

Effects of the Viscosity Ratio on Polyolefin Ternary Blends

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ABSTRACT: Polyolefin binary and ternary blends were prepared from polypropylene (PP), an ethylene- α -olefin copolymer (mPE), and high-density polyethylene (HDPE) on the basis of the viscosity ratio of the dispersed phase to the continuous phase. In PP/mPE/HDPE blends, fibrils were observed when the dispersed-phase (mPE/HDPE) viscosity was less than that of PP, or when the viscosity of mPE was less than that of PP, although the viscosity of mPE/HDPE was greater than that of PP. The notched impact strength

and mechanical properties such as the yield strength, flexural modulus, and hardness of PP/mPE binary blends further increased with the addition of HDPE according to the type of HDPE. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 4027–4036, 2004

Key words: polyolefins; blends; polyethylene (PE); viscosity; strength

INTRODUCTION

Blends based on isotactic polypropylene (PP) have been used in the automotive and electronics industries for injection molding because of their easy processing, low cost, and good thermal and mechanical properties. Recently, to improve the mechanical properties and coefficient of linear thermal expansion, researchers have devoted much attention to controlling the microstructures of multicomponent blends. A typical thermoplastic olefin successfully applied to automotive bumpers is the super olefin polymer developed by Toyota.^{1–4}

Many previous works have shown a strong dependence of the blend properties on the chemical characteristics of each component, the blending sequence, the blend composition, the viscosity ratio, and the adhesion between the dispersed phase and matrix.^{5,6} In particular, the blend properties of ternary blends are affected by the particle size and microstructure. The viscosity of each component is a very important factor for the morphology and mechanical properties.

Recently, ethylene- α -olefin copolymers have been widely used to incorporate PP as an impact modifier.^{7–14} Yamaguchi et al.,⁸ Craig et al.,⁹ and Nitta et al.¹⁰ claimed that higher α -olefin contents and long side chains of an ethylene- α -olefin copolymer yielded higher miscibility with PP in PP/ethylene- α -olefin copolymer blends because of decreased interfacial tension (γ). In high-density polyethylene (HDPE)/ethyl-

ene-octene copolymer (mPE) blends, Choe and co-workers^{14,14} claimed that the two materials were miscible in the melt state.

It is generally known that the toughness of PP can be improved by the addition of an elastomer, whereas mechanical properties such as the stiffness, hardness, and heat distortion temperature are reduced.

We have considered ternary blends of PP, HDPE, and mPE. The effect of the viscosity ratio on binary and ternary blends was examined in terms of the morphology, rheology, and mechanical and thermal properties of the blends. Three different types of PP and HDPE were used, leading to three series of blends: PPL, for which the PP viscosity was lower than that of mPE; PPM, for which the PP viscosity was close to that of mPE; and PPH, for which the PP viscosity was higher than that of mPE.

EXPERIMENTAL

Materials

The PP and HDPE samples used in this work were commercial grades produced by Korea Petrochemical Co., Ltd. (Ulsan, Korea). The PP samples included HF5003 [melt-flow rate (MFR) = 3.2 g/10 min], 1077M (MFR = 6.5 g/10 min), and 4017H (MFR = 15.0 g/10 min); the HDPE samples included M690, M850, and B502 (with MFRs of 10.3, 5.0, and 0.3 g/10 min, respectively). The mPE sample (Engage 8200) was produced by DuPont Dow Elastomers (Wilmington, DE) and had a 24 wt % 1-octene content and a density of 0.870 g/cm³. The important characteristics of these materials are listed in Table I. The complex viscosities (η^*) of the base resins, measured at 230°C with an Advanced Rheometrics Expansion System (Rheometrics, Piscataway, NJ), are shown in Figure 1.

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TABLE I
Characteristics of the Test Materials

	MFR (g/10 min)	Density (g/cm ³)	M_w (10 ⁵ g/mol)	Viscosity at 100 rad/s	Viscosity at 158.5 rad/s	η_0 (P)	Source
PP-L	15.0	0.90	2.20	2,658.3	2,102.9	10,397	4017H ^a
PP-M	6.5	0.90	2.65	3,717.0	2,861.4	23,308	1077M ^a
PP-H	3.2	0.90	3.51	5,179.6	3,906.5	46,431	HF5003 ^a
HD1	10.3	0.962	0.61	2,584.5	2,214.0	6,481	M690 ^a
HD2	5.0	0.965	0.86	4,227.8	3,509.8	17,980	M850 ^a
HD3	0.3	0.962	1.61	13,366.0	10,116.5	326,000	B502 ^a
mPE	5.0	0.870	—	4,001.3	3,392.6	7,880	Engage 8200 ^b

M_w = weight-average molecular weight. PP:MFR was measured under 2.16 kg at 230°C. HDPE and mPE:MFR were measured under 2.16 kg at 190°C; η_0 = Newtonian viscosity.

^a Korea Petrochemical Co.

^b DuPont Dow Elastomers; octene content = 24 wt %.

Preparation and characterization of the polymer blends

The blends were made with an Ikegai (Tokyo, Japan) PCM-45 45-mm corotating twin-screw extruder at 220 rpm and 230°C. Injection moldings were performed with a Nissei 35-oz injection molding machine (Tokyo, Japan) at a cylinder temperature of 230°C and at a mold temperature of 40°C. These samples were used to analyze the morphology and mechanical properties.

The thermal properties were determined with a PerkinElmer Pyris II (Wellesley, MA). The specimens

were heated to 200°C at 10°C/min and kept there for 1 min and then were cooled to -10°C at 10°C/min 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 an Advanced Rheometrics Expansion System at 230°C with a 25-mm parallel-plate fixture at a constant strain of 15%, which was within the linear viscoelastic limit tested by the strain sweep, and at an oscillatory angular frequency ranging from 0.1 to 500 rad/s.

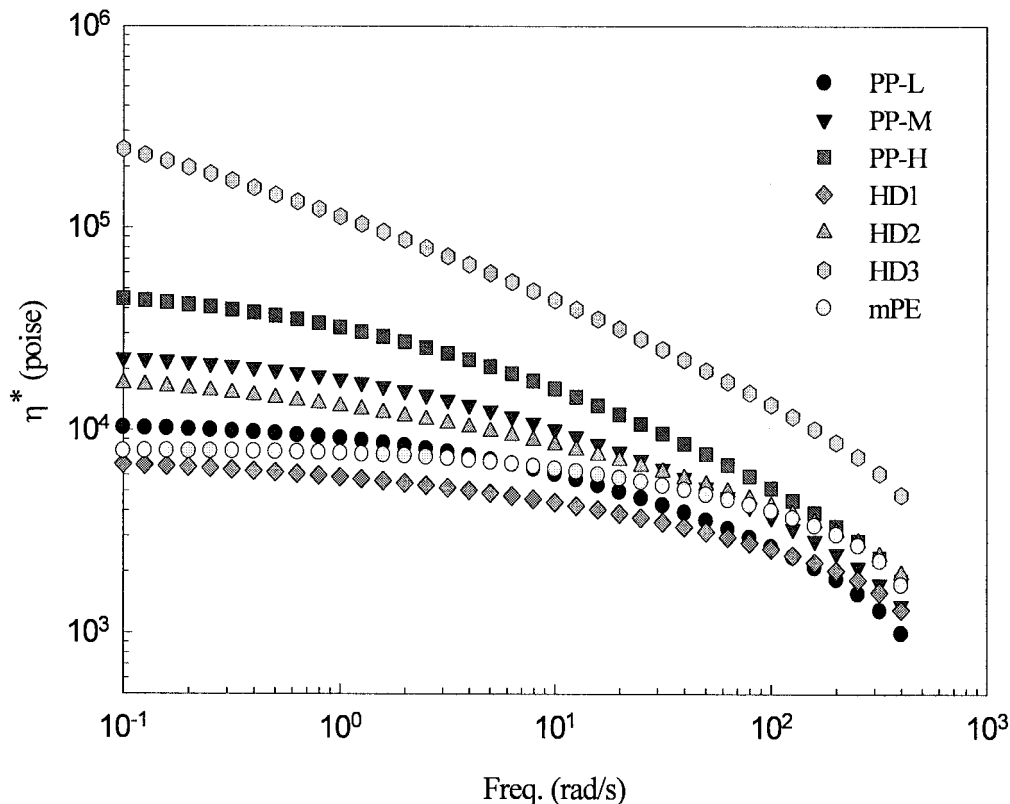


Figure 1 η^* of PP, HDPE, and mPE at 230°C.

TABLE II
Formulations of the Binary and Ternary Blends

	Sample no.	PP-L	PP-M	PP-H	mPE	HD1	HD2	HD3	MP-1	MP-2	MP-3
Binary blend	MP-1	—	—	—	66.7	33.3	—	—	—	—	—
	MP-2	—	—	—	66.7	—	33.3	—	—	—	—
	MP-3	—	—	—	66.7	—	—	33.3	—	—	—
	R-1	70	—	—	30	—	—	—	—	—	—
	R-2	—	70	—	30	—	—	—	—	—	—
	R-3	—	—	70	30	—	—	—	—	—	—
Ternary blend	PPL-1	70	—	—	—	—	—	—	30	—	—
	PPL-2	70	—	—	—	—	—	—	—	30	—
	PPL-3	70	—	—	—	—	—	—	—	—	30
	PPM-1	—	70	—	—	—	—	—	30	—	—
	PPM-2	—	70	—	—	—	—	—	—	30	—
	PPM-3	—	70	—	—	—	—	—	—	—	30
	PPH-1	—	—	70	—	—	—	—	30	—	—
	PPH-2	—	—	70	—	—	—	—	—	30	—
	PPH-3	—	—	70	—	—	—	—	—	—	30

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

mPE/HDPE binary blends (66.7/33.3 w/w) were prepared, and then these master pellets were used to prepare PP/mPE/HDPE ternary blends. The composition of the ternary blends was fixed at 7/2/1 (w/w/w) PP/mPE/HDPE. As a reference, a PP/mPE (7/3 w/w) binary blend was also prepared under the same extruding conditions used for the ternary blends. The formulations of all the blends in this work are listed in Table II.

RESULTS AND DISCUSSION

Morphology

The particle size and particle size distribution of polymer blends are very important with respect to the impact strength. According to previous studies, the dispersed particle size is smaller when the viscosity ratio is closer to unity and γ is lower.^{15–17}

Wu¹⁵ claimed that the particle diameter (a_n) could be estimated as follows:

$$a_n = \frac{4\gamma}{G\eta_m} \left(\frac{\eta_d}{\eta_m} \right)^{\pm 0.84} \quad \text{for } p > 1 : 0.84, p < 1 : -0.84 \quad (1)$$

where G is the effective shear rate; η_m and η_d are the viscosities of the matrix and dispersed phases, respectively; and p is the viscosity ratio (η_d/η_m).

As we know from eq. (1), a_n of the dispersed phase is mainly influenced by the matrix viscosity in a binary blend, but it is more complicated in a ternary blend.

In this work, 100 rad/s was used for G .

In our work, an oscillating frequency of 100 rad/s was used to calculate the melt viscosity. $\eta_{mPE/HDPE}/\eta_{PP}$ (p_{MP}) was above unity in the PPL-based ternary blends, so a_n was large in the ternary blends (Fig. 2). The p_{MP} values of MP1, MP2, and MP3 to PPL were 1.21, 1.37, and 1.82, respectively. The particle size of the PPM-based ternary blends showed a tendency similar to that of the PPL-based ternary blends.

All the PPH-based ternary blends showed a particle size of less than 1 μm , although p_{MP} was below unity (the p_{MP} values of MP1, MP2, and MP3 to PPH were 0.62, 0.70, and 0.94, respectively). Because of the high viscosity of PP-H, high interfacial shear stress, leading to the fine breakup of the dispersed phase, was obtained [Fig. 2(A–D)].

When p_{MP} was above unity, a fibril morphology was not observed. Fibrils were observed in the PPM-1 and PPH-1 blends with low viscosity ratios. For PPH-3 ($p_{MP} = 0.94$), mPE was oriented along the flow direction. Because the viscosity of PPH was higher than that of mPE and lower than that of HD3, mPE could form a skin, and HD3, forming a core, was hardly deformed because of the low interfacial shear stress between mPE and HD3 due to the low value of η_{mPE} . Therefore, the flow-direction morphology of PPH-3 was composed of fibrillar mPE and ellipsoidal HD3 droplets [Fig. 2(A–D)].

Fibrils in the PP/mPE/HDPE ternary blends were observed with p_{MP} was less than unity; this result is similar to the findings of Kim and Do¹⁸ for PP/EPR/polyethylene ternary blends. A fibril morphology was also observed when p_{MP} was greater than unity

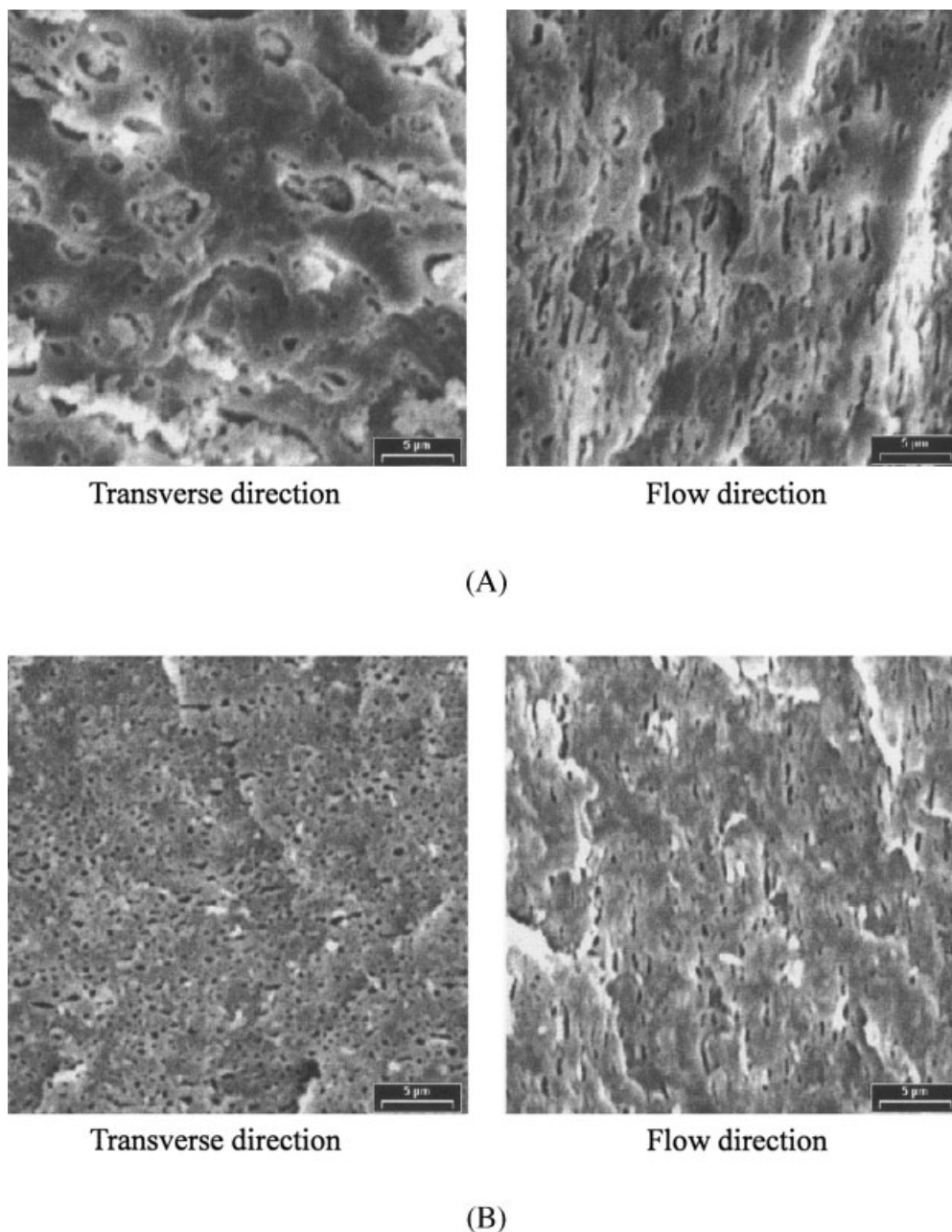


Figure 2 SEM micrographs of PP/mPE/HDPE (70/20/10) blends at 100 rad/s and 230°C: (A) PPL-3 ($p_{MP} = 1.82$), (B) PPM-2 ($p_{MP} = 0.98$), (C) PPH-1 ($p_{MP} = 0.62$), and (D) PPH-3 ($p_{MP} = 0.94$).

when the ternary blends contained low-viscosity mPE.⁷

Mechanical properties

The yield strength, flexural modulus, and hardness of PP dramatically decreased in the binary and ternary blends, but the notched impact strength increased by 14–23 times (Table III). The mechanical properties, except for toughness, decreased as the molecular weight of PP increased in all the blends. However, the toughness, flexural modulus, and hardness increased

as the molecular weight of HDPE increased in the ternary blends.

The yield strength, flexural modulus, and hardness increased considerably with the addition of HDPE to the PP/mPE binary blends, regardless of the molecular weight of HDPE. In general, the toughness increased as a_n of the dispersed phase decreased.^{16,17} However, in the PP/mPE/HDPE ternary blends, the toughness depended more on the molecular weight of PP and HDPE than a_n . Our results showed that the Izod impact strength increased with increasing particle size (Fig. 3). The addition of HDPE to the PP/mPE

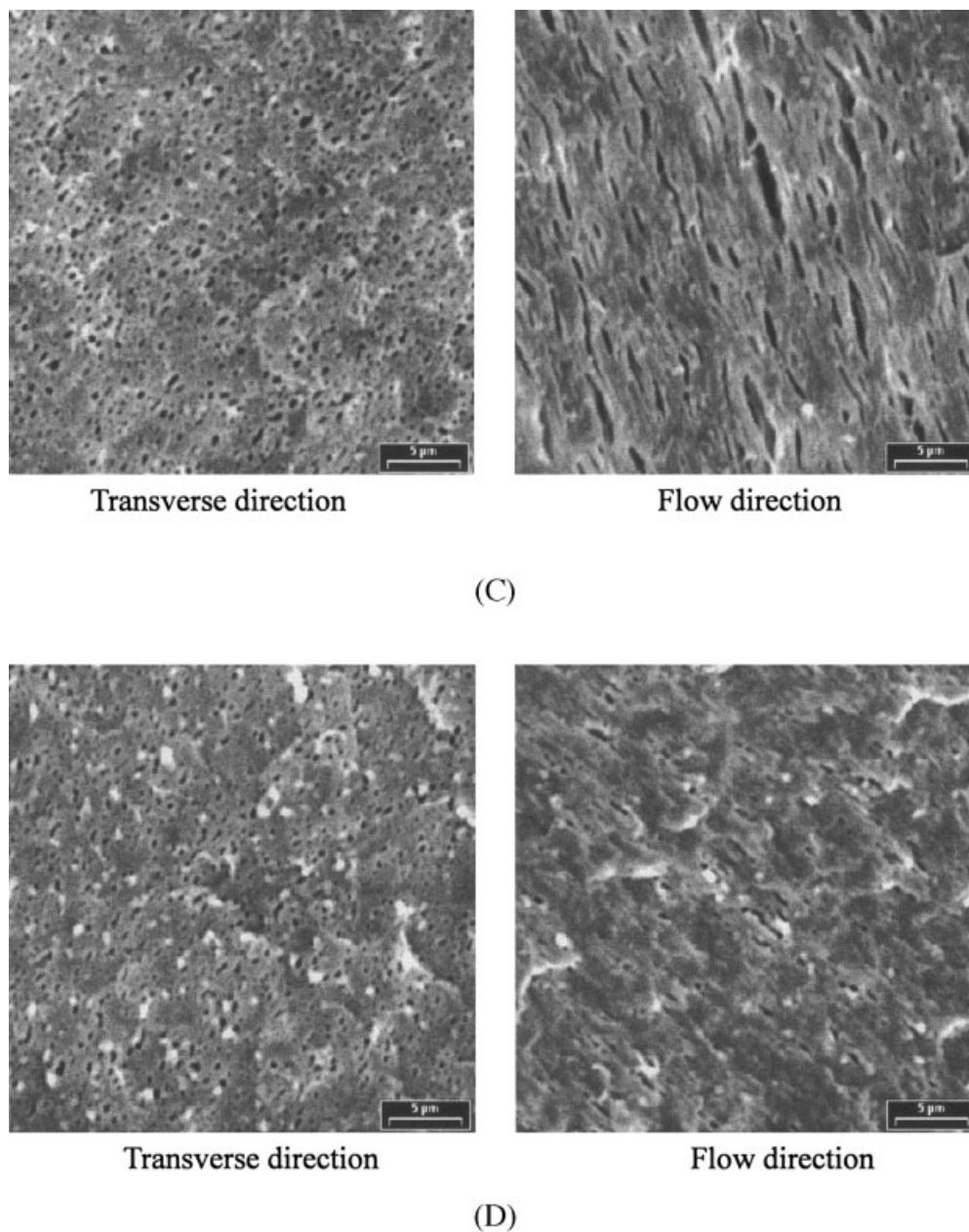


Figure 2 (Continued from the previous page)

binary blends significantly increased the mechanical strengths, and this was indicative of the reinforcing effects of HDPE in rubbery domains.

Thermal properties

The thermal properties of the blends are given in Table IV. T_m of HDPE is split into two parts: T_{mh} and T_{ml} . HDPE and mPE, having mutual ethylene units, could form partially miscible domains.¹⁹ Consequently, T_m should be lower than that of neat HDPE (Figs. 4 and 5).

T_c of HDPE decreased in the mPE/HDPE blends, whereas T_c of mPE increased (Table IV). This implies

that mPE provided HDPE with a dilution effect and that HDPE provided mPE with a nucleation effect.

T_m of mPE disappeared in all the blends, and T_c of mPE was clearly observed at 44–45°C in the PP/mPE binary blends but disappeared in the ternary blends. T_m and T_c of PP were unaffected by mPE and HDPE in the blends (Table IV) because of the incompatible nature of the blends.

Rheological properties

The η^* values of the ternary blends are given in Figure 6, which shows viscosity upturns at low frequencies,

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

Sample series	Sample	MFR at 230°C (g/10 min)	Tensile strength			Flexural modulus (kg ^f /cm ²)	Izod impact strength (kg ^f cm/cm)		Rockwell hardness (R scale)
			At yield (kg ^f /cm ²)	At break (kg ^f /cm ²)	Elongation (%)		23°C	-20°C	
Base polymer	PP-L	15.0	370	245	480	19,500	1.6	2.3	105.5
	PP-M	6.5	380	425	540	17,300	2.1	2.3	105.0
	PP-H	3.2	390	295	490	19,700	2.5	2.2	105.0
Binary blend	R-1	14.7	230	285	530	10,300	22.4	3.7	61.5
	R-2	9.5	230	300	500	9,900	38.3	6.9	60.0
	R-3	6.1	225	300	490	9,000	57.1	12.7	58.5
Ternary blend	PPL-1	15.8	280	305	620	12,400	11.8	2.8	75.5
	PPL-2	14.8	280	230	550	13,400	22.7	3.2	75.0
	PPL-3	13.1	280	235	570	13,500	33.2	3.6	77.5
	PPM-1	9.2	275	320	550	12,800	35.1	3.1	74.5
	PPM-2	8.7	280	255	550	12,900	41.0	3.3	75.0
	PPM-3	7.9	280	180	540	13,000	51.5	3.6	76.0
	PPH-1	6.3	275	250	510	12,300	49.0	3.3	72.5
	PPH-2	6.0	275	305	530	12,500	52.1	3.6	74.5
	PPH-3	5.6	275	245	540	12,500	60.1	3.7	74.0

which are indicative of two-phase systems with interparticle interactions.

The Cole–Cole plots of the mPE/HDPE binary blends are shown in Figure 7. Blends with a viscosity ratio close to unity (mPE/HD1 and mPE/HD2) show semicircles, but mPE/HD3 with a high viscosity ratio drifts away from a semicircle. For the PP-based blends, the Cole–Cole plots do not make semicircles, regardless of the viscosity ratio (Fig. 8). It can be concluded that all the blends investigated in this work were rheologically immiscible in the melt state, except for the mPE/HDPE blends.

CONCLUSIONS

HDPE was added to PP/mPE binary blends to improve the stiffness with the retention of toughness, and the effects were studied in terms of the viscosity ratios of each component.

a_n , when the viscosity ratio was below unity, was smaller than when the viscosity was above unity; this implied that the interfacial shear stress was more important than the viscosity ratio.

Fibrils were observed in the PP/mPE/HDPE ternary blends when p_{MP} was below unity. A fibril morphology was also observed, with p_{MP} greater than unity, when the viscosity of mPE was low, indicating that the mPE/HDPE blends had a skin–core morphology. With a skin–core morphology, some mPE in the skin formed fibrils.

The impact strength and tensile strength at yield, the flexural modulus, and the hardness increased with the addition of HDPE to the PP/mPE binary blends.

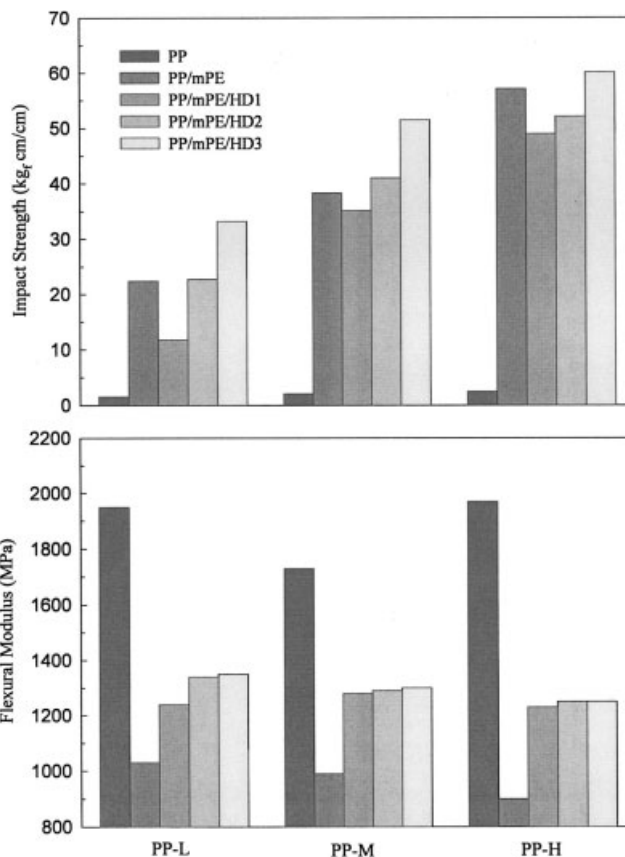


Figure 3 Notched Izod impact strength at room temperature and flexural modulus of PP, a PP/mPE (70/30) binary blend, and a PP/mPE/HDPE (70/20/10) ternary blend.

TABLE IV
Thermal Properties of the Base Polymers and Their Blends

Sample	Thermal properties							ΔH_c (J/g)	Crystallinity of PP (%)
	T_m (°C)		PP	ΔH_f (J/g)		T_c (°C)			
	T_{mt}	T_{mh}		HDPE	PP	mPE	PP and PE		
PP-L	—	—	162.4	—	93.3	—	116.1	105.9	44.6
PP-M	—	—	161.8	—	92.0	—	112.5	110.6	44.0
PP-H	—	—	163.1	—	96.3	—	115.5	109.5	46.1
R-1	—	—	161.7	—	64.4	45.1	115.4	74.2	44.0
R-2	—	—	162.4	—	67.2	44.7	113.8	70.6	45.9
R-3	—	—	161.7	—	65.5	44.4	114.1	72.3	44.8
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	—
PPL-1	125.1	127.1	161.4	14.4	64.2	—	113.1	93.0	43.9
PPL-2	126.4	129.4	161.7	15.2	64.6	—	114.5	92.7	44.2
PPL-3	126.7	129.4	162.4	12.3	59.5	—	115.5	84.6	40.7
PPM-1	125.5	127.5	161.8	12.6	62.3	—	113.5	88.9	42.6
PPM-2	128.1	129.7	162.1	15.1	62.0	—	115.1	85.1	42.4
PPM-3	126.4	128.7	161.7	15.4	60.2	—	115.9	89.6	41.1
PPH-1	125.4	127.1	162.1	14.8	62.3	—	113.1	87.8	42.6
PPH-2	128.1	129.4	162.4	15.0	62.3	—	114.1	90.4	42.6
PPH-3	127.1	128.7	162.4	15.1	61.3	—	115.8	87.7	41.9

ΔH_f = heat of fusion; ΔH_c = heat of crystallization.

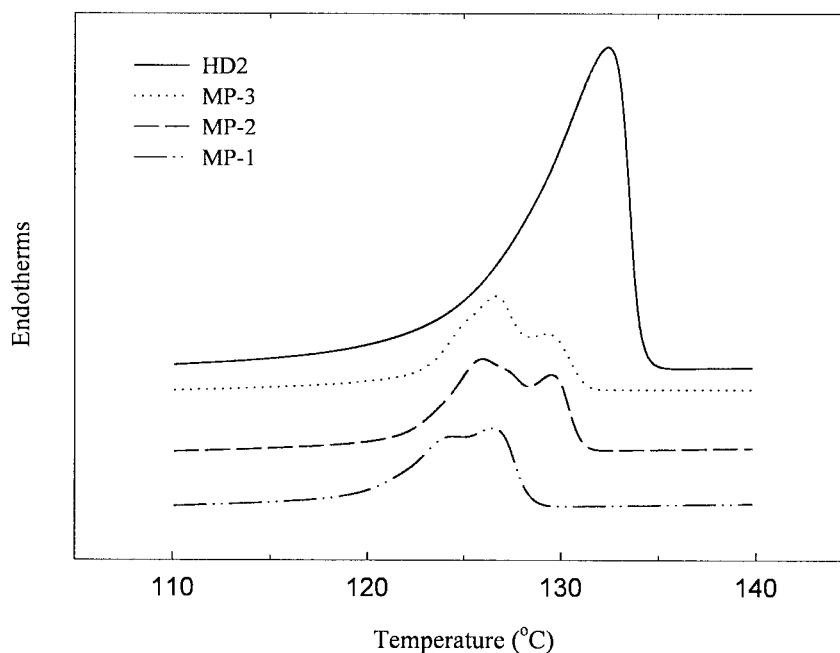


Figure 4 Melting endotherms of HD2 and HDPE in mPE/HDPE (66.7/33.3) binary blends.

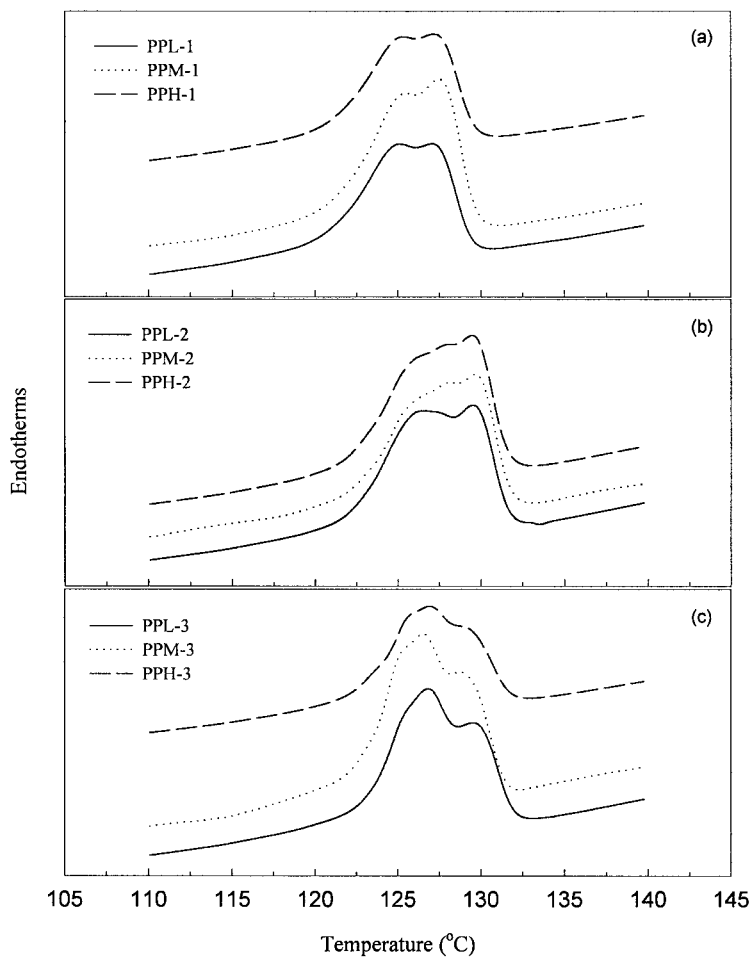


Figure 5 Melting endotherms of HDPE in PP/mPE/HDPE (70/20/10) ternary blends: (a) PP/mPE/HD1, (b) PP/mPE/HD2, and (c) PP/mPE/HDPE.

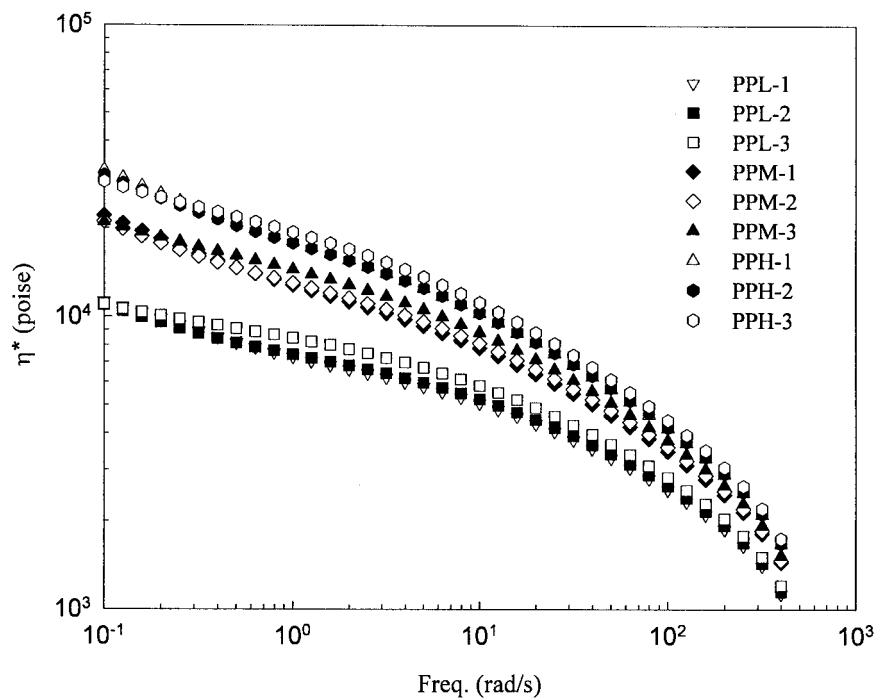


Figure 6 η^* of PP/mPE/HDPE (70/20/10) ternary blends at 230°C.

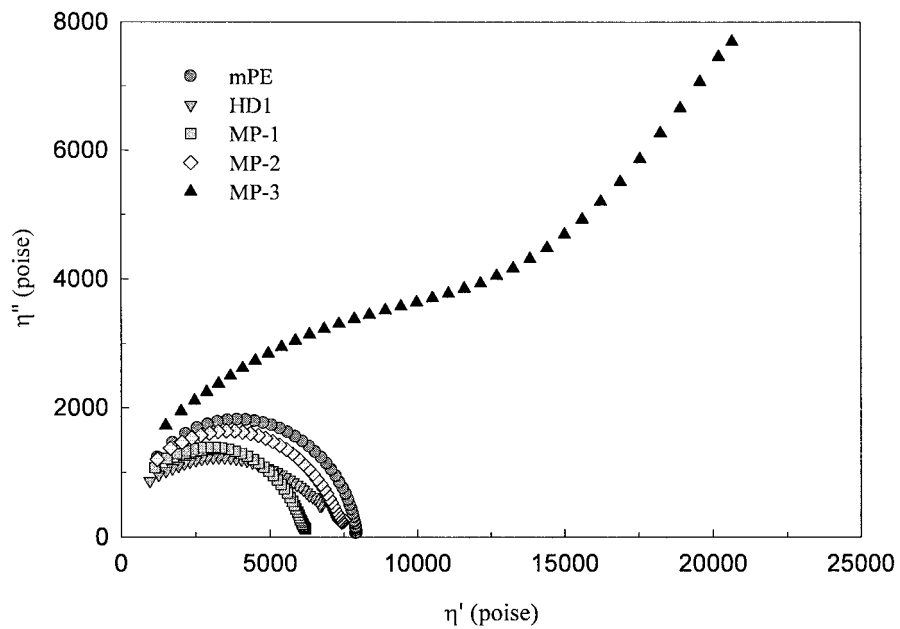


Figure 7 Cole-Cole plots for mPE, HDPE, and mPE/HDPE (66.7/33.3) binary blends at 230°C.

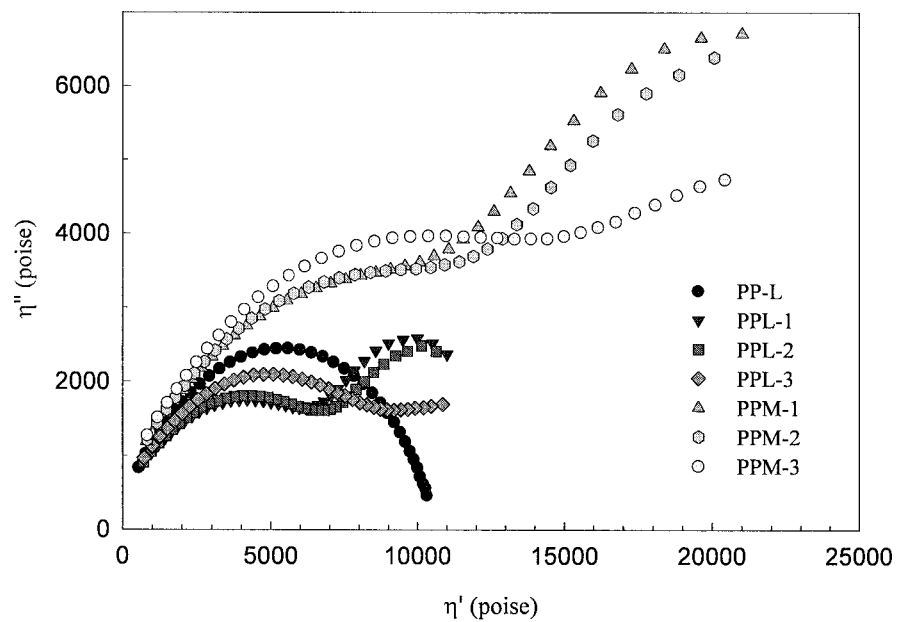


Figure 8 Cole-Cole plots for PP and PP/mPE/HDPE (70/20/10) ternary blends at 230°C.

Cocrystallization between HDPE and mPE, shown by double T_m 's in mPE/HDPE binary blends and PP/mPE/HDPE ternary blends, should contribute to the reinforcing effect of HDPE in the ternary blends.

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