

Reactive Extrusion of Polyolefin Ternary Blends

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SYNOPSIS

Reactive extrusion of polypropylene (PP)/ethylene-propylene-diene terpolymer (EPDM)/high-density polyethylene (PE) (80/10/10 by weight) blends were carried out using a co-rotating twin-screw extruder. The effects of peroxide and coagent concentrations and extruder rpm were studied in terms of rheological, morphological, thermal, and mechanical properties of the blends. Melt viscosity of the peroxide-treated blend increased and decreased over the untreated one depending on the amount of a coagent. Morphologically, interfaces blur with only a peroxide treatment, and significant domain reduction was obtained when peroxide and a coagent were used together. Both T_m (crystalline melting temperature) and T_g (glass transition temperature) of PP increased in the blend, whereas those of PE slightly decreased. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Although polypropylene (PP) has a most remarkable combination of physical properties, it has poor impact strength especially at low temperature due to the inherently high glass transition temperature and high crystallinity.^{1,2} The ethylene-propylene copolymer (EPM) and the ethylene-propylene-diene terpolymer (EPDM) are often used as impact modifiers for PP.³⁻⁶ Typical rubber-modified PP resins contain about 15% modifier, and effective impact toughening is obtained when small rubber particles (<0.5 μm in diameter) are distributed homogeneously in the PP matrix. On the other hand, certain mechanical properties such as modulus and tensile strength of PP are decreased by blending with rubbery materials. Therefore, part of the rubber was sometimes replaced by polyethylene (PE) to improve such properties in PP blends.⁷⁻⁹ In PP/EPDM/PE and PP/EPM/PE ternary blends, PE is preferentially dissolved in the rubber domain.

In the presence of peroxide, crosslinking is dominant for PE, whereas chain scission is for PP.¹⁰ Recently, multifunctional monomers called coagents are used alone and with a peroxide to promote

crosslinkability during reactive extrusion of polyolefins.^{11,12} When the coagent is added to the peroxide-initiated reactive extrusion of PP, the melt flow index (MFI) can be decreased depending on the relative concentration of coagent and peroxide.

This article considers the reactive ternary blends of PP/EPDM/PE (80/10/10 by weight). The blends were prepared using a twin-screw extruder (JSW TEX 30) at 230°C. A peroxide is used alone and in combination with a coagent. Viscoelastic properties of the melt and morphological, thermal, and mechanical properties of the injection-molded specimens of the blends were determined. The effect of the concentration of a multifunctional monomer as well as of peroxide was intensively investigated.

EXPERIMENTAL

Materials

Commercial grades of isotactic PP (weight-average molecular weight, $M_w = 380,000$, number-average molecular weight, $M_n = 54,000$, MFI [melt flow index] = 2.3 g/10 min [2.16 kg, 230°C]), high-density PE ($M_w = 235,000$, $M_n = 21,000$, MFI = 0.9 g/10 min [2.16 kg, 230°C]), and EPDM (Vistalon 3708P, ethylene content = 65 wt %, diene content = 3–4 wt %) were used for blending. Both PP and PE were kindly donated by the Korea Petrochemical Ind. Co.,

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Table I Formulation of Reactive PP/(EPDM/PE) Blends

Experiment No.	PP	MP ^a	Peroxide	Coagent
1	80	20	—	—
2	80	20	0.01	—
3	80	20	0.01	0.15
4	80	20	0.01	0.3
5	80	20	0.01	0.6
6	80	20	0.00	0.3
7	80	20	0.02	0.3
8	80	20	0.03	0.3

^a MP: master pellet prepared from EPDM/PE (60/40).

1,3-bis(*t*-butylperoxyisopropyl)benzene was used as a peroxide, and trimethylolpropanetriacrylate (TMPTA) was added as a multifunctional monomer. Irganox B561 (Ciba Geigy) was used as an antioxidant.

Compounding

Peroxide, the multifunctional monomer, and additives were premixed using a Super Floater (SFC-50, Kawata MFG). Blends were extruded in a corotating twin-screw extruder (JSW TEX30) at 230°C, 100 or 230 rpm, and the extrudates were injection-molded for mechanical tests and compression-molded for rheological tests. Peroxide and TMPTA concentrations were varied between 0–0.03 and 0–0.6 phr, re-

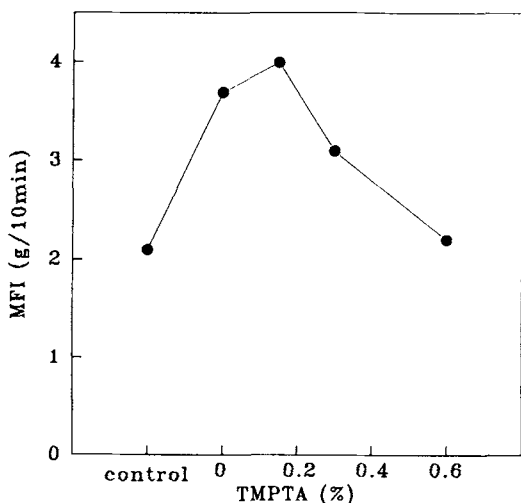


Figure 1 MFI of blends vs. TMPTA concentration (0.01% peroxide). (Control contains no peroxide, no TMPTA.)

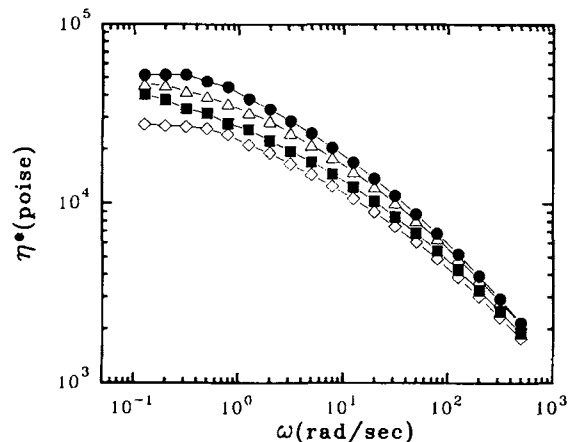


Figure 2 Complex viscosity of the blends vs. peroxide content (0.3 phr TMPTA) at 220°C: (●) 0.005, (△) 0.01, (■) 0.02, and (◇) 0.03 phr peroxide.

spectively. Compositions and recipes of the blends are listed in Table I. For ternary blends, EPDM/PE (60/40 by weight) master pellets were first prepared, followed by mixing with PP in a desired composition.

Measurements

MFI was measured following ASTM D 1238L, and the rheological properties, using an RDS (Rheometrics Dynamics Spectrometer 7700) with a parallel-plate fixture at 220°C. Morphologies of the injection-molded specimen were determined from a polarizing optical microscope and a scanning electron microscope (SEM, JSM 820) using the injection-molded specimen. SEM micrographs were taken from the cryogenically fractured (in liquid ni-

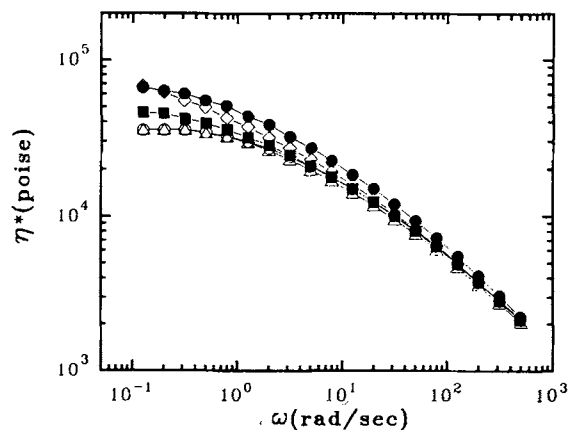


Figure 3 Complex viscosity of the blends vs. TMPTA content (0.01 phr peroxide) at 220°C: (●) untreated; (○) 0.0, (△) 0.15, (■) 0.3, and (◇) 0.6 phr TMPTA.

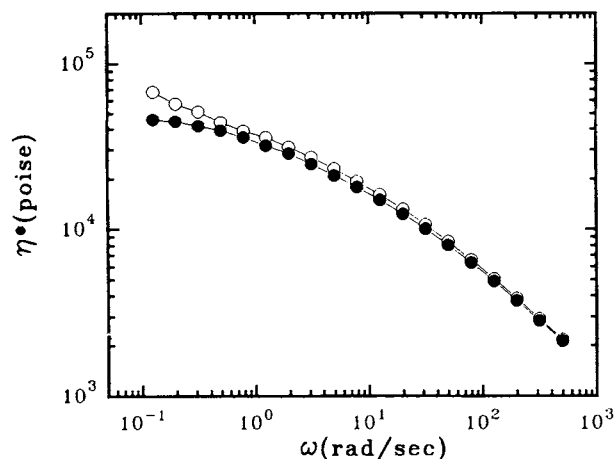


Figure 4 Effect of extruder rpm on the complex viscosity of the blends at 220°C (0.01 phr peroxide and 0.3 phr TMPTA): (○) 100 rpm; (●) 230 rpm.

trogen) surfaces, which were sputtered with gold before viewing. Thermal properties were determined using differential scanning calorimetry (DuPont 2100). Tensile properties were measured using the injection-molded specimen with a crosshead speed of 5 mm/min and the Izod impact test (ASTM D 256) with a notched $\frac{1}{8}$ in. specimen. The flexural modulus and hardness (Rockwell) were measured following ASTM D 790 and D 785, respectively. The above tests were done at room temperature. Error ranges of the mechanical tests were generally of 5–7%, and at least five runs were made to report the average.

RESULTS AND DISCUSSION

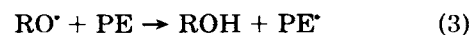
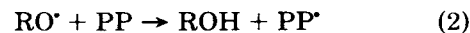
Reaction Mechanism

Since the major component of the ternary blends is PP (80%), generations of PP macroradicals, followed by main-chain scissions, are the main reactions during the peroxide-treated melt extrusion. However, the opportunity of crosslinking between PP macroradicals should be greatly enhanced by adding a proper amount of TMPTA to the peroxide system. Crosslinking and grafting will take place as the following simplified reaction schemes¹³:

Formation of the free radical:



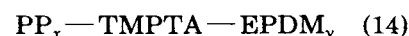
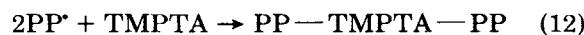
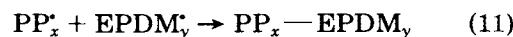
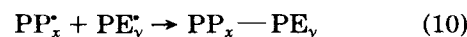
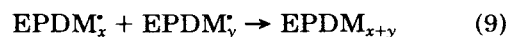
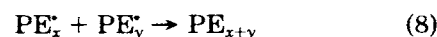
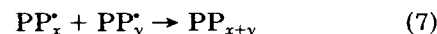
Radical transfer:



Chain scission of PP:



Grafting/crosslinking:



The chain scission (β -scission) [eq. (6)] will lead to reduction in M_w (molecular weight), whereas grafting and crosslinking reactions [eqs. (7)–(15)] result in increase in M_w .^{10,14} TMPTA is expected to minimize the chain scission by stabilizing the PP macroradicals [eq. (5)] and by enhancing the crosslinking efficiency by resolving the steric hindrance [eq. (12)].

Melt Properties

The MFI increases with peroxide treatment and with peroxide and TMPTA treatment when the amount of TMPTA is insufficient. This means that the crosslinking of PP is dominant over chain scission only with a sufficient amount of TMPTA (Fig. 1).

The effect of peroxide content (0.005–0.03 phr) at a fixed TMPTA content (0.3 phr) on the viscosity function of the blends is given in Figure 2. As ex-

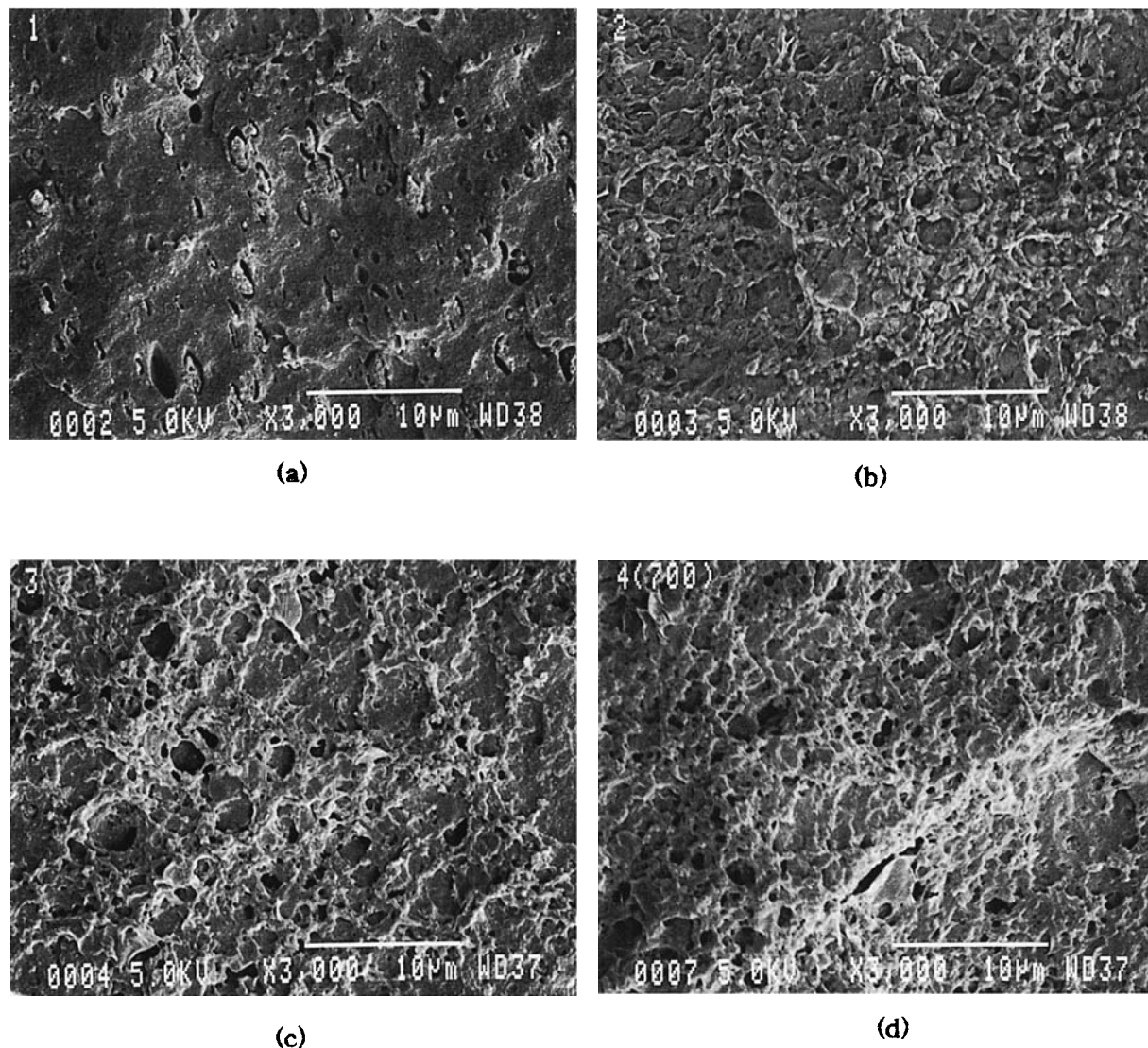


Figure 5 SEM micrographs of untreated and peroxide (0.01 phr)-treated blends vs. TMPTA content: (a) untreated; (b) 0.0; (c) 0.15; and (d) 0.3 phr TMPTA.

pected, the viscosity of the blends decreased monotonically with increasing peroxide content. The viscosity curve of the blend with 0.03 phr peroxide shows an extended Newtonian behavior at low frequency, indicating that the degradation of PP gives a narrower molecular weight distribution (MWD) as well as a lower average M_w .¹⁵

Melt viscosities of the blends as a function of TMPTA are shown in Figure 3. As expected, viscosity decreased with peroxide (0.15 phr) treatment. A relatively well-defined Newtonian plateau is obtained with 0 and 0.15 phr TMPTA. The MWD as well as the M_w of PP should decrease with peroxide treatment.¹⁰ This may imply that chain scission is preferred with high M_w species, whereas crosslinking

and chain extension are more feasible with low M_w species. As the TMPTA content increases, low-frequency viscosity increases as the crosslinking becomes significant.¹⁶ At 0.6 phr TMPTA, a sign of viscosity yield (upturn of viscosity at low frequency) is obtained, and the viscosity function tends to follow the rubbery material (a straight line in a log-log plot).

Figure 4 shows the effect of extruder rpm (100 and 230) on the melt viscosity of the ternary blends. Low screw speed gives a relatively higher viscosity due, in part, to the less shear degradation of PP under lower shear stress, but mostly to the longer residence time allowing more crosslinking to occur. However, under certain conditions, viz., at high per-

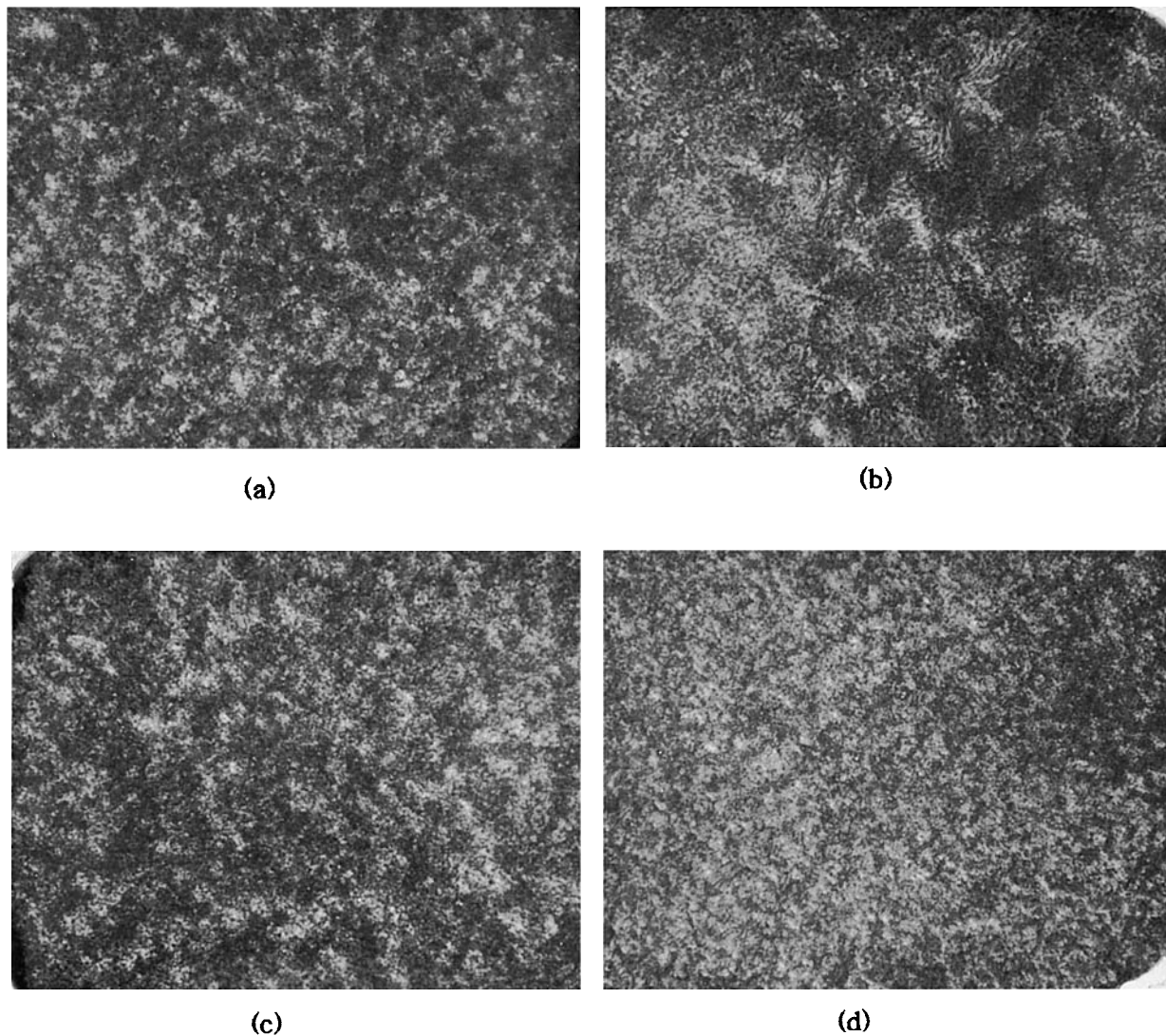


Figure 6 Polarizing optical micrographs of untreated and peroxide (0.01 phr)-treated blends vs. TMPTA content: (a) untreated; (b) 0.0; (c) 0.15; and (d) 0.3 phr TMPTA.

oxide and low coagent content, higher extrusion temperature and a longer residence time should allow more degradation of the polymers to occur.¹⁰

Morphology

Figure 5 shows fractured surfaces of the blends. It is seen that EPDM tends to surround PE in the PP matrix. With peroxide and coagent treatment, the dispersed domains are significantly decreased in size and the interface becomes a blur. This implies that block copolymers and/or graft copolymers between PP and EPDM and/or PE are formed *in situ* and act as an effective compatibilizer [eqs. (10), (11), (13), and (14)].¹³

Figure 6 shows polarizing optical micrographs of the ternary blends. The size of spherulites are significantly decreased with both peroxide and TMPTA treatment. This is probably due to the nucleating action of the crosslinks which were formed during extrusion.

Thermal Properties

Typical DSC thermograms of the blends are shown in Figure 7, where the melting endotherms are given as a function of TMPTA content. Detailed DSC data including T_m (crystalline melting temperature), T_c (crystallization temperature), ΔH_f (heat of fusion), and ΔH_c (heat of crystallization) are tabulated in Ta-

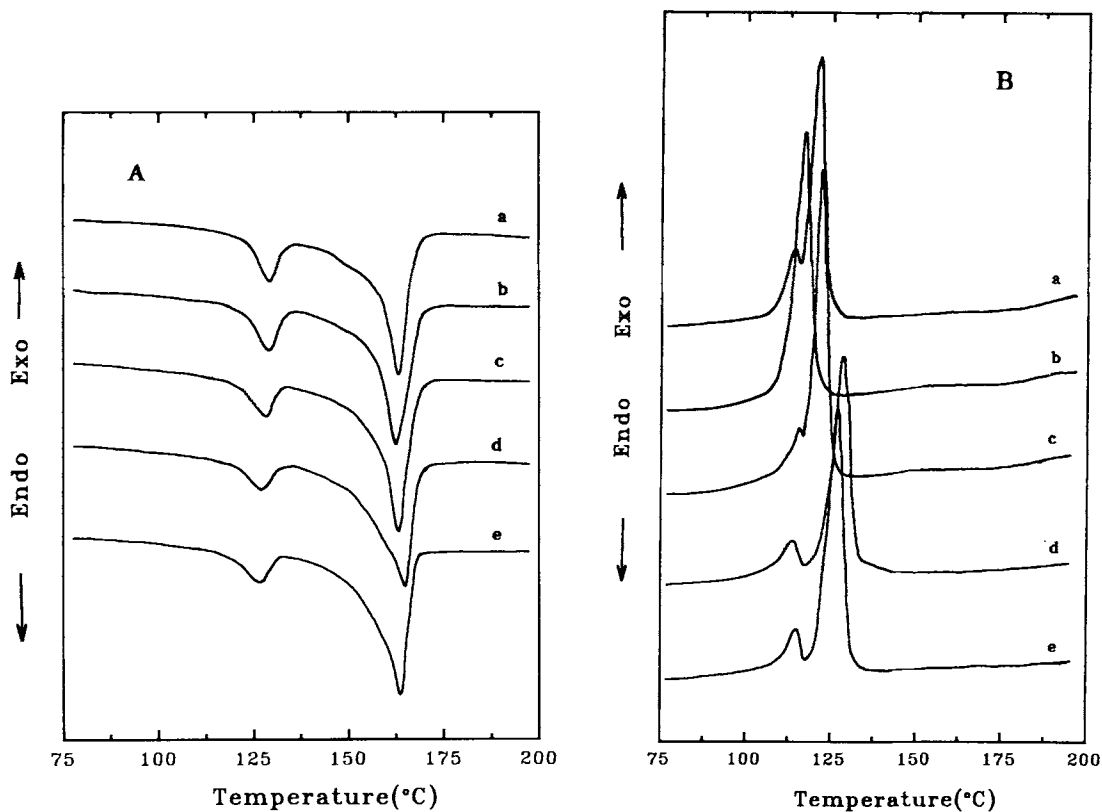


Figure 7 DSC thermograms of untreated and peroxide (0.01 phr)-treated blends vs. TMPTA content on (A) heating and (B) cooling: (a) untreated; (b) 0.0; (c) 0.15; (d) 0.3; and (e) 0.6 phr TMPTA.

ble II. With increase of peroxide and coagent content, the T_c of PP is increased by ca. 6°C with TMPTA and ca. 8°C with peroxide (T_m is almost unchanged). The T_m and T_c of PE is slightly decreased with the addition of additives. Depending upon the density, crosslinking may act as a local defect to reduce the

crystallinity, but a few crosslinks can also improve packing of the polymer chain into a crystalline structure at higher temperature since they can restrict the flow of the polymer.¹⁷⁻¹⁹ It seems that crosslinkings of PE act as a local defect, and those of PP, to augment the chain packing at higher temperature.

Table II Thermal Properties of Reactive PP/EPDM/PE Blends

Experiment No.	PP				PE			
	T_m ($^\circ\text{C}$)	ΔH_m (J/g)	T_c ($^\circ\text{C}$)	ΔH_c (J/g)	T_m ($^\circ\text{C}$)	ΔH_m (J/g)	T_c ($^\circ\text{C}$)	ΔH_c (J/g)
1	163.1	74.5	120.2	74.42	128.4	27.1	113.2	16.73
2	162.2	74.0	116.4	91.1	128.6	29.2	—	—
3	163.2	77.4	121.5	75.7	127.6	27.3	114.5	15.8
4	164.9	75.9	128.0	73.4	126.3	20.6	113.0	17.0
5	163.7	80.4	126.2	77.4	126.2	23.4	113.5	19.3
6	163.7	75.3	122.8	74.4	127.6	25.5	113.8	21.3
7	165.2	79.4	127.7	78.2	126.5	24.0	113.1	23.0
8	164.6	80.4	127.9	77.5	125.8	22.8	112.7	21.1

Table III Physical Properties and MFI of Peroxide and Multifunctional Monomer-treated PP/EPDM/PE Blends

Run No.	MFI (g/10 min)	Izod (kg cm/cm)	Hardness (Rockwell)	F/M (kgf/cm ²)	σ_y (kgf/cm ²)	ϵ (%)
1	2.1	12.5	74	12,300	300	510
2	3.7	11.9	74	11,500	285	520
3	4.0	11.7	75	11,700	280	520
4	3.1	16.1	77	12,200	280	550
5	2.2	15.4	78	12,400	280	550
6	2.3	13.9	75	11,900	290	540
7	3.6	12.9	76	11,800	270	560
8	5.0	12.4	77	11,700	270	570

F/M: flexural modulus; σ_y : yield strength; ϵ : elongation at break.

Mechanical Properties

Mechanical properties of the blends are shown in Table III and Figure 8. Peroxide alone causes a slight decrease in impact strength, modulus, and yield strength due to the main-chain scission of PP, as evidenced by the increased MFI. Impact strength increases only when a certain amount of TMPTA is added to the peroxide. This may imply that there is a minimum amount of TMPTA relative to the amount of peroxide used, which can contribute to the impact toughening, i.e., when the amount of TMPTA is insufficient, TMPTA neither can stabilize the PP macroradicals nor contribute to the crosslinking of PP. Then, chain scission is the dominant reaction, resulting in the decreased M_w of PP. With a lower average M_w of the matrix, the impact strength of the ternary blend should decrease. As the TMPTA concentration increases, impact strength increases over the untreated blend. This is due mainly to the increased M_w of PP by crosslinking as noted from the decreased MFI. The effect of increasing molecular weight of PP on the impact strength as well as on the other mechanical properties is twofold, i.e., to augment the blend property directly by the increased molecular weight and by the finer breakup of the dispersed phase due to the decreased viscosity ratio, viz., η (dispersed phase)/ η (matrix). In addition, the *in situ* formation of copolymers should also greatly contribute to the mechanical properties, especially to the impact strength of the blends by augmenting the interfacial adhesions between PP and the rubbery domains.

With the addition and increase of TMPTA, other mechanical properties (hardness, modulus, elongation at break) generally increase as compared to those of peroxide-alone-treated blends. This is ba-

sically due to the same reasons which contribute to the impact toughening, i.e., the increased molecular weight of PP, increased interfacial adhesions, and decreased particle size.

The effect of peroxide is to decrease modulus, yield strength, and impact strength of the blends due mainly to the main-chain scission (increased MFI) and to increase the hardness and elongation at break. The increase of elongation with peroxide treatment is related to the macromolecular parameters, i.e., higher peroxide loading leads to more degradation of PP, which results in decrease in MWD as well as in M_w . Following Tzoganakis et al.,²⁰ a lower MWD of PP gives higher elongation and possibly lower impact strength; the result agreed with ours.

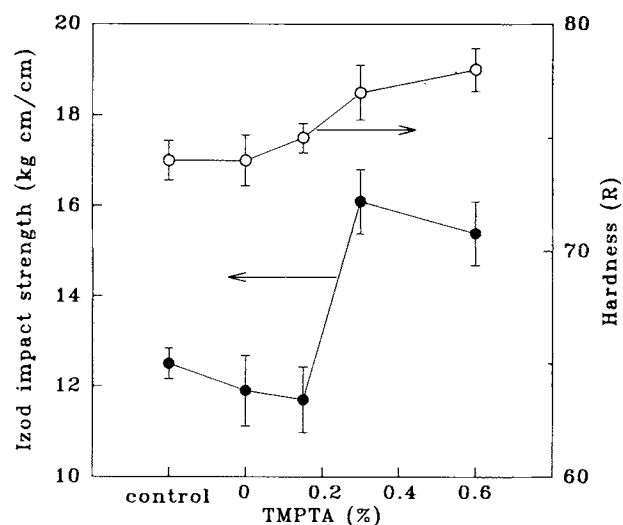


Figure 8 (●) Notched Izod impact strength and (○) hardness vs. TMPTA concentration (0.01% peroxide).

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