

# Effects of the Blending Sequence in Polyolefin Ternary Blends

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**ABSTRACT:** Ternary blends of isotactic polypropylene (PP), ethylene–octene copolymer (mPE), and high-density polyethylene (HDPE) were prepared by melt mixing in a twin-screw extruder with two different sequences of mixing: the simultaneous mixing of the three components (method I) and the premixing of mPE and HDPE followed by mixing with PP (method II). Regardless of the mixing sequence, mPE encapsulated HDPE in the PP matrix, although better mechanical properties were generally obtained with method

II. The domain size was mainly determined by the viscosity ratio of mPE to PP in method I and by the viscosity ratio of the binary blend (mPE/HDPE) to PP in method II. Specimens prepared by injection molding gave much finer dispersions than compression-molded specimens. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 804–811, 2004

**Key words:** polyolefins; blends; morphology

## INTRODUCTION

Isotactic polypropylene (PP) is used in a wide variety of applications because of its easy processability and good thermal and mechanical properties. However, it has relatively poor low-temperature toughness and dimensional stability. Consequently, PP has often been blended with various elastomers to improve the impact strength at low temperatures. Recently, it has become possible to produce blends with very high amounts of ethylene–propylene rubber (EPR) with a PP block copolymer technique in the reactor directly. This product is called *reactor-made thermoplastic olefin*.<sup>1</sup>

Blends of PP and elastomers, such as EPR,<sup>2–9</sup> ethylene–propylene–diene terpolymer,<sup>3,6,10,11</sup> ethylene/ $\alpha$ -olefin copolymer, and styrene–butadiene rubber,<sup>13</sup> are very important to the development of new products in the plastics industry. Recently, a number of researchers have attempted to control the microstructure in ternary blends. Changes in the interfacial tension of each component pair can be achieved with compatibilizers. There are two kinds of phase structures: (1) the components of the dispersed phase are dispersed separately and (2) one component is encapsulated by the other component of a

two-dispersed phase. It is generally known that mechanical properties such as the stiffness, hardness, and heat distortion temperature of PP/elastomer blends can be improved by the addition of inorganic fillers, but the toughness will be reduced. The morphology of an inorganic filler encapsulated with an elastomer can improve this problem. Therefore, composites with an encapsulated morphology generally have lower stiffness but higher impact strength than composites with a separated morphology. For an encapsulated morphology, an increase in the elastomer volume fraction leads to enhanced impact strength, but the reinforcing effects are reduced because the collision probability of the matrix with the inorganic filler decreases.<sup>13–16</sup>

The morphology of polymer blends can be controlled by many factors, such as the blending sequence, chemical characteristics, melt viscosity, extrusion conditions, and interfacial tension of each component. Stehling et al.<sup>9</sup> reported that two types of morphology were achieved through the control of the blending procedure in PP/EPR/high-density polyethylene (HDPE) ternary blends; the first was an encapsulation type, in which the HDPE particle was surrounded by an EPR shell, and the second was an interpenetrating type, which occurred only when EPR and HDPE were mixed before the addition of PP.

We report characteristics of PP-based ternary blends with a controlled micromorphology that can be altered by the blending sequence. This is based on the assumption that the morphology of ternary blends is affected by the variation of the collision probability.

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TABLE I  
Characteristics of the Tested Materials

	MFR <sup>a</sup> (g/10min)	Density (g/cm <sup>3</sup> )	$M_w$ (10 <sup>5</sup> g/mol)	Viscosity at 100 rad/s	$\eta_{\text{others}}/\eta_{\text{PP}}$ at 100 rad/s	$\eta_0$ (p)	Source
PP	6.5	0.90	2.65	3,717.0	1.00	23,308	1077M <sup>b</sup>
HD1	10.3	0.962	0.61	2,584.5	0.59	6,481	M690 <sup>b</sup>
HD2	5.0	0.965	0.86	4,227.8	1.14	17,980	M850 <sup>b</sup>
HD3	0.3	0.962	1.61	13,366.0	3.60	326,000	B502 <sup>b</sup>
mPE	5.0	0.870	—	4,001.3	1.08	7,880	Engage 8200 <sup>c</sup>
MP-1	7.1	—	—	3,221.2	0.87	—	mPE/HD1 (66.7/33.3)
MP-2	6.0	—	—	3,635.7	0.98	—	mPE/HD2 (66.7/33.3)
MP-3	4.0	—	—	4,849.4	1.30	—	mPE/HD3 (66.7/33.3)

$\eta_{\text{others}}$  = viscosity of other components;  $\eta_{\text{PP}}$  = viscosity of PP;  $\eta_0$  = Newtonian viscosity.

$M_w$  = weight-average molecular weight.

<sup>a</sup> For PP, MFR was measured under 2.16 kg at 230°C. For HDPE and mPE, MFR was measured under 2.16 kg at 190°C.

<sup>b</sup> Korea Petrochemical Industrial Co.

<sup>c</sup> DuPont Dow Elastomers. Octene content = 24 wt %.

That is, for simultaneous mixing, the particle diameter of the dispersed phase is determined by the interfacial tension and viscosity ratio of each components pair. In this case, if the dispersed component has high viscosity, this system has large particle diameters. However, when HDPE and the elastomer form a ternary blend with PP, the morphology is determined by the interfacial tension and viscosity ratio of the premixed binary blend to PP. The main purpose of this work is to study the influence of the mixing sequence and method of specimen preparation on the morphological and mechanical properties of ternary blends.

Recently, a great deal of work has been carried out with an ethylene/ $\alpha$ -olefin copolymer as an impact modifier.<sup>17-22</sup> To enhance compatibility with PP, we used an ethylene-octene copolymer (mPE) made with a metallocene catalyst as an impact modifier. HDPE was used as the third component to reinforce mPE and to reduce the cost. We also studied the effects of the viscosity ratio by adding three HDPEs with different molecular weights.

## EXPERIMENTAL

### Materials

The PP and HDPE samples used in these experiments were commercial grades from Korea Petrochemical Industrial Co., Ltd. (Ulsan, Korea) The PP sample (1077M) had a 6.5 g/10 min melt-flow rate (MFR), and the HDPEs (M690, M850, and B502) had 10.3, 5.0, and 0.3 g/10 min MFRs, as measured by ASTM D 1238. The mPE used was DuPont Dow Elastomers Engage 8200 with a 1-octene concentration of 24 wt % and a density of 0.870 g/cm<sup>3</sup> (Wilmington, DE). Some of the main characteristics of the materials are listed in Table I. The melt viscosities of the base resin measured at 230°C with the Rheometrics Advanced Rheometrics Expansion System (ARES) (New Castle, DE) are shown in Figure 1.

### Preparation of the polymer blends

The blends were made with an Ikegai (Japan) PCM-45 45-mm corotating twin-screw extruder at 220 rpm and 230°C. Two types of PP/mPE/HDPE ternary blends were prepared with the following blending procedures:

Method I. PP, mPE, and HDPE were mixed simultaneously.

Method II. mPE and HDPE were premixed, and this was followed by mixing with PP.

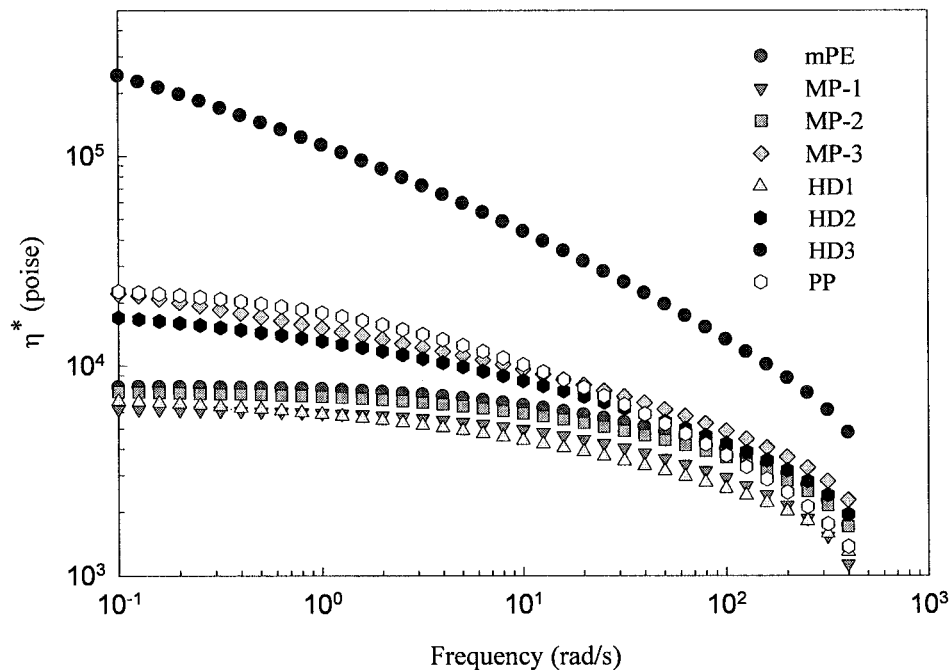
To avoid ambiguity, we identified the mixing conditions for all the blends, and the composition of the ternary blends was fixed at 7/2/1 (w/w/w) PP/mPE/HDPE. For reference, we also prepared a PP/mPE (7/3) binary blend.

### Characterization

Compression molding was performed with a hydraulic press at 250°C and 300 kg/cm<sup>2</sup> for 5 min, and injection molding was performed with a Nissei 35-oz injection-molding machine (Tokyo, Japan) at a cylinder temperature of 230°C and a mold temperature of 40°C. These samples were used to analyze the morphology and mechanical properties. The mechanical properties were measured according to an ASTM method.

The thermal properties were determined with a PerkinElmer Pyris II (Boston, MA). Specimens were heated to 200°C at 10°C/min and were kept there for 1 min and then cooled down to -10°C at a 10°C/min cooling rate to measure the crystallization temperature ( $T_c$ ). The samples were reheated under the same heating conditions to determine the melting temperature ( $T_m$ ).

The rheological properties were measured with ARES at 230°C with a 25-mm parallel-plate fixture at a



**Figure 1** Melt viscosities of PP, mPE, HDPE, and mPE/HDPE (66.7/33.3) binary blends at 230°C.

constant strain of 15% and at an oscillatory angular frequency of 0.1–500 rad/s.

The morphology of the dispersed phase was analyzed with a JEOL JSM-820 scanning electron microscope (Tokyo, Japan). The fracture surfaces for morphological observations were prepared by the breaking of the samples in liquid nitrogen. The surfaces were etched for 3 min in boiling *n*-heptane for the removal of mPE and then were coated with gold.

## RESULTS AND DISCUSSION

### Morphology

There are two types of morphologies in ternary blends: One of the dispersed components is encapsulated by the other dispersed component (encapsulation type), or the two dispersed components embed in the matrix separately (separation type).<sup>23–25</sup> Harkin's spreading coefficient was used to predict the morphology.<sup>24,25</sup> If component 1 is matrix in a ternary blend, Harkin's equation is

$$\lambda_{23} = \gamma_{13} - \gamma_{12} - \gamma_{23} \quad (1)$$

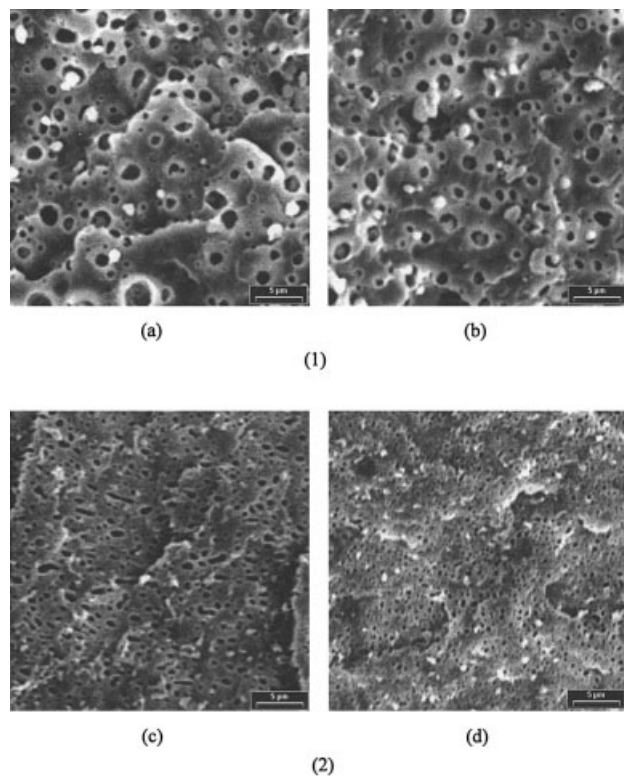
where  $\lambda_{23}$  is the spreading coefficient of phase 2 on phase 3 and  $\gamma_{ij}$  is the interfacial tension between *i* and *j* phases. If  $\lambda_{23}$  is positive, phase 3 will be encapsulated by phase 2. When  $\lambda_{23}$  and  $\lambda_{32}$  are both negative, components 2 and 3 will disperse separately in the matrix.

The collision probability of two minor components is an important factor in determining the microstructure in a ternary blend.<sup>16</sup> We used two types of blend-

ing sequences in our experiments. The collision probability of method II is higher than that of method I. The effect of the collision probability on the morphological and mechanical properties of PP/mPE/HDPE ternary blends was examined.

Figure 2 shows typical scanning electron microscopy (SEM) morphologies of PP/mPE/HD2 (7/2/1) ternary blends prepared by compression and injection molding. Depending on the method of specimen preparation, the particle sizes are significantly different: up to several micrometers for compression-molded specimens and submicrometer for injection-molded specimens. It seems that the particles are subjected to coalescence during compression molding and further break up during injection molding.

Obviously, injection-molded specimens show that method II produces a much finer morphology than method I. Because both specimens are prepared by injection molding, the different states of dispersions are due to the different blending methods. In method I, mPE and HD2, having similar viscosities, and PP are mixed simultaneously, and this is followed by the encapsulation of HD2 by mPE according to eq. (1). This sequence gives a large dispersed-phase domain size with a broad size distribution. On the contrary, when mPE and HD2 of similar viscosities are melt-blended, the blend viscosity is similar to or less than that of the virgin resins (Table I). When this binary blend is subjected to melt mixing with PP under shear, the viscosity ratio of the dispersed phase to PP is about the same as that of mPE or HD2 to PP, leading to a



**Figure 2** SEM morphology of (1) compression-molded and (2) injection-molded specimens of PP/mPE/HD2 (70/20/10) ternary blends: (a,c) method I and (b,d) method II.

particle size of HD2 or mPE that is smaller than that from method I. The migration of mPE molecules onto the particle surfaces will subsequently occur in the melt state according to eq. (1) and produce a core (HD2)–shell (mPE) morphology.

### Mechanical properties

The mechanical properties of the blends and base resins are given in Table II and Figures 3–5. The flex-

ural modulus, hardness, and elongation at break of the ternary blends are greater than those of the PP/mPE binary blends. This is primarily due to the reinforcing effects of HDPE for rubbery domains. The increase in these properties is greater with method II, mainly because of the finer dispersion, as can be observed from the SEM morphology.

The effects of the HDPE molecular weight on the mechanical properties of the ternary blends differ between the two methods. That is, the mechanical properties are improved with increasing HDPE molecular weight by method II but are reduced by method I. This is presumably due to the difficult breakup of high-molecular-weight HDPE when the three components are melt-mixed together, leading to a large dispersion by method I. However, in method II, the effect of the HDPE viscosity becomes less significant because the HDPE/mPE (1/2) blends are subjected to breakup during the second stage of mixing.

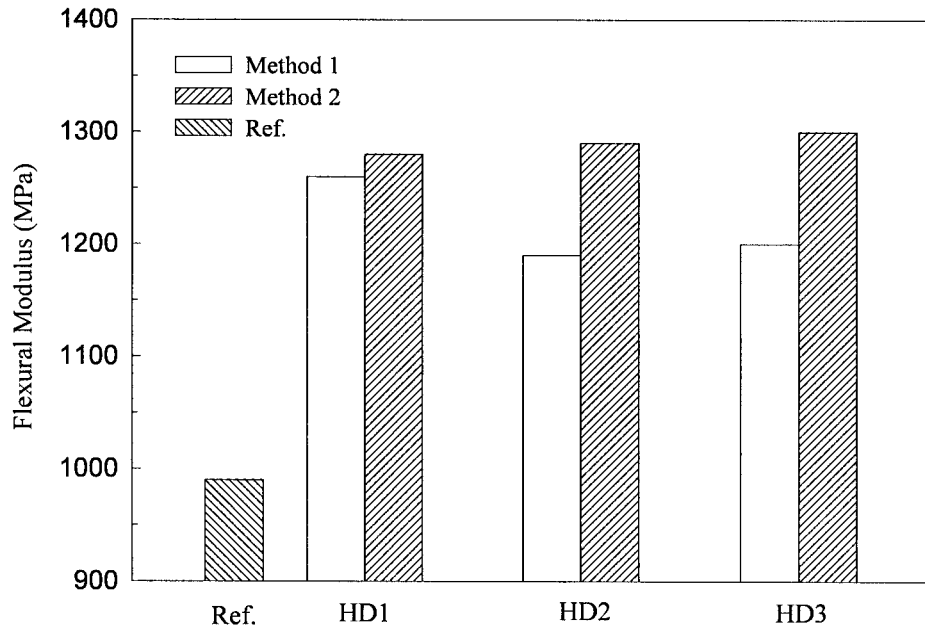
The notched impact strength of ternary blends decreases below that of the PP/mPE binary blend when the molecular weight of HDPE (HD1) is small, but it monotonically increases over the binary value as the molecular weight of HDPE (HD2 and HD3) increases (Fig. 6). This implies that there exists an optimum dispersion size for impact toughening.

### Thermal properties

The thermal properties of the blends are summarized in Table III. The crystalline  $T_m$  value of PP is virtually unchanged in the blends because of the immiscible nature of the blends. However, the melting peak of HDPE is reduced in the blends, and it is split into two (Fig. 7), which are conveniently denoted  $T_{mh}$  (high-temperature peak) and  $T_{ml}$  (low-temperature peak).  $T_{mh}$  should correspond to the melting of HDPE, and  $T_{ml}$  should correspond to the melting of HDPE–mPE cocrystallized domains. The reduction of  $T_{mh}$  and  $T_{ml}$  is greater with

**TABLE II**  
Mechanical Properties of PP, PP/mPE, and PP/mPE/HDPE Blends with Injection-Molded Specimens

Sample series	Sample	Formulation	MFR at 230°C (g/10 min)	Tensile strength			Flexural modulus (kg <sub>f</sub> /cm <sup>2</sup> )	Izod impact strength (kg <sub>f</sub> ·cm/cm)		Rockwell hardness
				At Yield (kg <sub>f</sub> /cm <sup>2</sup> )	At Break (kg <sub>f</sub> /cm <sup>2</sup> )	Elongation (%)		23°C	–20°C	
Method I	PP	PP	6.5	380	425	540	17,300	2.1	2.3	105.0
	Reference	PP/mPE	9.5	230	300	500	9,900	38.3	6.9	60.0
	M1-1	PP/mPE/HD1	10.2	275	300	560	12,600	34.7	3.2	73.5
	M1-2	PP/mPE/HD2	10.0	275	345	570	11,900	41.5	3.3	73.0
Method II	M1-3	PP/mPE/HD3	8.5	270	310	580	12,000	49.6	3.7	73.0
	M2-1	PP/(mPE/HD1)	9.2	275	320	550	12,800	35.1	3.1	74.5
	M2-2	PP/(mPE/HD2)	8.7	280	255	550	12,900	41.0	3.3	75.0
	M2-3	PP/(mPE/HD3)	7.9	280	180	540	13,000	51.5	3.6	76.0



**Figure 3** Flexural moduli of a PP/mPE (70/30) binary blend and PP/mPE/HDPE (70/20/10) ternary blends (injection-molded specimens).

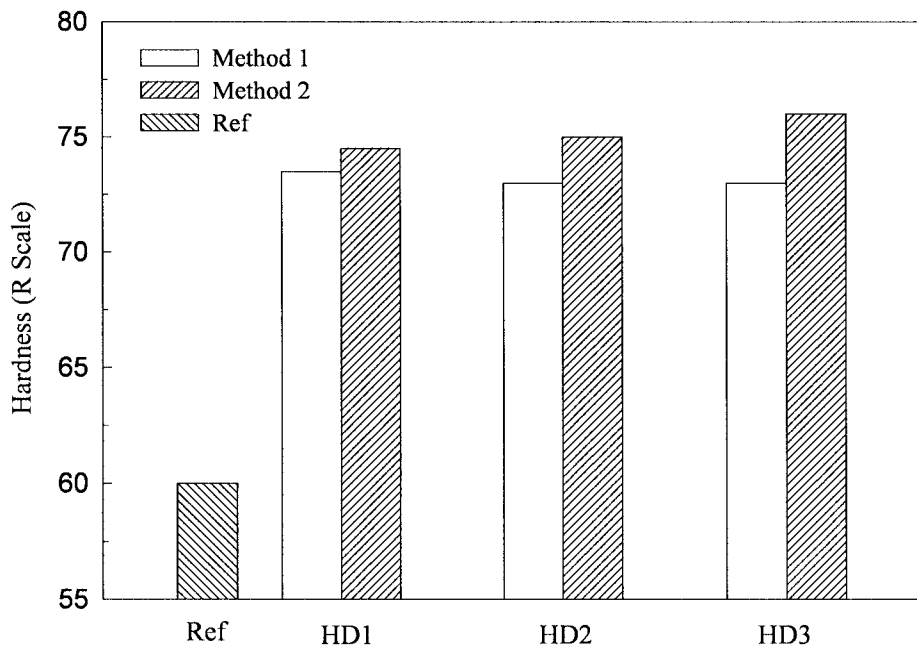
method II, likely because of the intimate mixing, which is caused by a high collision probability.

$T_c$ 's of PP and HDPE in the blends are not affected by the method of preparation or the molecular weight of HDPE. However,  $T_c$  for mPE is observed only with M1-3 at 46.4°C. This implies that when the viscosity of HDPE is high, mPE and HDPE form separate disper-

sion in the PP matrix when they are simultaneously blended with PP.

#### Rheological properties

The complex viscosities ( $\eta^*$ ) of the blends are shown in Figure 8. The viscosity functions of the blends



**Figure 4** Rockwell hardness of a PP/mPE (70/30) binary blend and PP/mPE/HDPE (70/20/10) ternary blends (injection-molded specimens).

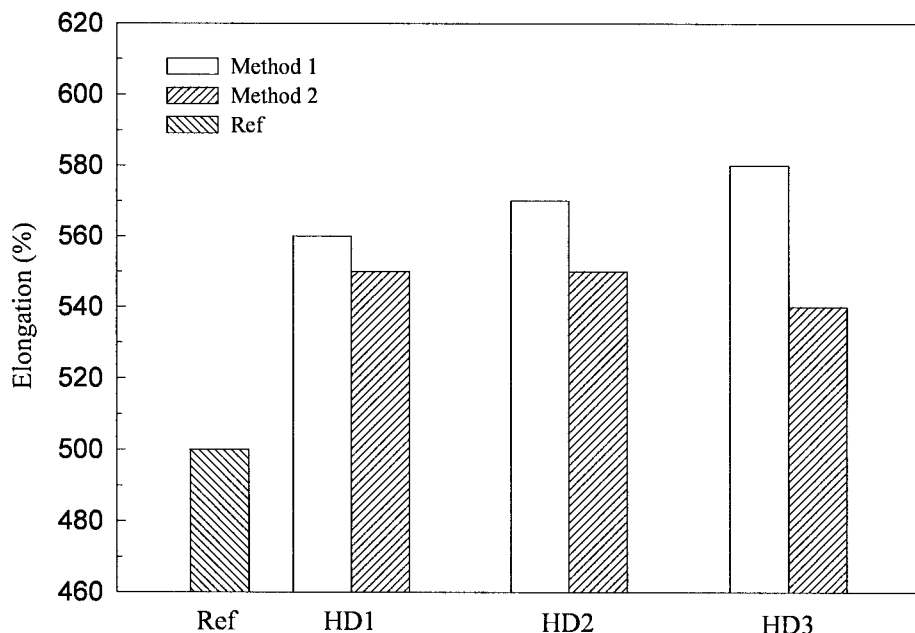


Figure 5 Elongation at break of a PP/mPE (70/30) binary blend and PP/mPE/HDPE (70/20/10) ternary blends (injection-molded specimens).

show an upturn at low frequencies, and this implies that the dispersed phases form three-dimensional networks. Among them, the PP/mPE blend shows the highest tendency of yield, and the ternary blend containing HD3 shows the lowest. This implies that network formation becomes difficult as the particle size increases.

### CONCLUSIONS

The effects of the blending sequence and method of specimen preparation on the mechanical, thermal, and rheological properties and morphology of PP/mPE/HDPE ternary blends have been investigated. Regarding the morphology of the ternary blends, the HDPE

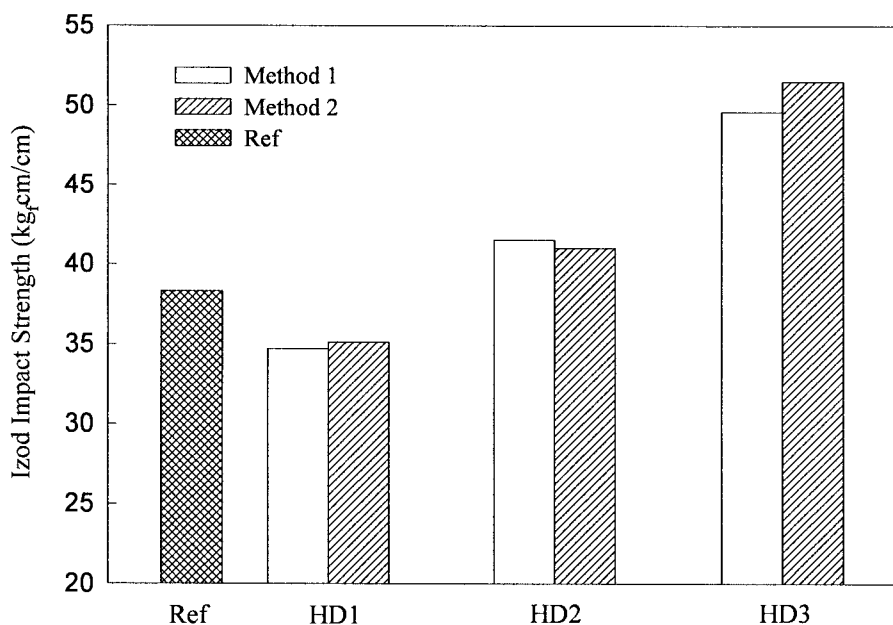


Figure 6 Notched Izod impact strength of a PP/mPE (70/30) binary blend and PP/mPE/HDPE (70/20/10) ternary blends (injection-molded specimens at room temperature).

TABLE III  
Thermal Properties of PP, PP/mPE, and PP/mPE/HDPE Blends

Sample	Thermal properties						Crystallinity of PP (%)
	$T_m$ (°C)		PP	$\Delta H_f$ (J/g)	$T_c$ (°C)	$\Delta H_c$ (J/g)	
	$T_{ml}$	$T_{mh}$					
mPE	—	60.4	—	11.8	44.1	26.0	—
PP	—	—	161.8	92	112.5	110.6	44.0
Reference	—	—	162.4	67.2	44.7/113.8	70.6	45.9
HD1	—	129.7	—	199.3	114.8	201.5	—
HD2	—	132.4	—	216.5	116.9	222.9	—
HD3	—	132.4	—	199.8	117.8	215.0	—
MP-1	124.4	126.4	—	58.9	48.1/112.1	55.8	—
MP-2	126.1	129.4	—	64.1	48.1/114.8	63.8	—
MP-3	126.8	129.4	—	61.8	49.4/116.5	57.6	—
M1-1	126.1	127.8	162.4	15.3/64.3	113.1	89.8	44.0
M1-2	128.4	130.1	162.1	14.2/60.9	115.2	90.1	41.6
M1-3	127.1	130.1	162.4	14.4/61.5	46.4/115.8	2.3/91.1	42.0
M2-1	125.5	127.5	161.8	12.6/62.3	113.5	88.9	42.6
M2-2	128.1	129.7	162.1	15.1/62.0	115.1	85.1	42.4
M2-3	126.4	128.7	161.7	15.4/60.2	115.9	89.6	41.1

$\Delta H_f$  = heat of fusion;  $\Delta H_c$  = heat of crystallization.

particles are encapsulated by mPE in the PP matrix, regardless of the blending sequence.

In method I, mPE and HDPE are first separately dispersed in PP, and this is followed by the encapsulation of HDPE by mPE in a core (HDPE)–shell (mPE) morphology. This gives rise to an additional

increase in the domain size to the one originally determined by the viscosity ratio of mPE to PP. However, in method II, the domain size is determined by the viscosity ratio of the premixed binary blend (mPE/HDPE) to PP, which is close to or rather smaller than the ratio of mPE to PP. Conse-

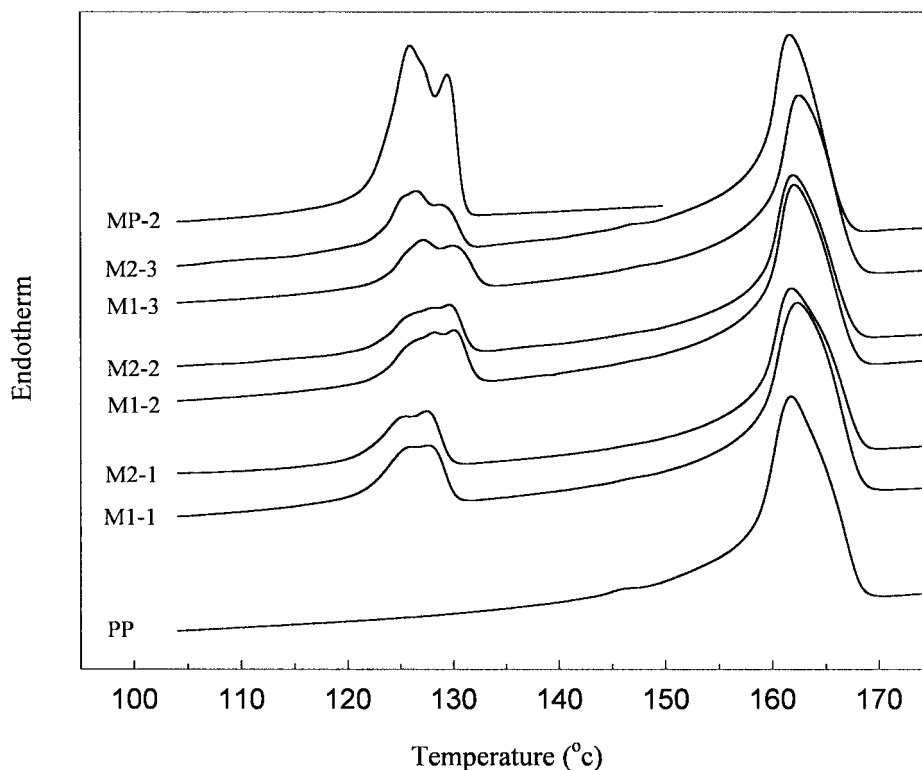
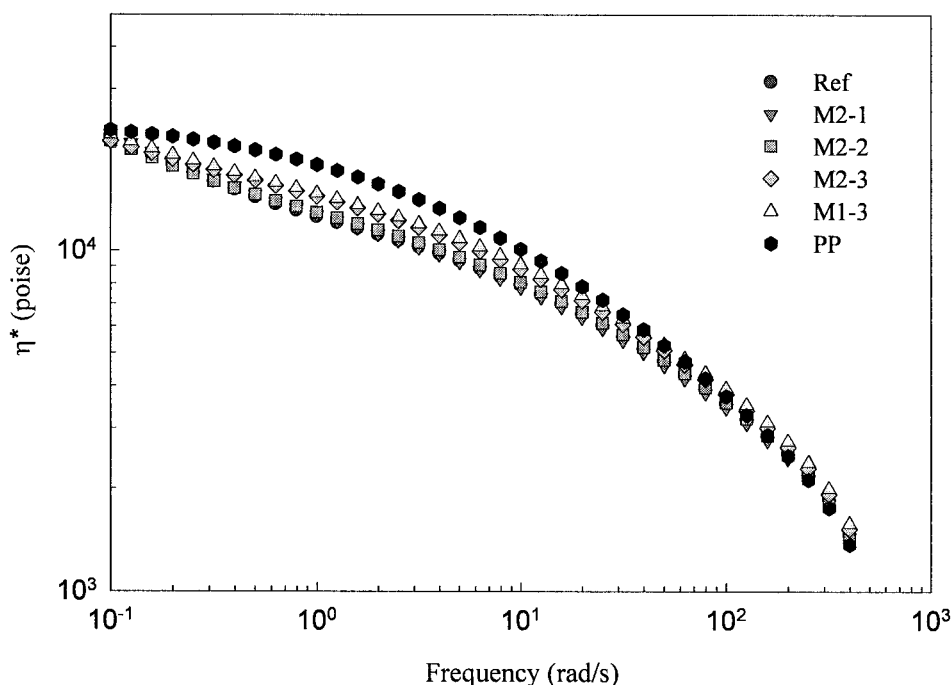


Figure 7 Melting endotherms of HDPE and PP in PP/mPE/HDPE (70/20/10) ternary blends.



**Figure 8** Melt viscosities for PP, a PP/mPE (70/30) binary blend, and PP/mPE/HDPE (70/20/10) ternary blends at 230°C.

quently, a finer domain size results, and the method of specimen preparation, as well as the mixing sequence, exerts effects on the blend properties via morphology control.

SEM of injection-molded specimens shows a much finer domain morphology than SEM of compression-molded specimens. This implies that particles are subjected to further coalescence during compression and break up during injection molding. This is why better mechanical properties are obtained.

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