

# Thermoplastic Vulcanizates Based on Epoxidized Natural Rubber/Polypropylene Blends: Effect of Compatibilizers and Reactive Blending

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**ABSTRACT:** Epoxidized natural rubber (ENR) was prepared using the performic epoxidation method. TPVs based on ENR/PP blends were later prepared by melt-mixing processes via dynamic vulcanization. The effects of blend ratios of ENR/PP, types of compatibilizers, and reactive blending were investigated. Phenolic modified polypropylene (Ph-PP) and graft copolymer of maleic anhydride on polypropylene molecules (PP-g-MA) were prepared and used as blend compatibilizers and reactive blending components of ENR/Ph-PP and ENR/PP-g-MA blends. It was found that the mixing torque, apparent shear stress and apparent shear viscosity increased with increasing levels of ENR. This is attributed to the higher viscosity of the pure ENR than that of the pure PP. Furthermore, there was a higher compatibilizing effect because of the chemical interaction between the polar groups in ENR and PP-g-MA or Ph-PP. Mixing torque, shear flow properties (i.e., shear stress and shear viscosity) and mechanical properties (i.e.,

tensile strength, elongation at break, and hardness) of the TPVs prepared by reactive blending of ENR/Ph-PP and ENR/PP-g-MA were lower than that of the samples without a compatibilizer. However, the TPVs prepared using Ph-PP and PP-g-MA as compatibilizers exhibited higher values. We observed that the TPVs prepared from ENR/PP with Ph-PP as a compatibilizer gave the highest rheological and mechanical properties, while the reactive blending of ENR/PP exhibited the lowest values. Trend of the properties corresponds to the morphology of the TPVs. That is, the TPV with Ph-PP as a blend compatibilizer showed the smallest rubber particles dispersed in the PP matrix, while the reactive blending of ENR/PP-g-MA showed the largest particles. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4729–4740, 2006

**Key words:** natural rubber (NR); thermoplastic vulcanizate (TPV); polypropylene; reactive blending

## INTRODUCTION

Thermoplastic elastomers (TPEs) exhibit functional properties of conventional vulcanized rubber, yet can be processed on thermoplastic fabrication equipment. Such materials can be produced either as block copolymers or as blends. The great majority of TPEs have hetero-phase morphology. The TPEs based on polyolefin rubber-thermoplastic compositions have developed along two distinctly different lines. One consists of a simple blend and classically meets the definition of a thermoplastic elastomeric olefin (TPO). In the other class, the rubber phase is dynamically vulcanized giving rise to thermoplastic vulcanizates (TPVs) or dynamic vulcanizates (DVs). The TPVs are characterized by finely dispersed micron-sized crosslinked rubber particles distributed in a thermoplastic matrix.<sup>1</sup>

Most polyolefin TPEs are based on ethylene-propylene-diene monomer (EPDM) and nitrile rubber (NBR) or a modification of them. Interest in natural rubber (NR) and thermoplastic blends has increased recently. These materials are known as thermoplastic natural rubbers (TPNRs). Thermoplastics blended with NR include polypropylene,<sup>2–10</sup> low-density polyethylene,<sup>11,12</sup> high-density polyethylene,<sup>11,13,14</sup> ultra-low-density polyethylene,<sup>15</sup> linear low-density polyethylene,<sup>16</sup> chlorinated polyethylene,<sup>17,18</sup> polystyrene<sup>19,20</sup> polyamide,<sup>6,21</sup> ethylene-vinyl acetate copolymer (EVA)<sup>22</sup> and poly(methyl methacrylate).<sup>23,24</sup> Apart from raw NR, modified forms of NR have also been used to prepare TPNRs. Epoxidized natural rubber (ENR) is one of the modified forms currently used to prepare TPNRs. This is done through blending of ENR with polar thermoplastics such as poly(vinyl chloride)<sup>25,26</sup> and poly(ethylene-co-acrylic acid).<sup>27</sup> Graft copolymers of NR with PMMA<sup>23,28</sup> have also been used to prepare TPNRs.

In this work, an attempt was made to prepare TPNRs based on epoxidized natural rubber and polypropylene (PP) blends via dynamic vulcanization. Various levels of ENR, various types of blend com-

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**TABLE I**  
**Compounding Formulation**

Ingredients	Quantity (phr)
ENR-30	100
ZnO	5.0
Stearic acid	2.5
Wingstay L	1.0
TBBS	0.5
Sulphur	2.0

patibilizers (i.e., NR-*g*-MA and Ph-PP) and reactive blending of ENR/PP-*g*-MA and ENR/Ph-PP were studied. Rheological, mechanical, and morphological properties of the blends were investigated.

## EXPERIMENTAL

### Materials

High ammonia (HA) concentrated natural rubber latex, manufactured by Yala Latex Co., Yala, Thailand, was used as a raw material for a preparation of the ENR. The nonionic surfactant used to stabilize the latex during epoxidation was Teric N30 (alkylphenol ethoxylate), which was manufactured by Huntsman Corp. (Ascot Vale Vic, Australia). The formic acid used as a reactant for the preparation of ENRs was manufactured by Fluka Chemie (Buchs, Switzerland). Hydrogen peroxide used as a coreactant for the preparation of the ENRs was manufactured by Riedel De Haën (Seelze, Germany). The thermoplastic blend component, polypropylene, used was of injection grade MD with MFI of 12 g/10 min at 230°C and specific gravity of 0.91, supplied by the Thai Polypropylene Co., Rayong, Thailand. The zinc oxide used as an activator was manufactured by Global Chemical Co., Samutprakarn, Thailand. The stearic acid used as an activator was manufactured by Imperial Chemical Co., Pathumthani, Thailand. The sulfur used as a vulcanizing agent was manufactured by Ajax Chemical Co., Samutprakarn, Thailand. The *N*-*tert*-butyl-2-benzothiazolesulphenamide (Santocure TBBS) used as an accelerator was manufactured by Flexsys (USA).

### Preparation of ENRs

ENR latex was prepared using high-ammonia concentrated NR latex with a dry rubber content of ~60%. Details for the preparation process of the ENR are described elsewhere.<sup>29</sup> The reaction time was set according to the level of epoxide groups in the ENR products, as described in our previous work.<sup>29</sup> The level of the epoxide content in the ENR products was later confirmed by infrared spectroscopy via a calibration curve. In this work, the ENR with epoxide groups

of 30 mol % (i.e., ENR-30) was prepared and used throughout the work.

### Preparation of graft copolymer of maleic anhydride and polypropylene (PP-*g*-MA)

Maleic anhydride was first dried in a vacuum oven at 40°C for 24 h. The reaction was carried out in a melt state using a Brabender Plasticorder PLE 331 (Duisberg, Germany) at 180°C. PP (100 parts by weight) and maleic anhydride (7 parts) were added into the mixing chamber and mixed at a rotor speed of 60 rpm for 2 min. Dicumyl peroxide (2 parts) was then added and mixing was continued for 2 min. The quantity of MA (7 parts) was used based on the works of Saiwaree,<sup>30</sup> who observed the maximum grafting efficiency of the MA onto PP molecules by using this condition. The PP-*g*-MA products were later cut into small pieces with a Bosco plastic grinder (Samutprakarn, Thailand). The sample was purified by extracting with acetone. Infrared spectroscopy was used to confirm the grafted MA on the PP molecules.

### Preparation of phenolic modified polypropylene (Ph-PP)

Phenolic modified polypropylene was prepared using a Brabender Plasticorder by mixing process according to the work of George et al.<sup>31</sup> PP (100 parts by weight) and dimethylol phenolic resin (SP-1045) (4 parts) were mixed at 180°C with a rotor speed of 60 rpm for 3 min. Stannous dichloride (SnCl<sub>2</sub>) (0.8 parts) was then added and mixing was continued for 2 min. The products were later cut into small pieces with a Bosco plastic grinder. The sample was purified by extracting with acetone. Infrared spectroscopy was used to characterize the Ph-PP products.

### Preparation of thermoplastic vulcanizates (TPVs)

ENR was first compounded using a two-roll mill at room temperature using the compounding formulations as shown in Table I and the mixing schedule in Table II. Thermoplastic vulcanizates of ENR/PP blends were prepared using dynamic vulcanization

**TABLE II**  
**Mixing Schedule**

Descriptions	Mixing time (min)
Rubber mastication	5
ZnO	2
Stearic acid	2
Wingstay L	2
TBBS <sup>a</sup>	2
Sulphur	2

<sup>a</sup> *N*-*tert* Butyl-2-benzothiazolesulphenamide.

during melt mixing using a Brabender Plasticorder PLE 331 (Duisberg, Germany). Mixing was performed at 180°C. The PP was first preheated for 6 min in the mixer without rotation. The polymer was then melted for 2 min at a rotor speed of 60 rpm. Compatibilizer was later added (i.e., PP-g-MA or Ph-P), and mixing was continued for 1 min. The ENR compound was then incorporated and mixing was continued until a plateau mixing torque was observed. The blend products were cut into small pieces with a Bosco plastic grinder (Samutprakarn, Thailand). Various blends ratios of ENR/PP (i.e., 25/75, 40/60, 50/50, 60/40, and 75/25) were studied. In the preparation of TPVs by reactive blending, two types of modified PP (i.e., PP-g-MA and Ph-PP) were each used instead of the pure PP in a Brabender Plasticorder using various blend ratios of ENR/PP-g-MA and ENR/Ph-PP.

Torque versus mixing time was plotted for each blend. Furthermore, rheological, mechanical and morphological properties, and swelling behavior of the TPVs were investigated.

### Rheological characterization

Rosand single bore capillary rheometer (model RH7, Rosand Precision, Gloucestershire, UK) was used to characterize shear flow properties in terms of the relationship between apparent shear stress and shear viscosity with apparent shear rate. The test was carried out at a wide range of shear rates (5–1600 s<sup>-1</sup>) at a test temperature of 200°C. The dimension of the capillary die used was 2-mm diameter, 32-mm length, and 90° entry angle with an aspect ratio (L/D) of 16/1. The material was first preheated in the rheometer's barrel for 5 min under a pressure of ~3–5 MPa to get 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 of shear rates

controlled by a program via a microprocessor. During the test, the pressure drop across a capillary channel and melt temperature was captured via a data acquisition system. The apparent values of shear stress, shear rate, and shear viscosity were calculated using the derivation of the Poiseuille law for capillary flow<sup>32</sup>:

$$\text{Apparent wall shear stress (Pa); } \tau = \frac{R\Delta P}{2L} \quad (1)$$

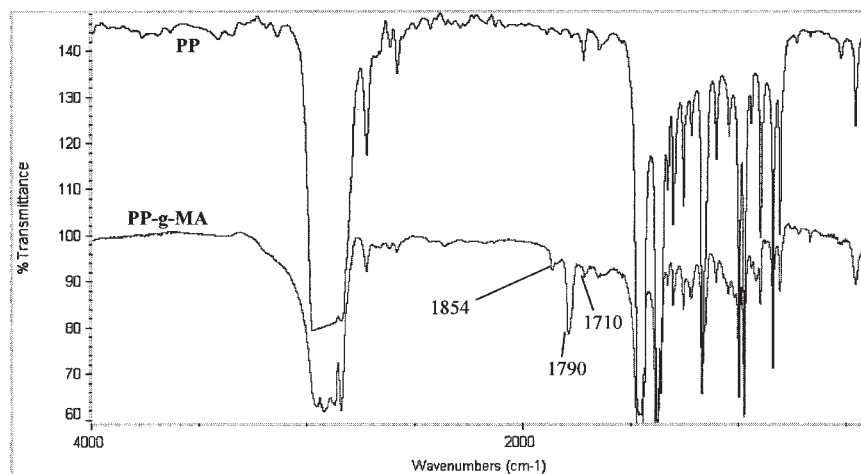
$$\text{Apparent wall shear rate (s}^{-1}\text{); } \dot{\gamma}_{\text{app}} = \frac{4Q}{\pi R^3} \quad (2)$$

$$\text{Apparent shear viscosity (Pa s); } \eta_s = \frac{\tau}{\dot{\gamma}_{\text{app}}} \quad (3)$$

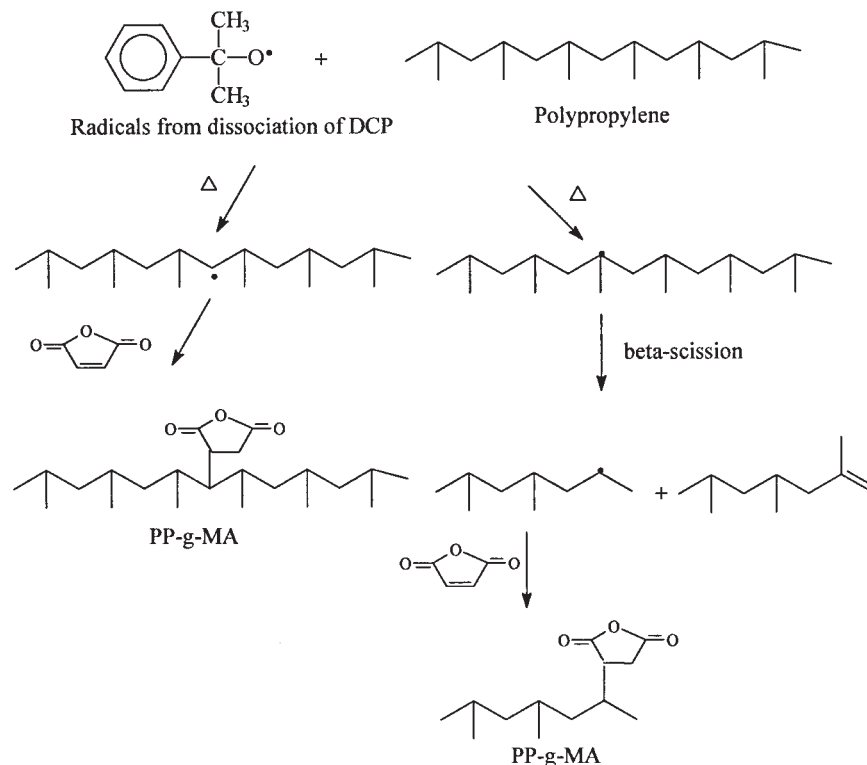
where  $\Delta P$  is the pressure drop across the channel (Pa),  $Q$  is the volumetric flow rate (m<sup>3</sup> s<sup>-1</sup>),  $R$  is the capillary radius (m), and  $L$  is the length of the capillary (m). The values of  $R$  and  $L$  used in this work were 1 and 32 mm, respectively.

### Mechanical testing

Tensile testing of the samples was performed at 25 ± 2°C at a crosshead speed of 500 mm/min according to ASTM D412. The instrument used was Hounsfield Tensometer, model H 10 KS, manufactured by the Hounsfield Test Equipment Co., UK. The dumbbell-shaped specimens, 2 mm thick, were prepared by thermoplastic injection molding machine with a capacity of 90 tons (clamping force), Welltec Machinery, Hong Kong. Hardness of the samples was measured using indentation shore A, according to ASTM D1415.



**Figure 1** Infrared spectra of PP and of PP-g-MA prepared using MA of seven parts by weight of PP.



**Scheme 1** Proposed grafting mechanism of PP-g-MA during melt reactive process.

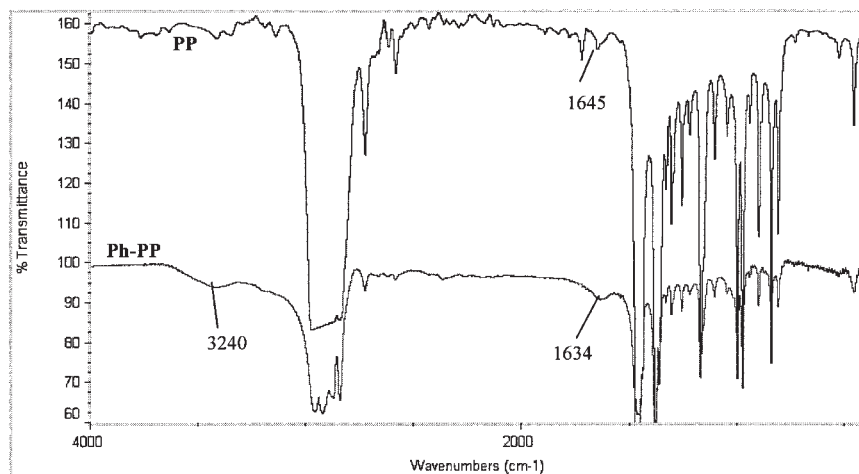
### Morphological studies

Morphological studies were carried out using a Leo scanning electron microscope, model VP 1450, manufactured by Leo Co., Cambridge, UK. Molded samples of the thermoplastic vulcanizates were cryogenically cracked in liquid nitrogen to avoid any possibility of phase deformation. The PP phase was extracted by immersing the fractured surface into hot xylene for 10 min. The samples were later dried in vacuum oven at

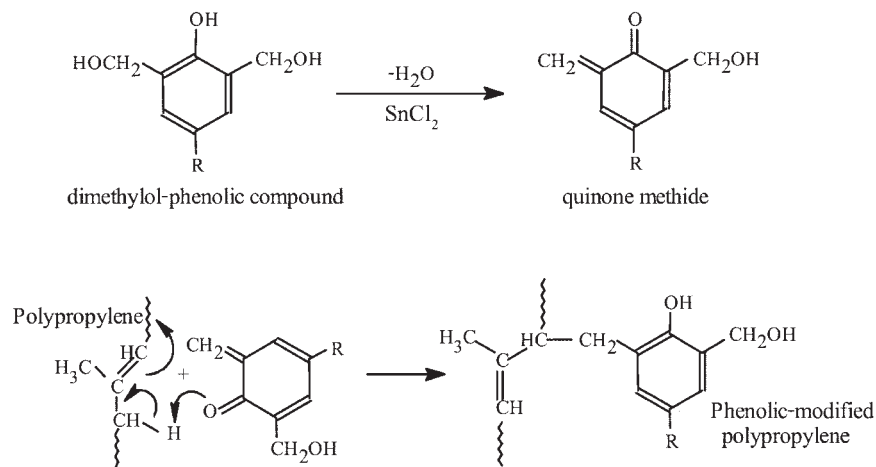
40°C for 3 h. The dried surfaces were later gold-coated and examined by the scanning electron microscope.

### Swelling behavior

TPVs based on the various ENR/PP blends were weighed and inserted into test tubes containing test liquids and placed in an oven at 30°C. In this work, diesel oil and a mixture of toluene/isooctane (50%



**Figure 2** Infrared spectra of PP and phenolic modified polypropylene (Ph-PP).



**Scheme 2** Mechanism of reaction between dimethylol phenolic resin and polypropylene.

v/v) were used as the test liquids. The test specimens were immersed in the test liquids for 72 h. The samples were removed from the solvents and blotted with filter paper to remove excess solvent from the surface of the sample. The TPVs were then weighed to an accuracy of 0.1 mg at a fixed temperature of 30°C. The degree of swelling was calculated as follows:

$$\text{Degree of swelling (\%)} = \frac{(W_s - W_0) \times 100}{W_0} \quad (4)$$

where  $W_0$  and  $W_s$  are weights of specimens before and after immersing in the test liquids, respectively.

## RESULTS AND DISCUSSION

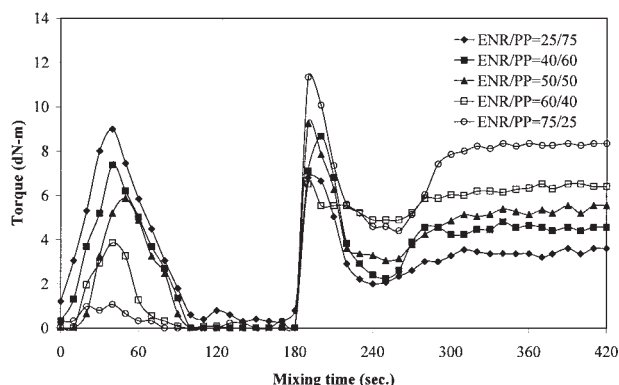
### Preparation of graft copolymer of maleic anhydride and polypropylene (PP-g-MA)

Figure 1 shows infrared spectra of PP-g-MA compared with polypropylene. Because unreacted MA gives rise to absorption bands in the same region as the grafted anhydride, complete elimination of the unreacted MA is of great importance. This was done by extracting the crude product from the reaction with acetone before characterizing with FTIR (Perkin-Elmer, 1600 Series). In Figure 1, an intense characteristic band at 1790  $\text{cm}^{-1}$  and a weak absorption band at 1854  $\text{cm}^{-1}$  were observed. These bands can be assigned to grafted anhydride, which are due to symmetric (strong) and asymmetric (weak) C=O stretching vibration of succinic anhydride rings, respectively.<sup>33</sup> Also, a very low content of C=O stretching vibration of succinic acid at 1710  $\text{cm}^{-1}$  was observed. This peak can be assigned to grafted maleic acid, which was a product of ring-opening of succinic anhydride because of moisture. This proves the presence of grafted anhydride on the PP molecules. A possible reaction mechanism was therefore proposed similar to a grafting mechanism of

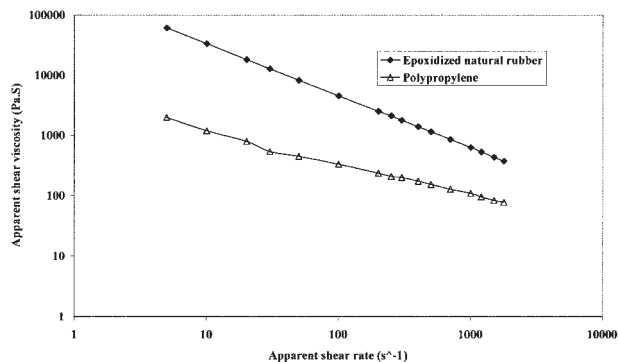
PP-g-MA proposed by Shi et al.,<sup>34</sup> as shown in Scheme 1.

### Preparation of phenolic modified polypropylene (Ph-PP)

Figure 2 shows infrared spectra of polypropylene and phenolic modified polypropylene. A weak absorption band at 1645  $\text{cm}^{-1}$  in the PP molecules indicates the presence of trace quantities of —C=C— double bonds in the PP molecules. This is a reactive site of the PP molecules with dimethylol phenolic resin in the presence of halogen donor, such as  $\text{SnCl}_2$ . In an infrared spectrum of purified Ph-PP, a characteristic band at 3420  $\text{cm}^{-1}$  and a weak absorption band at 1634  $\text{cm}^{-1}$  were observed. These bands can be assigned symmetric —OH stretching of phenolic compound and symmetric —C=C stretching vibration of conjugated double bonds in the benzene ring, respectively. Therefore, a possible reaction mechanism is postulated, as shown in Scheme 2.<sup>31</sup>



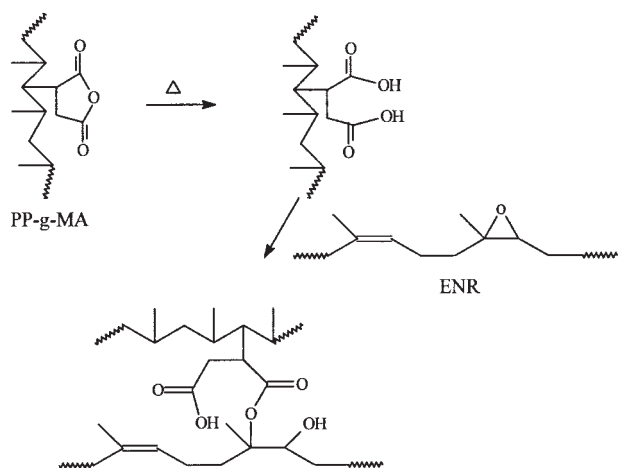
**Figure 3** Torque-time curves for various types of TPVs based on 60/40 ENR/PP blends using PP-g-MA as a blend compatibilizers.



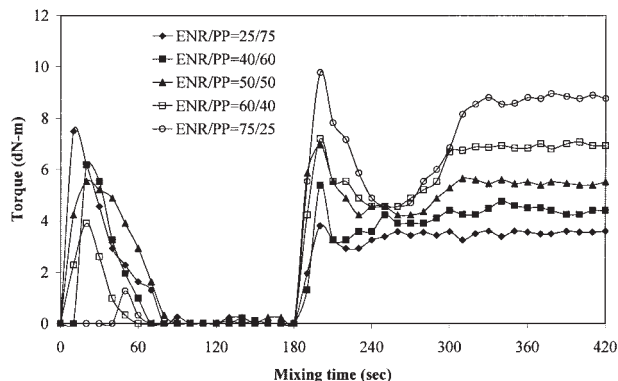
**Figure 4** Relationship of apparent shear viscosity and shear rate of pure epoxidized natural rubber and pure PP.

### Mixing torques

The torque-time curves of the TPVs prepared from various blend ratios ENR/PP using PP-g-MA as a blend compatibilizer are shown in Figure 3. PP was first charged into the mixing chamber and preheated for 6 min without using the rotor. This was to warm and dry the material. The rotors were later started, and mixing was continued for 2 min. The torque rose sharply when the rotors were started because of the resistance exerted on the rotors by the unmelted PP. A reduction of torque was later observed because the PP melted on account of mechanical shearing and heat transfer from the heating oil. Upon incorporation of the ENR compound with vulcanizing agents (i.e., accelerator (TBBS) and sulfur) the mixing torque again sharply rose because of resistance of the unmelted material. A reduction of torque was again observed. The mixing torque eventually rose sharply due to vulcanization during the melt mixing process, i.e., dynamic vulcanization. Constant mixing torque was observed after a mixing time of  $\sim 300$  s. The mixing



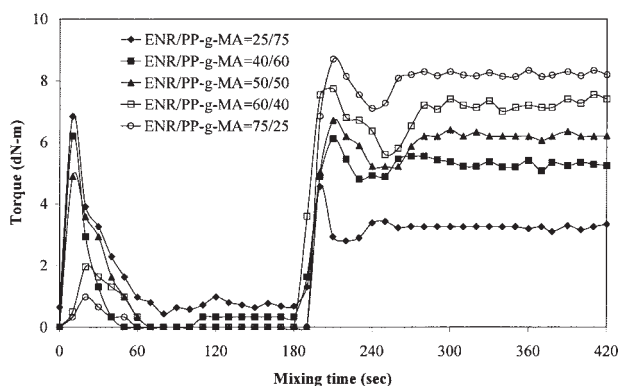
**Scheme 3** Possible mechanism of compatibilization of ENR/PP blends by PP-g-MA.



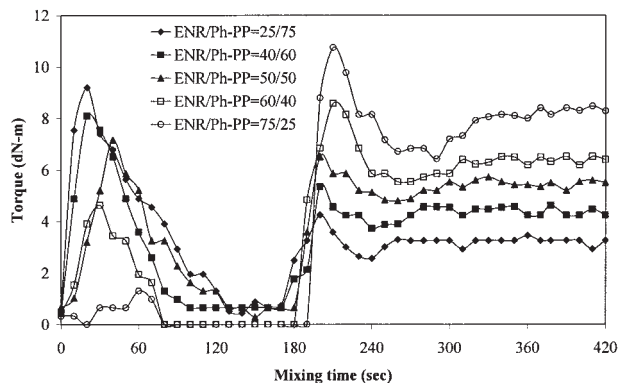
**Figure 5** Torque-time curves for various types of TPVs based on 60/40 ENR/PP blends using Ph-PP as a blend compatibilizers.

was continued until a total mixing time of 420 s was reached. In Figure 3, the levels of the final mixing torque increased with increasing levels of ENR compound. Therefore, the mixing torque of the ENR/PP with PP-g-MA as a compatibilizer was ordered as follows: ENR/PP = 75/25 > ENR/PP = 60/40 > ENR/PP = 50/50 > ENR/PP = 40/60 > ENR/PP = 25/75. This was an influence of the higher viscosity of the pure ENR than that of the pure PP, as shown in Figure 4. Also, the chemical interaction between polar groups in the ENR molecules with succinic anhydride groups of the PP-g-MA molecules might be another reason for the increasing trend of mixing torque. The grafted MA groups on PP molecules are capable of ring-opening to form succinic acid which is possible to further react with oxirane groups in the ENR molecules, such as the proposed results of the reaction (Scheme 3). The PP backbone in the PP-g-MA is capable of compatibilizing with the PP in the blend component. Consequently, the blend with higher content of ENR generated a higher chemical interaction between its molecules and the PP molecules.

Figure 5 shows the torque-time curves of the TPVs

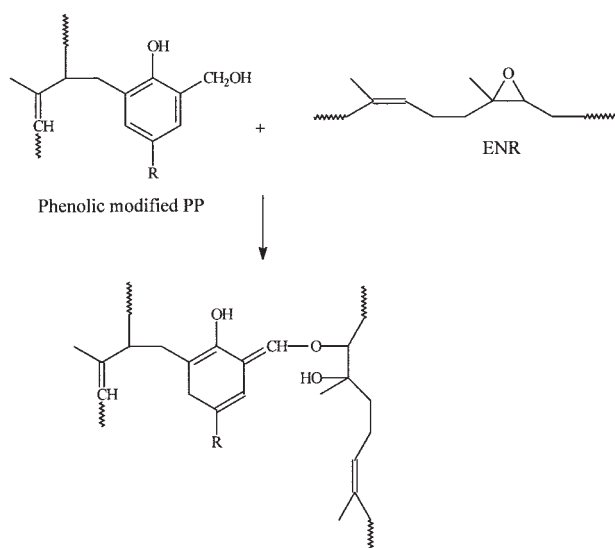


**Figure 6** Torque-time curves for various types of TPVs based on reactive blending of 60/40 ENR/PP-g-MA.

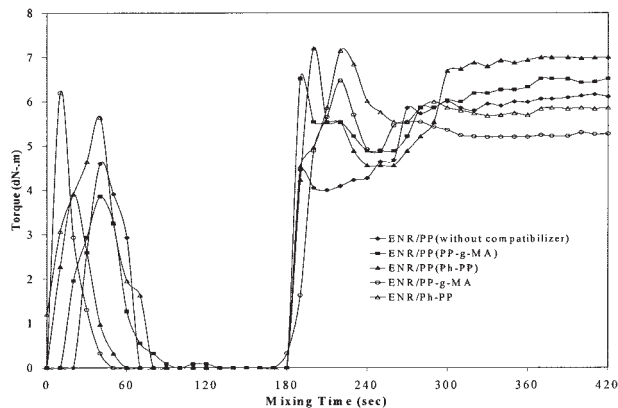


**Figure 7** Torque-time curves for various types of TPVs based on reactive blending of 60/40 ENR/Ph-PP.

prepared from ENR/PP blends with Ph-PP as a compatibilizer. Figures 6 and 7 show the torque-time curves of the TPVs prepared from a reactive blending of ENR/PP-g-MA and ENR/Ph-PP, respectively. It can be seen that the trend of the final mixing torque for various types of the TPVs showed the same as in the case of using PP-g-MA as a compatibilizer in Figure 3. The higher viscosity of the pure ENR and the compatibilizing effect of Ph-PP caused an increasing trend of mixing torque upon increasing levels of ENR compound as shown in Figure 5.<sup>31</sup> That is, the phenolic modified PP is capable of reacting with ENR molecules as indicated in Scheme 4. In Figures 6 and 7, apart from viscosity of the pure ENR, the chemical interaction between polar groups in the ENR molecules and polar functional groups in modified PP (i.e., succinic anhydride in PP-g-MA and methylol and hydroxyl groups in the Ph-PP) was also the reason for an increasing trend of the mixing torque.



**Scheme 4** Possible mechanism of compatibilization of ENR/PP blends by Ph-PP.

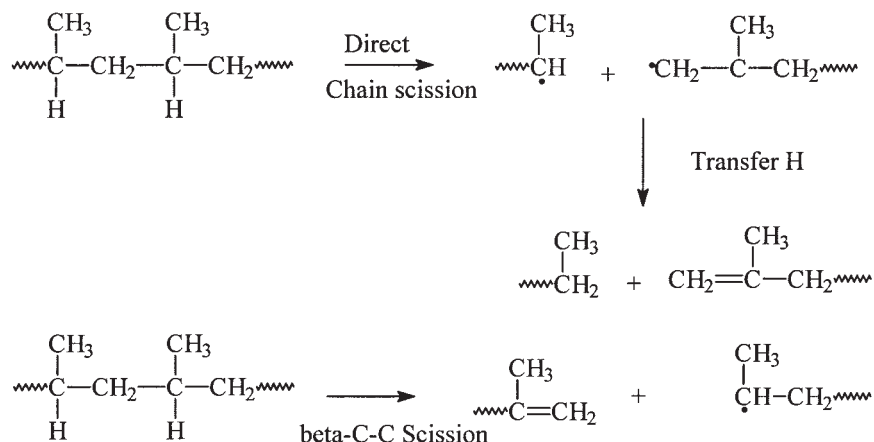


**Figure 8** Torque-time curves for various types of TPVs based on 60/40 ENR/PP blends using various types of compatibilizers and reactive blending.

Figure 8 shows a comparison of the torque-time curves of various types of the TPVs prepared from 60/40 ENR/PP blends using PP-g-MA and Ph-PP as compatibilizers and reactive blending of ENR/PP-g-MA and ENR/Ph-PP. We see that the TPVs prepared from reactive blending of ENR/PP-g-MA and ENR/Ph-PP exhibited lower final mixing torques than that of the TPV prepared without a compatibilizer. This is attributed to the degradation of PP molecules during modification under shearing action at high temperature. The chain scission of the PP molecules was more pronounced in the preparation of PP-g-MA because of incorporation of DCP. This led to a  $\beta$ -scission of the PP molecules as indicated in Scheme 1. Also, various types of chain scissions occurred during melt processing under very high shearing action as indicated in reaction Scheme 5. Therefore, the TPVs prepared from a reactive blending of ENR/PP-g-MA exhibited the lowest mixing torque. In Figure 8, the TPVs prepared from ENR/PP blends using Ph-PP and PP-g-MA exhibited higher final mixing torque than that of the blend without a compatibilizer. This proves a compatibilizing affect of the two types of blend compatibilizers. However, the system with Ph-PP exhibited higher mixing torque than that of the system with PP-g-MA. Therefore, Ph-PP provided the best compatibilizing affect on the blend of ENR and polypropylene in this work.

### Rheological properties

Plots of apparent shear stress versus shear rate of thermoplastic vulcanizates prepared from ENR/PP blends via dynamical vulcanization are showed in Figure 9. It was found that the shear stress increased with an increase of shear rate. Furthermore, at a given shear rate, the apparent shear stress increased with an increasing level of ENR compounds. The results correspond to the trend of mixing torque in Figure 5. This



Scheme 5 Possible mechanism of compatibilization of ENR/PP blends by Ph-PP.<sup>31</sup>

is attributed to the higher viscosity of the pure ENR than that of the pure PP. Also, increasing the level of ENR caused increasing chemical interaction between the polar functional groups of the Ph-PP and ENR molecules. This gives rise to an increasing trend of a compatibilizing effect on the ENR/PP blends with Ph-PP acting as a blend compatibilizer.

The effect of apparent shear viscosity on shear rate of the TPVs prepared from ENR/PP blend with Ph-PP as a compatibilizer is shown in Figure 10. We found that shear viscosity decreased with an increasing of the shear rate. This proves that all types of the TPV melts are pseudoplastic (possessing shear-thinning behavior) in nature. Shear viscosity at a given shear rate shows the same trend as the shear stress. That is, the level of shear viscosity at a given shear rate is ranked as follows: ENR/PP = 75/25 > ENR/PP = 60/40 > ENR/PP = 50/50 > ENR/PP = 40/60 > ENR/PP

= 25/75. This is attributed to the viscosity of the parent polymers and compatibilizing effect of the Ph-PP.

Plots of apparent shear stress versus shear rate and apparent shear viscosity versus shear rate of thermo-plastic vulcanizates prepared from 60/40 ENR/PP blends via dynamic vulcanization using various types of blend compatibilizers and reactive blending are shown in Figures 11 and 12, respectively. It was found that the reactive blending of ENR/PP-g-MA and ENR/Ph-PP exhibited lower shear stress and viscosity than that of the blend without compatibilizer. However, the blends with Ph-PP and PP-g-MA as compatibilizers showed higher shear stress and viscosity. The results agree with the trend of the final mixing torque in Figure 8. Degradation of polypropylene during chemical modification in a molten state may be responsible for the lower rheological property values of

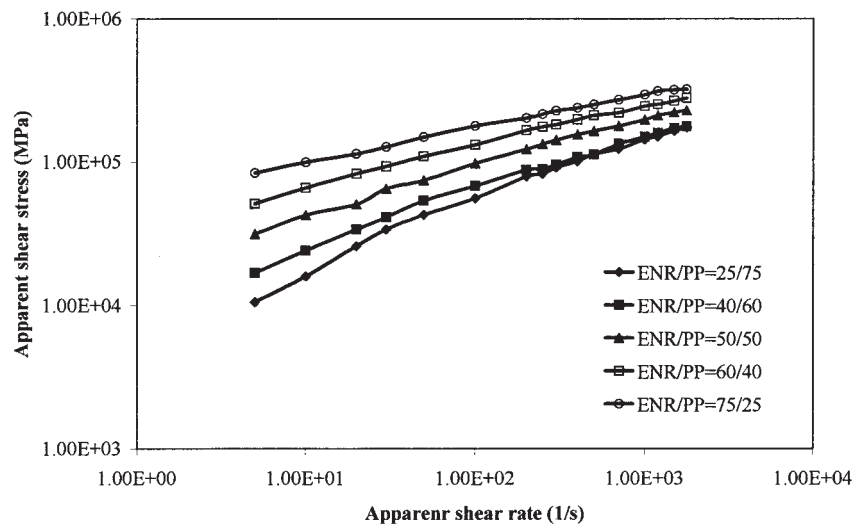
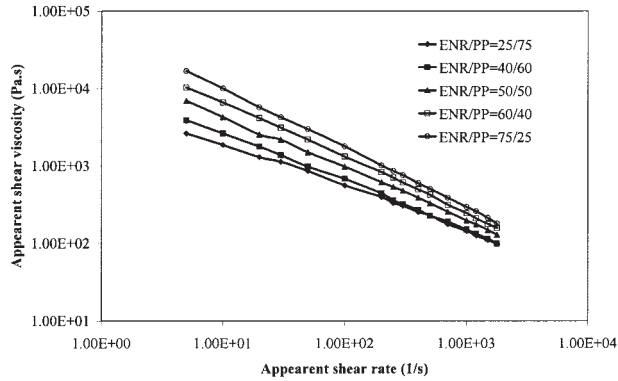
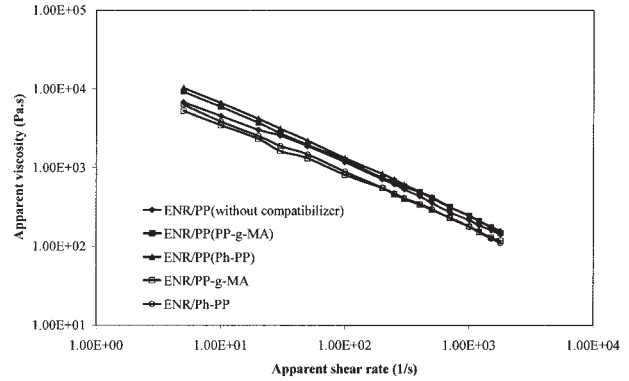


Figure 9 Relationship between apparent shear stress and apparent shear rate of ENR/PP blend with various blend ratios using Ph-PP as a compatibilizer.





**Figure 10** Relationship between apparent shear viscosity and apparent shear rate of ENR/PP blend with various blend ratios using Ph-PP as a compatibilizer.



**Figure 12** Relationship between apparent shear viscosity and apparent shear rate of ENR-30/PP blend at a blend ratio of 60/40 with various types of blend compatibilizers and reactive blending.

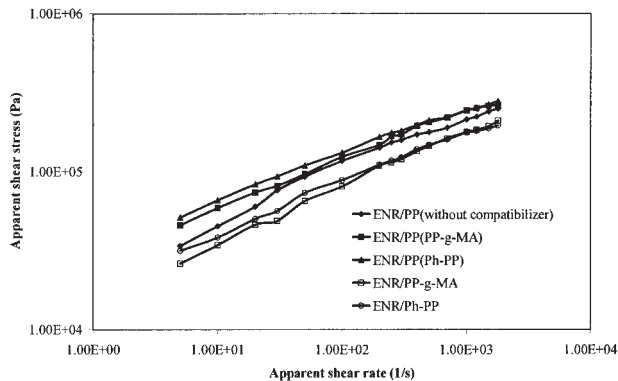
the blends. To confirm the trend of apparent shear stress and shear viscosity, plots of apparent shear stress and shear viscosity against types of compatibilizers and reactive blending at a constant shear rate of  $50 \text{ s}^{-1}$  were constructed and are shown in Figures 13 and 14, respectively. We observed the rank of apparent shear stress and shear viscosity as follows: ENR/PP blend with Ph-PP as a compatibilizer > ENR/PP blend with PP-g-MA as a compatibilizer > ENR/PP blend without a compatibilizer > ENR/Ph-PP > ENR/PP-g-MA. It can be seen that the trend of mechanical properties corresponds to the trend of mixing torque, shear stress, and shear viscosity. Therefore, it is concluded that the Ph-PP provided the best compatibilizing performance for ENR/PP blend in this work.

**Mechanical properties**

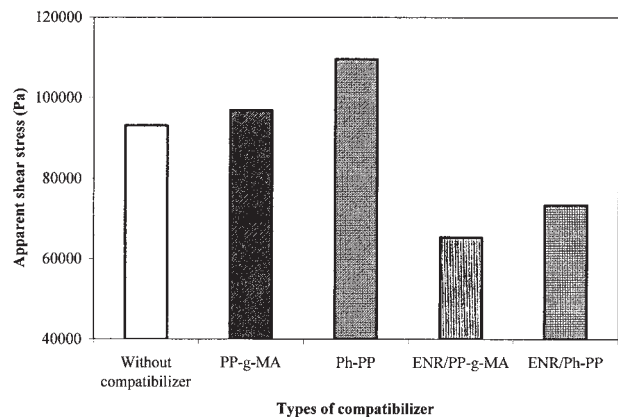
Effects of different blend ratios and compatibilizer systems on mechanical properties (i.e., tensile strength, elongation at break and hardness) of thermo-plastic vulcanizates prepared from 60/40 ENR/PP blend are given in Figures 15–17, respectively. It can be seen that the TPVs with Ph-PP as a compatibilizer provided the maximum values of tensile strength,

elongation at break and hardness while the reactive blending of ENR/PP-g-MA exhibited the lowest values. Therefore, mechanical properties of the TPVs prepared using various types of compatibilizers can be ranked as follows: ENR/PP blend with Ph-PP as a compatibilizer > ENR/PP blend with PP-g-MA as a compatibilizer > ENR/PP blend without a compatibilizer > ENR/Ph-PP > ENR/PP-g-MA. It can be seen that the trend of mechanical properties corresponds to the trend of mixing torque, shear stress, and shear viscosity. Therefore, it is concluded that the Ph-PP provided the best compatibilizing performance for ENR/PP blend in this work.

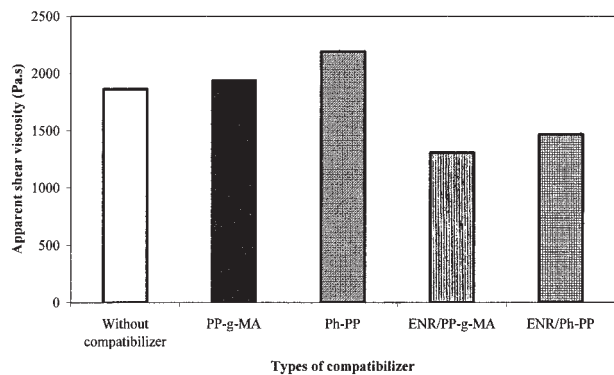
A decreasing trend of the tensile strength (Fig. 15) and hardness (Fig. 17) of TPVs was observed upon increasing levels of ENR. This is due to a decreasing trend of PP, which provides strength and hardness properties to the material. However, increasing levels of the ENR caused an increasing trend of the elonga-



**Figure 11** Relationship between apparent shear stress and apparent shear rate of ENR-30/PP blend at a blend ratio of 60/40 with various types of blend compatibilizers and reactive blending.



**Figure 13** Comparison of apparent shear stress at an apparent shear rate of  $50 \text{ s}^{-1}$  for ENR-30/PP blend at a blend ratio of 60/40 with various types of blend compatibilizers and reactive blending.



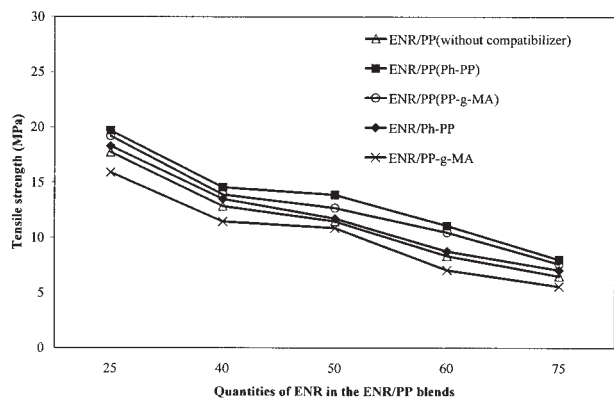
**Figure 14** Comparison of apparent shear viscosity at an apparent shear rate of  $50 \text{ s}^{-1}$  for ENR-30/PP blend at a blend ratio of 60/40 with various types of blend compatibilizers and reactive blending.

tion at break (i.e., in Fig. 16). This is attributed to an increasing in the elastomeric component in the TPVs.

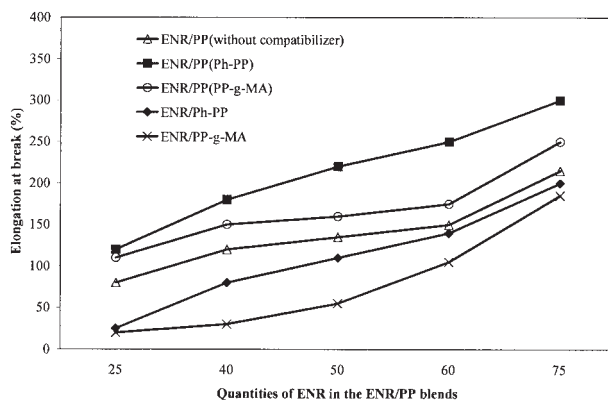
Figure 18 shows tension set, which we determined by extending the TPV's specimen at 100% elongation for 10 min. The dimension of the specimen was measured comparing before and after elongation. The tension set of the TPVs with elongation at break lower than 100% (Fig. 16) could not be determined. In Figure 18, it can be seen that the TPVs prepared from ENR/PP blends with Ph-PP as a compatibilizer exhibited the lowest tension set. This means this set of TPVs exhibited very high nature of elastomer. The tension set of other types of TPVs can be ordered as follows: ENR/PP-g-MA > ENR/Ph-PP/ENR/PP blend without compatibilizer > ENR/PP with PP-g-MA as a compatibilizer > ENR/PP with Ph-PP as a compatibilizer. This indicates an increasing trend of elastomeric properties of the TPVS.

### Morphological studies

The etched cryogenic fracture surfaces of the TPVs based on 60/40 ENR/PP blends using various types of

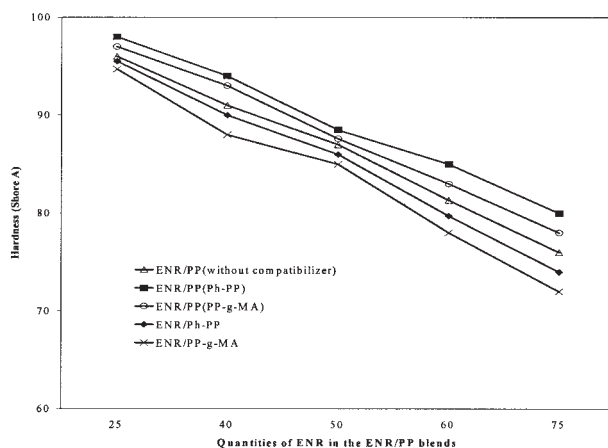


**Figure 15** Tensile strength of ENR-30/PP blends at various blend ratios using various types of blend compatibilizers and reactive blending.

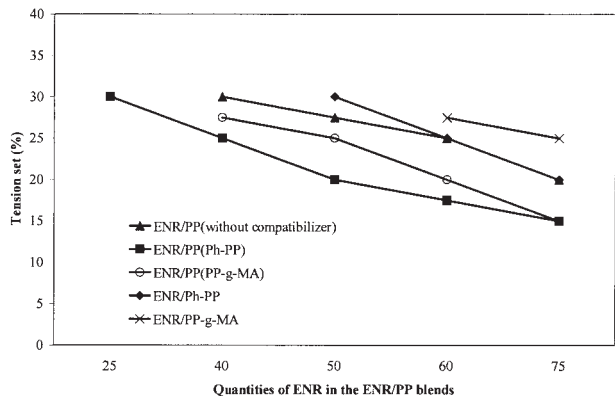


**Figure 16** Elongation at break of ENR-30/PP blends at various blend ratios using various types of blend compatibilizers and reactive blending.

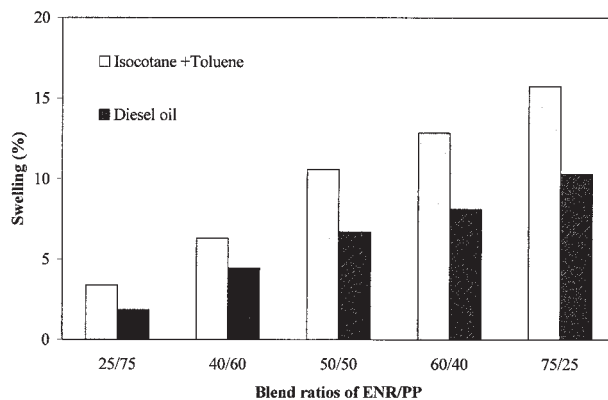
blend compatibilizers are shown in Figure 19. The thermoplastic phase was preferentially extracted using xylene. As a result, the PP was dissolved at an elevated temperature and left vulcanized rubber particles adhering to the surfaces. The two phase morphology is obvious. It was also found that smaller spheres of dispersed rubber phases were observed for the TPVs based on ENR/PP blends with Ph-PP (Fig. 19 (B)) and PP-g-MA (Fig. 19 (C)) as compatibilizer. This corresponds to higher tensile strength and elongation at break for these two types of TPVs (Figs. 15 and 16). The other types of the TPVs (i.e., reactive blending of ENR/PP-g-MA and ENR/Ph-PP) exhibited larger size vulcanized rubber particles dispersed in the PP matrix. That is, the vulcanized rubber particles are larger than that of the TPVs prepared without a compatibilizer. This causes lower mechanical strength in terms of tensile strength, elongation at break and hardness for these types of TPVs.



**Figure 17** Hardness of ENR-30/PP blends at various blend ratios using various types of blend compatibilizers and reactive blending.



**Figure 18** Tension set of ENR-30/PP blends at various blend ratios using various types of blend compatibilizers and reactive blending.

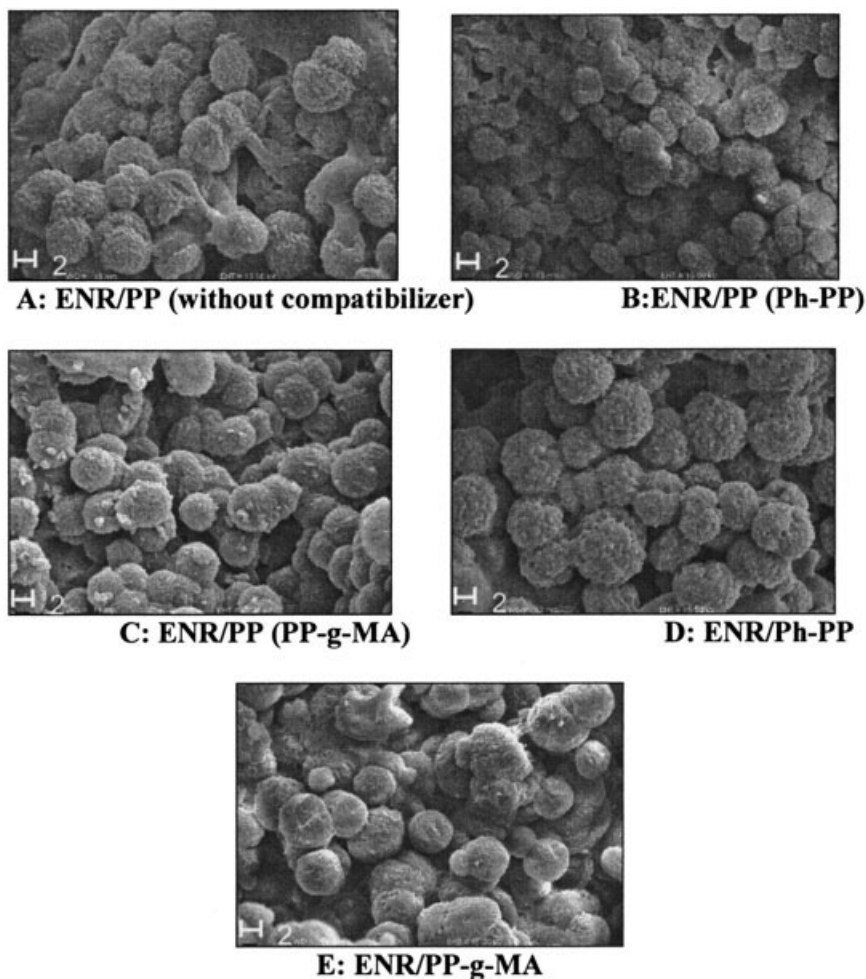


**Figure 20** Swelling resistance for various types of TPVs based on ENR/PP blends using various blend ratios and various types of blend compatibilizers and reactive blending.

**Swelling behavior**

Figure 20 shows the degree of swelling for the TPVs based on ENR/PP blends using various types of the

compatibilizers and reactive blending. It can be seen that abruptly decreasing trends of swelling occurred upon increasing the level of the ENRs. Therefore, in-



**Figure 19** SEM micrographs of various types of TPVs based on 60/40 ENR/PP blends using various types of blend compatibilizers and reactive blending.

creasing polarity because of the increasing levels of the ENR resulted in lower swelling capacity of the TPVs in the nonpolar solvent, diesel oil. However, a higher degree of swelling was observed in the mixed solvent, toluene/isooctane (50% v/v). This may be attributed to the high solubility of PP in toluene.

### CONCLUSIONS

Epoxidized natural rubber was successfully prepared using the performic epoxidation method. TPVs based on ENR/PP blends were later prepared by a melt-mixing process. Dynamic vulcanization of the blends was performed via sulfur vulcanization system. The influence of various blend ratios of ENR/PP and types of compatibilizers and reactive blendings was investigated. Phenolic modified PP and PP-g-MA were synthesized in a molten state and used as blend compatibilizers and blend components of a reactive blending of ENR/Ph-PP and ENR/PP-g-MA blends. It was found that the mixing torque, apparent shear stress, and apparent shear viscosity increased with increasing levels of ENR. This is attributed to higher viscosity of the pure ENR than that of the pure PP and a higher compatibilizing effect because of the chemical interaction between the polar groups in ENR and PP-g-MA or Ph-PP. Mixing torque, shear flow properties (i.e., shear stress and shear viscosity), and mechanical properties (i.e., tensile strength, elongation at break and hardness) of the TPVs prepared by reactive blending of ENR/Ph-PP and ENR/PP-g-MA were lower than that of the system without a compatibilizer. However, the TPVs prepared using Ph-PP and PP-g-MA as compatibilizers exhibited higher value. It is concluded that the TPVs prepared from ENR/PP with Ph-PP as a compatibilizer gave the highest rheological and mechanical properties, while the reactive blending of ENR/PP exhibited the lowest value. Trend of the properties corresponds to the size of vulcanized ENR dispersed domains in the PP matrix. That is, the TPV with Ph-PP as a blend compatibilizer showed the smallest dispersed rubber particles, while the reactive blending of ENR/PP-g-MA showed the largest particles.

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