclude, at least tentatively, that UHMWPE may be miscible

with the conventional polyethylenes in the melt state. This result is similar to that of LLDPE/LDPE blends obtained by Bader and Chung.²⁴ It may be interesting to investigate the miscibility between various polyethylene blends by neutron scattering technique.³³ However, it is beyond the scope of this study.

In the DSC studies, we observed the contrasting results between the blends of UHMWPE with conventional polyethylenes, i.e., LLDPE, HDPE, and LDPE. Cocrystallization takes place in the former two blends while separate crystals are formed in the latter blend. This may be attributed to differences in chain linearity where the former two systems are essentially linear while the latter is of branched type. The slight movement of the T_m and T_c of the UHMWPE component in the UHMWPE/LDPE blends in Figure 6(c) may be a consequence of melting temperature depression, which has been commonly observed in other crystallizable blend systems. On the basis of Flory-Huggin theory,³⁴ the melting temperature depression results are further analyzed to determine the interaction parameter between the dissimilar chains. In the present case, such analysis is not attempted because the interaction parameter for similar polyethylene chains may be close to zero.

The light scattering results strongly suggest that separate crystals as well as separate superstructures are formed between UHMWPE and LDPE. In a recent study by Kyu et al.,²⁷ crystallization takes place separately in the LLDPE/LDPE blends; however, the LDPE component crystallizes within the preformed LLDPE spherulites. This suggests that the crystallization of the blends should be studied at different structural levels. The observation of a single four-lobe Hv pattern in the UHMWPE/LLDPE and UHMWPE/HDPE may not be an adequate proof of cocrystallization. However, according to a previous study,¹⁷ poorly mixed UHMWPE/LLDPE and UHMWPE/HDPE blends indeed show dual scattering patterns.

According to the studies of Paul and Robertson³¹ negative deviations are generally seen in tensile strength and elongation at break vs. composition curves of immiscible HDPE/PP blends. The modulus, however, varies more or less linearly with the composition regardless of the miscibility between the components. This kind of negative deviation is also observed in the poorly mixed blends of UHMWPE/LLDPE, UHMWPE/HDPE, and UHMWPE/LDPE. The validity of the linear additivity rule in the tensile properties vs. composition may be associated with the formation of cocrystals between UHMWPE and linear polyethylene. However, in the blends of UHMWPE/branched LDPE where separate crystals are formed, the tensile properties deviate from the simple additivity rule.

The present study is consistent with the studies of Kyu, Hu, and Stein,²⁷ who found that cocrystallization takes place between LLDPE and HDPE, whereas separate crystals are formed in the LLDPE/LDPE blends. The general conclusion may be drawn from those studies that mixtures of linear and linear polyethylene chains have an ability to cocrystallize together while blends of linear and branched polyethylenes tend to form separate crystals. It should be very interesting to investigate the effect of chain branching on the cocrystallization and miscibility of polyethylene blends using well-controlled side chain branches. This will be the subject of future study.

References

1. A. Ciferri and I. M. Ward, Eds., *Ultrahigh Modulus Polymers*, Applied Science, Basing, Essex, U.K., 1979.
2. A. E. Zachariades and R. S. Porter, Eds. *The Strength and Stiffness of Polymers*, Dekker, New York, 1983.
3. P. Smith and P. J. Lemstra, *J. Mater. Sci.*, **15**, 505 (1980).
4. J. Boer, H. J. van den Berg, and A. J. Pennings, *Polymer*, **25**, 513 (1984).
5. J. Smook and A. J. Pennings, *J. Mater. Sci.*, **19**, 31 (1984).
6. S. Kavesh and D. C. Provorsek, U.S. Pat. 4,413,110 (1983).
7. M. Matsuo and R. St. J. Manley, *Macromolecules*, **15**, 985 (1982).
8. A. E. Zachariades and J. Logan, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 821 (1983).
9. T. Kanamoto, A. Tsuruta, K. Tanaka, T. Takeda, and R. S. Porter, *Polym. J.*, **15**, 327 (1983).
10. K. Furuhashi, T. Yokokawa, and K. Miyasaka, *J. Polym. Sci. Polym. Phys. Ed.*, **22**, 133 (1984).
11. K. Miyasaka, Proceedings of the International Symposium on Fiber Science and Technology, August 1985, Hakone, Japan, p. 27.
12. P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949)
13. A. E. Zachariades and T. Kanamoto, AIChE Annual Meeting Symposium, November 25-30, 1984.
14. A. Plochocki, in *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic, New York, 1978, p. 319.
15. A. S. Speed, *Plast. Eng.*, (Jul.), 39 (1982).
16. M. M. Dumoulin, L. A. Utracki, and J. Lara, *Polym. Eng. Sci.*, **24**, 117 (1984).
17. T. Kyu and P. Vadhar, *Polym. Eng. Sci.*, in press.
18. Y. Suetsugu and J. L. White, *J. Appl. Polym. Sci.*, **28**, 1481 (1983).
19. K. F. Wissbrun, *J. Rheol.*, **25**, 619 (1981).
20. H. Sugiyama, D. N. Lewis, J. L. White, and J. F. Fellers, *J. Appl. Polym. Sci.*, **30**, 2329 (1985).
21. C. D. Han and T. C. Yu, *J. Appl. Polym. Sci.*, **15**, 1163 (1971).
22. C. D. Han and Y. W. Kim, *J. Appl. Polym. Sci.*, **19**, 2831 (1975).
23. V. N. Kuleznev, I. V. Konyuk, G. V. Vinogradov, and I. D. Dmitrieva, *Kolloid Z.*, **27**, 540 (1965).
24. M. K. Bader and C. I. Chung, *Soc. Plast. Eng. 43rd, ANTEC*, 918 (1985).
25. P. Smith and R. St. J. Manley, *Macromolecules*, **12**, 483 (1979).
26. A. Donatelli, *J. Appl. Polym. Sci.*, **23**, 3071 (1979).
27. T. Kyu, S. R. Hu, and R. S. Stein, *J. Polym. Sci. Polym. Phys. Ed.*, in press.
28. R. S. Stein and M. V. Rhodes, *J. Polym. Sci. A-2*, **8**, 489 (1970).
29. W. Chu and R. S. Stein, *J. Polym. Sci., A-2*, **8**, 489 (1970).
30. T. Hashimoto, Y. Murakami, N. Hayashi, and H. Kawai, *Polym. J.*, **6**, 132 (1974).
31. D. R. Paul and R. E. Robertson, *J. Appl. Polym. Sci.*, **17**, 2579 (1973).
32. O. Olabisi, L. M. Robeson, and M. T. Shaw, *Polymer-Polymer Miscibility*, Academic, New York, 1979.
33. J. S. Higgins and R. S. Stein, *J. Appl. Crystallogr.*, **11**, 346 (1978).
34. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, NY, 1955.

Received January 17, 1986

Accepted February 10, 1986