Influence of Compatibilizers on the Rheological, Mechanical, and Morphological Properties of Epoxidized Natural Rubber/Polypropylene Thermoplastic Vulcanizates

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ABSTRACT: In polymeric materials combining desirable properties, compatibility between constituent components of incompatible blends is necessary. The influence of two types of blend compatibilizers, a graft copolymer of maleic anhydride and polypropylene (PP) and phenolic-modified PP, on the rheological, mechanical, and morphological properties of epoxidized natural rubber/PP thermoplastic vulcanizates was investigated at varied concentrations. All properties improved in a range of loading levels of compatibilizers at 0–7.5 wt % of PP. This was attributed to a chemical interaction between the different phases caused by the functionalized compatibilizers. Increasing chemical interaction between interfaces improved the interfacial tension and led to a microscale size of the dispersion. A decreasing trend in the properties was observed at compatibilizer levels higher than 7.5 wt % of PP because of segregation, which led to a third blend component dispersed in the PP matrix. The compatibilizers behaved as lubricants in the polymer melt flow. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2436–2443, 2008

Key words: blending; elastomers; miscibility; morphology; polypropylene (PP); rubber; thermoplastics

INTRODUCTION

Thermoplastic elastomers based on thermoplastic/elastomer blends with excellent mechanical properties have been prepared by a melt-mixing process via dynamic vulcanization: the vulcanization of the rubber during melt-mixing with thermoplastic. These thermoplastic elastomers have been classified as thermoplastic vulcanizates (TPVs).[1–3] TPV compositions with good properties were obtained, even though the rubber and plastic were thermodynamically incompatible.[1,4]

In incompatible blends, the adhesion between the various phases is rather poor. Physical forces applied to the blend are not transferred to the dispersed phase. As a result, some properties are significantly lower than expected by the nature of the parent components. Conversion of these incompatible blends into useful polymeric materials with a combination of desirable properties of each component requires compatibilization.[5] Compatibilizing agents or compatibilizers have been applied to TPVs to promote interaction between the phases. They are becoming a rapidly growing field because they provide a convenient procedure for changing the mechanical, thermal, or chemical properties of existing materials without the expense of synthesizing new polymers.[6] Therefore, the objective of compatibilization is to obtain a stable and reproducible dispersion that leads to the desired morphology and properties.[5,7] A number of studies have been done on the preparation of TPVs with various reactive or additive compatibilizers, such as *m*-phenylenemaleimide, polystyrene-modified natural rubber, glycidyl methacrylate-grafted polypropylene (PP), and block copolymers.[7–11] Nakason and coworkers[12,13] recently reported the effect of a graft copolymer of maleic anhydride and polypropylene (PP-*g*-MA) and phenolic-modified polypropylene (Ph-PP) on properties of TPVs based on maleated natural rubber/PP blends and epoxidized natural rubber (ENR)/PP blends using a sulfur vulcanization system. They found that the blend compatibilizers promoted compatibility between the constituent components and resulted in an improvement of the useful properties.

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In this study, the effects of the types of compatibilizers (i.e., PP-*g*-MA and Ph-PP) at various loading levels on the rheological, mechanical, and morphological properties of TPVs with a peroxide curing system were investigated.

EXPERIMENTAL

Materials

The PP used in this study was PP700J, with a melt flow index (MFI) of 11.5 g/10 min and a specific gravity of 0.90, and was manufactured by the Thai Polypropylene Co., Ltd. (Rayong, Thailand). ENR with a level of epoxide groups of 20 mol % (i.e., ENR-20) was synthesized in-house by an *in situ* performic epoxidation method. Emulvin W, a nonionic surfactant used to stabilize the latex, was manufactured by Bayer (Wuppertal, Germany). The maleic anhydride (MA) used to prepare PP-*g*-MA was manufactured by Riedel-de Haen (Seelze, Germany). The phenolic resin, SP-1045, used to prepare Ph-PP compatibilizer was obtained from Schenectady International, Inc. (Freeport, NY). The stannous dichloride used as a Lewis acid catalyst in the preparation of Ph-PP was manufactured by Fluka Chemical (Buchs SG, Switzerland). Dicumyl peroxide (DCP), which was used as a free-radical initiator in the preparation of PP-*g*-MA and as a curing agent of ENR, was manufactured by PT. Nof Mas Chemical Industries (Jagarta, Indonesia). Triallyl cyanurate (TAC), which was used as a coagent in the peroxide curing system, was manufactured by Fluka Chemical. The polyphenolic additive Wingstay L, which was used as an antioxidant, was manufactured by Eliokem, Inc. (Akron, OH).

Preparation of ENR

ENR was prepared in house from high-ammonia-concentrated NR latex with 60% dry rubber content. An *in situ* performic epoxidation method was performed by the reaction of formic acid with peroxide in diluted latex with 20% dry rubber content. The reaction temperature was kept at 50°C for 7 h to gain ENR with a level of epoxide groups of 20 mol % (i.e., ENR-20), according to a calibration curve described by Nakason et al.[14] The ENR latex was coagulated by heating to a temperature above the cloud point of the nonionic surfactant Emulvin W (i.e., 63°C). The coagulum was sheeted out with a crepe mill and thoroughly washed with water. The ENR was finally dried at 60°C for several hours.

Preparation of the PP-*g*-MA compatibilizer

MA was first dried in a vacuum oven at 40°C for 24 h. A Brabender plasticorder PLE 331 (Duisberg, Germany) was used to prepare PP-*g*-MA. The reaction was carried out in the molten state at 180°C. PP (100 parts by weight) and MA (5 parts by weight of PP) were added to the mixing chamber and then mixed at a rotor speed of 60 rpm for 2 min. DCP (1 part by weight of PP) was later added and mixed for another 1 min. The PP-*g*-MA product was ground into small pieces with a Bosco plastic grinder (Bosko Engineering, Co., Ltd., Samutprakarn, Thailand). The sample was then purified by extraction with acetone before lateron was used.

Preparation of the Ph-PP compatibilizer

Ph-PP was prepared with an internal mixer, the Brabender plasticorder, at 180°C with a rotor speed of 60 rpm. PP (100 parts by weight) was first mixed in a mixing chamber with 4 parts by weight of dimethylol phenolic resin (SP-1045) for 3 min. Stannous dichloride at 0.8 parts by weight was later added, and mixing was continued for 2 min.[15] The product was cooled to room temperature and ground into small pieces with the Bosco plastic grinder. Before use, the sample was purified by extraction with acetone.

Preparation of TPVs based on ENR/PP blends

TPVs based on 60/40 ENR/PP blends were prepared by melt mixing with the Brabender plasticorder. The compounding formulation is shown in Table I. In this study, dynamic vulcanization was performed with DCP as a curing agent and TAC as a coagent. The mixing was performed at 180°C and at a rotor speed of 60 rpm. PP was first incorporated into the mixing chamber without rotation for 5 min to preheat it. The PP was then mixed for 3 min. Antioxidant (i.e., Wingstay L) and ENR were added to the mixing chamber, and mixing was continued for another 3 min. A blend compatibilizer (i.e., PP-*g*-MA or Ph-PP) was then incorporated into the mixing chamber, and mixing was continued for 2 min. A coagent (TAC) was added and mixed for 1 min before the DCP curative was added. The mixing was continued for 5 min until a plateau mixing torque

TABLE I
Compounding Formulation

Ingredient	Quantity (phr)
ENR	60
PP	40
ZnO	1.5
Wingstay L	2.0
TAC	4.0
DCP	5.52 (20)[a]

[a]The number within parentheses represents milliequivalents of peroxides per 100 parts of pure ENR rubber.

was reached. The blend products were then cut into small pieces with the Bosco plastic grinder. In this study, the two types of blend compatibilizers (i.e., PP-g-MA and Ph-PP) were each studied at various concentrations: 0, 2.5, 5.0, 7.5, 10.0, and 15.0 wt % of PP.

Molecular structure characterization

A thin film of the compatibilizers (i.e., PP-g-MA and Ph-PP) was formed by compression molding at 180°C with a hydraulic pressure of 6.9 MPa. A Fourier transform infrared spectrophotometer (model Omnic ESP Magna-IR 560, Nicolet Instrument Corp., Madison, WI) was later used to characterize the molecular structures of the prepared compatibilizers. The wavelengths of the mid-IR region (i.e., the ranges of wave number from 4000 to 400 cm^{-1}) were exploited.

Rheological characterization

Rheological properties of the blends were tested with a Rosand single-bore capillary rheometer (model RH7, Rosand Precision, Ltd., Gloucestershire, United Kingdom). The samples were tested at a shear rate range of 50–1800 s^{-1} at 190°C. The capillary die used had a diameter of 2 mm, a length of 32 mm, and an entry angle of 90°. The material was first preheated in the barrel for 5 min under a pressure of 3–5 MPa to obtain a compact mass. The excess molten material was then automatically purged until no bubbles were observed. The test was then carried out at a set shear rate in a program controlled by a microprocessor. During the test, the pressure drop across the capillary channel and melt temperature were captured via the data-acquisition system. The apparent values of the shear stress and shear viscosity were characterized as a function of apparent shear rate.

Mechanical testing

The 60/40 ENR/PP TPVs pellets were injected into dumbbell-shaped specimens with a Weltec thermoplastic injection-molding machine (Weltec Machinery, Ltd., Hongkong, China) with a clamping of 90 tons. Tensile properties, in terms of tensile strength, elongation at break, and tension set, were tested with a Hounsfield tensometer (model H 10 KS, Hounsfield Test Equipment Co., Ltd., Raydon, UK) at a crosshead speed of 500 mm/min and at room temperature according to ISO 37.

Morphological studies

Morphological studies were carried out with a scanning electron microscope (model VP 1450, Leo Co.,
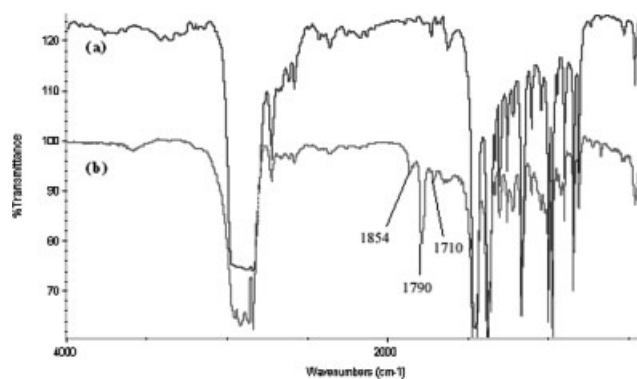
Figure 1 IR spectra of (a) pure PP and (b) PP-g-MA.[13]

Ltd., Cambridge, United Kingdom). Injection-molded samples of the NR/PP TPVs were cryogenically fractured in liquid nitrogen to prevent any possibility of phase deformation during the fracture process. The PP phase was preferentially extracted by immersion of the fractured surface into xylene at 110°C for 30 min. The samples were later dried in a vacuum oven at 40°C for 12 h to eliminate contamination of the solvent. The dried surfaces were gold-coated before they were characterized by scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Characterization of the compatibilizers: PP-g-MA and Ph-PP

The Fourier transform infrared spectra of the pure PP and PP-g-MA are shown in Figure 1 New absorption bands at 1790 and 1854 cm^{-1} were observed in spectrum of PP-g-MA [i.e., Fig. 1(b)]. This confirmed the presence of carbonyl groups (—C=O) of the cyclic anhydride after the grafting reaction. These peaks were assigned to symmetric and asymmetric C=O stretching vibration modes of succinic anhydride groups, respectively.[16–19] Also, the majority of the grafted MA on the PP molecules was the cyclic succinic anhydride. This was because a weak absorption peak was observed at a wave number of 1710 cm^{-1}. This peak was assigned to C=O stretching vibrations of carboxylic acid, which resulted from the ring-opening reaction of the succinic anhydride groups. This reaction took place as a result of moisture and hydrogen-donor molecules with hydroxyl or amino functions.[18] A proposed reaction mechanism of PP and MA was described by Nakason et al.[13] Alkoxy radicals from DCP first abstracted hydrogen atoms from the PP main chain, which resulted in reactive PP molecules. They later reacted with MA molecules to form the PP-g-MA.

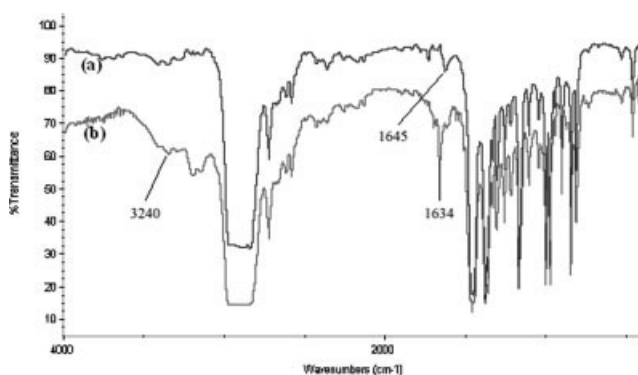The IR spectra comparison between pure PP and Ph-PP are shown in Figure 2 A weak absorption

Figure 2 IR spectra of (a) pure PP and (b) Ph-PP.[13]

Figure 3 Relationship between the apparent shear viscosity and apparent shear rate of 60/40 ENR/PP TPVs with PP-*g*-MA compatibilizer.

band at 1645 cm^{-1} was observed for the pure PP molecules and indicated the presence of —C=C— double bonds in this special grade of PP (one double bond per PP molecule). The unsaturated sites were active for reacting with dimethylol phenolic compound in the presence of a Lewis acid (i.e., SnCl$_2$·2H$_2$O). A probable reaction mechanism of PP and dimethylol phenolic resin molecules was reported previously.[13] That is, the quinone methide derived from a dimethylol-phenolic compound reacted with unsaturation in PP molecules to yield a rearrangement of hydrogen and oxygen atoms. As a result, the Ph-PP compatibilizer was formed. The results of the grafting reaction showed new absorption peaks at a wave number of 3420 cm^{-1}. This was assigned to a symmetric stretching vibration of the O—H bond in the phenolic resin molecules. The second peak was observed at 1654 cm^{-1}, which was assigned to the presence of the —C=C— conjugated double bond in the benzene ring of the resin.

In addition, the viscosity of neat PP and newly prepared compatibilizers was discussed in term of MFI. The MFI values of neat PP and Ph-PP measured at 230°C were 11.5 and 10.9 g/10 min (2.16-kg load), respectively. The MFI of Ph-PP was marginally lower than that of the neat PP, even though it was sheared under high temperature (i.e.,180°C) for 5 min. However, the influence of chemical interaction between the polar functional groups was higher than the effect of shearing action. Therefore, the lower MFI was consequent. The MFI of PP-*g*-MA compatibilizer was 22.7 g/10 min. The viscosity was very low compared with the neat PP and Ph-PP. This was a result of the β-chain scission of PP molecules in the presence of DCP during the grafting mechanism.

Rheological properties of ENR/PP TPVs with PP-*g*-MA compatibilizers

The relationship between the apparent shear viscosity and apparent shear rate (i.e., the viscosity curve)
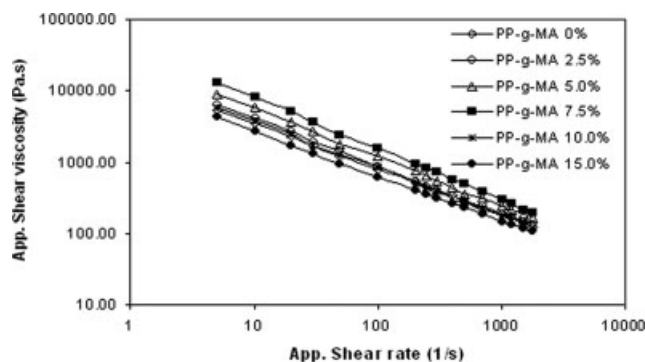
is shown in Figure 3 All TPVs exhibited pseudoplastic behavior (i.e., shear thinning behavior). At a given shear rate, the apparent shear viscosity increased with increase loading levels of PP-*g*-MA until it reached a maximum value at a loading level of 7.5 wt %. Chemical interaction between the polar functional groups in the PP-*g*-MA and ENR molecules might have been a reason for the increasing trend of apparent shear viscosity. A possible mechanism of compatibilization of the ENR/PP blend by PP-*g*-MA is shown in Scheme 1. The nonpolar PP segments in the PP-*g*-MA molecules were capable of miscibility with the PP molecules of the blend component. This led to a reduction in the interfacial tension and an increase in the interfacial adhesion. As a result, fine micrometer-size vulcanized ENR particles were dispersed in the PP matrix. Increasing levels of the PP-*g*-MA higher than 7.5 wt % also caused a decreasing trend in the apparent shear viscosity. This was attributed to the formation of micelles in the continuous PP matrix at high concentrations of
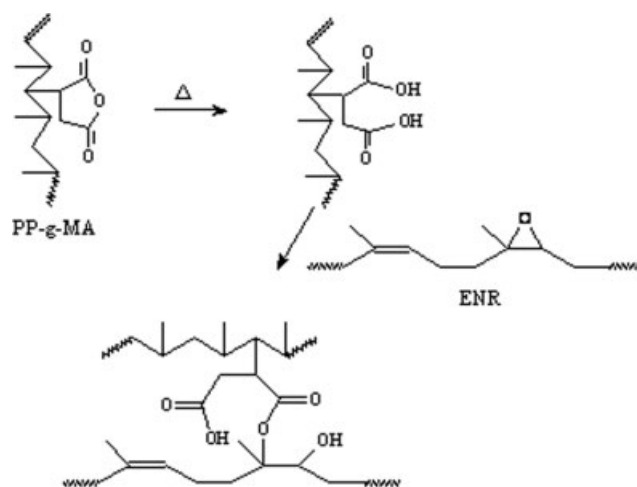
Scheme 1 Possible mechanism of compatibilization of ENR/PP blends by PP-*g*-MA.[13]
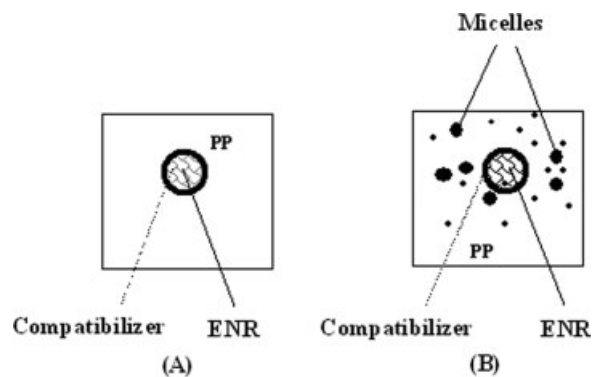
Figure 4 Schematic representation of the formation of micelles in a 60/40 ENR/PP blend: (a) at the optimum level of the compatibilizer and (b) above the critical micelle concentration.

Figure 6 Relationship between the apparent shear viscosity and apparent shear rate of 60/40 ENR/PP TPVs with Ph-PP compatibilizer.

Rheological properties of ENR/PP TPVs with Ph-PP compatibilizers

Figures 6 and 7 show the viscosity curves (i.e., plot of apparent shear viscosity and shear rate) and the relationship of apparent shear viscosity and the concentration of Ph-PP at constant apparent shear rates of 60/40 ENR/PP TPVs, respectively. At a given shear rate, increasing trends of apparent shear viscosity were observed in the range of Ph-PP loading levels of 0–7.5 wt % of PP. The maximum apparent shear viscosity was also observed at a loading level of Ph-PP = 7.5 wt %. This was similar to the trend of the viscosity curves in the case of TPVs with PP-g-MA compatibilizer (Fig. 3). This was attributed to a maximum compatibilizing effect or chemical interaction between the PP and ENR phases at a loading level of Ph-PP = 7.5 wt %, as in the reaction mechanism shown in Scheme 2.

In Figure 7, the PBDs in the shear viscosity of the ENR/PP blend with Ph-PP compatibilizer is also shown. Therefore, we concluded that the 60/40 ENR/PP blends with Ph-PP compatibilizer were partly compatible blends.

PP-g-MA, as shown schematically in Figure 4 Therefore, the micelles dispersed in the matrix acted as lubricants for the blend system.

Trends of the apparent shear viscosity with increasing content of PP-g-MA compatibilizer at constant apparent shear rates are shown in Figure 5 The shear viscosity indicated positive deviation blends (PBD) according to the log-additive rule:[20]

$$\log \eta_\beta = \sum w_I \log \eta_I \qquad (1)$$

where η_I and η_β are the viscosity of the ith component and that of the blend, respectively, and w_I is the weight fraction of the ith component.

Compatible or partially compatible blends normally lead to a positive deviation in rheological properties, such as the viscosity and die swell, and are termed PBDs. We, therefore, concluded that the blends of 60/40 ENR/PP with PP-g-MA compatibilizer were partly compatible blends.
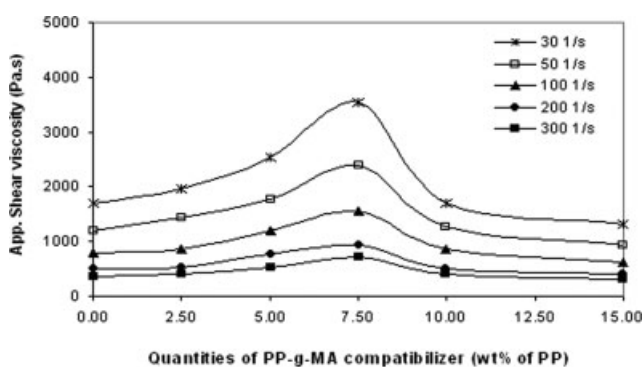

Figure 5 Apparent shear viscosity at constant shear rates of 60/40 ENR/PP TPVs with various quantities of PP-g-MA compatibilizer.
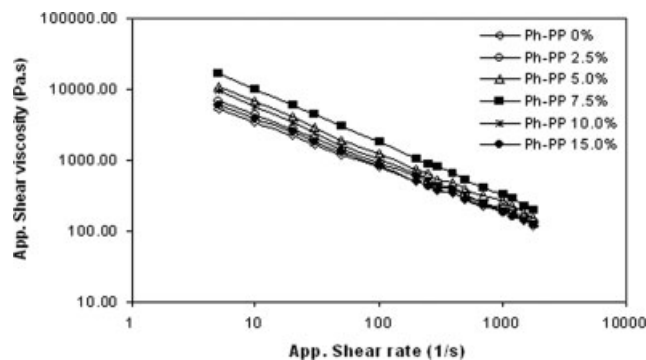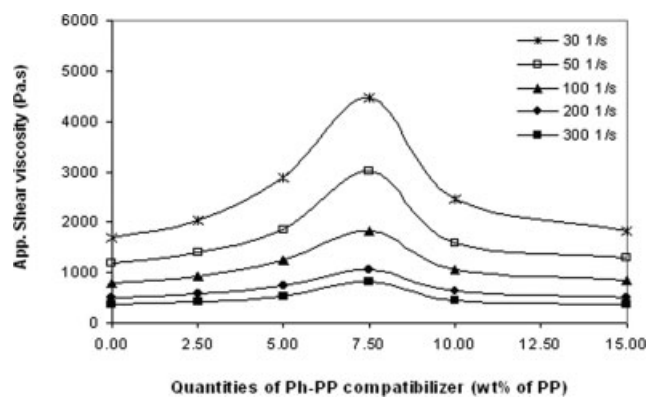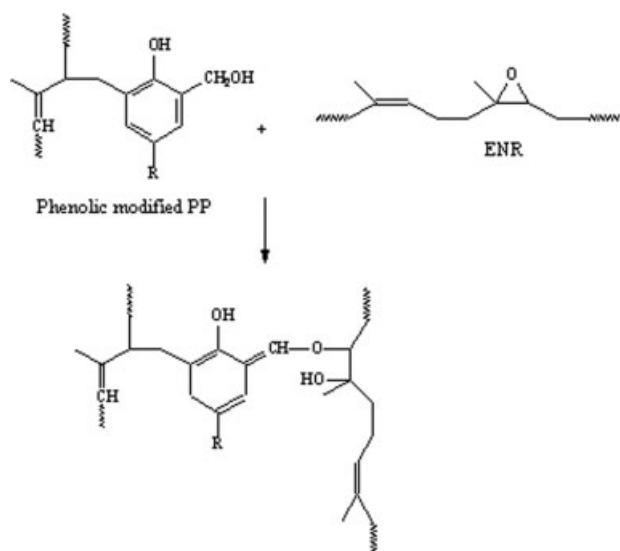

Figure 7 Apparent shear viscosity at a constant shear rate for 60/40 ENR/PP TPVs with various quantities of Ph-PP compatibilizer.

Scheme 2 Possible mechanism of compatibilization of ENR/PP blends by Ph-PP.[13]

Figure 9 Elongation at break of 60/40 ENR/PP TPVs as a function of the types and quantities of compatibilizers.

Mechanical properties of ENR/PP TPVs

The influence of the compatibilizers on the mechanical properties (i.e., tensile strength, elongation at break, and tension set) of 60/40 ENR/PP TPVs is shown in Figures 8–10. Tensile strength and elongation at break first increased with increasing loading levels of the compatibilizers up to 7.5 wt %. Higher contents of the compatibilizers caused a decreasing trend in these properties. At each fixed loading level of compatibilizers, the TPVs with Ph-PP compatibilizer exhibited somewhat superior tensile strength and elongation at break to that of the blends with PP-g-MA compatibilizer. As shown in Figure 10, the tension set of the TPVs without compatibilizer (i.e., 0%) and those with PP-g-MA compatibilizer (2.5 wt % of PP) could not be determined. This was because failures of specimen occurred at elongations at break lower than 100%. The TPVs with Ph-PP compatibilizer exhibited a somewhat superior tension set to
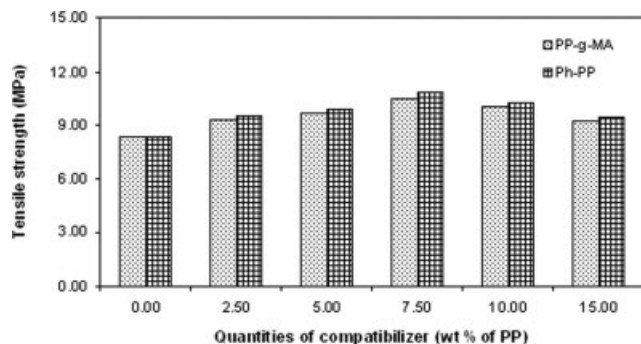
that of the TPVs with PP-g-MA. That is, a lower tension set value was observed for the TPVs with Ph-PP compatibilizer. Furthermore, all TPVs exhibited a tension set lower than 50%. This indicated good elastomeric properties of the TPVs at the tested conditions. Therefore, the presence of compatibilizers, even at low concentrations, caused an improvement in the mechanical properties of the TPVs compared with the control (i.e., 60/40 ENR/PP TPVs with 0% compatibilizer). Therefore, we concluded that the compatibilizers not only reduced the interfacial tension between the phases but also promoted a stable dispersion of the vulcanized ENR domains in the blends. This led to improvement in the desired properties of the TPVs.

Morphological studies

SEM micrographs of the etched cryogenic fracture surfaces of 60/40 ENR/PP TPVs with different types and concentrations of compatibilizers in are shown in Figure 11. The PP at the surface of samples was extracted and dissolved by hot xylene. As a result, the vulcanized rubber particles adhered at the surface were observed at the surface of the specimens. Therefore, it was clear that the small spheres of the vulcanized rubber particles dispersed in the PP matrix for the TPVs

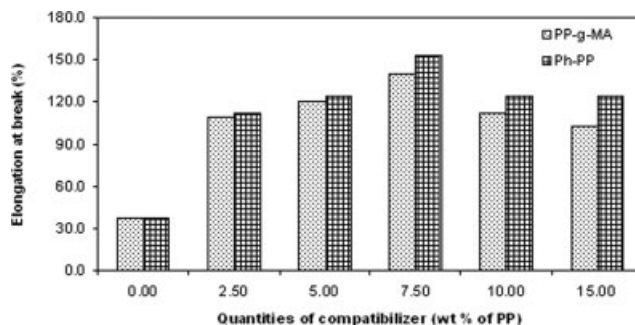Figure 8 Tensile strength of 60/40 ENR/PP TPVs as a function of the types and quantities of compatibilizers.
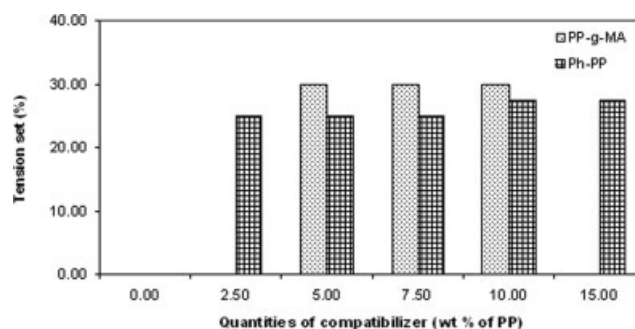

Figure 10 Tension set of 60/40 ENR/PP TPVs as a function of the types and quantities of compatibilizers.
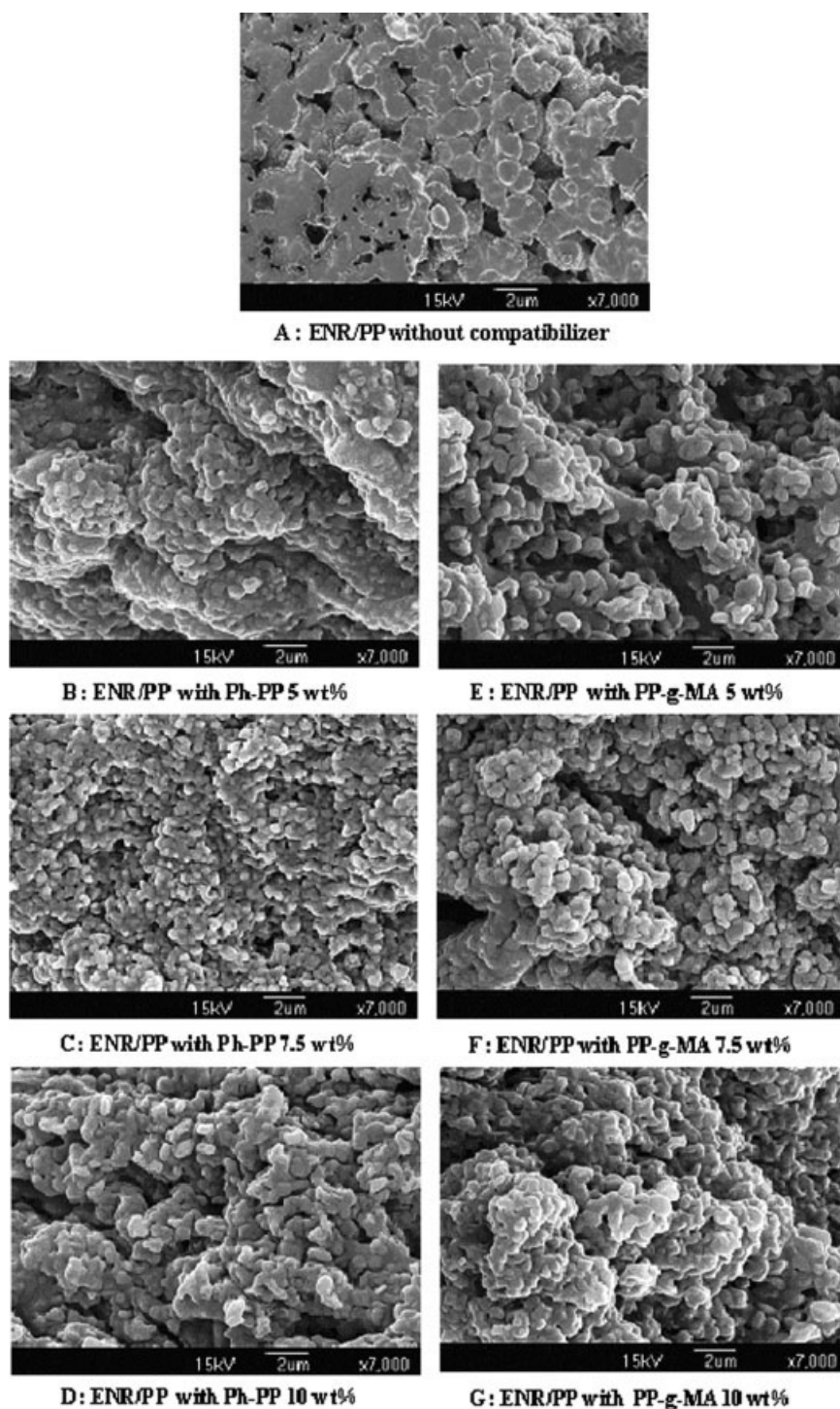
Figure 11 SEM micrographs of ENR/PP TPVs with various types and concentrations of compatibilizers.

with both type compatibilizers. Sizes of dispersed vulcanized ENR domains of the TPVs with two types of compatibilizer at 5, 7.5, and 10 wt % were compared. TPVs with compatibilizers at 7.5 wt % showed the smallest particle sizes of the disperse vulcanized rubber domains in the PP matrix. That is, the particle size was smaller than 1 μm. The particle sizes of the TPVs

with higher or lower loading levels of compatibilizers were larger than that of the TPV with compatibilizer at 7.5 wt %. Furthermore, as shown in Figure 11, TPVs with Ph-PP compatibilizer showed smaller dispersed vulcanized rubber domains, which correlated to a higher mechanical strength and viscosity of the TPVs, as described earlier.

CONCLUSIONS

Incompatible blends of ENR and PP can be improved to partially compatibility with the suitable reactive compatibilizers PP-*g*-MA and Ph-PP. We found a positive deviation in rheological properties (i.e., apparent shear viscosity) according to the log-additive rule for the ENR/PP blend with PP-*g*-MA and Ph-PP compatibilizers. Both types of blend compatibilizers provided the ENR/PP TPVs with superior mechanical properties (i.e., tensile strength, elongation at break, and tension set), even at a low loading level. Furthermore, the TPVs with Ph-PP compatibilizer exhibited somewhat superior mechanical properties to those of the PP-*g*-MA compatibilizer. The optimum mechanical properties were observed in the TPVs with a loading level of blend compatibilizers at 7.5 wt %. This was attributed to high chemical interaction between the polar groups of the ENR and polar functional groups of the compatibilizer molecules. The PP segments in the compatibilizer molecules were also capable of compatibilizing with PP molecules in the blend component. The smallest vulcanized rubber domains were observed in the TPVs with Ph-PP. This corresponded to higher rheological and mechanical properties of this type of the blend.

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