

Effect of Viscosity Ratio, Rubber Composition, and Peroxide/Coagent Treatment in PP/EPR Blends

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SYNOPSIS

Effect of viscosity ratio ($\eta_{\text{EPR}}/\eta_{\text{PP}}$), propylene (C_3) content of (ethylene-propylene copolymer (EPR)), and peroxide/coagent treatment on polypropylene (PP)/EPR (80/20 by weight) melt blends were studied in terms of morphological, rheological, thermal, and mechanical properties. As the viscosity ratio increases from approximately 0.8 to 1.2, domain size increased (submicron–1.5 μm), and the degree of supercooling (ΔT) for crystallization increased (37.4–47.8°C) due to the decreased crystallization temperature (T_{cc} , 122.2–110.8°C). This resulted in larger spherulite size and increased hardness, modulus, and yield strength. With high C_3 EPR, total crystallinity (ΔH_f) of PP decreased, together with the mechanical properties, except the impact strength. With peroxide/coagent treatment, the spherulite size significantly decreased. The notched Izod impact strength decreased with increasing viscosity ratio, but significantly increased with high C_3 EPR and with peroxide/coagent treatments. The results were interpreted in terms of domain size and shape, chemical affinity between PP and EPR, copolymer formation, and main chain scission of PP. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polypropylene (PP) has well-balanced physical properties and processability, although it has poor impact strength, especially at low temperature due to the inherently high glass transition temperature and high crystallinity.^{1,2} Ethylene-propylene copolymer (EPR) and ethylene-propylene-diene terpolymer are often used as impact modifiers for PP.^{3–5} Typical rubber-modified PP resins contain about 20% modifier, and effective impact toughening is obtained when small rubber particles (<0.5 μm in diameter) are evenly distributed in the PP matrix. Recently it has also been claimed that PP crystalline lamellae can be dispersed in a matrix consisting of networked amorphous PP and EPR, where EPR can form fibrils along the flow direction during injection.⁶ The domain morphology is closely related to the properties and it should

depend on several factors including blend compositions, viscosity ratio of EPR to PP ($\eta_{\text{EPR}}/\eta_{\text{PP}}$), and interfacial conditions.

In the presence of peroxide, chain scission is the dominant reaction for PP.⁷ Recently multifunctional monomers called coagents were used alone and with a peroxide to promote crosslinkability during reactive extrusion of polyolefins.^{8–10} When the coagent is added to the peroxide-initiated reactive extrusion of PP, main chain scissions are decreased due to the stabilization of macroradicals via resonance, and crosslinking reactions are favored because the steric hindrance is resolved.^{11,12} In polyolefin blends, crosslinking between the different components leads to the formation of graft or block copolymers that should act as compatibilizers.

We considered the particles in matrix morphology in a PP/EPR (80/20 by weight) blend, where the morphology was fixed by the low rubber content. The effect of viscosity ratio, propylene (C_3) content of EPR, and peroxide/coagent treatment were studied in terms of morphological, rheological, thermal, and mechanical properties of the blends.

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EXPERIMENTAL

Materials

Table I lists the PP and EPRs used in the present experiments, with their melt viscosities in Figure 1. One type of isotactic PP, and six types of EPR were chosen so that the viscosity ratio ($\eta_{\text{EPR}}/\eta_{\text{PP}}$) greater than (EPR-h, EPR-H), smaller than (EPR-l, EPR-L) and approximately equal to (EPR-m, EPR-M) unity are obtained with two types of EPR having significantly different levels of C_3 (26–28% for EPR-h, -m, -l, and 42–44% for EPR-H, -M, -L). The viscosity functions of EPR-l, EPR-m, and EPR-h were practically the same as EPR-L, EPR-M, and EPR-H, respectively, and they are not shown in the figure. 1,3-Bis(*t*-butylperoxyisopropyl) benzene and trimethylolpropanetriacrylate (TMPTA) were used as peroxide and coagent, respectively, together with an antioxidant (Irganox B561, Ciba Geigy).

Compounding

Peroxide, multifunctional monomer, and additives, when employed, were premixed using a Super Floater (SFC-50, Kawata MFG). Blending was done in a corotating twin screw extruder (JSW TEX30) with L/D of 30 at 30 rpm using a temperature profile 210, 220, 230, and 220°C. Extrudates were injection molded for mechanical tests and compression molded for rheological tests. Basic formulations of the blends are listed in Table II.

Measurements

The rheological properties of the base resins were measured using an Rheometrics Dynamics Spectrometer 7700 with a parallel plate fixture at 210°C. For the blends, a capillary rheometer with L/D of

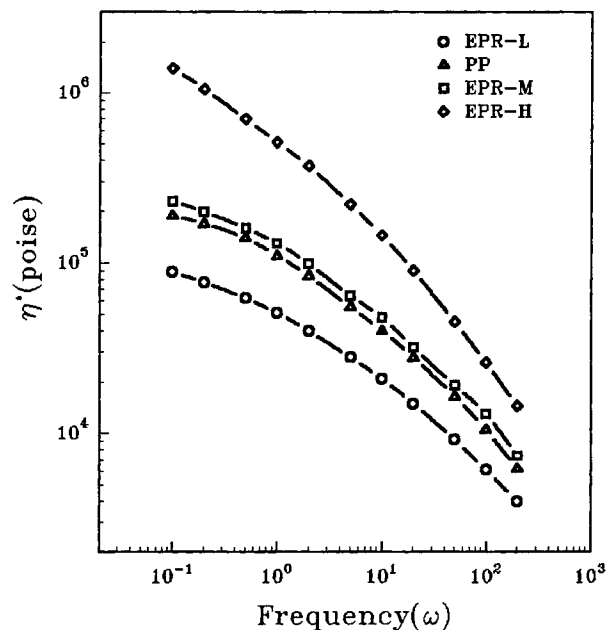


Figure 1 Melt viscosities of PP and EPR (210°C).

25 was used to measure the melt viscosity at 220°C. Morphologies of the injection molded specimen were determined from a polarizing optical microscope (POM) and a scanning electron microscope (SEM, JSM 820) using the injection molded specimen. SEM micrographs were taken from the cryogenically fractured (in liquid nitrogen) surfaces, which were sputtered with gold before viewing. Thermal properties were determined using differential scanning calorimetry (DuPont 2100). Tensile properties were measured using injection molded specimens with a crosshead speed of 5 mm/min and an Izod impact test (ASTM D 256) with a notched $\frac{1}{8}$ -in. specimen. Flexural modulus and hardness (Rockwell) were measured following ASTM D 790 and D 785, respectively. The above tests were done at room tem-

Table I Melt Index, Mooney Viscosity, and C_3 Content of Base Materials

	MI (g/10 min)	MV	C_3 (%)	Product Name, Maker
PP	2		> 99	5014L, Korea Petrochem.
EPR-h		90	28	KEP570, Kumho
EPR-m		38	26	KEP510, Kumho
EPR-l		24	26	KEP020P, Kumho
EPR-H		93	42	EPT4095, Mitsui
EPR-M		40	42	EPT3045, Mitsui
EPR-L		23	44	EPT4021, Mitsui

MI, melt index; MV, mooney viscosity; and C_3 , propylene content of EPR.

Table II Basic Formulations of PP/EPR Binary Blends

Run	PP	EPR-1	EPR-m	EPR-h	EPR-L	EPR-M	EPR-H	Peroxide	Coagent
1	80	20	—	—	—	—	—	—	—
2	80	—	20	—	—	—	—	—	—
3	80	—	—	20	—	—	—	—	—
4	80	—	—	—	20	—	—	—	—
5	80	—	—	—	—	20	—	—	—
6	80	—	—	—	—	—	20	—	—
7	80	20	—	—	—	—	—	0.01	—
8	80	20	—	—	—	—	—	0.01	0.1
9	80	20	—	—	—	—	—	0.01	0.2
10	80	20	—	—	—	—	—	0.01	0.3
11	80	—	20	—	—	—	—	0.01	0.3
12	80	—	—	20	—	—	—	0.01	0.3

Weight percent for peroxide and coagent is based on resin and rubber.

perature, and at least five runs were made to report the average.

RESULTS AND DISCUSSION

Morphology

Effect of Viscosity Ratio: Runs 1–3

SEM morphology of runs 1, 2, and 3 are shown in Figure 2, where the dominant morphology is the particles in the matrix. Particle size monotonically increases with the increasing viscosity ratio, which is varied from approximately 0.8 to 1.2, based on the value at ω (frequency) = 10^2 rad/s, and approximately corresponds to the compounding conditions. Following Wu,¹² who did experiments in a broad range of viscosity ratios, the finest breakup of the dispersed phase was obtained when the viscosity ratio approached unity. In our experiments, the range of viscosity ratio was narrow and close to unity, and the particle size was approximately the minimum and seemed inversely proportional to the shear rate imposed on the dispersed phase:

$$\frac{\dot{\gamma}_d}{\dot{\gamma}_m} = \frac{\eta_m}{\eta_c}$$

In this equation $\dot{\gamma}$ is the shear rate, and subscript d and m designate dispersed phase and matrix, respectively. This equation is simply obtained by assuming shear stress continuity at the interfaces.¹³

Figure 3 is the POM morphology of runs 1, 2, and 3, which shows that the size of PP spherulite increases with the increase of viscosity ratio. This im-

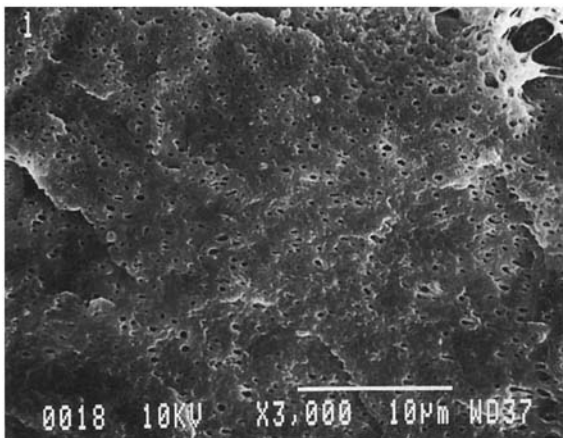
plies that EPR provides PP with nucleating sites. With increasing viscosity ratio, rubber domains increase in size and the PP–EPR interfacial areas are decreased.

Effect of C₃ Content: Runs 4–6

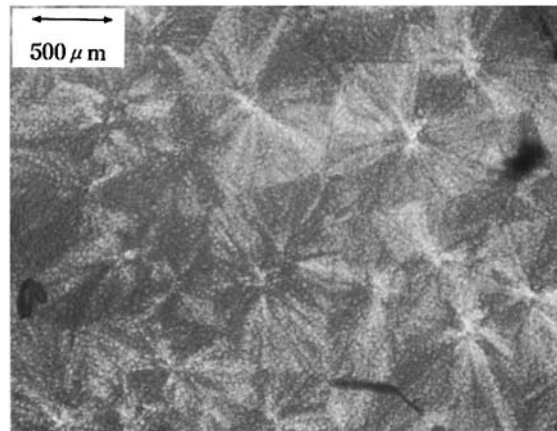
Figure 4 shows the SEM morphology of runs 4, 5, and 6, which have similar viscosity ratios with runs 1, 2, and 3, respectively, but with higher (42–44%) C₃ contents. Apparently no significant difference is seen in SEM morphology, as compared with the above three runs. That is, particle size increases with the increase of viscosity ratio, and at the same viscosity ratio particle size is practically the same with those having significantly low C₃ content of EPR. It seems that the rubber particle size in PP/EPR blends is primarily governed by the viscosity ratio. Rubber particles are more likely to be elliptic at lower viscosity ratio; and they become spherical at higher viscosity ratio, indicative of difficult deformability at the higher viscosity ratio.

Effect of Peroxide/Coagent Treatment: Runs 8–10 and 12

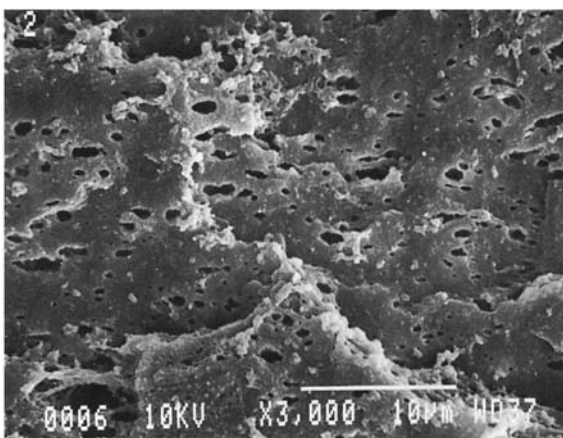
The effect of peroxide/coagent treatment was studied with the smallest particles (run 1). With peroxide/coagent treatment (Fig. 5) particle size increases. When this result is compared with the effect of viscosity ratio on domain size, the viscosity ratio should have been increased by peroxide/coagent treatment, implying the dominant reactions are main chain scission of PP. However, as the relative amount of coagent is increased (runs 8–10) domain size decreases to some extent, presumably due to



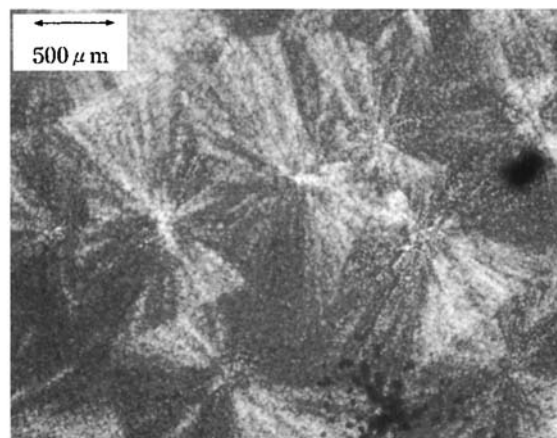
run #1



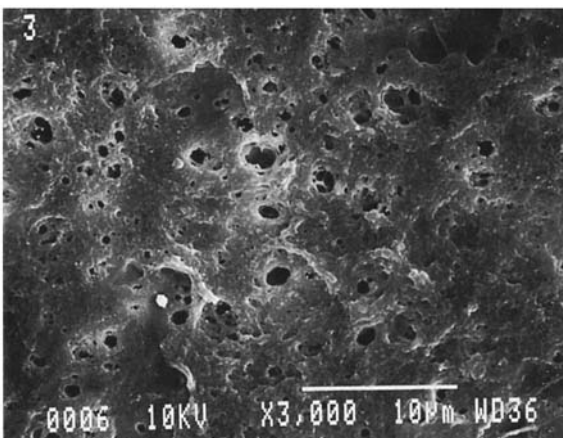
run #1



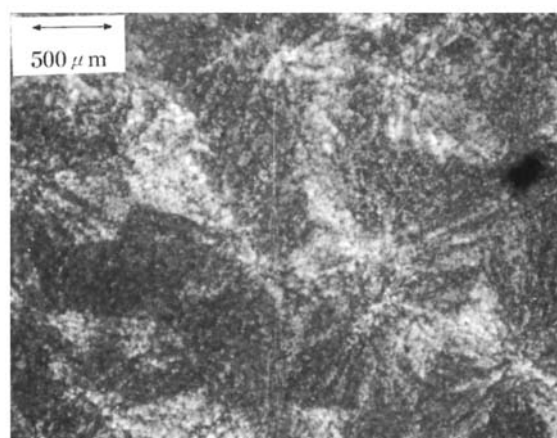
run #2



run #2



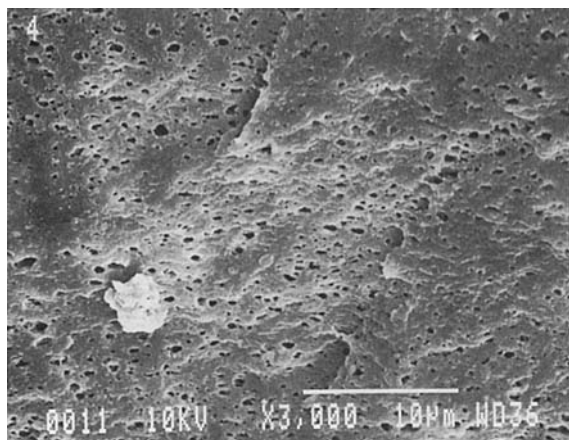
run #3



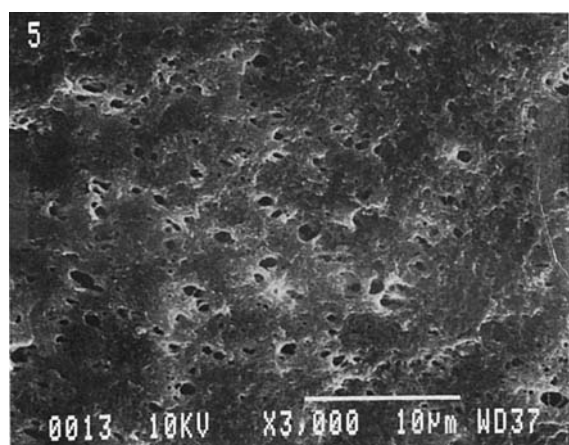
run #3

Figure 2 SEM micrographs of PP/EPR blends (runs 1–3).

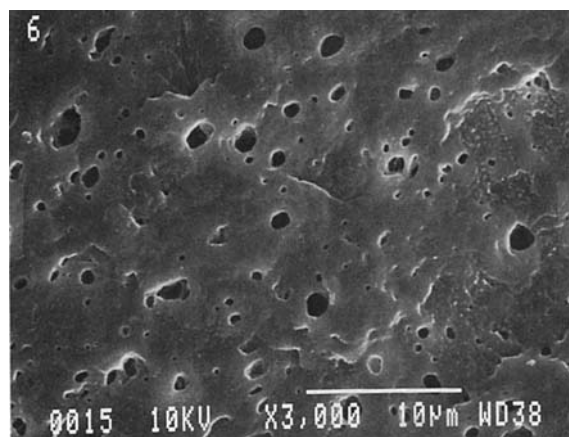
Figure 3 POM morphologies of PP/EPR blends (runs 1–3).



run #4



run #5



run #6

Figure 4 SEM micrographs of PP/EPR blends with C_3 content (42–44%) EPR (runs 4–6).

the stabilization effect of TMPTA. When the peroxide/coagent (0.01/0.3) was treated for the blends having the largest viscosity ratio (the largest domain size; run 3), the dispersed domains increased greatly (run 12).

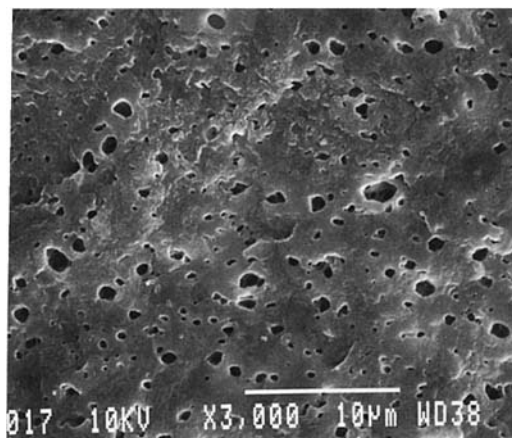
The above observations imply that certain types of PP/EPR copolymers are formed *in situ*, and are interposed at the interfaces to modify the interfacial tension. Because the same grade of PP is being used as matrix, the extent of crosslinking and degradation of PP should be the same, retaining the viscosity ratio unchanged. Then the extent of compatibilization by copolymer formation should explain the difference in the increase in domain size with peroxide/coagent treatment (run 10 vs. 12). With originally (untreated) larger particles, interfacial areas and hence the interfacial reactions to form PP/EPR copolymers are not likely to occur significantly, leading to insufficient compatibilization.

Figure 6 shows the effect of peroxide/coagent treatment on POM morphology. The size of PP spherulites is significantly decreased with peroxide/coagent treatment, although the effect of coagent content is not seen.

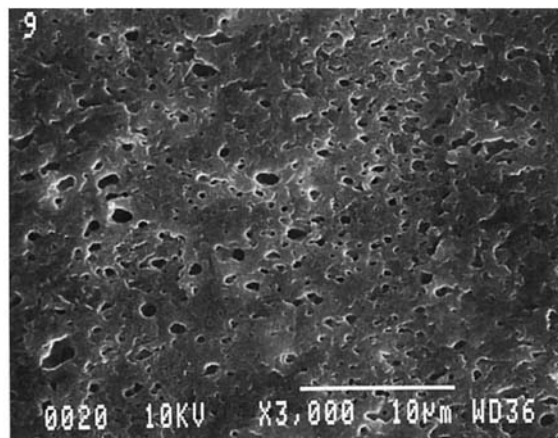
Rheology

Figure 7 shows typical melt viscosities of the blends, i.e., the effect of peroxide/coagent treatment. With peroxide/coagent (0.01/0.1) treatment (run 8), melt viscosity is decreased below the untreated one (run 1). However, as the coagent content is increased (0.01/0.3, run 10), viscosity is increased. This means that at low coagent content the main chain scission reaction of PP is dominant. However, as the coagent content increases relative to the peroxide content, the chain scission reactions are suppressed and/or crosslinking reactions are increased. The decrease of PP viscosity with peroxide/coagent treatment is consistent with the SEM morphology change. However, the increase of melt viscosity with increasing coagent content is not seen in the SEM and POM morphologies. This may imply that melt rheology is more sensitive to the structure variation of the polymer than the solid-state morphology.

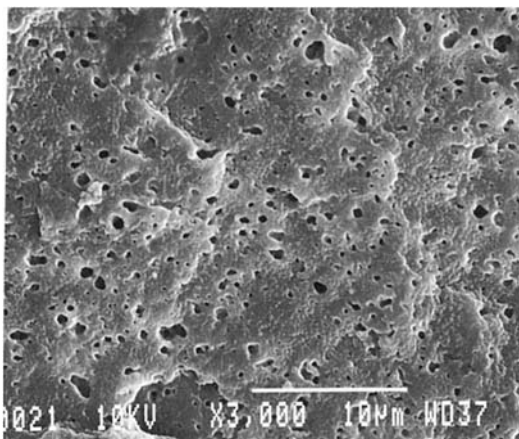
Figure 8 shows the effect of peroxide/coagent (0.01/0.3) treatment in relation to the viscosity ratio (runs 10–12). The original higher viscosity ratio gave lower blend viscosity with peroxide/coagent treatment. This is in line with the larger particle size that gives smaller hydrodynamic volume under motion and smaller particle-particle interactions, leading to lower viscosity. In addition, smaller in-



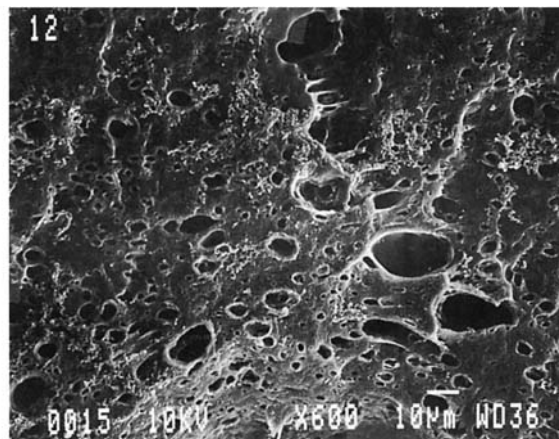
run #8



run #9



run #10



run #12

Figure 5 Effects of peroxide/coagent treatment in PP/EPR blends (runs 8–10 and 12).

terfacial interactions with larger particles should also contribute to the lower melt viscosity of the blends.

Thermal Properties

Thermal properties of the PP/EPR blends are summarized in Table III.

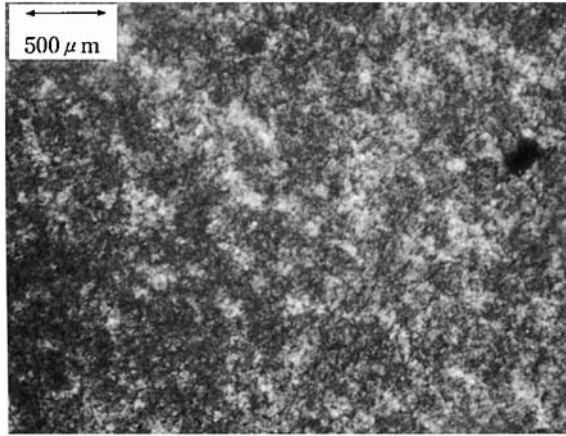
Effect of Viscosity Ratio: Runs 1–3

With the increase in viscosity ratio, the crystallization temperature upon cooling (T_{cc}) decreased over 10°C , while keeping the crystalline melting temperature (T_m) unchanged. This gives a high degree of

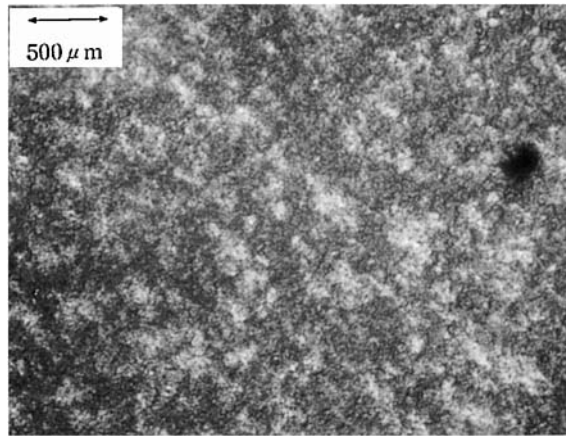
supercooling (ΔT). The results seem in line with the SEM morphology (Fig. 2), where the larger viscosity ratio yielded larger dispersed particles and smaller interfacial areas. Then crystallization occurred only with a higher degree of supercooling; and with fewer nucleation sites, the nuclei grew larger until they met the others.

Effect of C_3 Content

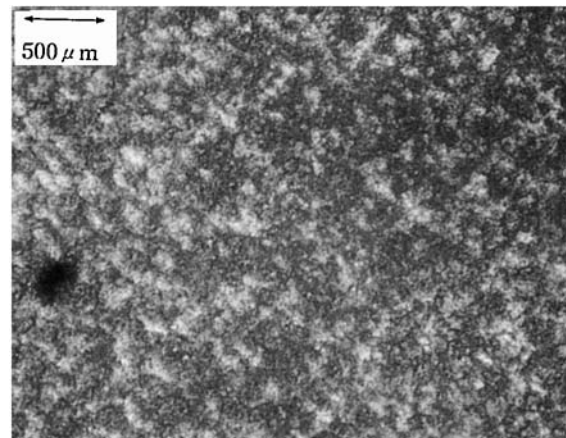
At the same viscosity ratios (runs 1 vs. 4, 2 vs. 6, and 3 vs. 6), EPR with lower C_3 content generally has low T_m , T_{cc} , and ΔH_f (heat of fusion) of PP. This is presumably due to the dilution effect of high C_3



run #8



run #9



run #10

Figure 6 POM morphologies of peroxide/coagent treated PP/EPR blends (runs 8–10).

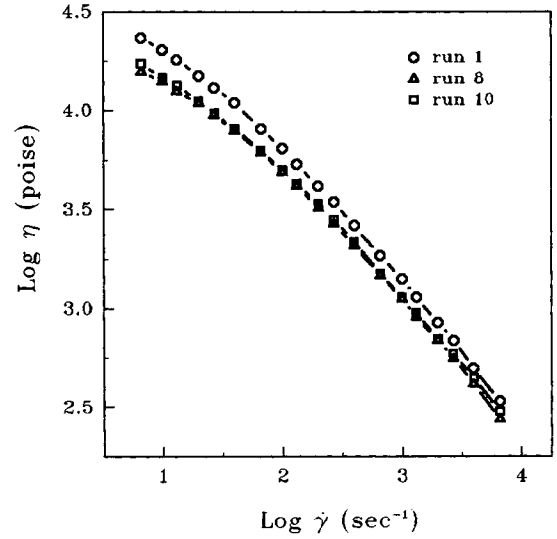


Figure 7 Effects of peroxide/coagent treatment on melt viscosity (runs 1, 8, and 10).

EPR for PP due to the better chemical affinity and interfacial interactions with PP.

Mechanical Properties

Mechanical properties of the PP/EPR blends are shown in Table IV.

Effect of Viscosity Ratio: Runs 1–3

Hardness, flexural modulus, yield, and break strength generally increased and elongation at break

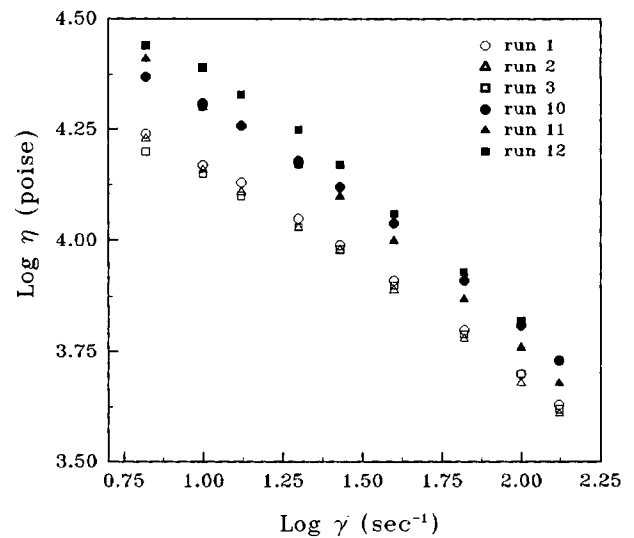


Figure 8 Effects of viscosity ratio on melt viscosity for peroxide/coagent (0.01/0.3) treated blends (runs 10–12).

Table III Thermal Properties of PP/EPR Binary Blends

Run	T_m (°C)	ΔH_f (J/g)	T_{cc} (°C)	ΔT
1	159.6	81.1	122.2	37.4
2	158.4	83.4	114.0	44.4
3	158.6	82.5	110.8	47.8
4	158.3	77.6	111.6	46.7
5	158.6	78.9	111.1	47.5
6	158.0	81.4	110.1	48.0
7	158.0	79.3	109.8	48.2
8	160.6	81.1	116.8	43.8
9	161.6	75.4	119.2	42.4
10	161.2	83.6	120.6	40.6
11	161.8	79.5	121.8	40.0
12	161.9	81.0	121.5	40.4

T_m , crystalline melting temperature; T_{cc} , crystallization temperature upon cooling; $\Delta T = T_m - T_{cc}$; and ΔH_f , heat of fusion.

decreased with the increase of viscosity ratio. It seems that the increased mechanical properties are related to the larger spherulite size because the PP amorphous domains are reinforced with PP crystalline lamellae.⁶

Impact strength of run 1 was approximately threefold those of runs 2 and 3. The greater impact toughening obtained with run 1 was due to the smaller particle size (submicron in diameter). Although the particle size increased in run 3 compared with run 2, its impact strength was slightly increased, probably due to the spherical shape of the rubber domains.¹⁴

Effect of C_3 Content: Runs 4–6

At the same viscosity ratio, EPR with high C_3 content generally has poor mechanical properties, except impact strength. The poor mechanical properties with high C_3 EPR seems, at least in part, due to the lower crystallinity (ΔH_f) of PP, which on the other hand is caused by the dilution effect of high C_3 EPR to PP. However, with increased chemical affinity of high C_3 EPR with PP, the interfacial interactions should increase, and this gives relatively high impact strength to the blends. It may be noted that the rubber domains of high C_3 EPR were more or less spherical, as compared with run 2, and the decrease in impact strength with increasing viscosity ratio was monotonic because the domain geometry was similar in three of the runs.

Effect of Peroxide/Coagent Treatment: Runs 7–12

Mechanical properties of the blends are increased with peroxide (without coagent) treatment (run 7). The effect of adding and increasing coagent at fixed peroxide content is not unique. Hardness is increased, yield strength is decreased, and break strength, elongation at break, and impact strength are decreased followed by an increase. The lowest impact strength of run 8 seems due to the large particle size, perhaps caused by the insufficient amount of coagent produced *in situ*. The effect of peroxide to augment the mechanical properties seems to work via the modification of PP molecular parameters, in addition to the copolymer formation. With peroxide treatment, average molecular weight is decreased,

Table IV Mechanical Properties of PP/EPR Binary Blends

Run	Hardness (R)	F/M (kg/cm ²)	Y/S (kg/cm ²)	B/S (kg/cm ²)	I/S (kg·cm/cm)	ϵ_b (%)
1	61	9700	240	330	46.9	510
2	66	10100	255	315	16.0	470
3	68	10400	260	330	17.3	480
4	49	8900	220	305	62.7	470
5	55	9500	240	310	38.4	460
6	66	10500	260	330	22.2	480
7	60	10500	265	315	49.6	540
8	69	10900	250	285	27.0	520
9	68	10300	245	285	72.8	530
10	67	10000	240	295	77.7	530
11	66	9700	245	315	78.6	550
12	72	10800	245	215	7.3	560

FM, flexural modulus; YS, yield strength; BS, break strength; IS, notched impact strength; and ϵ_b , elongation at break.

and molecular weight distribution is believed to become narrower.^{10,15}

The effect of peroxide/coagent (0.01/0.3) treatment was most pronounced in impact strength (run 1 vs. 10, 2 vs. 11). However, with originally (untreated) too large particles (run 3), peroxide/coagent treatment lowered the PP viscosity and augmented the viscosity ratio further, resulting in the decrease in impact strength below the untreated blend (run 12).

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