

# Thermoplastic Vulcanizates Based on Epoxidized Natural Rubber/Polypropylene Blends: Effect of Epoxide Levels in ENR Molecules

Charoen Nakason, Puripong Wannavilai, Azizon Kaesaman

Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani, Thailand

Received 28 July 2005; accepted 11 December 2005

DOI 10.1002/app.23926

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Epoxidized natural rubbers (ENR) with various levels of epoxide groups were prepared. Thermoplastic vulcanizates based on 75/25 ENRs/PP blends with Ph-PP compatibilizer were later prepared by dynamic vulcanization using sulfur curing system. Influence of various levels of epoxide groups on rheological, mechanical morphological properties, and swelling resistance of the TPVs was investigated. It was found that the mixing torque, apparent shear stress, apparent shear viscosity, tensile strength, and hardness properties increased with increasing levels of epoxide groups in the ENR molecules. This may be attributed to increasing level of chemical interaction between the methylol groups of the Ph-PP molecules and polar functional groups of the ENR molecules. Also, the PP segments in the

Ph-PP molecules are capable of compatibilizing with the PP molecules used as a blend composition. In SEM micrographs, we observed finer dispersion of vulcanized rubber domains as increasing levels of epoxide contents. This corresponds to increasing trend of strength and hardness properties of the TPVs. An increasing trend of tension set and a decreasing trend of elongation at break were observed as increasing levels of epoxide groups in the ENR molecules. This is because of higher rigidity of the vulcanized ENR phase with higher epoxide groups. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3046–3052, 2006

**Key words:** epoxidized natural rubber; thermoplastic vulcanizate; polypropylene; rheological properties

## INTRODUCTION

Thermoplastic elastomers (TPEs) play more and more important role in polymer industry because of their good processability and their elastomeric properties.<sup>1</sup> TPE based on NR/thermoplastic blends is called as “thermoplastic natural rubber (TPNR)” blends. They are a family of materials prepared by blending natural rubber and thermoplastics in varying proportion. As the composition of the blend varies, materials with a wide range of properties are obtained. Polypropylene is considered to be the best choice for blending with NR because of its high softening temperature of about 150°C and low glass transition temperature ( $T_g$ ) for the blend.<sup>2</sup> This gives rise to a very versatile applicable over a wide range of temperatures. Furthermore, the dimensional stability at elevated temperatures and the low cost and abundant supply of NR are the main reasons to drive an intention to develop this class of

materials.<sup>3–5</sup> Epoxidized natural rubber (ENR) has also been widely used to prepare the TPNR by blending with various types of thermoplastics, particularly polar thermoplastics. These include poly(vinyl chloride),<sup>6–8</sup> poly(ethylene-co-acrylic acid),<sup>9</sup> and poly(methyl methacrylate).<sup>10–12</sup> Blending of ENR with non-polar thermoplastics, such as polypropylene may encounter a serious problem with the incompatibility. In our previous work, we reported properties of TPNR in a form of thermoplastic vulcanizates (TPVs) based on ENR/PP blends by using two different routes to improve the blend compatibility. One was adding a third component (i.e., phenolic modified polypropylene, Ph-PP and graft copolymer of maleic anhydride and polypropylene, PP-g-MA) which facilitated compatibilization of ENR and PP blends. The other was introducing a reactive blending of ENR/Ph-PP and ENR/PP-g-MA, leading to a modification of the polymer interface in two-phase blends.<sup>13</sup>

In this study, a suitable type and level of compatibilizer (i.e., Ph-PP at 5 wt % of PP) was used to prepare the TPVs.<sup>13</sup> The influence of quantities of epoxide groups in the ENR molecules was studied. That is, rheological, mechanical, morphological properties, and swelling behavior of the TPVs were investigated.

Correspondence to: C. Nakason (ncharoen@bunga.pn.psu.ac.th).

Contract grant sponsor: National Metal and Materials Technology Center; contract grant number: MT-B-46-POL-18-199-G.

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

Ingredients	Quantities (phr)
ENR <sup>a</sup>	100
ZnO	5.0
Stearic acid	2.5
Wingstay L	1.0
TBBS	0.5
Sulphur	2.0

<sup>a</sup> Various levels of ENRs (i.e., ENR-10, ENR-20, ENR-30, ENR-40, and ENR-50).

## EXPERIMENTAL

### Materials

Polypropylene (PP) used in the present study as a blend component was of injection molding grade, manufactured by Thai Polypropylene, Rayong, Thailand with an MFI value of 12 g/10 min at 230°C. High ammonia (HA) concentrated natural rubber latex was used as a raw material for the preparation of ENR, manufactured by Yala Latex, Yala, Thailand. The non-ionic surfactant used to stabilize the latex during epoxidation was Teric N30 (alkylphenol ethoxylate), which was manufactured by Huntsman Australia Pty, (Ascot Vale Vic, Australia). The formic acid used as a reactant for the preparation of ENRs was manufactured by Fluka Chemie (Buchs, Switzerland). The hydrogen peroxide used as a coreactant for the preparation of the ENRs was manufactured by Riedel De Haën (Seelze, Germany). The dimethylol phenolic resin (SP-1045) used to prepare phenolic modified polypropylene (Ph-PP) was manufactured by Schenectady International, Freeport. The zinc oxide used as an activator was manufactured by Global Chemical, Samutprakarn, Thailand. The stearic acid used as an activator was manufactured by Imperial Chemical, Pathumthani, Thailand. The sulfur used as a vulcanizing agent was manufactured by Ajax Chemical, Samutprakarn, Thailand. The *N-tert*-butyl-2-benzothiazolesulphenamide (Santocure TBBS) used as an accelerator, manufactured by Flexsys (USA). The polyphenolic additive, Wingstay<sup>®</sup> L, used as an antioxidant was manufactured by Eliokem (OH).

### Preparation of epoxidized natural rubber

The ENR latices were prepared using high-ammonia concentrated latex with a dry rubber content of ~60%. Details for the preparation process of the ENRs are described elsewhere.<sup>14</sup>

The latex was first diluted to 20% DRC and stabilized against coagulation by adding 10 wt % of a nonionic surfactant Teric N30. Hydrogen peroxide and formic acid were then added to form *in situ* performic acid. The reaction temperature was kept at

50°C. The latices were later coagulated in methanol and washed thoroughly with distilled water. The rubber was then dried in a vacuum oven at 40°C for 24 h and characterized with infrared spectroscopy. The reaction time of the epoxidation was set according to the required level of epoxide groups in the ENR products as described in our previous work.<sup>14</sup> The level of the epoxide contents in the ENR products was later confirmed by infrared spectroscopy via a calibration curve. In this work, the ENRs with various levels of epoxide groups at ~10, 20, 30, 40, and 50 mol % epoxide, corresponding to ENR-10, ENR-20, ENR-30, ENR-40, and ENR-50, respectively, were used in this study.

### Preparation of phenolic modified polypropylene

The Ph-PP used as a blend compatibilizer was prepared using a Brabender Plasticorder by mixing process. Details for the preparation process are described elsewhere.<sup>13,15</sup> Hundred parts by weight of polypropylene and four parts by weight of dimethylol phenolic resin (SP-1045) were mixed at 180°C and 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 blend product was later cut into small pieces with a Bosco plastic grinder (Samutprakarn, Thailand). The sample was purified by extracting with acetone and characterized using infrared spectroscopy.

### Preparation of thermoplastic vulcanizates

ENR was first compounded using a two-roll mill at a room temperature using compounding formulations as shown in Table I and the mixing schedule in Table II. Thermoplastic vulcanizates of ENR/PP blends were prepared via dynamic vulcanization during melt mixing using a Brabender Plasticorder PLE 331 (Duisberg, Germany). Mixing was performed at 180°C. 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. Ph-PP was then added as a blend compatibilizer, and mixing was continued for 1

**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.

**TABLE III**  
Chemicals Used for a Preparation of TPVs Based on 75/25 ENR/PP Blends

Chemicals	Quantities (part by wt of rubber)
ENR	75.00
PP	25.00
Ph-PP <sup>a</sup>	1.25
ZnO	3.75
Stearic acid	1.88
Wingstay L	0.75
TBBS	0.38
Sulphur	1.50

<sup>a</sup> 5% by weight of polypropylene.

min. Various types of ENR compounds were each 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 (Smutprakarn, Thailand). ENRs with various levels of epoxide groups at 10, 20, 30, 40, and 50 mol % were each blended with polypropylene to prepare the TPVs. A blend ratio of ENR/PP was fixed at 75/25 throughout the work. Therefore, various quantities of chemicals used in part by weight of rubber were listed in Table III.

### Rheological characterization

Shear flow properties of the polymer melts in terms of relationship between apparent shear stress and shear viscosity with apparent shear rate were measured using Rosand single bore capillary rheometer (model RH7, Rosand Precision, Gloucestershire, UK). The experiment was performed at a wide range of shear rates of 5–1800 s<sup>-1</sup>) at 180°C. Dimension of a capillary die used were a 2 mm diameter, 32 mm length, and 90 ° entry angle with the aspect ratio (L/D) of 16/1. The TPV based on 75/25 ENR/PP blends was first incorporated into a rheometer's barrel and preheated for 5 min under a pressure of ~3–5 MPa to get a compact mass. The piston was set to move downward automatically at a piston speed of 5 mm/min for 30 s. This was to purge the excess of molten material and eliminate bubbles present in the melt. The test was then carried out at a set of shear rates in 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. Equations used to calculate the shear flow properties were described elsewhere.<sup>16</sup>

### Mechanical testing

Tensile testing was performed at 25°C ± 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, UK. The dumbbell shaped specimens of the TPVs with 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 also measured using indentation shore A, according to ASTM D1415.

### Morphological studies

Morphological studies were carried out using a Leo scanning electron microscope, model VP 1450, manufactured by Leo (Cambridge, UK). Injection molded samples of the TPVs prepared from ENR/PP blends were cryogenic cracked in liquid nitrogen. This is to avoid any possibility of phase deformation during cracking process. The PP phase was preferentially extracted by immersing the fractured surface into a hot xylene for 10 min. The samples were later dried in vacuum oven at 40°C for 3 h to eliminate the contamination of the solvent. The dried surfaces were later gold-coated and examined by scanning electron microscope.

### Swelling behavior

TPVs based on the various types of 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, a mixture of toluene/isooctane (50% v/v), and engine oil 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 according to ASTM 471:

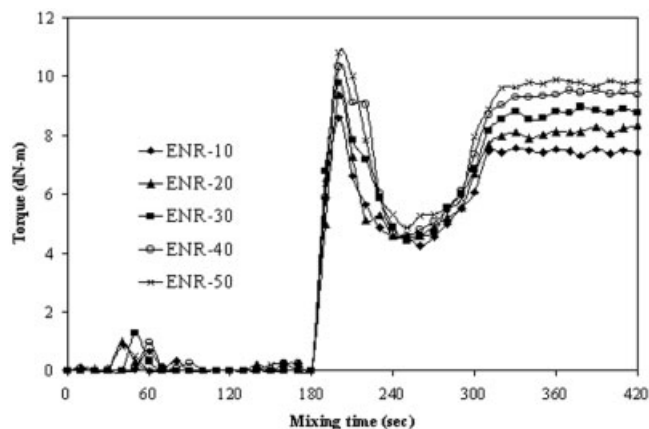
$$\text{Degree of swelling (\%)} = \frac{(W_s - W_0)}{W_0} \times 100 \quad (1)$$

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

## RESULTS AND DISCUSSION

### Mixing torques

The torque–time curves of the TPVs prepared from 75/25 ENR/PP blends using ENRs with various levels of epoxide groups are shown in Figure 1. It is seen that the torque rose marginally when the rotors were started because of the resistance exerted on the rotors by the unmelted PP. The torque did not rise sharply as in the case of blend ratios with higher PP in a blend

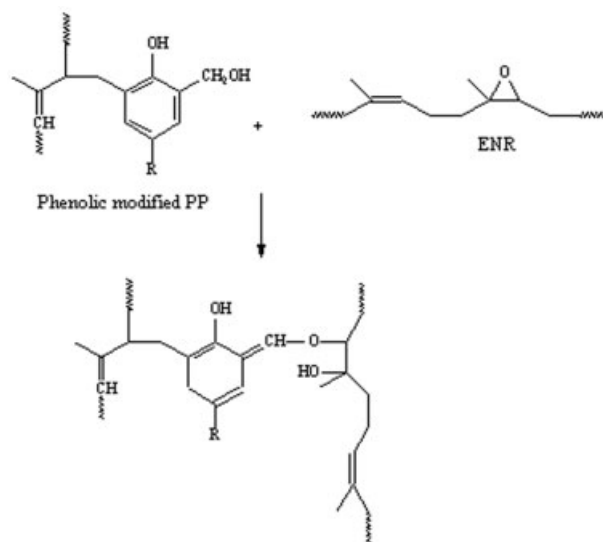


**Figure 1** Mixing torque-time of TPVs based on 75/25 ENR/PP blends using ENRs with various levels of epoxide groups and Ph-PP compatibilizer.

composition.<sup>13</sup> This is attributed to quantity of material not high enough to generate a force on a torque transducer. A reduction of torque was later observed because of melting of the PP. ENR compounds with other chemicals (i.e., as indicated in Table I) were later added. We observed abruptly increasing of the mixing torque because of resistance of the unmelted rubber compounds. A reduction of torque was again observed because of melting of the ENR phase. The mixing torque eventually rose sharply because of dynamic vulcanization of the ENR. A constant mixing torque was later observed after a mixing time of  $\sim 320$  s. The mixing was continued until a total mixing time of 420 s when a plateau mixing torque was reached. It is seen that the levels of the final mixing torque increased with increasing levels of epoxide groups in the ENR compounds. That is, the mixing torques of TPVs with various levels of epoxide groups can be ordered as follows: ENR-50 > ENR-40 > ENR-30 > ENR-20 > ENR-10. This may be attributed to chemical interaction between polar groups in the ENR molecules with free methylol phenolic groups in the Ph-PP molecules as a proposed possible mechanism of compatibilization in a reaction Scheme 1.<sup>13</sup> The PP backbones in the Ph-PP are capable of compatibilizing with the PP molecules used as a blend component. As a consequent, the blend with higher levels of epoxide groups exhibited a higher chemical interaction between their molecules and the PP molecules.

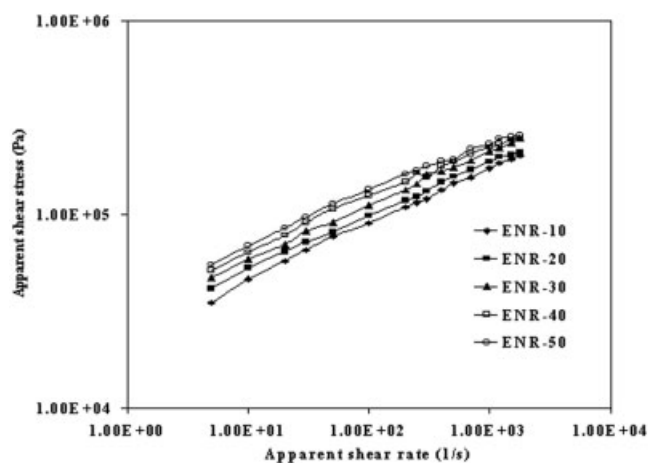
### Rheological properties

Plots of apparent shear stress versus shear rate (i.e., flow curves) of thermoplastic vulcanizates prepared from 75/25 ENR/PP blends with Ph-PP via dynamic vulcanization are showed in Figure 2. It can be seen that the shear stress increased with an increase in shear rate. At a given shear rate, the apparent shear

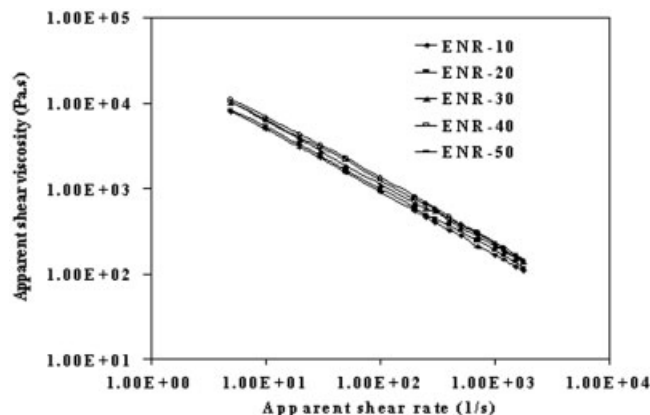


**Scheme 1** Possible mechanism of compatibilization of ENR/PP blends by Ph-PP.<sup>13</sup>

stress increased with an increasing level of epoxide groups in the ENR molecules. This confirms increasing trend of chemical interaction between ENR and PP phase upon increasing levels of the epoxide groups. That is, the compatibilizing effect of Ph-PP via an interaction of free methylol groups and epoxide groups in the ENR molecules. Also, PP segments of Ph-PP molecules are miscible with PP molecules of the blend component. Figure 3 shows relationship between apparent shear viscosity and apparent shear rate (i.e., viscosity curves) of the TPVs prepared from 75/25 ENR/PP blends with Ph-PP compatibilizer. It was found that shear viscosity decreased with an increase in shear rate. Therefore, all types of the TPV melts are pseudoplastic (or shear-thinning behavior)



**Figure 2** Relationship between apparent shear stress and shear rate of TPVs based on 75/25 ENR/PP blends using ENRs with various levels of epoxide groups and Ph-PP compatibilizer.

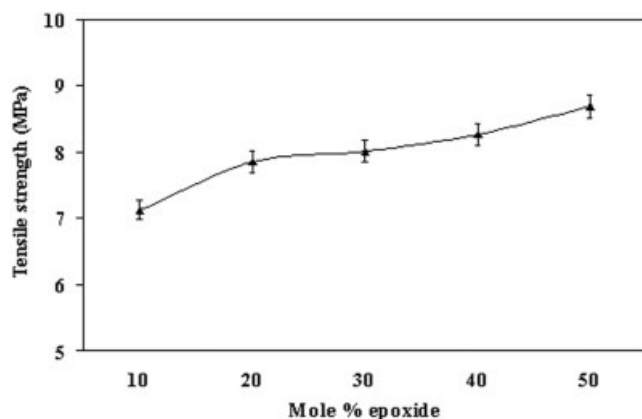


**Figure 3** Relationship between apparent shear viscosity and shear rate of TPVs based on 75/25 ENR/PP blends using ENRs with various levels of epoxide groups and Ph-PP compatibilizer.

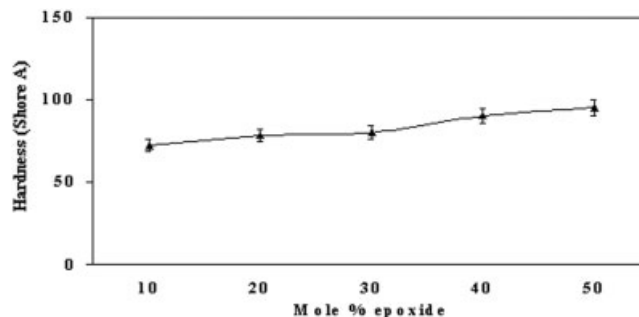
in nature. Shear viscosity at a given shear rate shows the same trend as the shear stress. That is, the level of shear viscosity at a given shear rate can be ordered as follows: ENR-50 > ENR-40 > ENR-30 > ENR-20 > ENR-10. This is attributed to the chemical interaction between ENR and PP phase via a compatibilizing effect of the Ph-PP.

### Mechanical properties

Effect of levels of epoxide groups in the ENR molecules on tensile strength and hardness of the thermo-plastic vulcanizates prepared from 75/25 ENR/PP blends is shown in Figures 4 and 5, respectively. We observed an increasing trend of tensile strength and hardness with an increasing concentration of epoxide groups in the ENR molecules. Therefore, the trends of tensile strength and hardness of the TPVs with various levels of ENRs are ordered as follows: ENR-50



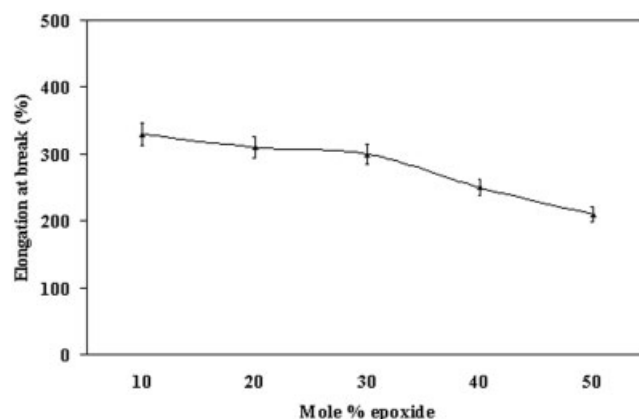
**Figure 4** Tensile strength of TPVs based on 75/25 ENR/PP blends using ENRs with various levels of epoxide groups and Ph-PP compatibilizer.



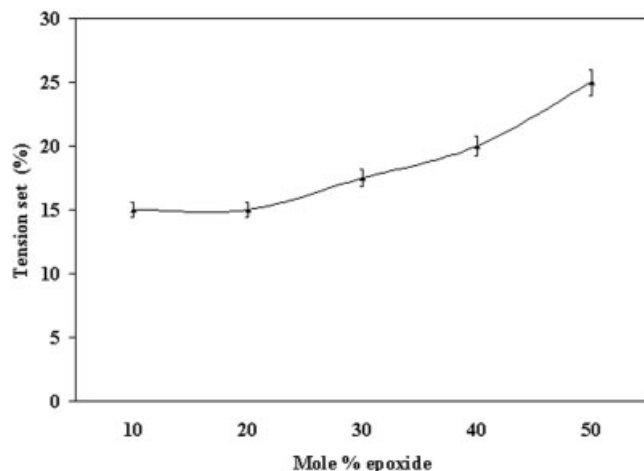
**Figure 5** Hardness of TPVs based on 75/25 ENR/PP blends using ENRs with various levels of epoxide groups and Ph-PP compatibilizer.

> ENR-40 > ENR-30 > ENR-20 > ENR-10. This might be attributed to increasing surface energy between the interface of PP and ENR phases upon increasing levels of the epoxide groups. That is, the polar part of Ph-PP (i.e., a free methylol group) increased its capability to interact with the polar groups in the ENR molecules with higher epoxide groups. A similar level of compatibilization between PP segments in the Ph-PP molecules and PP of a blending component remained the same. Furthermore, the vulcanized rubber network of ENR with higher epoxide content is stronger because of higher chemical interaction within and between ENR molecules via the polar groups. This causes a formation of permanent covalent or hydrogen bonds and leads to a formation of harder and more rigid materials. Therefore, higher mechanical strength was observed upon increasing levels of epoxide groups in the ENR molecules.

Figure 6 shows elongation at break of the TPVs prepared from 75/25 ENR/PP blends using various types of ENRs. We observed a decreasing trend of the elongation at break with increasing levels of epoxide groups in the ENR molecules. This is attributed to



**Figure 6** Elongation at break of TPVs based on 75/25 ENR/PP blends using ENRs with various levels of epoxide groups and Ph-PP compatibilizer.



**Figure 7** Tension set of TPVs based on 75/25 ENR/PP blends using ENRs with various levels of epoxide groups and Ph-PP compatibilizer.

increasing rigidity of the ENR molecules. That is, higher epoxide contents caused higher chemical interaction between the ENR molecules and less level of unsaturation. As a consequence, increase of  $T_g$  of the ENRs was observed.<sup>14</sup> This leads to lowering elastomeric characteristics (i.e., extensibility and permanent set) of the ENR vulcanizates. The permanent set in terms of tension set was also determined by extending the TPV's specimen at 100% elongation for 10 min. The dimension of the specimen was later measured comparing between before and after elongation, as results shown in Figure 7. It is seen that the tension set increased with increasing levels of epoxide groups. It means the TPVs decrease their elastomeric nature upon increasing levels of epoxide groups. However, all TPVs' specimens exhibited tension set value lower than 25%. This reveals that these types of the TPVs have good elastomeric properties for various industrial applications.

### Swelling behavior

Figure 8 shows a degree of swelling of the TPVs based on 75/25 ENR/PP blends using various types of ENRs with Ph-PP compatibilizer. It was found that the levels of swelling of the TPVs for all types of solvents decreased with increasing contents of epoxide groups in the ENR molecules. The mixed solvents of isooctane and toluene (50% v/v) showed the highest degree of swelling, i.e., the lowest resistance to the solvent. This may be attributed to closed solubility parameters of polypropylene (i.e., 7.9–9.4 (cal/cm<sup>3</sup>)<sup>1/2</sup>) and toluene (i.e., 8.9 (cal/cm<sup>3</sup>)<sup>1/2</sup> 17,18). This causes dissolving or swelling of polypropylene phase in toluene. Diesel oil and engine oil are more nonpolar characteristics. Therefore, the TPVs exhibited higher degree of solvent

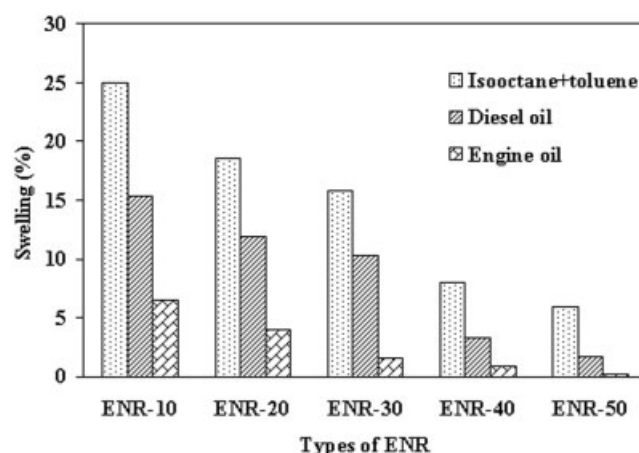
resistance in these two types of solvents. The TPVs prepared from 75/25 ENR-50/PP blend exhibited the highest levels of solvent resistance particularly with the engine oil because of its high polarity.

### Morphological studies

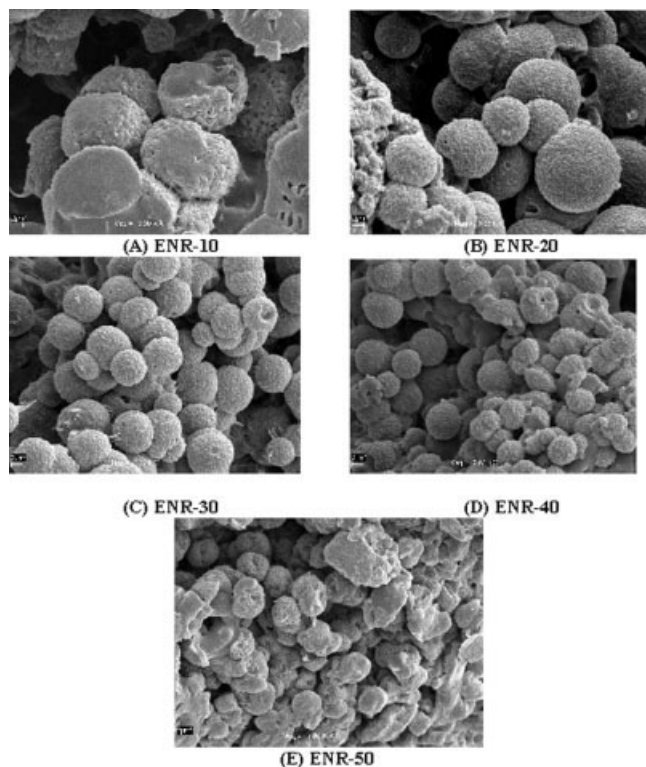
The solvent-etched cryogenic fracture surfaces of the TPVs based on 75/25 ENR/PP blends using various types of ENRs are shown in Figure 9. The PP phase was preferentially extracted using hot xylene. Therefore, the thermoplastic phase was dissolved in xylene at an elevated temperature and left vulcanized rubber spherical particles adhere at the surfaces. Also, previous location of PP phase was changed to be a cavitation. The two phase morphology of the TPVs was therefore confirmed. We also observed small spheres of dispersed vulcanized rubber phases in the PP matrix. Sizes of dispersed vulcanized rubber domains decreased with an increase in levels of epoxide groups in the ENR molecules. That is, increasing trend of polarity of the rubber phase caused higher chemical interaction between the ENR and PP molecules via the compatibilization of Ph-PP. As a result, higher interfacial adhesion between ENR and PP phase was obtained. This causes a decreasing trend of sizes for vulcanized rubber domains with increasing level of epoxide groups. This correspond to higher strength and hardness properties of the TPVs with high levels of epoxide groups in the ENR molecules, as shown in Figures 4 and 5, respectively.

### CONCLUSIONS

ENRs with various levels of epoxide groups were successfully prepared by performic epoxidation method. TPVs based on 75/25 ENR/PP blends with



**Figure 8** Swelling behavior of TPVs based on 75/25 ENR/PP blends using ENRs with various levels of epoxide groups and Ph-PP compatibilizer.



**Figure 9** SEM of various levels of TPVs based on 75/25 ENR/PP blends.

Ph-PP compatibilizer were later prepared by melt-mixing processes via dynamic vulcanization with sulfur curing system. Influence of various types of ENRs on properties of the TPVs was investigated. We found that the mixing torque, apparent shear stress, apparent shear viscosity, tensile strength, and hardness increased with increasing levels of epoxide groups in the ENR molecules. This is attributed to an increase in chemical interaction between the methylol groups in the Ph-PP molecules and polar functional groups in the ENR molecules upon increasing levels of epoxide groups. Also, the PP segments in the Ph-PP molecules are capable of compatibilizing with the PP molecules in the blend composition. This causes smaller sizes of

dispersed vulcanized rubber domains with increasing epoxide content in the ENRs. A decreasing trend of resistance to permanent set (i.e., tension set) and elongation at break was observed with increasing level of epoxide groups in the ENR molecules. This is because of increasing rigidity of the vulcanized ENR phase with higher epoxide contents. Therefore, the rubber exhibited lower extensibility and higher  $T_g$ . We also found that solvent resistance (i.e., lower swelling) of the TPVs increased with an increasing level of the epoxide groups in the ENR molecules.

Special scholarship granted by Graduate School, Prince of Songkla University, Thailand to one of us (Mr. Puripong Wannavilai) is gratefully acknowledged.

## References

- Legge, N. R.; Holden, G.; Schroeder, H. E., Eds. *Thermoplastic Elastomer: A Comprehensive Review*; Hanser: New York, 1987.
- Ibrahim, A.; Dahlan, M. *Prog Polym Sci* 1998, 23, 665.
- Tinker, A. J.; Icenogle, R. D.; Whittle, I. *Rubber World*; March 25, 1989.
- Tinker, A. J.; Icenogle, R. D.; Whittle, I. *Rubber Plast News* 1988, 17, 80.
- Tinker, A. J. *NR Technol* 1981, 18, 30.
- Ishiaku, U. S.; Shaharum, A.; Isamail, H.; Ishak, Z. A. M. *Polym Int* 1997, 45, 83.
- Ratnam, C. T.; Zaman, K. *Polym Degrad Stab* 1999, 65, 99.
- Mousa, A.; Ishiaku, U. S.; Ishak, Z. A. M. *Polym Test* 2000, 19, 193.
- Mohanty, S.; Nando, G. B. *Polymer* 1997, 38, 1395.
- Thiraphattaraphun, L.; Kiatkamjornwong, S.; Prasassarakich, P. *J Appl Polym Sci* 2001, 81, 428.
- Nakason, C.; Panklieng, Y.; Kaesaman, A. *J Appl Polym Sci* 2004, 92, 3561.
- Nakason, C.; Toprakon, A.; Kaesaman, A. *J Appl Polym Sci* 2005, 98, 1251.
- Nakason, C.; Wannavilai, P.; Kaesaman, A. *J Appl Polym Sci* 2006, 100, 4729.
- Nakason, C.; Kaesaman, A.; Klinpituksa, P.; Songklanakarin, J. *Sci Technol* 2001, 23, 415.
- George, S.; Varughese, K. T.; Thomas, S. *Polymer* 2000, 41, 5485.
- Nakason, C.; Kaesaman, A.; Samoh, Z.; Homsin, S.; Kiatkamjornwong, S. *Polym Test* 2002, 21, 449.
- Michaels, A. S.; Vieth, W. R.; Alcalay, H. H. *J Appl Polym Sci* 1968, 12, 1621.
- Sperling, L. H. *Introduction to Physical Polymer Science*, 3rd ed.; Wiley: New York, 2001; p 66.