

Polypropylene / Ethylene-Propylene 공중합체 Blend : Rheology, Morphology, 열적, 기계적 성질

김 병 규 · 김 면 수 · 김 국 중* · 하 만 호*
부산대학교 고분자공학과 · *대한유화(주) 연구개발실
(1988년 11월 7일 접수)

Polypropylene/Ethylene-Propylene Copolymer Blends : Rheology, Morphology, Thermal and Mechanical Properties

Byung Kyu Kim, Myun Soo Kim, Kook Choong Kim*, and Man Ho Ha*
Dept. of Polymer Science & Engineering, Pusan National University, Pusan 609-735, Korea
**R & D Division, Daehan Petrochemical Co. Ltd., Ulsan, Korea*
(Received November 7, 1988)

요약 : isotactic PP와, ethylene 대 propylene의 중량조성이 50:50인 랜덤 공중합체 EPM을 용융블렌딩하여 얻어진 blend물에 대하여 RDS(Rheometrics Dynamic Spectrometer), DSC 및 Instron을 이용하여 유성학적, 열적, 기계적 성질을 각각 측정하였다. 또한 사출시편을 액체질소 온도에서 파괴, 파단면의 SEM 사진으로 부터 blend물의 morphology를 관찰하였다. 그러나 본 연구에서는 iPP/EPM blend물의 유성학적 특성을 중점적으로 검토하였으며, 아울러 blend 조성과 유성학적 거동이 blend물의 morphology, 기계적 및 열적 성질에 미치는 영향을 검토하였다.

Abstract : Melt blends of isotactic polypropylene with ethylene(50)-propylene(50) random copolymer have been studied. Measurements included rheological properties from a capillary rheometer and RDS, thermal properties from differential scanning calorimetry, and mechanical properties from Instron. Morphology was determined from cryogenically fractured surfaces of injection molded tensile specimen using a scanning electron microscopy. With an emphasis on rheology measurement, this paper considers the effects of composition ratio and melt property on the microstructure, mechanical and thermal properties of the blends.

INTRODUCTION

Blends of isotactic polypropylene with elastomeric impact modifier are gaining increasing demands beyond the conventional applications of high

impact polypropylene. Among many of thermo-plastic elastomers, those prepared from isotactic polypropylene and ethylene-propylene copolymer (EPM) are nowadays industrially important over the full range of their composition.¹

PP/EPM blends are generally incompatible, and therefore phenomena such as segregation, stratification and phase inversion are to be expected as in other two phase polymer systems.¹⁻⁵ Earlier works in this area mainly devoted to macroscopic properties. Morphology and structure of the blends were also studied fairly extensively in terms of elastomer particle size and its distribution, and also from the crystal structure of PP.^{1,4} Besides the high impact strength especially at low temperature, easy processing is also of prime importance for thermoplastic elastomers. However works on melt properties are sparse.

This paper primarily considers the rheological behavior of iPP/EPM blends. In addition, an attempt was also made to interpret the mechanical and thermal properties in terms of composition ratio and melt property.

EXPERIMENTALS

Polymers used in the present study were the commercially available extension grade of iPP (Deahan Petrochemicals, 4017 grade) and EPM (ethylene/propylene=50/50 random copolymer). Blends were prepared by melt blending in a twin screw compounding machine with $L/D=30$, using a temperature profile 210, 220, 230, 220°C of first, second, third, and the die zones, respectively at screw speed 30 rpm, which approximately corresponds to shear rate of 200 1/s.

Blending was carried out in two stages, i.e., master pellet of iPP 50/EPM50 was first prepared, and the desired composition was obtained from dilution of the master pellet with iPP. For iPP40/EPM60 blend, extra EPM was added at the second stage of the blending. The iPP homopolymer and iPP50/EPM50 blend received the same thermal and shear histories with those of other blend samples.

Rheological properties were measured from a capillary-type rheometer ($L/D=40$, $D=1.0$ mm) and RDS (cone-and-plate type, cone angle=1 rad, dia=1"). Both rheometers were operated isothermally at 210°C. Entrance correction was

ignored by using a capillary of large L/D ratio, however, the wall shear rate was corrected following Rabinowitsch procedure.

Thermal properties of the blends were determined using DSC (du Pont 1090 B) in nitrogen atmosphere. Samples were first heated to 180°C (i.e., 20°C above the melting temperature of iPP) and kept at that temperature for 5 minutes. The melted samples were cooled to room temperature at 20°C/min. Thermograms were recorded during the second heating cycle at a rate of 10°C/min.

Mechanical properties were determined from an injection molded plaque following ASTM procedures. Tensile tests were carried out using the Instron 4202 with a 1-500kg load cell and a crosshead speed of 50mm/min. Dumbbell specimen of thickness 3mm, width 25mm, and gauge length 80mm were punched out using a cutter.

Morphological texture of the blend was observed from scanning electron microscopy (SEM). SEM photographs were taken from cryogenically fractured surface at the liquid nitrogen temperature, perpendicular to the plane of injection molded sheet, and sputtered with gold before viewing.

RESULTS AND DISCUSSION

Complex viscosity and steady shear viscosity of the blends are respectively shown in Figs. 1 and 2. The viscosity of EPM is approximately one order of magnitude higher than that of iPP throughout the frequency range tested. It is also seen that blend viscosity increases monotonically with EPM content.

The viscosity as a function of composition is summarized in Fig. 3. The viscosities measured at low ($\omega=0.1$ rad/s) and at moderate ($\omega=10$ rad/s) frequencies (RDS data) reasonably follow the simple additive rule. However the viscosities measured at high ($\dot{\gamma}=10^3$ 1/s) rate of shear (capillary data) show negative deviation a little as the EPM content increases. The difference may in part be due to the different deformation in capillary flow (high shear data) and oscillatory flow (low and moderate frequency data). This possibility

was however excluded since viscosity functions measured from the two types of rheometer showed basically same tendency for the entire range of shear rate overlapped.

Another observation on the rheological com-

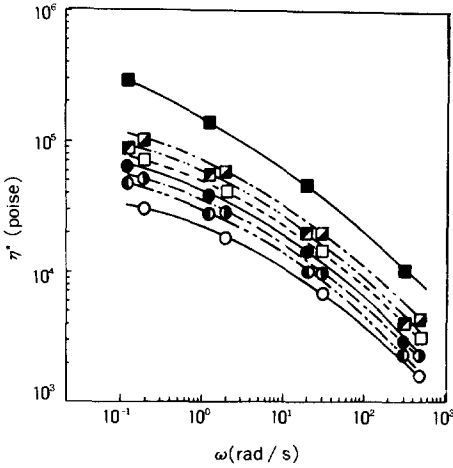


Fig. 1. Complex viscosity vs. frequency for iPP / EPM blend system : iPP / EPM=100 / 0 (○); 90 / 10(●); 80 / 20(◐); 70 / 30(◑); 60 / 40(□); 50 / 50(◒); 40 / 60(◓); 0 / 100 (■).

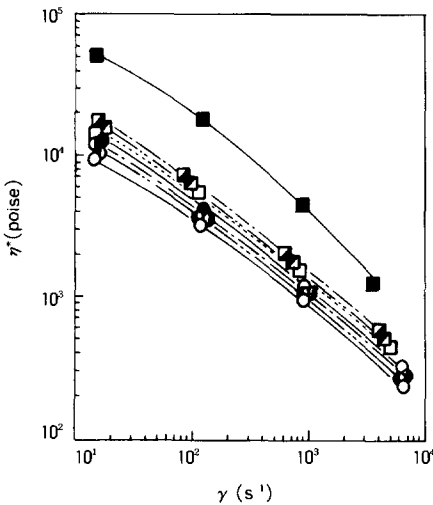


Fig. 2. Steady shear viscosity vs. shear rate for iPP / EPM blend system. Same symbols as in Fig. 1.

patibility of polymer blends can be made through the Cole-Cole plots.^{6,7} In such a plot, a drift from semicircle is present for incompatible blends, however incompatible drifts do not appear for homopolymer and compatible blends. In Fig. 4 the Cole-Cole plot for the iPP / EPM blends is presented. Evidently no incompatible drift is seen from the figure.

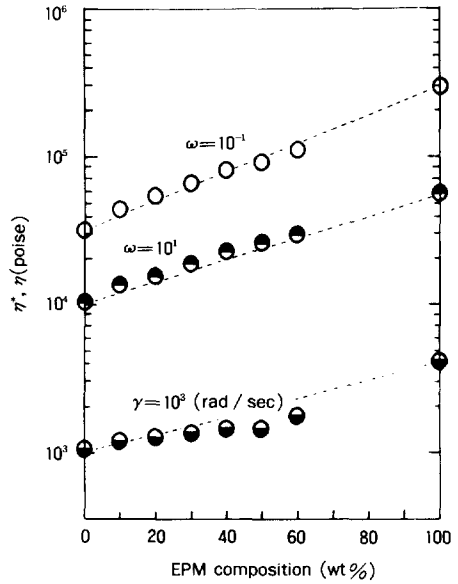


Fig. 3. Viscosity vs. EPM composition for iPP / EPM blend system.

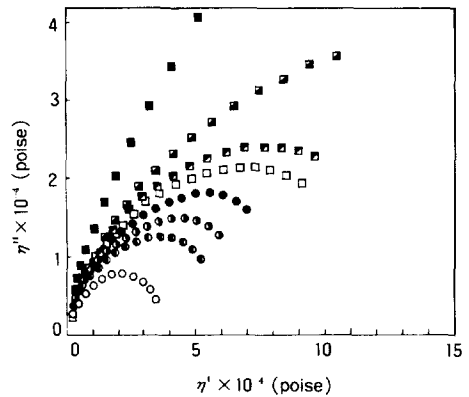


Fig. 4. Cole-Cole plot for iPP / EPM blend system. Same symbols as in Fig. 1.

Storage modulus, loss modulus and loss tangent are given in Figs.5~7. Again as the EPM content increases, the moduli monotonically increase. It should be mentioned that the $\tan\delta$ for EPM is typical of rubbery materials, i.e., a linear dependence of $\tan\delta$ on $\log\omega$. The same result is observed for iPP40/EPM60 blend, and this should be an indication of phase inversion around this composition. An earlier paper by Danesi and

Porter¹ also reported, from morphological observation, that the phase inversion occurs between iPP60/EPM40 and iPP40/EPM60. Our morphological texture, to be discussed later, also indicated a completely different state of dispersion on going from iPP50/EPM50 to iPP40/EPM60 blends.

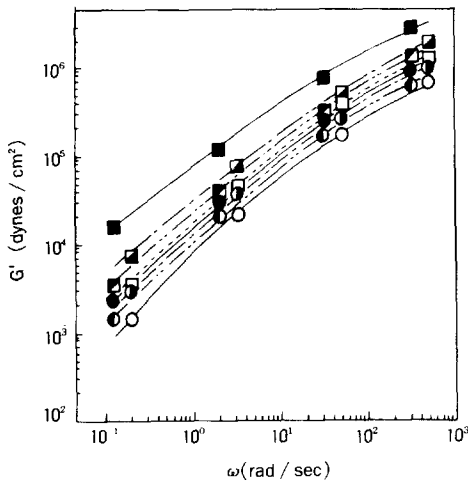


Fig. 5. Storage modulus vs. frequency for iPP / EPM blend system. Same symbols as in Fig. 1.

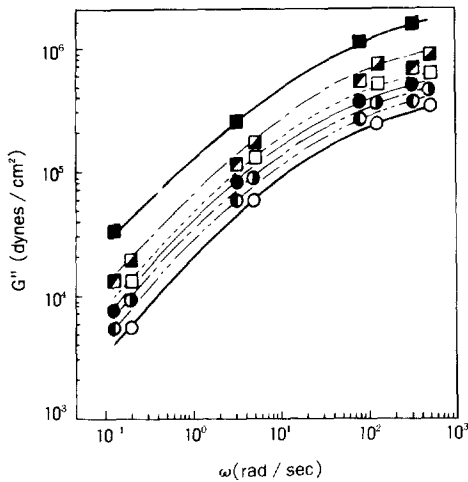


Fig. 6. Loss modulus vs. frequency for iPP / EPM blend system. Same symbols as in Fig. 1.

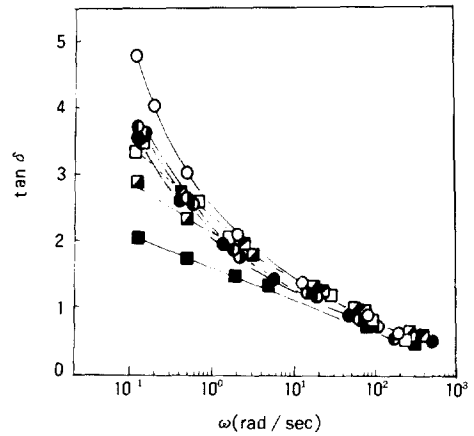


Fig. 7. Loss tangent vs. frequency for iPP / EPM blend system. Same symbols as in Fig. 1.

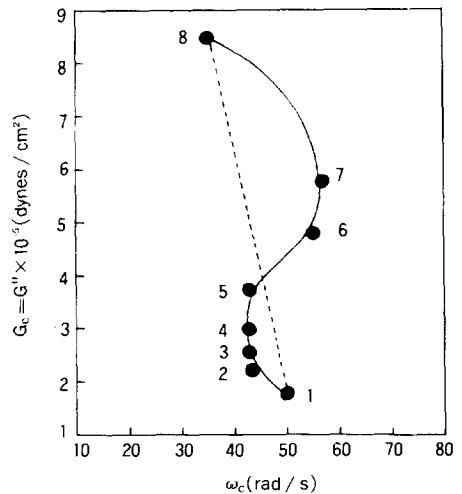


Fig. 8. Coordinates of $G'=G''$ cross-over point : G_c vs. ω_c for iPP / EPM blend system : iPP / EPM=100 / 0 (1); 90 / 10 (2); 80 / 20 (3); 70 / 30 (4); 60 / 40 (5); 50 / 50 (6); 40 / 60 (7); 0 / 100(8).

The crossover point $G_c = G' = G''$ at $\omega = \omega_c$ is a measure of molecular weight and its distribution for iPP.⁸ In Fig. 8 the values of G_c for the present iPP / EPM blends are plotted. It is interesting to note that G_c and ω_c for the blends are rather closer to iPP, the lower viscosity component. Such was also found for LLDPE / iPP / EPM ternary blends.⁸

Morphological textures of the iPP / EPM blends are given in Fig. 9. The vacancy that EPM particle left upon fracture is seen in Figs. 9 (a)-(e). The EPM domain is larger and has a shape approximating to a sphere for iPP90 / EPM10 blend. As the EPM content increases up to 40%, the hole is reduced in size and becomes elliptical which is indicative of more deformation. Also noted is the increase of craze formation with EPM content. Polarized light micrographs for iPP / EPM blends by others⁴ also showed the same state of dispersion with EPM content up to 40% EPM, the highest EPM content they tested. Following ref. (4), an impact modifier is an effective nucleating agent for α type of spherulites, and reduces the average spherulite size as well.

In iPP50 / EPM50 blend (Fig. 9(e)) the EPM domain becomes irregular in shape and larger in size. Probably, at this composition, the diffusion

of EPM into the amorphous region of iPP is not driven further by molecular action, and a competition to occupy continuous phase seems evident between the two constituents resulting in an unstable phase morphology. The possibility of EPM dissolution in iPP amorphous domain could be inferred from the smaller fractional area of EPM domain in SEM micrographs compared to the blend composition.

A completely different morphological texture is observed for iPP40 / EPM60 blend. Here a fibril-in-matrix structure or a highly elongated morphology is obvious. This could be explained as follows : At this composition, EPM may possibly be continuous phase, and iPP be droplet phase. Since the viscosity of iPP is approximately one order lower than that of EPM, the rate of deformation and hence the amount of deformation in iPP phase is greater than that of continuous EPM phase resulting in a breakup of the droplet. This of course assumes the continuity of shear stress at the interface. With the breakup of iPP droplet into smaller ones, the elongational deformation exercised in injection molding should result in a stratification of iPP droplets.

The effect of EPM on the crystallization of iPP was determined from DSC. Melting peak temperature and heat of fusion are respectively

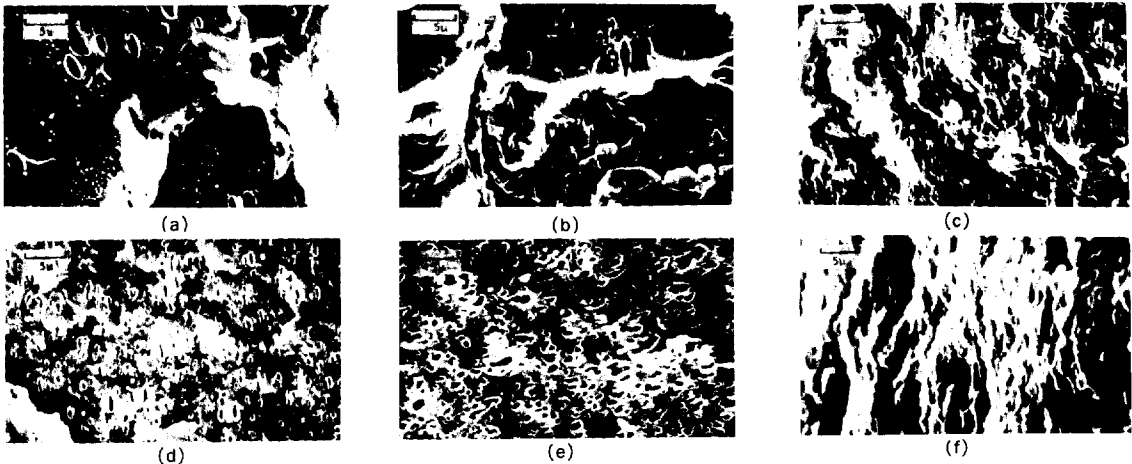


Fig. 9. Scanning electron micrographs of cryogenically fractured surfaces. (a):iPP90 / EPM10, b:80 / 20, c:70 / 30, d:60 / 40, e:50 / 50, f: 40 / 60).

given in Figs. 10 and 11. Approximately up to 1°C of melting point depression is observed with EPM inclusion. This could be within the experimental error, however the tendency was reproducible. Upon comparing the experimentally determined heats of fusion with the calculated values (Fig. 11), one notices that the total crystallinity is essentially independent of rubber content. In

short, an impact modifier provides iPP with more nucleation sites and smaller crystalline domain

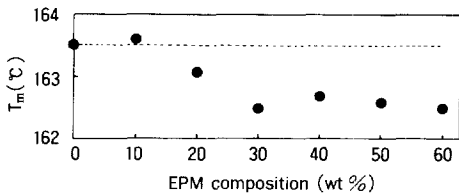


Fig. 10. Melting peak temperature (T_m) vs. EPM composition for iPP/EPM blend system.

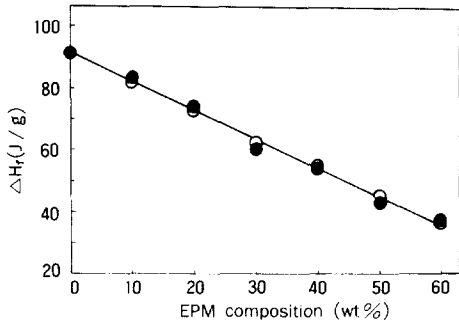


Fig. 11. Heat of fusion vs. EPM composition for iPP/EPM blend system : (●) experimental data; (○) calculated values.

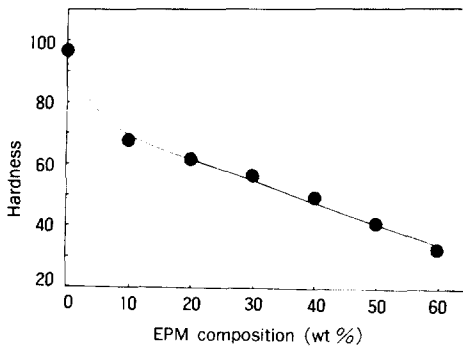


Fig. 12. Hardness vs. EPM composition for iPP/EPM blend system.

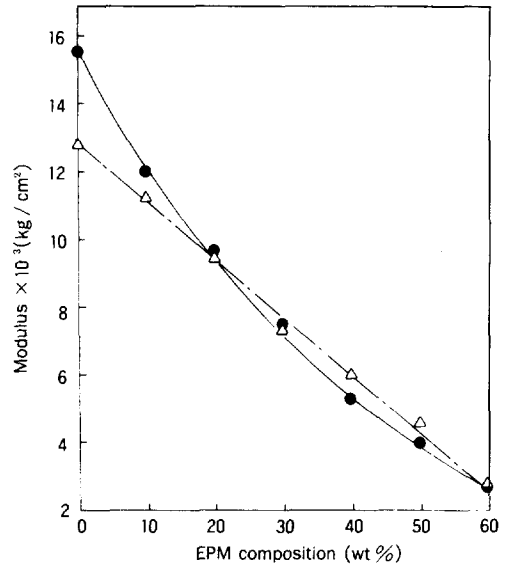


Fig. 13. Flexural (●) and Young (Δ) modulus vs. EPM composition for iPP/EPM blend system.

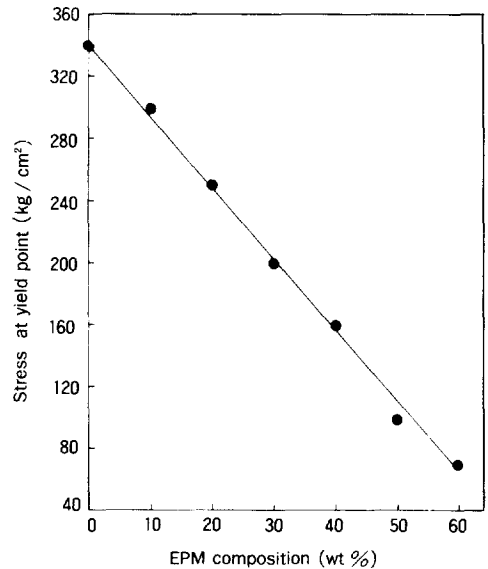


Fig. 14. Stress at yield point vs. EPM composition for iPP/EPM blend system.

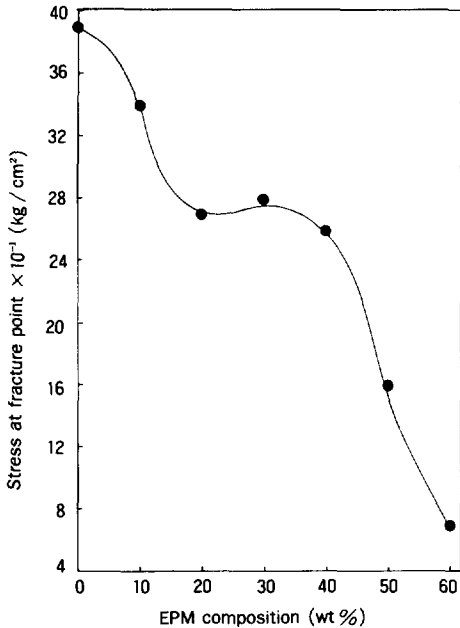


Fig. 15. Stress at fracture point vs. EPM composition for iPP/EPM blend system.

size. The effect, however seems marginal.

Mechanical properties of iPP/EPM blends are shown in Figs. 12~15. Flexural modulus and hardness show negative deviation from the simple additive rule whereas the Young's modulus and yield stress decrease linearly with EPM content. Negative deviation in mechanical properties is probably due to the two phase structure of the blends. Fracture stress indicates a sharp drop with EPM content up to 20% EPM, and was kept nearly constant up to 40% EPM followed by a sharp decrease again. The fracture stress trend seems in line with the state of dispersion (Fig. 9). Large particle size coupled with its unequal spatial distribution should be responsible for the rapid drop of fracture stress at low EPM contents (10,20%). At intermediate contents, EPM particle has been reduced in size with improved size and spatial distributions. The second rapid drop in fracture stress appeared at 40~60% EPM is probably due to the increased particle size and irregular shape together with the phase inversion.

The blends of iPP with EPM apparently posed some complexity in interrelating the rheological behavior with mechanical properties. Rheologically, iPP/EPM blends are generally favored for simple additive rules of compatible blends. Cole-Cole plots again did not show any incompatible drifts.

The morphological textures showed an obvious contradiction to the melt flow properties. A better interpretation of the rheology data should therefore rely on other aspect than the compatibility. The measured rheological behavior of the blends should be of a noninteractive system, i.e., the droplets have little interaction.⁵ The noninteractive nature of the blend was also obvious from the thermal measurements, i.e., heat of fusion measured gave the same values as calculated ones with the marginal effect of EPM on iPP melting temperature.

The mechanical properties of the blends, to some extent, should be related to the viscoelastic properties of the melt. This is via the rheology morphology interaction. Presently, the viscosity of EPM is approximately one order of magnitude higher than that of iPP. Therefore with EPM as a minor, the deformations of EPM droplet phase do not follow the iPP continuous phase deformation, resulting in a droplet-in-matrix structure. However with iPP as a minor, deformation of dispersed phase should be greater than that of continuous EPM phase resulting in a fibril-in-matrix structure. The mechanical response should find closer relationship with morphology rather than with rheology since the mechanical response and morphology are solid state properties, whereas the rheological property is of melt state. Presently measured mechanical properties are of generally incompatible blends, consistent with our morphological observations.

REFERENCES

1. S. Dansei and R. Porter, *Polymer*, **19**, 448 (1978).
2. C. D. Han, J. W. Kinn, and G. Chen, *J. Appl. Polym. Sci.*, **19**, 2831(1975).
3. B. L. Lee and J. White, *Trans. Soc. Rheol.*,

- 19, 481(1975).
4. J. Karger-Kocsis, A. Kallo, A. Szafner, and G. Bodor, *Polymer*, **20**, 37(1979).
 5. C. D. Han, "Multiphase Flow in Polymer Processing", Academic Press, New York, 1981.
 6. C. Wisnie, G. Marin, and P. H. Monge, *Eur. Polym. J.*, **21**, 479(1985).
 7. C. Wisnie, G. Marin, and P. H. Monge, *Eur. Polym. J.*, **7**, 691(1984).
 8. M. Domoulin, C. Farha, and L. Utraki, *Polym. Eng. Sci.*, **24**, 1319(1984).