Pergamon

S0014-3057(96)00106-1

Eur. Polym. J. Vol. 32, No. 12, pp. 1387–1393, 1996

0014-3057/96 $15.00 + 0.00

EFFECT OF VISCOSITY RATIO AND PEROXIDE/COAGENT TREATMENT IN PP/EPR/PE TERNARY BLENDS

I. H. DO,[1] L. K. YOON,[1] B. K. KIM[1] and H. M. JEONG[2]

[1]Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735 and
[2]Department of Chemistry, Ulsan University, Ulsan 680-749, South Korea

(Received 14 August 1995; accepted in final form 22 November 1995)

Abstract—Ternary blends of PP/EPR/PE (isotactic polypropylene/ethylene–propylene rubber/high density polyethylene) (80/10/10 by weight) were prepared using a corotating twin screw extruder. The effect of the viscosity ratio of a rubber domain (EPR + PE) to a matrix PP (η_{EPR}/η_{PP}), and peroxide/coagent treatment on the micrograph (POM), rheology, and mechanical properties of the blend have been studied. Rubber domain size was easily controlled by the addition of PE. When PE satisfying $\eta_{PE} < \eta_{EPR}$ was added, the rubber domain size decreased, and vice versa. With increasing viscosity ratio, the rubber domain size increased and the crystallization temperature (T_{cc}) of PP and impact strengths of the blend decreased. The effects of peroxide treatment on domain size seem dual, i.e. originally small domains become larger and vice versa. By contrast, the addition of coagent reduced the domain size and improved the interfacial adhesions. The spherulite size increased somewhat with peroxide treatment, and significantly decreased with coagent treatment. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Although polypropylene (PP) has well balanced physical properties and easy processability, it needs improvement in impact toughness, especially at low temperature, and flexibility, [1–3]. For this reason, PP has long been blended with elastomeric polyolefins, typically with EPR (ethylene–propylene rubber) and EPDM (ethylene–propylene diene terpolymer) [4–6]. In PP/EPR or PP/EPDM blends, the level of rubber (5–65%) affects the properties of the simple blends, which are fairly straightforward as an average of the ingredients[7]. With 5–20% EPR, low temperature impact strength and toughness are improved with some retention of rigidity. As the level of rubber increases, the blends became semi-elastomer with moderate modulus, and eventually fully elastomeric materials.

In elastomer modified thermoplastic, rubber particle size is important and affects the mechanical properties. The optimum particle size ranges from 0.5 μm to several μm depending on the conditions. With rubber inclusion, certain mechanical properties, such as tensile strength and modulus, are inevitably reduced [8, 9]. The magnitude of tensile property decrease can be suppressed by adding the high-density polyethylene (PE) into the binary blends [10–12]. When PE is added to the PP/rubber blend, PE is preferentially dissolved in the rubbery domain, which is thermoplastically unstable and continues to grow in the melt state [13, 14]. It has often been observed that, in such a thermoplastically unstable system, the component viscosity ratio has an important role in determining the morphology and mechanical properties of the blend [1, 15]. With regard to the viscosity effect, a number of contributions have been devoted to PP/rubber blends. However, to the knowledge of the present authors, studies on the effect of the viscosity ratio in the PP/EPR/PE system are sparse.

Peroxide is often used for the postreactor modification of polyolefins [16–20]. In the presence of peroxide, polyolefins may lead to oxidative degradation, crosslinking, or chain scission mainly depending on the type of polymer, i.e. the structure of the pendant group determines the preferred reaction pathway. In the case of PP, the positive induction effect of the methyl group facilitates a homolytic scission of the C–H bonds and the tertiary macroradical formed will readily undergo chain scission. In addition, the pendant methyl groups provide PP with steric hindrance for the coupling reaction of two macroradicals. For PE, such an effect or hindrance does not exist, and hence crosslinking reactions by the combination of secondary macroradicals dominate. Since the role of peroxide is to produce the macroradicals, it accelerates chain scission for PP and crosslinking for PE. In the case of EPR, the ethylene/propylene ratio determines the preferred reaction, which in general and in our case is the crosslinking since ethylene content is approximately threefold (74/26). The crosslinking of PP in the presence of peroxide is facilitated by the addition of a coagent, which is typically a reactive polyfunctional monomer of a methacrylate or allyl compound. The effect of various types of coagents on the reactive extrusion of PE, PP and natural rubber have been reported earlier [20–23]. The role of coagent seems twofold, i.e. to remove the steric hindrance for coupling, and to minimize the main chain scission by stabilizing the macroradicals via resonance. In blends, cross-cure between the different polymers can also be formed, leading to the formation of graft or block copolymers. This type of copolymer formed *in situ* during extrusion can act as an effective compatibililzer of the blends.

Table 1. Physico-chemical properties of base polymers

	T_m (°C)	MFI (g/10min)	Mw (10^4g/mol)	MV	C3 (%)	Manufacturer
PP1	162	3.0	38	—	100	5014L, Korea Petrochem
PP2	163	7.5	25	—	100	4017, Korea Petrochem
HDPE1	136	4.8	9.7	—	—	M850, Korea Petrochem
HDPE2	129	0.8	18.6	—	—	E308, Korea Petrochem
HDPE3	131	0.07	23.5	—	—	F500, Korea Petrochem
EPR	—	—	—	24	26	-KEP020P, Kumbo

PP: MFI under 2.16kg load at 230°C, PE: MFI under 2.16kg load at 190°C.

We consider the effect of viscosity ratio of rubber domain (EPR + PE) on matrix PP, and peroxide/coagent treatment in PP/(EPR/PE) (80/(10/10)) ternary blends. Two types of isotactic PP, three types of PE, and one type of EPR were used with and without peroxide/coagent to prepare a total of 12 ternary bends. Morphology, rheology, thermal and mechanical properties of the blends were studied.

EXPERIMENTAL

Materials

Table 1 lists PP, EPR and PE used in the present experiments with their melt viscosities in Fig. 1. The basic formulations of these blends are shown in Table 2. The viscosity ratio of rubber domain to PP ($\eta_{EPR\text{-}PE}/\eta_{PP}$) was largely determined by PP and EPR, and it was further modified by adding PE of various viscosities to EPR domains. According to the viscosity ratio the blends are divided into four series:

Series 1 (runs 1–3) $\eta_{PE} < \eta_{EPR} < \eta_{PP}$

Series 2 (runs 4–6) $\eta_{EPR} < \eta_{PE} < \eta_{PP}$

Series 3 (runs 7–9) $\eta_{EPR} < \eta_{PP} < \eta_{PE}$

Series 4 (runs 10–12) $\eta_{PP} < \eta_{EPR} < \eta_{PE}$

In Series 1, 2 and 3, viscosity of EPR is smaller than PP, whereas viscosity of EPR is greater than PP in Series 4. Viscosity of rubber domain is further decreased below EPR in Series 1, and increased above PP in Series 4, by adding PE of different viscosities. Each series consists of three runs: untreated, peroxide (0.01phr) alone treated, and peroxide (0.01)/coagent (0.3) treated runs.

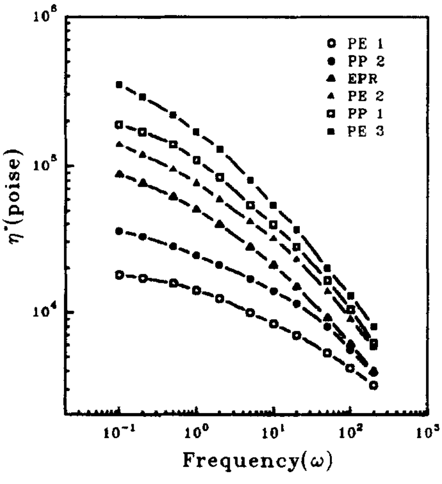

Fig. 1. Melt viscosities of PP, EPR and PE (210°C).

Compounding

Peroxide, multifunctional monomer and additives were premixed using a Super Floater. Blends were prepared in two stages using a corotating twin screw extruder (PEX-30, JSW) with L/D = 30, and at 30rpm. Typical temperature profile was 210–220–230–220°C of first, second, third and die zone. Master pellets of EPR/PE (50/50) were first prepared, followed by blending with PP in the second stage. Extrudates were pelletized and dried prior to characterization and injection molding.

Measurements

The rheological properties of the base resins and blends were measured using an RDS (Rheometrics Dynamics Spectrometer 7700) with a parallel plate fixture at 220°C. Blend viscosity was measured from a capillary rheometer, with L/D = 25, at 220°C using the dried pelletized chips. 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 (Du Pont 2100). Tensile properties were measured using the injection molded specimen with crosshead speed 5mm/min and Izod impact test (ASTM D 256) with notched 1/8″ specimen. Flexural modulus and hardness (Rockwell) were measured following ASTM D 790 and D 785, respectively. The above tests were done at room temperature, and at least five runs were made to report the average.

RESULTS AND DISCUSSION

Morphology

In steady shear flows, the deformation of a dispersed phase can be determined by two dimensionless parameters, viz. the viscosity ratio (λ) and capillary number (κ) defined below [24, 25]:

$$\lambda = \frac{\eta_d}{\eta_m} \tag{1}$$

$$\kappa = \frac{\eta_m\dot{\gamma}}{v/D} \tag{2}$$

where η_d and η_m are the viscosity of dispersed and continuous phases, respectively, and $\dot{\gamma}$, v and D are the shear rate, interfacial tension and droplet diameter, respectively. The numerator of equation (2) is the shear stress ($\sigma = \eta_m\dot{\gamma}$) imposed on the continuous phase by screw rotation, and this force is transferred to the dispersed phase, with the magnitude determined by the interfacial conditions. Assuming shear stress continuity at the interfaces, the shear rate imposed on the dispersed phase is given by [26, 27]

$$\dot{\gamma}_d = \frac{\eta_m}{\eta_d}\dot{\gamma} \tag{3}$$

Table 2. Basic formulations of the blends

Run	PP1	PP2	EPR	PE1	PE2	PE3	Peroxide*	Coagent*
Binary	80	—	20	—	—	—	—	—
1	80	—	10	10	—	—	—	—
2	80	—	10	10	—	—	0.01	—
3	80	—	10	10	—	—	0.01	0.3
4	80	—	10	—	10	—	—	—
5	80	—	10	—	10	—	0.01	—
6	80	—	10	—	10	—	0.01	0.3
7	80	—	10	—	—	10	—	—
8	80	—	10	—	—	10	0.01	—
9	80	—	10	-	—	10	0.01	0.3
10	—	80	10	—	—	10	—	—
11	—	80	10	—	—	10	0.01	—
12	—	80	10	—	—	10	0.01	0.3

*Weight % based on total polymers.

At given screw rpm, dispersed phase deformability is inversely proportional to the viscosity ratio. Equation (2) can be written as

$$\kappa = \frac{\eta_d \gamma_d}{v/D} \tag{4}$$

Then the numerator of equation (4) is the driving stress for the dispersed phase deformation, the denominator is the interfacial stress which acts as the resistance against deformation, and deformation occurs only for κ greater than the critical value.

Figure 2 shows the SEM micrographs of Series 1 blends, together with the PP/EPR binary blend for comparison. It is seen that the rubber domains of Series 1 blends, regardless of peroxide/coagent treatment, are much smaller than those of the binary blend. This is mainly due to the lowered viscosity of the rubbery domain with the addition of PE since PE is preferentially dissolved in the EPR domain. In the presence of peroxide alone rubber domains increased in size a small amount and were deformed elliptically along the flow direction in the mold. With the addition of coagent, the interfaces become blurred, indicative of improved interfacial adhesion.

The increased and deformed rubber domains with peroxide alone are probably due to the main chain scission of PP, leading to the increased viscosity ratio and hence difficult breakup of rubber domains [equation (3)]. With the addition of coagent, chain scission of PP is suppressed, and cross-cures between

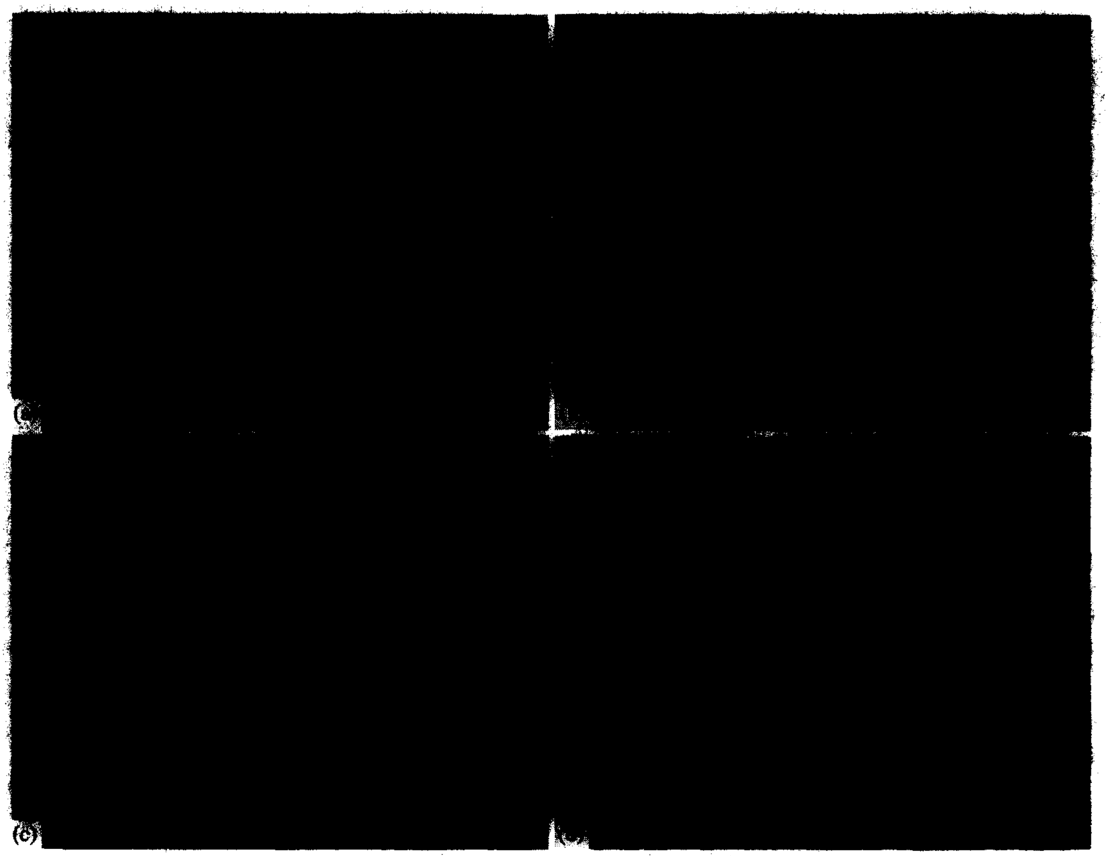

Fig. 2. SEM micrographs of (a) PP/EPR binary and Series 1 blends [(b) untreated, (c) peroxide treated, (d) peroxide/coagent treated].

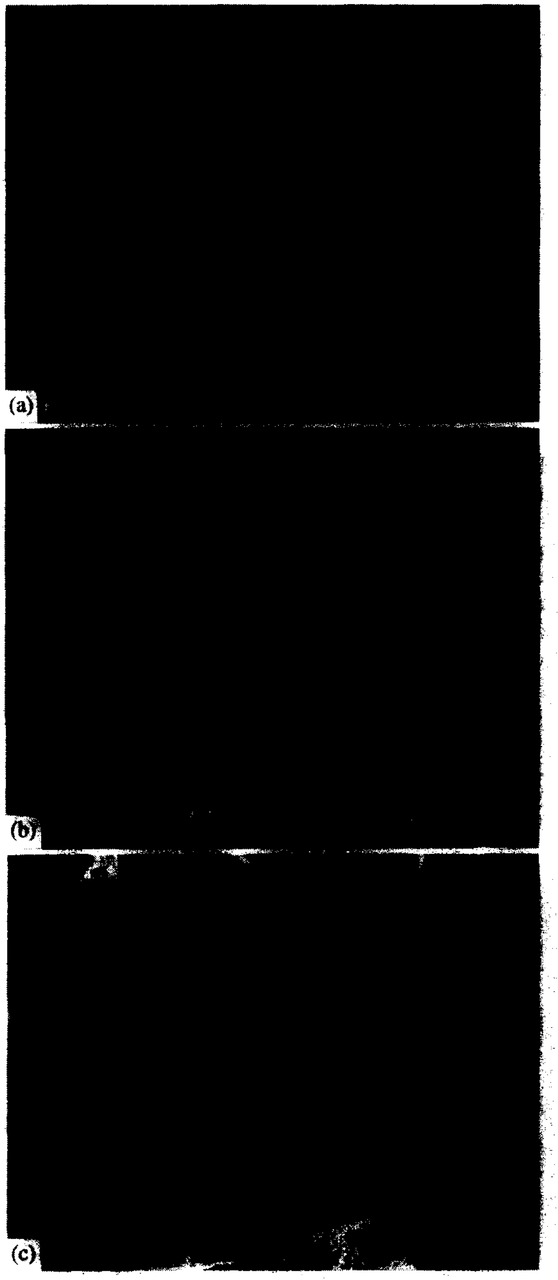

Fig. 3. SEM micrographs of Series 2 blends: (a) untreated, (b) peroxide (0.01) treated, and (c) peroxide (0.01)/coagent (0.3) treated.

PP and rubber domain are augmented to form more copolymers, which are preferentially interposed at the PP–rubber interfaces to reduce the interfacial tensions, resulting in the decreased interfacial stress [equation (4)].

Figure 3 shows SEM micrographs of Series 2 blends. The untreated blend (Fig. 3(a)) shows significantly larger rubber domains, up to several μm. However, the domain size is decreased to approx. 1 μm with peroxide treatment (Fig. 3(b)), and it is further decreased with blurred interfaces with the addition of coagent (Fig.3(c)). Domain reduction with peroxide alone implies that a certain amount of copolymer can be formed even with peroxide alone, and the amount increased with the addition of coagent.

Figure 4 shows typical POM morphology of the blends as a function of peroxide and coagent treatment (runs 4–6). The spherulite of PP is increased a small amount with peroxide treatment. However, it is significantly decreased with the addition of coagent. This tendency was generally observed with other series of blends, and the tendency should be related to the thermal properties of the blends to follow. SEM morphology showed a domain reduction with peroxide and a further reduction in domain size with improved interfaces with the addition of coagent. It seems that the lowered

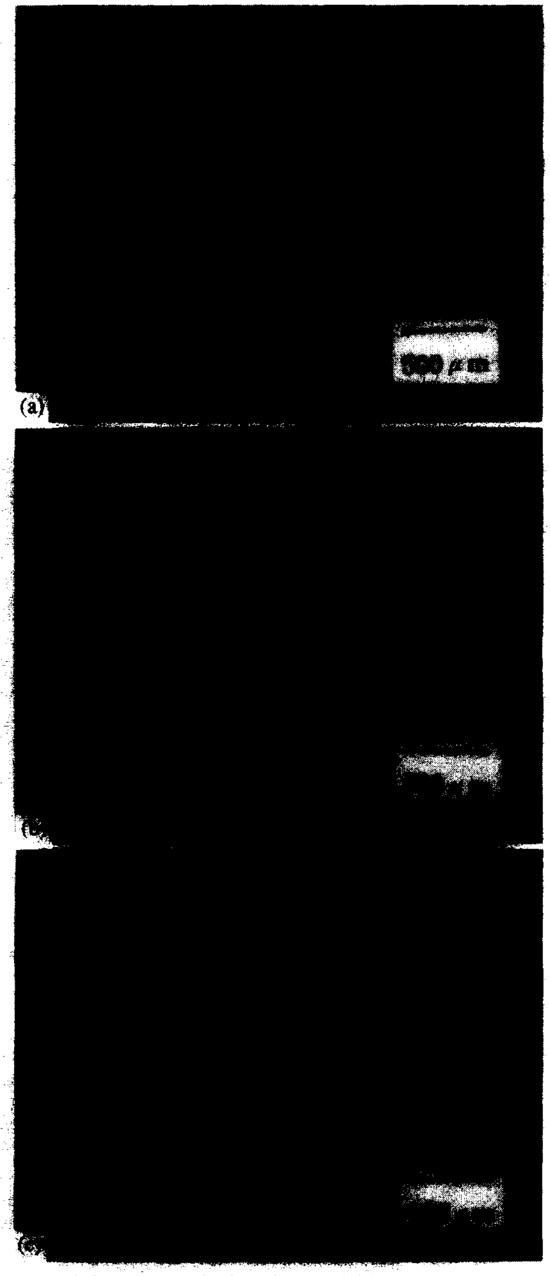

Fig. 4. POM morphologies of Series 2 blends: (a) untreated, (b) peroxide (0.01) treated, and (c) peroxide (0.01)/coagent (0.3) treated.

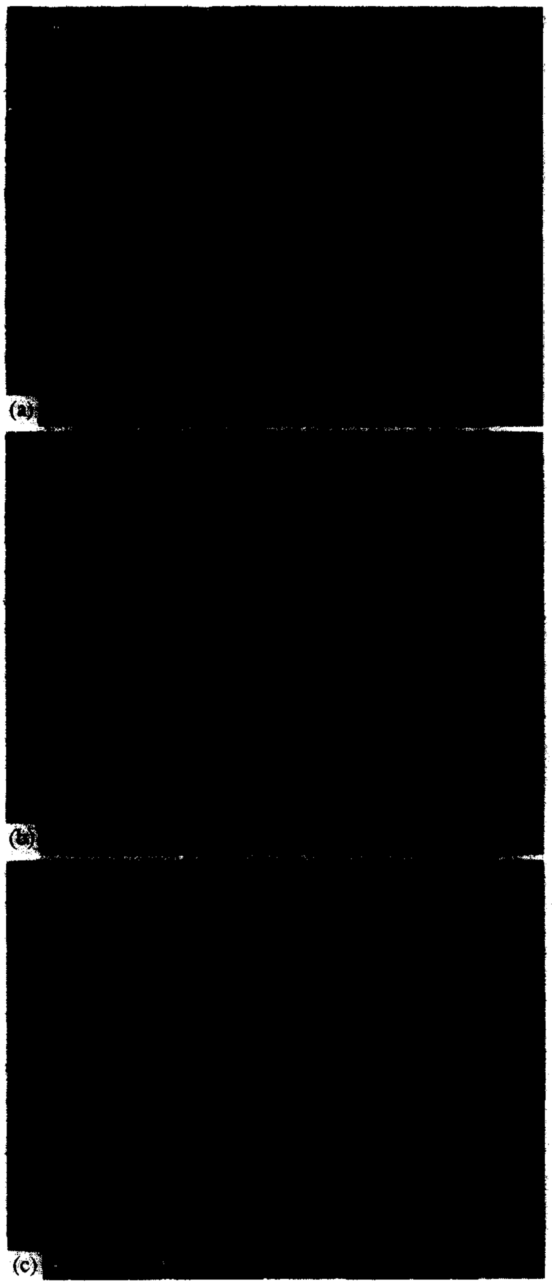

Fig. 5. SEM micrographs of Series 3 blends: (a) untreated, (b) peroxide (0.01) treated, and (c) peroxide (0.01)/coagent (0.3) treated.

molecular weight of PP, and hence the lowered viscosity, induced the crystallization at a slightly lower temperature. In general, lower temperature crystallization of a given polymer gives smaller spherulites due to fast nucleation and slow rate of crystal growth.

Figure 5 shows the SEM micrographs of Series 3 blends, which are similar in domain size to Series 2. Viscosity of PE added to this series is greater than that of PP, and the rubber domain viscosity is higher (assuming additivity of viscosity) than that of Series 2. It seems that the difference is insignificant to modify the domain morphology greatly.

Figure 6 shows the SEM micrographs of Series 4 blends. Due to the large viscosity ratio, the break-up of the rubber domain is a minimum, up to approx. 4–5 μm in the major dimension. This more or less decreases with peroxide alone treatment, a dramatic reduction in size as well as interface improvement is obtained with the addition of coagent.

From the morphology study, it seems that the domain size is largely governed by the viscosity ratio, i.e. the smaller the viscosity ratio, the smaller the domain size. Peroxide generally contributes to the reduction in domain size via the formation of copolymers. When the compatibilizing effect of the copolymers is greater than the increased viscosity ratio due to main chain scission of PP, domain size

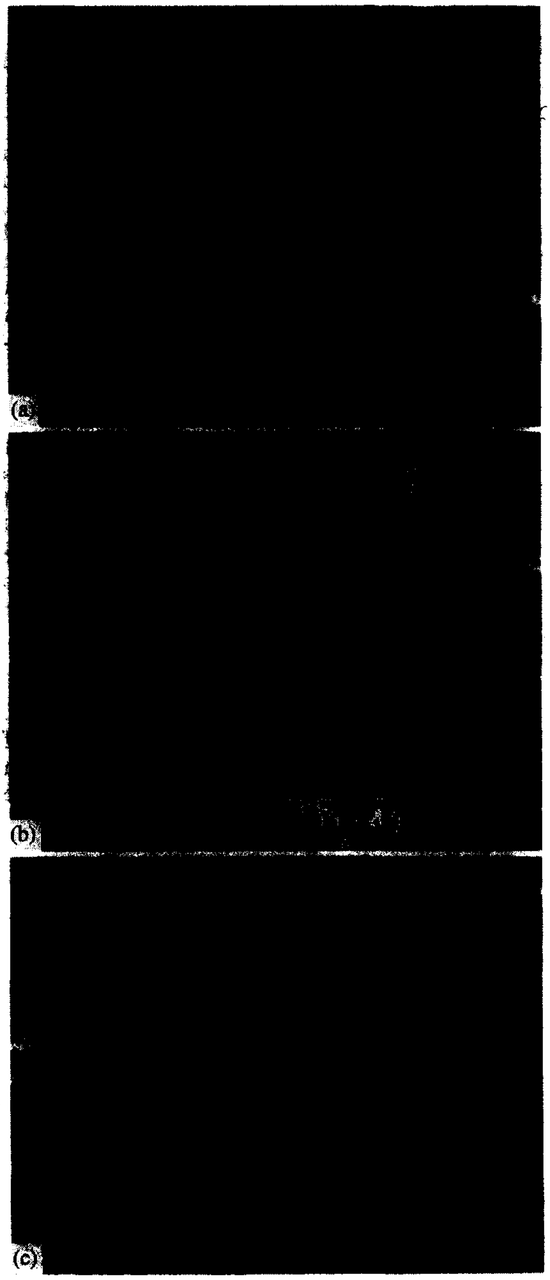

Fig. 6. SEM micrographs of Series 4 blends: (a) untreated, (b) peroxide (0.01) treated, and (c) peroxide (0.01)/coagent (0.3) treated.

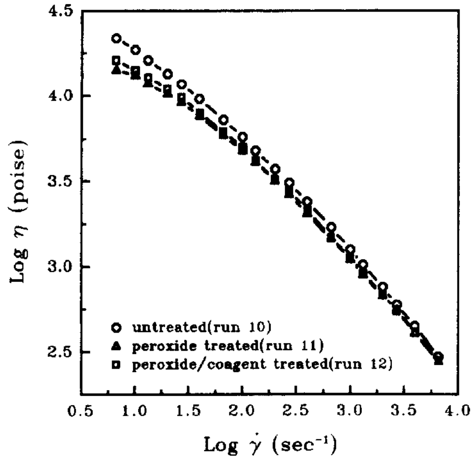

Fig. 7. Melt viscosities of PP/(EPR/PE) blends as a function of peroxide and coagent (210°C).

decreases with improved interfaces. However, when the domain size of untreated blends is too small, main chain scission of PP may contribute to the coalescence of fine rubber domains to a large and deformable size since coalescence is more feasible in less viscous media. However, addition of coagent seems essential to reduce to domain size, probably via the effective formation of copolymers and stabilization of PP macroradicals.

Rheology

Typical melt viscosity of the blend as a function of peroxide and coagent are shown in Fig. 7 As expected, melt viscosity of the blends is decreased with peroxide treatment, and it is increased a small amount with coagent addition, but below the untreated one. This implies that coagents suppress the main chain scission of PP and/or augment the crosslinking reactions.

Thermal properties

Table 3 shows the thermal properties of the blends. As compared with the binary blend, T_{cc} and ΔH_f of PP are decreased in the ternary blend (Run 1). With increasing viscosity ratio, crystallization temperature increases, and hence the degree of supercooling (ΔT) decreases for PP. Though marginal, peroxide treatment gives lower T_{cc} of PP, in general. However, with the addition of coagent, T_{cc} is increased while keeping the T_m essentially unchanged, leading to the decreased degree of supercooling and increased crystallinity (ΔH_f) for PP. On the other hand, total crystallinity and T_m of PE is decreased with peroxide and coagent treatment. The lowered T_{cc} of PP with peroxide treatment seems due to decreased viscosity of PP by main chain scission, which makes the chain folding of PP plausible at low temperature. With the addition of coagent, crosslinkings as well as chain scission are obtained. Extensive crosslinks should disturb the crystallinity. However, a few crosslinks can also improve packing of the polymer chains into a crystalline structure at even higher temperature since they can restrict the unfolding of polymer chains from packed stack to melt pool. Such restrictions make chain packing plausible even at higher temperature, leading to the increased T_{cc}. Fine break-up of the dispersed phase should contribute to the increased number of dispersed domains and areas of nucleation sites leading to the smaller spherulites of the blends. The decrease of T_m and ΔH_f for PE is mainly due to the formation of copolymers and their dilution effect on PE crystallization since most copolymers formed are preferentially interposed at the interfaces.

Finally it should be mentioned that Series 4 demonstrates the most favourable thermal properties, regardless of peroxide and coagent treatment. This series shows the lowest T_{cc} and ΔT, and the greatest ΔH_f for PP.

Mechanical properties

Table 4 shows the mechanical properties of the blends. As compared with the PE/EPR binary blends, addition of PE gives increased hardness, modulus and yield strength in spite of decreased ΔH_f of PP, due to the rubber domains reinforcement, with crystalline polymers. Hardness generally increases with peroxide, alone and with coagent. Impact strength of the untreated blends decreased with increasing viscosity ratio and peroxide treatment and

Table 3. Thermal properties of PP/EPR/PE ternary blends

	PE				PP			
Run	T_m (°C)	ΔH_f (J/g)	T_{cc} (°C)	ΔT (°C)	T_m (°C)	ΔH_f (J/g)	T_{cc} (°C)	ΔT (°C)
Binary	—	—	—	—	159.6	81.1	122.2	37.4
1	133.8	32.1	114.8	19.0	162.2	64.7	114.8	47.4
2	131.0	36.1	114.7	16.3	159.3	67.1	114.7	44.6
3	129.1	32.8	121.3	7.8	160.9	72.2	121.3	39.6
4	128.8	32.8	115.5	13.3	159.2	70.5	115.5	43.7
5	128.2	32.2	113.6	14.6	158.4	69.2	113.6	44.8
6	126.0	28.5	114.5	11.5	159.9	72.8	122.0	37.9
7	126.8	30.8	115.5	11.3	157.5	60.9	115.5	42.4
8	128.1	26.8	113.4	14.7	158.7	58.9	113.4	45.3
9	126.6	28.6	114.7	11.9	160.5	72.6	122.0	38.5
10	128.5	29.6	115.5	13.0	164.8	82.5	123.1	41.7
11	128.5	29.4	114.8	13.7	164.9	81.2	123.1	41.7
12	126.4	27.9	113.9	12.5	165.3	84.9	125.6	39.7

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

Table 4. Mechanical properties of PP/EPR/PE ternary 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 (%)
Binary	61	9700	240	330	46.9	510
1	75	11,700	300	275	29.2	470
2	77	12,000	295	250	15.3	500
3	81	12,300	290	300	18.0	550
4	76	11,800	305	260	31.6	480
5	77	12,100	290	230	12.6	490
6	79	12,500	285	310	23.2	570
7	77	12,200	310	250	13.6	490
8	78	12,300	300	260	11.7	510
9	78	12,200	285	260	19.8	560
10	84	13,300	305	225	7.4	560
11	83	13,000	295	210	7.3	610
12	83	12,900	285	205	12.3	610

F/M: flexural modulus,
Y/S: yield strength,
B/S: break strength,
I/S: notched impact strength,
ϵ_b: elongation at break.

decreases with coagent addition. The decrease of impact strength with increasing viscosity ratio is directly related to the increased domain size, and the decrease with peroxide should be related to the main chain scission of PP, whereas the increase with coagent is related to the improved rubber–PP interfaces via the compatibilizing effect of copolymers formed *in situ*. Flexural modulus and yield strength slightly increase and decrease with coagent treatment, respectively.

Acknowledgement—This research has been supported by the Korea Science and Engineering Foundation (Grant number 94-0502-08-03-3). The financial support is gratefully acknowledged.

REFERENCES

1. Synnott, D. J., Sheidan, D. F. and Kontos, E. G., in *Thermoplastic Elastomers from Rubber–Plastic Blends*, ed. S. K. De and A. K. Bhowmick. Ellis Horwood, New York, 1990.
2. Mathew, N. M. and Tinker, A. J., *J. Nat. Rubb. Res.*, 1986, **1**, 240.
3. Hoppner, D. and Wendorff, J. H., *Colloid Polym. Sci.*, 1990, **268**, 500.
4. Karger-Kocsis, J. and Csikai, I., *Polym. Eng. Sci.*, 1987, **27**, 241.
5. Plochocki, A. P., in *Polymer Blends*, ed. D. R. Paul and S. Newman. Academic Press, New York, 1987, Chap. 21.
6. Kresge, E. N., in *Polymer Blends*, ed. D. R. Paul and S. Newman. Academic Press, New York, 1987, Chap. 20.
7. Bonner, J. G. and Hope, P. S., in *Polymer Blends and Alloys*, ed. M. J. Flokes and P. S. Hope. Blackie, London, 1993.
8. Murphy, N. S., Kotliar, A. M., Sibilia, J. P. and Sacks, W., *J. Appl. Polym. Sci.*, 1986, **31**, 2569.
9. Stehling, F. C., Huff, T., Speed, C. S. and Wissler, G., *J. Appl. Polym. Sci.*, 1981, **26**, 2693.
10. Kolarik, J. and Lednicky, F., in *Polymer Composites*, ed. B. Sedlacek. Walter de Gruyter, Berlin, 1986, p. 537.
11. Kucera, J. and Kolarik, J., in *Polymer Composites*, ed. B. Sedlacek. Walter de Gruyter, Berlin, 1986, p. 543.
12. Pukanszky, B., Kolarik, J. and Lednicky, F., in *Polymer Composites*, ed. B. Sedlacek. Walter de Gruyter, Berlin, 1986, p.553.
13. Levij, M. and Maurer, F. H. J., *Polym. Eng. Sci.*, 1988, **28**, 670.
14. Dorazio, L., Greco, R., Mancarella, C., Martuscelli, E., Ragosta, G. and Silvestre, C., *Polym. Eng. Sci.*, 1982, **22**, 536.
15. Kim, B. K., Kim, M. S. and Kim, K. J., *J. Appl. Polym. Sci.*, 1993, **48**, 1271.
16. Al Malaika, S. and Amir, E. J., *J. Nat. Rubb. Res.*, 1986, **1(2)**, 104.
17. Chodaok, I. and Lazar, M., *Agnew. Makromol. Chem.*, 1982, **106**, 153.
18. Borsig, E., Fiedlerova, A. and Lazar, M., *J. Macromol. Sci. Chem.*, 1981, **A16**(2), 513.
19. Tzoganakis, C., Vlachopoulos, J. and Hamielec, A. E., *Polym. Eng. Sci.*, 1988. **28**, 170.
20. Kim, K. J. and Kim, B. K., *J. Appl. Polym. Sci.* 1994, **48**, 981.
21. Kim, K. J. and Kim, B. K., *Eur. Polym. J.*, 1992, **28**(12), 1487.
22. Kim, B. K. and Kim, K. J., *Adv. Polym. Technol.*, 1993. **12**(3), 263.
23. Yoon, L. K., Choi, C. H. and Kim, B. K., *J. Appl. Polym. Sci.*, 1995, **56**, 239.
24. Utracki, L. A., Dumoulin, M. M. and Toma, P., *Polym. Eng. Sci.*, 1986, **26**, 34.
25. Utracki, L. A. and Shi, Z. H., *Polym. Eng. Sci.*, 1992, **32**, 1824.
26. Han, C. D., *Multiphase Flow in Polymer Processing*. Academic, New York, 1989.
27. Bird, R. D., Stewart, W. E. and Lightfoot, E. N., *Transport Phenomena*. Wiley, New York, 1960.
28. Birley, A. W., Haworth, B. and Batchelor, J., *Physics of Plastics*. Hanser, Munich, 1991.