

Reactive Extrusion of PP/Natural Rubber Blends

LEE KEUN YOON, CHI HOON CHOI, and BYUNG KYU KIM*

Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, South Korea

SYNOPSIS

Reactive extrusion of polypropylene (PP)/natural rubber (NR) (90/10) blends was conducted in the presence of a peroxide[1,3-bis(*t*-butylperoxy)benzene] and coagent (trimethylolpropanetriacrylate, TMPTA). Effects of peroxide and coagent content were studied in terms of melt index (MI), melt viscosity, morphology, thermal, and mechanical properties. At a constant content of the coagent, melt viscosity increased at a low and decreased at a high content of the peroxide. On the other hand, melt viscosity increased monotonically with the coagent concentration at constant peroxide content. The increase and decrease of viscosity were interpreted in terms of crosslinking and chain scission of PP, which governed the rubber domain size and mechanical properties of the reactive blends. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polypropylene (PP) has a most remarkable combination of various physical properties and processability. However, PP has poor impact strength, especially at low temperature, due to its high glass transition temperature and high crystallinity.^{1,2} An ethylene-propylene copolymer and ethylene-propylene-diene terpolymer, which contain a propylene unit in their structures, are often used as impact modifiers for PP.³⁻⁵ 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 homogeneously distributed in the PP matrix.

Toughening of PP with natural rubber (NR) has also been considered. However, due to the chemically dissimilar structure of these two polymers, phase separation is generally larger than the optimum, and interfacial bonding is poor in their physical blends. Therefore, chemical additives such as peroxide⁷ and *m*-phenylenebismaleimide² have been added to the systems to obtain interpolymers. Such *in situ*-produced copolymers (graft or block copolymers) are likely to be interposed at the interfaces and reduce

the interfacial tension. The result is size reduction and improved interfacial bondings.

The effect of peroxide in the melt extrusion of PP and NR could be in opposite directions in terms of a molecular weight change upon extrusion. Peroxide-initiated reactive extrusion of polyolefin may lead to oxidative degradation, crosslinking, or chain scission depending on the type of polymer, compounding conditions, and partial pressure of oxygen (Fig. 1).⁷ With regard to the polymer, the structure of the pendant group (R) determines the preferred reaction pathway. In the case of PP (R = CH₃), 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 even under a low partial pressure of oxygen. At high oxygen pressure, oxidative degradation predominates. In addition, the pendant methyl groups provide PP with steric hindrance for the coupling of two macroradicals. For polyethylene (PE), such an effect or hindrance does not exist, and, hence, crosslinking reactions by the combination of secondary macroradicals dominate.^{8,9} Since the role of peroxide is to produce the macroradical, it accelerates chain scission for PP and crosslinking for PE. In the case of NR, crosslinking is dominant over chain scission.⁷

With regard to the compounding conditions, for PP, chain scission is preferred over crosslinking at low peroxide concentration and higher temperature,

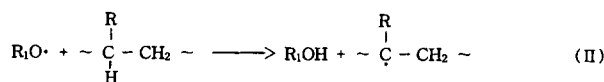
* To whom correspondence should be addressed.

since chain scission is a monomolecular reaction and has higher activation energy than has crosslinking.¹⁰ Practically, the peroxide-initiated degradation of PP is used for the production of controlled-rheology resin with tailor-made properties:

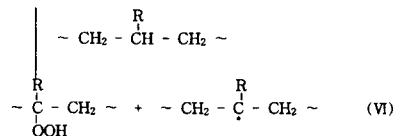
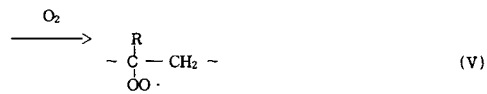
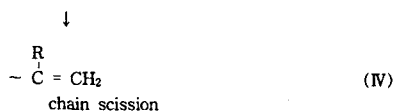
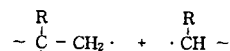
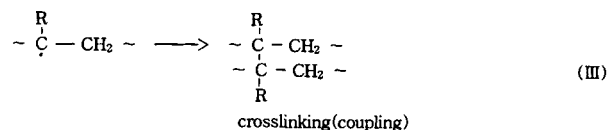
Degradation of peroxide



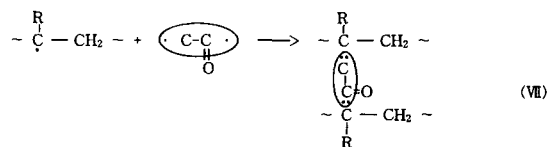
Generation of macroradical



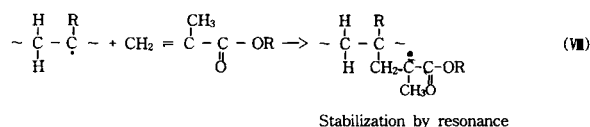
Macroradical reactions



oxidative degradation



crosslinking by coagent



Stabilization by resonance

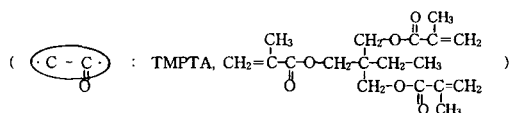


Figure 1 Possible reaction schemes.

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 methacrylate or allyl compounds. The effects of various types of coagents on the reactive extrusion of PE and PP have been reported earlier.¹¹⁻¹³ The role of coagent seems twofold, i.e., to remove the steric hindrance for coupling (Fig. 1-VII) and to minimize the β -scission by stabilizing the macroradicals via resonance (Fig. 1-VIII).

We consider the reactive melt blends of PP with NR at a specific composition of 90/10 (PP/NR). The effects of peroxide (0–0.05 phr) and coagent (0–1.0 phr) are studied in terms of morphology and thermal, melt, and mechanical properties.

EXPERIMENTAL

NR (SMR CV50) and isotactic PP ($M_n = 54,000$, $M_w = 380,000$, melt index [MI] = 2.3 g/10 min [2.16 kg, 230°C], Korea Petrochemicals) as received, were used for blending. Peroxide and the coagent used were 1,3-bis(*t*-butylperoxy)benzene (liquid), and trimethylolpropanetriacrylate (TMPTA) (liquid). First grades of these reagents were used without further purification. Irganox 1010 and Irgafos 168 were added as an antioxidant for NR and PP.

Extrusion was done in a corotating twin-screw extruder with $L/D = 30$ and $D = 2.5$ cm. The master batch was first prepared at 180°C, 350 rpm, followed by reactive extrusion at 230°C. During the reactive extrusion, minute amounts of volatile products were formed, and these were removed in the degassing zone of the extruder, where a vent hole is provided.

Thermal properties were measured by differential scanning calorimetry (DSC, DuPont 1090). Samples of injection-molded specimens were first heated to 200°C at 20°C/min and cooled down to room temperature, recording the crystallization temperature (T_c). The crystalline melting temperature (T_m) was measured during the second heating cycle.

The MI of extrudates was measured at 210°C, 2.16 kg loading, using a Monsanto capillary rheometer according to ASTM 1238. Melt viscosity was measured using an RDS (Rheometric Spectrophotometer, type II) rheometer with a parallel-plate fixture. Discs measuring 12.5 mm (radius) \times 1.2 mm (height) were compression-molded, and measurements were done isothermally at 220°C, 15% strain level.

Morphologies were studied using a scanning electron microscopy (SEM). SEM micrographs were

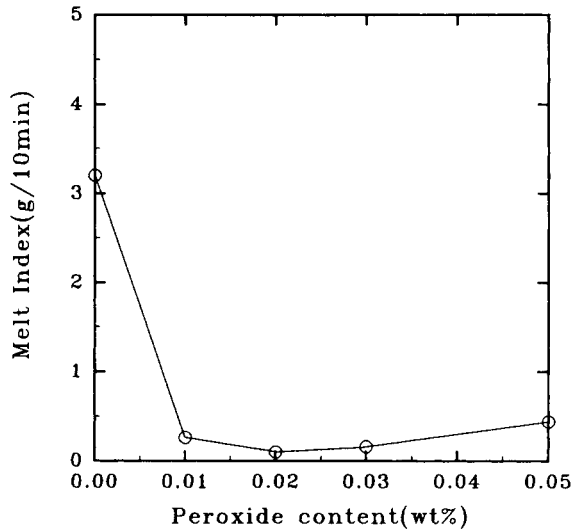


Figure 2 Melt index vs. peroxide content of the blend (0.6 phr TMPTA).

taken from cryogenically (in liquid nitrogen) fractured surfaces of injection-molded tensile specimens. Surfaces were sputtered with gold before viewing.

Specimens for mechanical tests were injection-molded at 230°C, and tests were made following the standard ASTM procedure. Tensile tests (ASTM D638) were made on an Instron using 1/4 in. specimens with a crosshead speed of 50 mm/min and an Izod impact test (D256), with notched 1/8 in. specimens. The above tests were done at room temperature, and at least five runs were made to report the average.

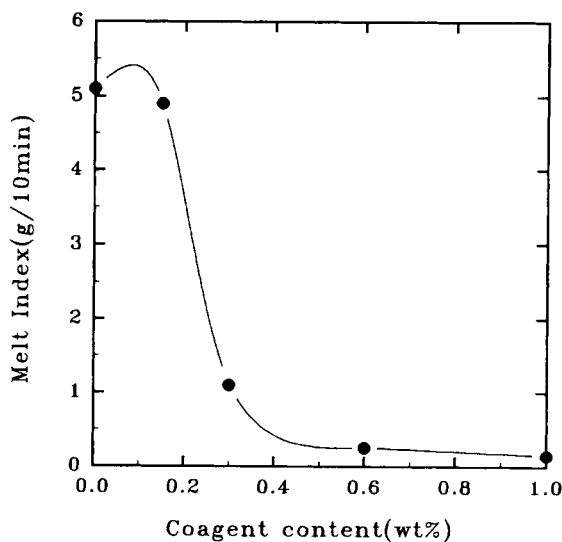


Figure 3 Melt index vs. coagent content of the blend (0.01 phr peroxide).

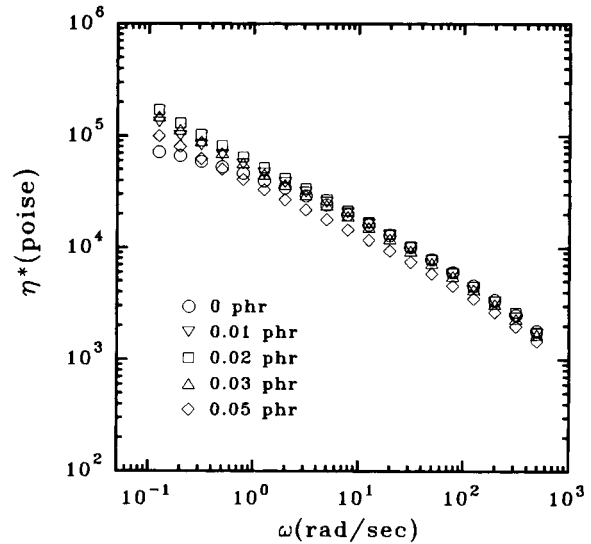


Figure 4 Complex viscosity of the blends vs. peroxide content at 220°C (0.6 phr TMPTA).

RESULTS AND DISCUSSION

Melt Properties

The MI of the extrudates as a function of peroxide content and of coagent content is shown in Figures 2 and 3, respectively. At constant TMPTA (0.6 phr), MI decreases sharply with 0.01 phr peroxide and slowly with 0.02 phr, beyond which it increases mildly. The dramatic decrease of MI with peroxide indicates that TMPTA alone does not contribute to the crosslinking significantly and it does so only with

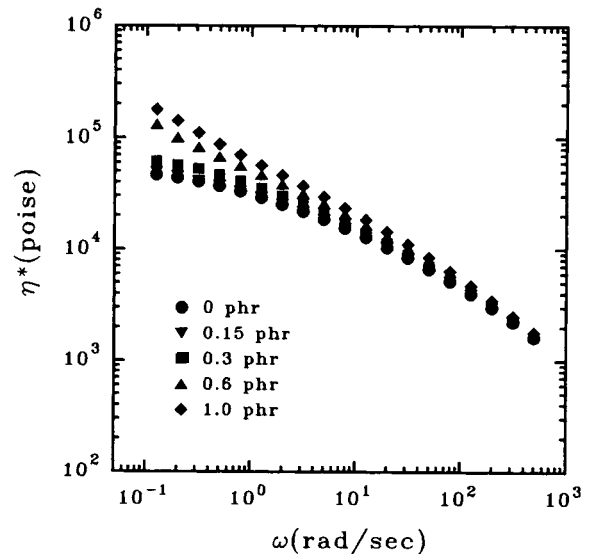


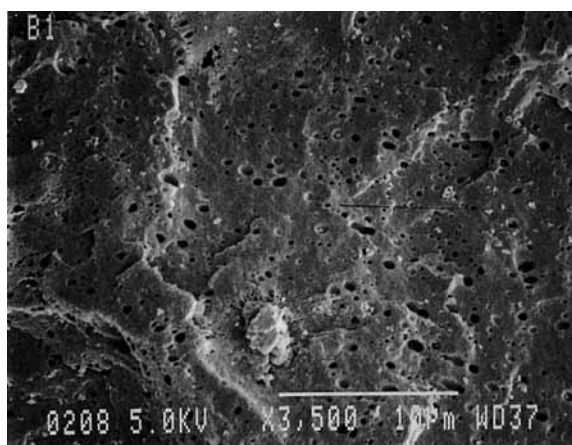
Figure 5 Complex viscosity of the blends vs. coagent content at 220°C (0.01 phr peroxide).

peroxide (Fig. 1-II). However, with more peroxide, more macroradicals are formed and the added TMPTA is insufficient to bridge (Fig. 1-VII) and stabilize (Fig. 1-VIII) the PP macroradicals. It seems that the balance is obtained at about 0.02 phr peroxide.

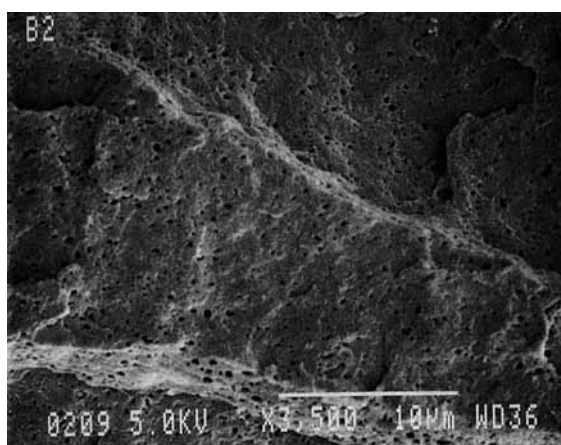
At constant peroxide content (0.01 phr), MI is almost not changed with 0.2 phr TMPTA (Fig. 3), implying that there may be a critical content of TMPTA needed. As the TMPTA content increases from 0.2 to 0.3 phr, a dramatic drop of MI from ca. 5 to 2 is obtained. This implies that macroradicals formed by peroxide are mostly crosslinked via TMPTA. The number of macroradicals produced

during melt extrusion, and, hence, the amount of coagent to stabilize and crosslink the macroradicals, should be proportional to the amount of peroxide added. Therefore, further addition of TMPTA gives only a slight decrease of MI.

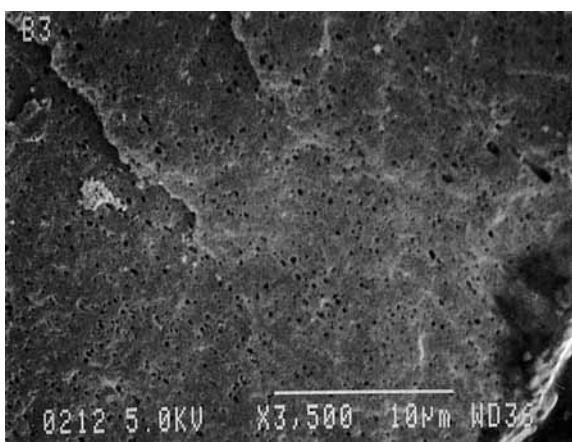
Although the MI is a quick guide to the melt processability, it corresponds to the viscosity of a single shear rate, which is generally low. The rubber-toughened PP is generally processed at a high shear rate, and high shear viscosity data are useful.⁷ Figures 4 and 5 show the melt viscosity of the blends, prepared with different amounts of peroxide and coagent, respectively. Low shear viscosity increases with peroxide up to 0.02 phr and decreases beyond



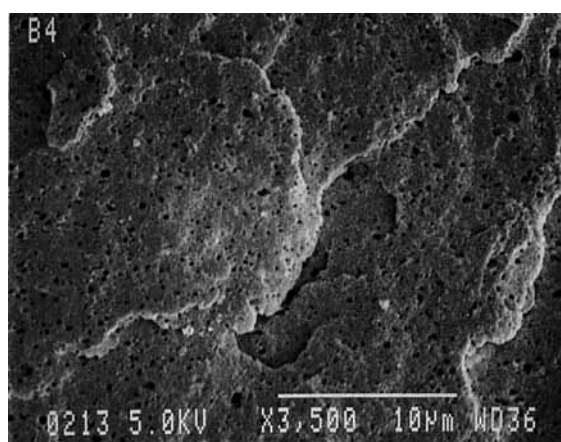
a)



b)

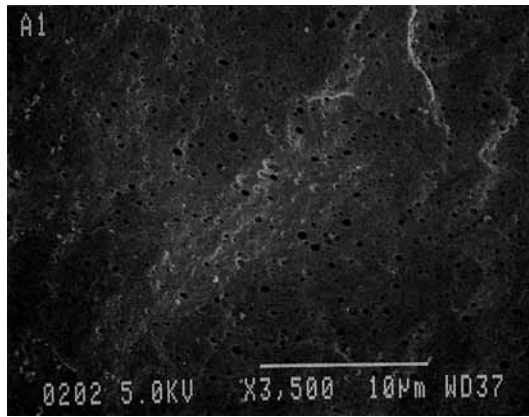


c)

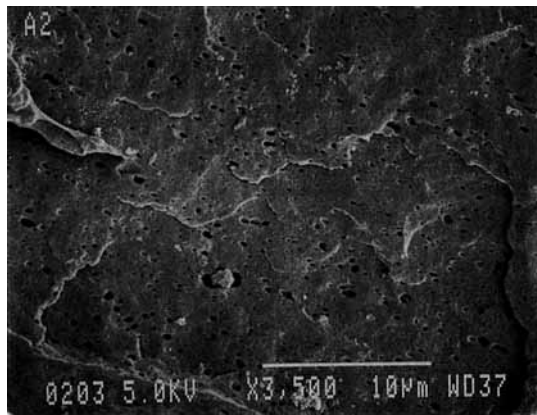


d)

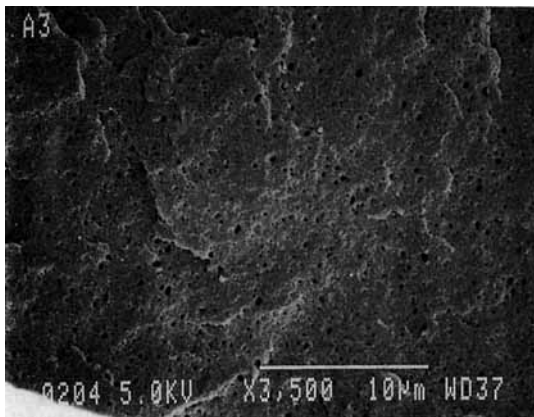
Figure 6 SEM micrographs of the blends vs. peroxide content (0.6 phr TMPTA): (a) 0.01; (b) 0.02; (c) 0.03; (d) 0.05 phr.



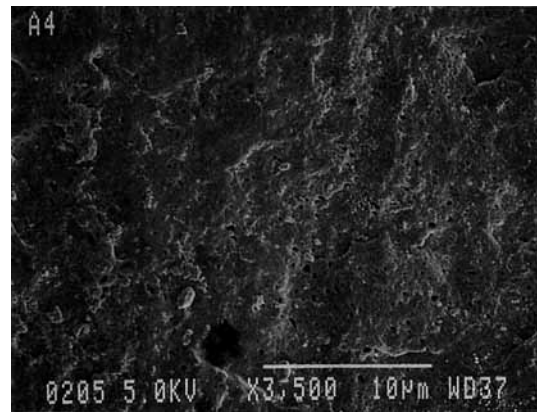
a)



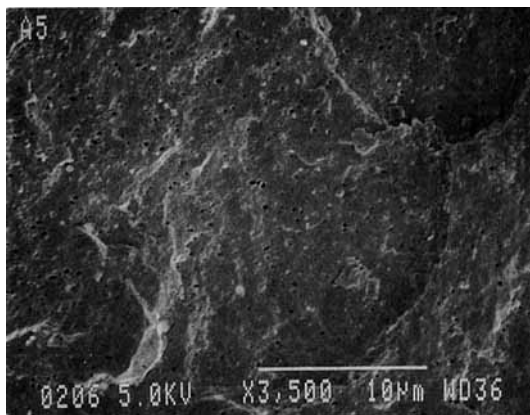
b)



c)



d)



e)

Figure 7 SEM micrographs of the blends vs. coagent content (0.01 phr peroxide): (a) 0; (b) 0.15; (c) 0.3; (d) 0.6; (e) 1.0 phr.

that content, a result consistent with the MI measurement (Fig. 2). The viscosity function of 0.02 phr peroxide tends to show a viscosity upturn at low frequencies. In a multiphase flow, such viscosity yield is obtained when the dispersed domains are interconnected to form a three-dimensional network or aggregates.¹⁴⁻¹⁶ However, the morphology measurement described later does not confirm this. Thus, the increase and decrease of the melt viscosity with peroxide is due to the crosslinking and degradation of the matrix.

As expected, the melt viscosity monotonically increases with the coagent content, showing a well-defined viscosity yield at 0.6 and 1.0 phr (Fig. 5). If

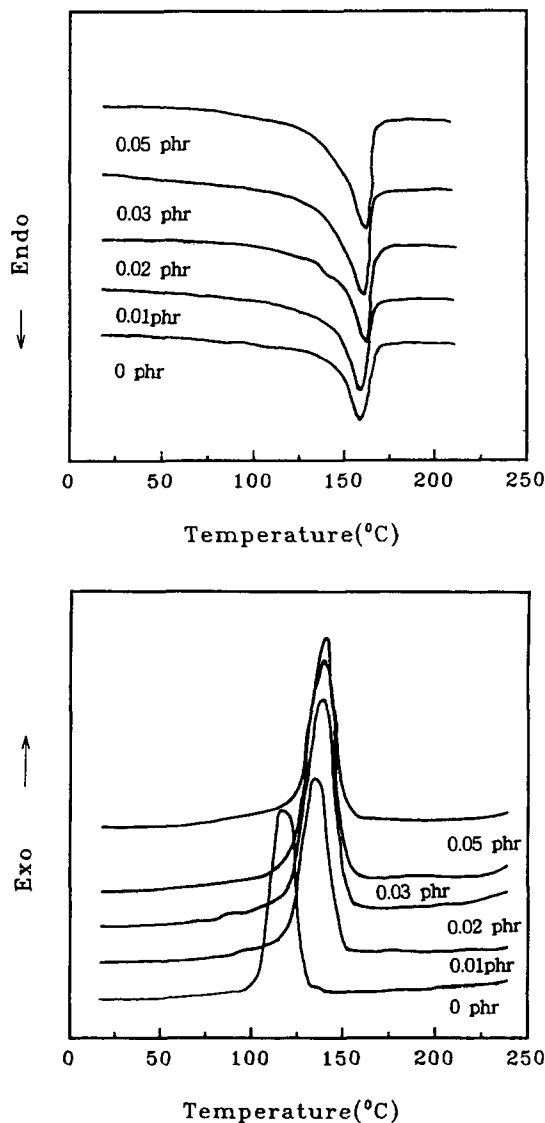


Figure 8 DSC thermograms of the blends vs. peroxide content (0.6 phr TMPTA): (a) heating; (b) cooling.

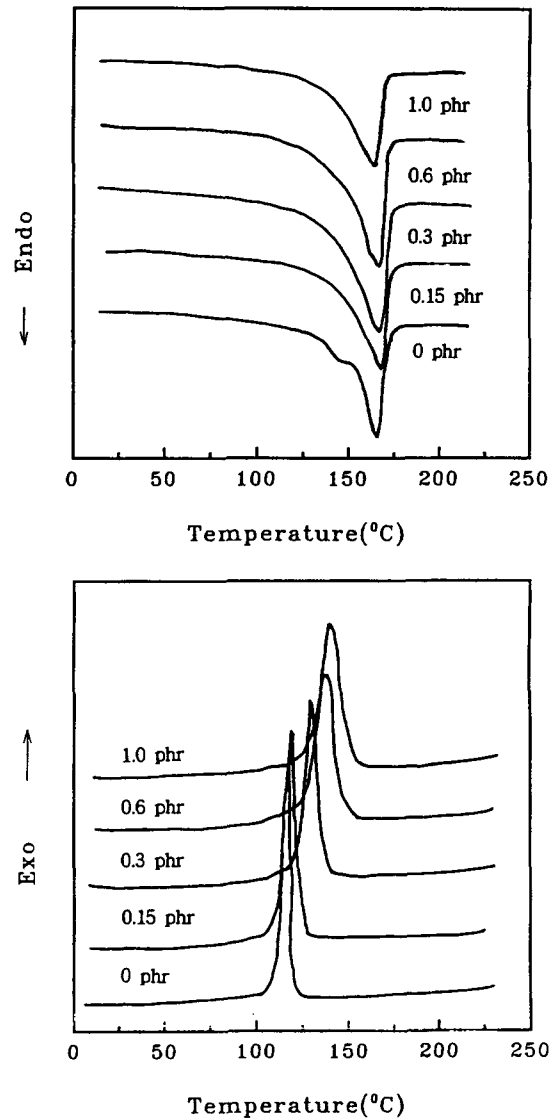


Figure 9 DSC thermograms of the blends vs. coagent content (0.01 phr peroxide): (a) heating; (b) cooling.

the viscosity yield is caused by the heterogeneity of the blend, i.e., by the suspension of NR domains in PP, viscosity yield is more plausible with less crosslinked PP since coalescence of NR particles is more feasible in a less viscous matrix. Therefore, it is convincing that the yield obtained at high TMPTA content is due to the crosslinking of PP, and the effect of NR crosslinking seems insignificant.

Morphology

SEM micrographs of the blends as a function of peroxide content are shown in Figure 6. The rubber domains are independently dispersed in the PP ma-

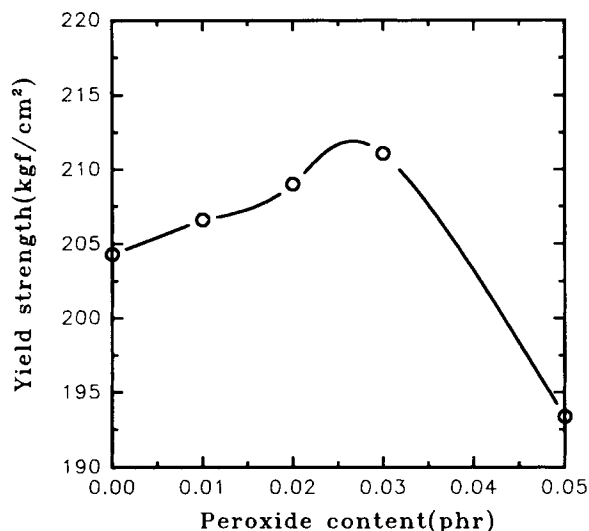


Figure 10 Yield strength of the blends vs. peroxide content (0.6 phr TMPTA).

trix, and they are neither connected in three dimensions nor form aggregates. The dispersed domains (holes) are largest for the control (no peroxide added), decrease with 0.02 and 0.03 phr, and increase with 0.15 phr peroxide. The reduction of domain size is due to the compatibilizing effect of the interpolymers, which were formed *in situ* during melt extrusion, and to the increased viscosity of the PP matrix by crosslinking. With greater matrix viscosity, greater interfacial shear stress and, hence, finer breakup of the dispersed phase are obtained.¹⁷ The relative significance between the compatibilizing ef-

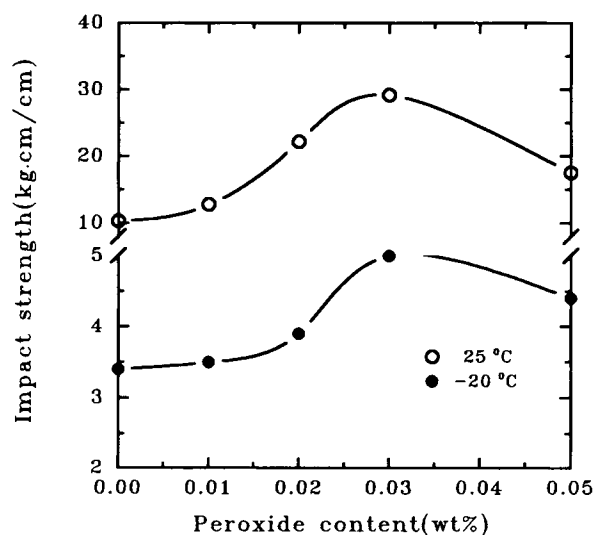


Figure 11 Impact strength of the blends vs. peroxide content (0.6 phr TMPTA).

fect and viscosity effect is not clear. However, since more interpolymers are expected to form with more peroxide, the increase of droplet size with 0.05 as compared to 0.03 phr peroxide probably indicates that the viscosity effect is more significant.

Figure 7 shows the effect of TMPTA on the domain size, where a monotonic decrease with the TMPTA content is seen, except with 0.15 phr, where the domain size is practically unchanged from the control containing no TMPTA, like MI and the melt viscosity. The variation of domain size with TMPTA content is consistent with the viscosity variation, again suggesting that the main factor to control the domain size is the matrix viscosity. However, the viscosity ratio of NR to PP, rather than the viscosity of PP, should be considered in determining the dispersed domain size, and further study should be directed toward the dispersed phase characterization.

Thermal Properties

Figure 8 shows the DSC thermograms of the blends prepared with different contents of peroxide. The melting peak temperature (T_m) of PP is, however, practically unchanged with the peroxide content. The crystallization temperature (T_c) is significantly increased with peroxide, as compared to the control of the coagent-alone-treated blend. At a constant content of peroxide, T_m is slightly increased with TMPTA, but T_c is significantly increased, in proportion to its content (Fig. 9).

Extensive crosslinking should disturb the crystallinity.¹⁸ However, a few crosslinks can also im-

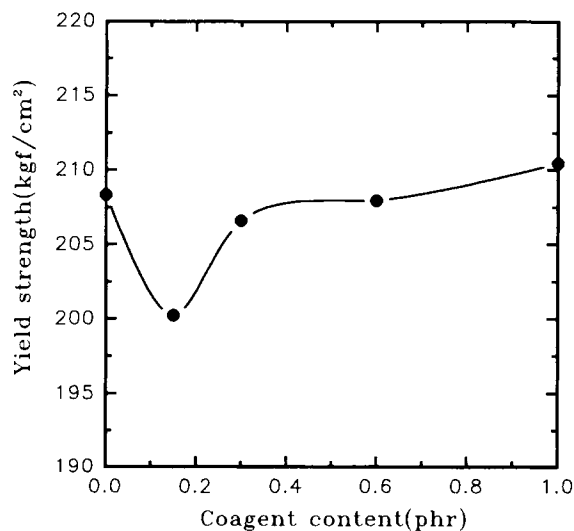


Figure 12 Yield strength of the blends vs. coagent content (0.01 phr peroxide).

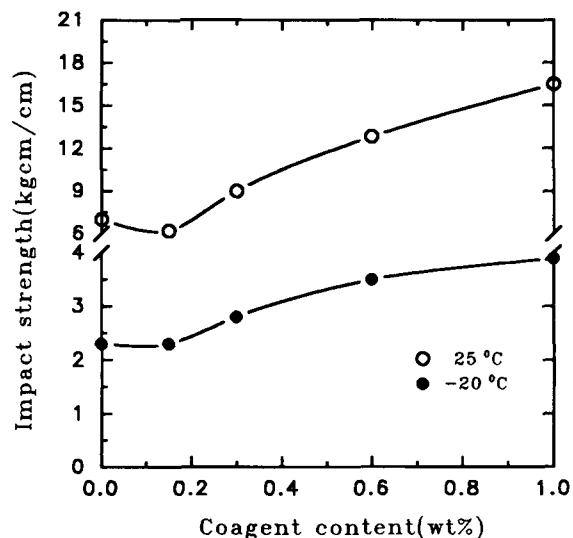


Figure 13 Impact strength of the blends vs. coagent content (0.01 phr peroxide).

prove 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_c .^{11-13,18} However, the crosslinks should also act as local defects, not allowing close packing of the polymer chains, and, hence, the increase of T_m could be marginal as compared to T_c .

Mechanical Properties

Yield strength (Fig. 10) and impact strength (Fig. 11) increase smoothly with peroxide up to 0.03 phr and decrease with 0.05 phr. The increase and decrease are due mainly to the crosslinking and chain scission of PP. At constant peroxide content, yield (Fig. 12) and impact strength (Fig. 13) generally increase with TMPTA content, except with 0.15 phr, where a minimum is generally obtained. It is noted that impact strength is increased significantly with

only peroxide/coagent treatment, implying that the crosslinking of the matrix improves such a property without sacrificing other properties.

REFERENCES

1. D. J. Synnott, D. F. Sheidan, and E. G. Kontos, in *Thermoplastic Elastomers from Rubber-Plastic Blends*, S. K. De and A. K. Bhowmick, Eds., Ellis Horwood, New York, 1990.
2. N. M. Mathew and A. J. Tinker, *J. Nat. Rubb. Res.*, **1**, 240 (1986).
3. D. Hoppner and J. H. Wendorff, *Colloid Polym. Sci.*, **268**, 500 (1990).
4. N. K. Kalfoglou, *Angew. Makromol. Chem.*, **129**, 103 (1985).
5. K. C. Dao, *Polymer*, **25**, 1527 (1984).
6. J. Karger-Kocsis and V. N. Kuleznev, *Polymer*, **23**, 6999 (1982).
7. S. Al Malaika and E. J. Amir, *J. Nat. Rubb. Res.*, **1**(2), 104 (1986).
8. I. Chodaok and M. Lazar, *Agnew. Makromol. Chem.*, **106**, 153 (1982).
9. E. Borsig, A. Fiedlerova, and M. Lazar, *J. Macromol. Sci. Chem. A*, **16**(2), 513 (1981).
10. C. Tzoganakis, J. Vlachopoulos, and A. E. Hamielec, *Polym. Eng. Sci.*, **28**, 170 (1988).
11. K. J. Kim and B. K. Kim, *J. Appl. Polym. Sci.*, **48**, 981 (1994).
12. K. J. Kim and B. K. Kim, *Eur. Polym. J.*, **28**(12), 1487 (1992).
13. B. K. Kim and K. J. Kim, *Adv. Polym. Technol.*, **12**(3), 263 (1993).
14. C. D. Han, *Multiphase Flow in Polymer Processing*, Academic Press, New York, 1989.
15. L. A. Utracki, *Polymer Alloys and Blends*, Hanser, New York, 1989.
16. T. O. Ahn, C. K. Kim, B. K. Kim, H. M. Jeong, and J. D. Huh, *Polym. Eng. Sci.*, **30**, 341, (1990).
17. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York, 1960.
18. A. W. Birley, B. Harworth, and R. Muhta, *Physics of Plastics*, Hanser, Munich, 1991.

Received August 30, 1994

Accepted September 20, 1994