

Thermoplastic Vulcanizates Based on Poly(methyl methacrylate)/Epoxidized Natural Rubber Blends: Mechanical, Thermal, and Morphological Properties

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Received 22 February 2005; accepted 17 March 2005

DOI 10.1002/app.21908

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

ABSTRACT: Epoxidized natural rubbers (ENRs) with epoxide levels of 10, 20, 30, 40 and 50 mol % were prepared. The ENRs were later used to prepare thermoplastic vulcanizates (TPVs) by blending them with poly(methyl methacrylate) (PMMA) using various formulations. Dynamic vulcanization, using sulfur as a vulcanizing agent, was performed during the mixing process. The mixing torque increased as the ENR contents and epoxide molar percentage increased. This was because of an increasing chemical interaction between the polar groups of the blend components, particularly at the interface between the elastomeric and thermoplastic phases. The ultimate tensile strength of the TPVs with ENR-20 was high because of strain-induced crystallization. ENRs with epoxide levels >30 mol % exhibited an increase of tensile strength because of increasing levels of chemical interaction between the molecules and the different phases. The

hardness of the TPVs also increased with increased epoxide levels but decreased with increased contents of ENRs. Two morphology phases with small domains of vulcanized ENR particles dispersed in the PMMA matrix were observed from scanning electron microscopy micrographs. The TPVs based on ENR-20 and ENR-50 showed smaller dispersed rubber domains than those of the other types of ENRs. Furthermore, the size of the vulcanized rubber domain decreased with increasing amounts of PMMA in the blends. The decomposition temperature of the TPVs also increased as both the levels of ENRs in the blends and the epoxide molar percentage increased. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1251–1261, 2005

Key words: thermoplastic vulcanizates; epoxidized natural rubber; poly(methyl methacrylate); morphology; properties

INTRODUCTION

Thermoplastic elastomers (TPEs) are rubbery materials with properties and functional performance similar to those of conventional vulcanized rubber. Furthermore, they can be processed in a molten state as a thermoplastic polymer.¹ The field of TPEs based on polyolefin rubber/thermoplastic compositions has grown along two distinctly different classes. One class consists of a simple blend, and it meets the classic definition of a thermoplastic elastomeric olefin. In the other class, the rubber phase is dynamically vulcanized giving rise to a thermoplastic vulcanizate (TPV) or dynamic vulcanizate. The TPVs are characterized by finely dispersed micron-sized crosslinked rubber particles distributed in a thermoplastic matrix.² Interest in natural rubber

(NR) and thermoplastic blends has also increased recently. These materials are known as thermoplastic NRs (TPNRs). Thermoplastics blended with NR include polypropylene,^{3–10} low-density polyethylene,^{8,11,12} high-density polyethylene,^{13,14} linear low-density polyethylene,^{15–17} polystyrene,¹⁸ polyamide 6,¹⁹ poly(methyl methacrylate) (PMMA),^{20–23} and ethylene–vinyl acetate copolymer.²⁴ Modified forms of NR have also been used to prepare TPNRs via both simple blending and dynamic vulcanization (i.e., TPVs). Epoxidized NR (ENR) is one of the modified forms currently used to prepare TPNRs. This has been done by blending the ENR with thermoplastics such as poly(vinyl chloride)^{25–27} and PMMA.²² Graft copolymers of NR with PMMA,^{21,28} polystyrene,¹⁸ and glycidyl methacrylate–styrene copolymer²³ have also been used to prepare TPNRs.

In this work, an attempt was made to prepare TPNRs based on ENR and PMMA blends by dynamic vulcanization using a sulfur vulcanization system. ENRs with various levels of epoxide or epoxirane rings and various blend ratios were used. After dynamic vulcanization, the mechanical, ther-

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Contract grant sponsor: Thailand Research Fund; contract grant number: RSA 4580040.

mal, and morphological properties as well as the swelling behavior of the TPVs were investigated.

EXPERIMENTAL

Materials

High ammonia concentrated NR latex (Yala Latex Co., Ltd., Yala, Thailand) was used as a raw material for preparation of the ENR. The nonionic surfactant used to stabilize the latex during epoxidation was alkylphenol ethoxylate (Teric N30, Huntsman Corp. Australia Pty Ltd, Ascot Vale, Australia). Formic acid was employed as a reactant for the preparation of ENRs (Fluka Chemie, Buchs, Switzerland). Hydrogen peroxide (Riedel De Haën, Seelze, Germany) was used as a coreactant for the preparation of the ENRs. The PMMA used as a blend component was injection-molding grade (TPI Polyacrylate Co., Ltd., Rayong, Thailand) and had a melt flow index of 14 g/10 min at 230°C. Zinc oxide (Global Chemical Co., Ltd, Samutprakarn, Thailand) and stearic acid were used as activators (Imperial Chemical Co., Ltd, Pathumthani, Thailand). The vulcanizing agent was sulfur (Ajax Chemical Co., Ltd, Samutprakarn, Thailand), and the accelerator was *N-tert-butyl-2-benzothiazolesulfenamide* (Santocure TBBS, Flexsys). The polyphenolic additive used as an antioxidant was Wingstay L (Eliokem Inc.).

Preparation of ENRs

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

TABLE I
Compounding Formulations

Ingredients	Quantities (phr)			
PMMA	60	50	40	30
ENR ^a	40	50	60	70
ZnO	2	2.5	3	3.5
Stearic acid	1	1.25	1.5	1.75
Wingstay L	0.2	0.25	0.3	0.35
TBBS	0.4	0.5	0.6	0.7
Sulfur	0.8	1	1.2	1.4

^a ENR with 10, 20, 30, 40 and 50 mol % epoxide groups.

TABLE II
Mixing Schedule

Descriptions	Mixing time (min)
PMMA	2
ENRs	1
ZnO + stearic acid	1
TBBS	2
Sulfur	until plateau mixing torque
Wingstay L	until mixing time of 10 min

TBBS, *N-tert-butyl-2-benzothiazolesulfenamide*.

Preparation of TPVs

TPVs of ENR/PMMA blends were prepared via dynamic vulcanization during melt mixing using a Brabender plasticorder (PLE 331, Duisberg, Germany). Mixing was performed at 180°C. PMMA was first preheated for 6 min in the mixer without rotation. The polymer was then melted for 2 min at a rotor speed of 40 rpm. ENR was added, and mixing was continued for 3 min. Other ingredients were then incorporated as the compounding formulations shown in Table I and the mixing schedule in Table II. The blend products were later cut into small pieces with a Bosco plastic grinder (Samutprakarn, Thailand). A torque versus mixing time curve was plotted for each blend. Various types of ENRs with epoxide levels of 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. Furthermore, various rubber contents (i.e., 40, 50, 60, and 70 wt %) were blended with PMMA according to the blending formulations shown in Table I.

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 a Hounsfield Tensometer H 10 KS, manufactured by the Hounsfield Test Equipment Co., Ltd (Surrey, U.K.). Dumbbell-shaped specimens with 2-mm thickness were prepared by a Weltec thermoplastic injection-molding machine (Welltec Machinery Ltd., Hong Kong) using a clamping force of 90 ton. The hardness (International Rubber Hardness Degrees, IRHD) of the samples was also measured using a Wallace Dead Load Hardness Tester according to ASTM D 1415.

Swelling behavior

TPVs based on the various ENR/PMMA blends were weighed and inserted into test tubes contain-

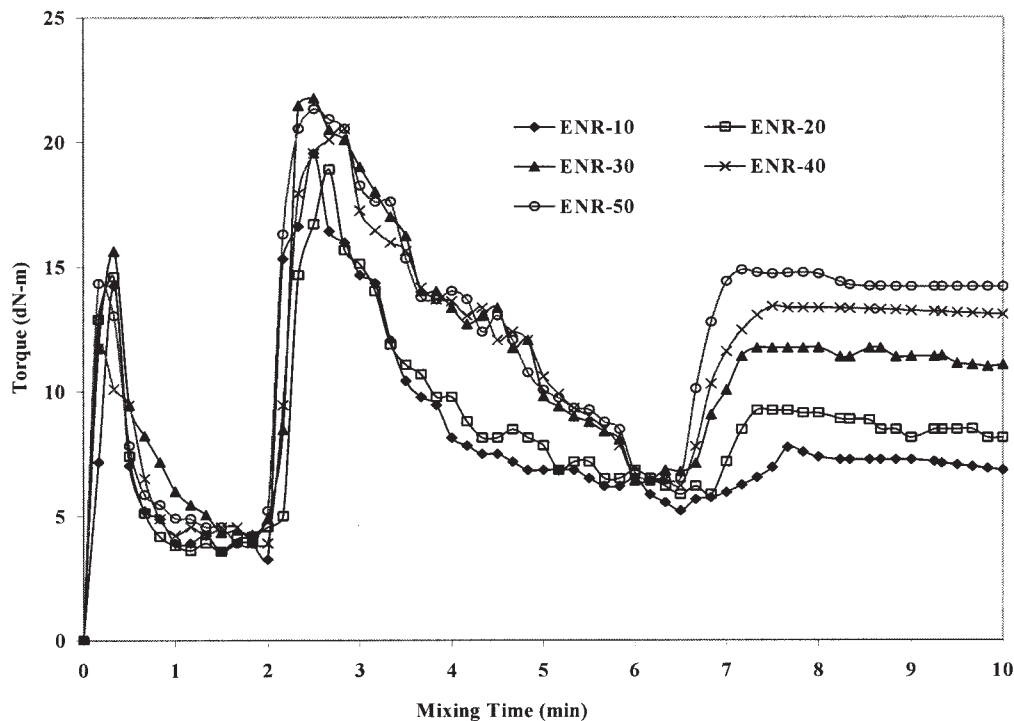


Figure 1 Torque-time curves for various types of TPVs based on 50/50 ENR/PMMA blends using various types of ENRs.

ing test liquids and placed in an oven at 30°C. In this work, diesel oil and a mixture of 50% (v/v) toluene/isooctane 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:

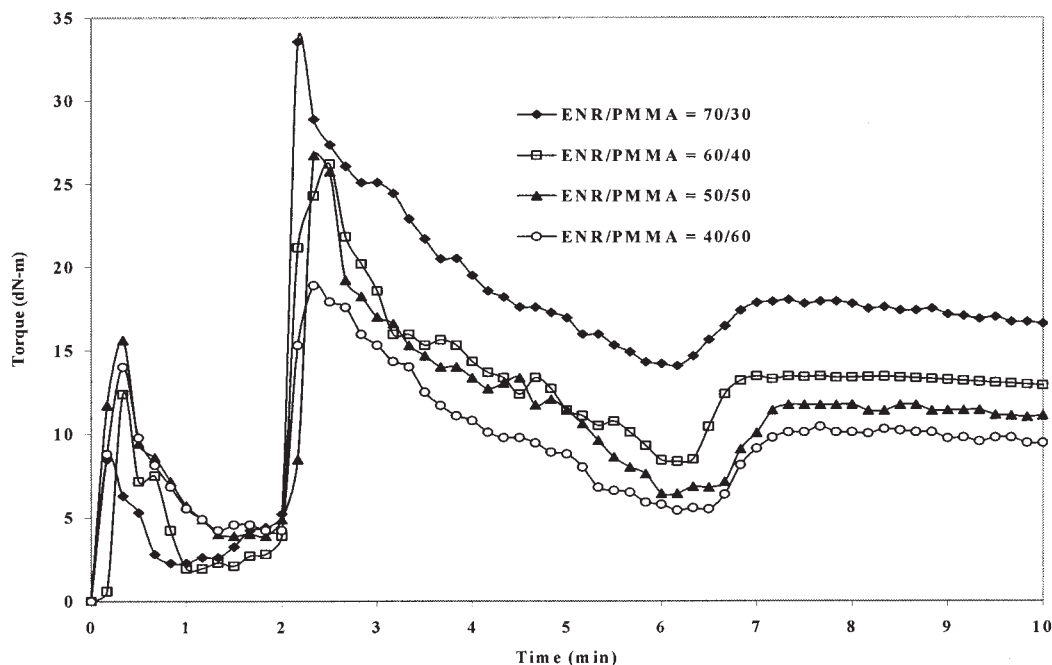


Figure 2 Torque-time curves for TPVs based on ENR-30/PMMA blends using various blend ratios.

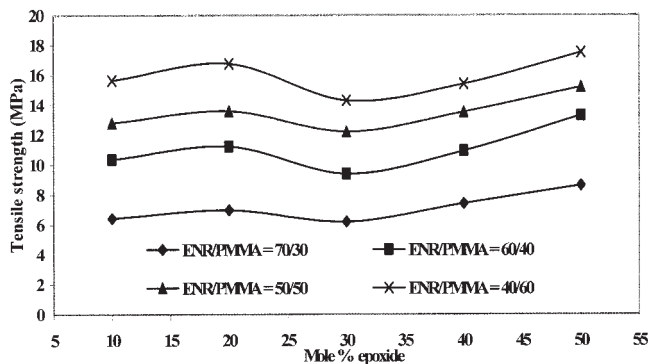


Figure 3 The tensile strength of TPVs based on ENR/PMMA blends with various types of ENRs and blend ratios.

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

where W_o and W_s are the weights of the specimens before and after immersion in the test liquids, respectively.

Morphological study

Morphological studies were carried out with a scanning electron microscopy (SEM) microscope (Leo-1450 VP, Cambridge, U.K.). The cryogenic fracture surfaces of the molded samples were prepared in liquid nitrogen to avoid any possibility of phase deformation. The PMMA phase was preferentially extracted using methyl ethyl ketone/acetone. The samples were dried in a vacuum oven at 40°C for 6 h, and then the dried

surfaces were coated with gold and examined with the SEM microscope.

Characterization of thermal properties

Thermogravimetric analysis was carried out under a nitrogen atmosphere at a heating rate of 20°C/min in a Shimadzu TGA-50 thermal analyzer (Kyoto, Japan). A constant sample weight was used in all cases. Thermograms were recorded from room temperature to 800°C. The temperature at which the rate of mass loss was maximum, which is called the decomposition temperature (T_d), was determined from the differential thermogravimetry curve.

RESULTS AND DISCUSSION

Mixing torque

The torque–time curves of the TPVs prepared from various types of ENRs with a fixed blend ratio of 50/50 ENR/PMMA are shown in Figure 1. PMMA was first charged into the mixing chamber and preheated for 6 min without using the rotor, which 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 PMMA. A reduction of torque was later observed because the PMMA melted because of mechanical shearing and heat transfer from the heating oil. Upon incorporation of ZnO and stearic acid, a reduction of the mixing torques was still observed. However, after adding vulcanizing agents (TBBS ac-

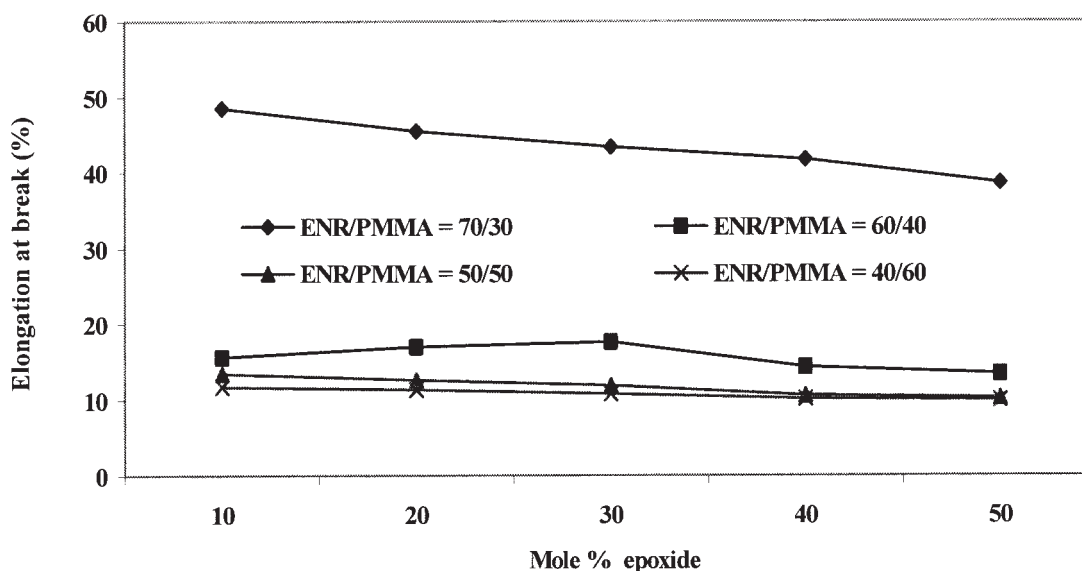


Figure 4 The elongation at break of TPVs based on ENR/PMMA blends with various types of ENRs and blend ratios.

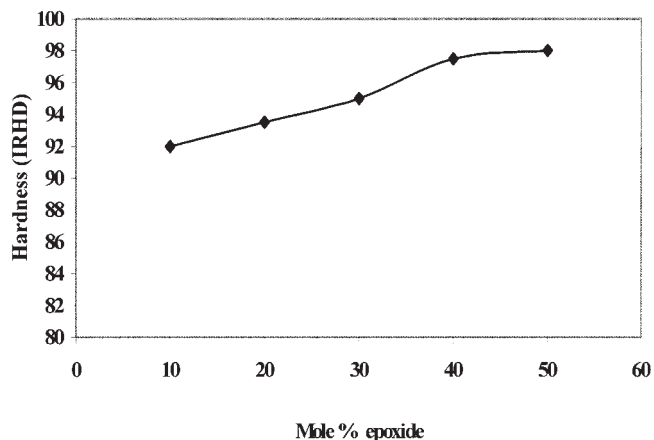


Figure 5 The hardness of TPVs based on 50/50 ENR/PMMA blends with various levels of mole percents of epoxide.

celerator and sulfur) the mixing torques again rose because of dynamic vulcanization. Constant mixing torques were observed after a mixing time of approximately 8 min. The antioxidant (Wingstay L) was finally added to protect the TPVs during the fabricating process and service life. The mixing was continued until a total mixing time of 10 min was reached.

Figure 1 shows that the levels of the mixing torque increased with increasing levels of epoxide groups. That is, ENR-10 exhibited the lowest mixing torque whereas ENR-50 showed the highest value. Therefore, the mixing torque of the ENR/PMMA blends was in the order ENR-10 < ENR-20 < ENR-30 < ENR-40

< ENR-50. This was the result of the influence of the chemical interaction between polar groups in the PMMA and ENR molecules and particularly at the interface. Consequently, the ENRs with higher levels of epoxide groups generated a higher chemical interaction between their molecules and the PMMA molecules.

Figure 2 shows the torque–time curves of the TPVs prepared from ENR-30/PMMA blends with various rubber contents. A similar trend for the mixing torque shown in Figure 1 was found. In a typical case, the mixing torque increased with increasing contents of ENR-30 in the blend composition. This may be attributed to both the higher content of small rubber domains dispersed in the PMMA matrix and the higher shear viscosity for the pure ENR-30 than that of the pure PMMA, as indicated in our earlier work.²² Therefore, the mixing torques of the TPVs from the ENR-30 and PMMA blends was in the order 70/30 > 60/40 > 50/50 > 40/60.

Tensile properties

The effects of different levels of epoxide groups in the ENRs on the ultimate tensile strength of the TPVs prepared from ENR/PMMA blends are shown in Figure 3. It can be seen that the tensile strength increased with increasing quantities of PMMA in the blends. This may be attributed to the higher tensile strength of the PMMA (i.e., 55 MPa) than that of the ENRs. Furthermore, the tensile strength slightly increased with increasing levels of epoxide groups from 10 to 20 mol

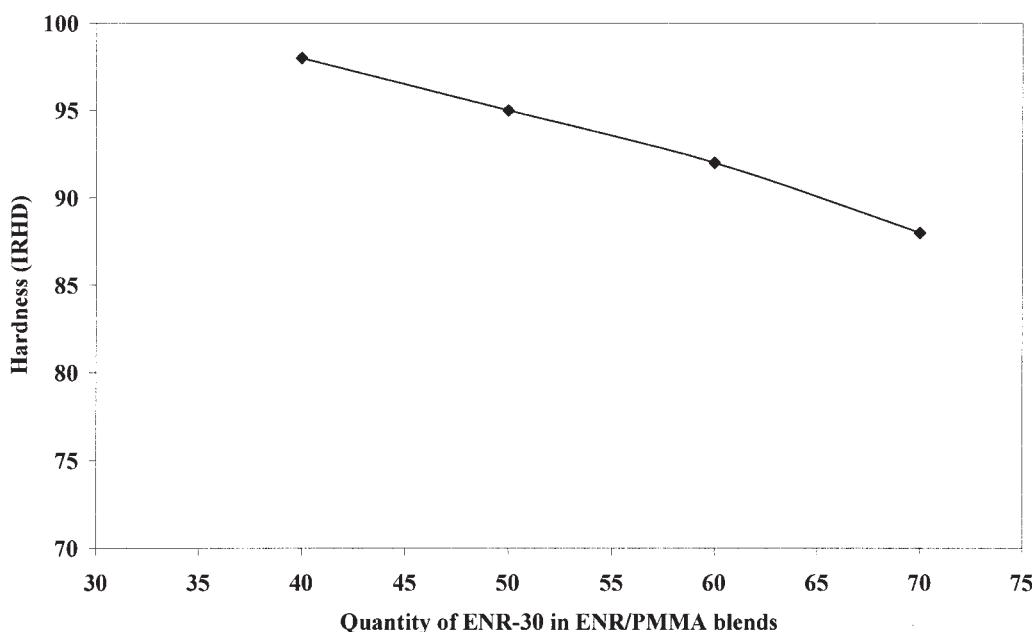


Figure 6 The hardness of TPVs based on ENR-30/PMMA blends with various blend ratios.

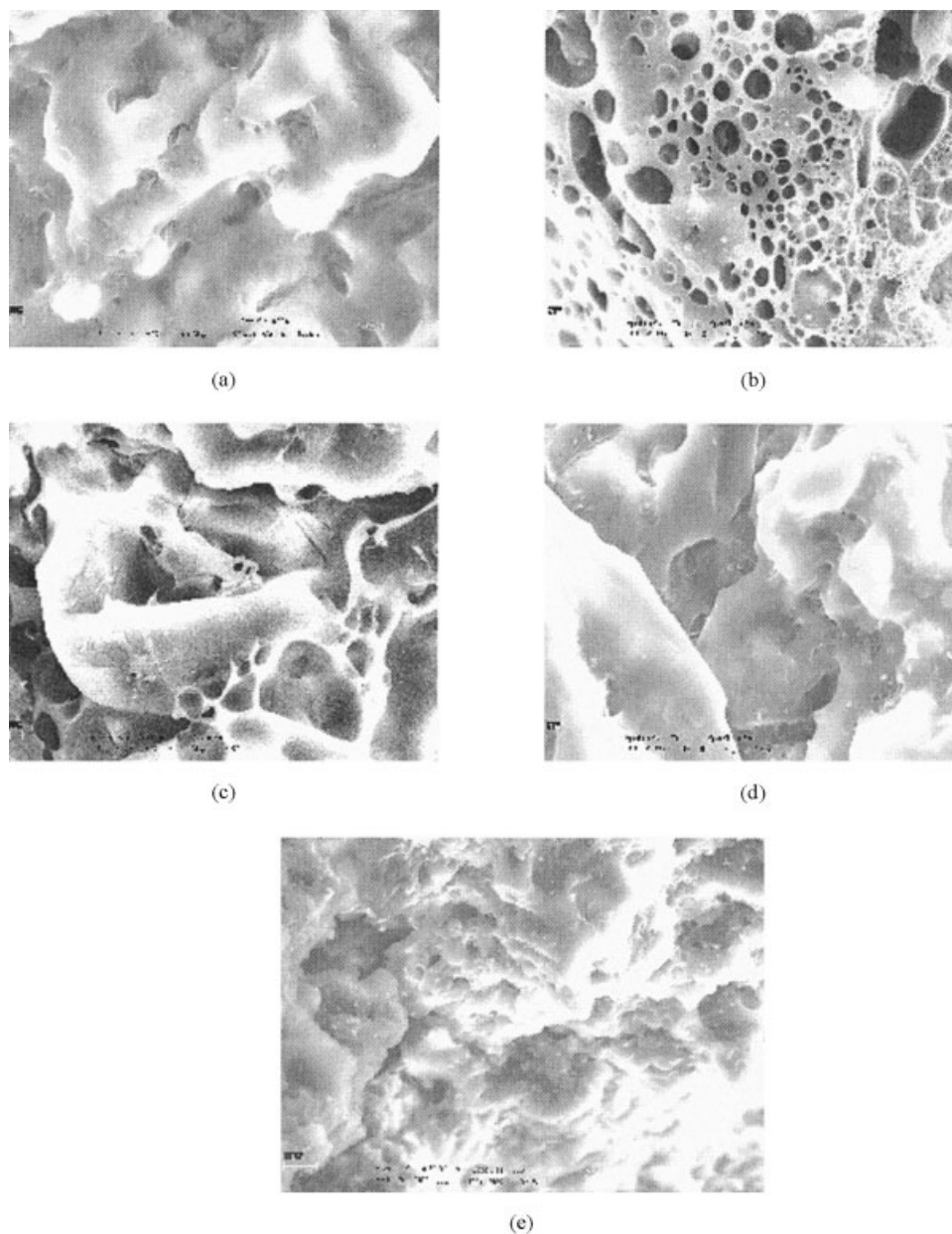


Figure 7 Electron micrographs of the cryogenic fracture surfaces of TPVs based on 60/40 ENR/PMMA blends: (a) ENR-10, (b) ENR-20, (c) ENR-30, (d) ENR-40, and (e) ENR-50.

%. Upon increasing the levels of epoxide groups to 30 mol %, a decreasing trend of the tensile strength was observed. The tensile strength again increased as levels of the epoxide groups higher than 30 mol % were used. High levels of strain-induced crystallization may be the reason for the high tensile strength of ENR-20.³⁰ More irregularity of the molecular structure of the ENR molecules with levels of epoxide groups higher than 20 mol % caused a decreasing trend of the strain-induced crystallization. Chemical interactions between the polar functional groups increased as levels of epoxide groups in the ENR molecules increased.

However, in ENR-20, the influence of strain-induced crystallization was more pronounced. Therefore, the increasing ultimate tensile strength of the TPVs using ENRs with >30 mol % epoxide might be the result of an increasing trend of the polarity. Higher chemical interactions between ENR molecules as well as lower interfacial tension between ENRs and PMMA phases were the main reasons for the increasing trend of the tensile strength in the latter case.

Figure 4 shows the elongation at break of the TPVs. It can be seen that the ultimate elongation slightly decreased with the increased levels of epoxide groups.

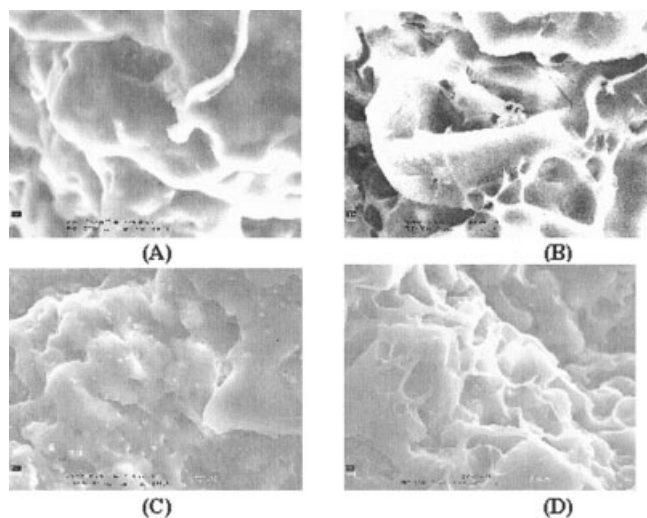


Figure 8 Electron micrographs of the cryogenic fracture surfaces of TPVs based on ENR-30/PMMA blends: (a) 70/30 ENR-30/PMMA, (b) 60/40 ENR-30/PMMA, (c) 50/50 ENR-30/PMMA, and (d) 40/60 ENR-30/PMMA.

A higher degree of chemical interaction between ENR molecules and between different phases caused higher chain stiffness. Therefore, lower elongation at break was observed. The influence of the strain-induced crystallization was not observed in this case. Increasing contents of ENRs in the TPVs caused an increasing trend in the elongation at break. However, very poor ultimate elongation was observed for the TPVs with ENR content lower than 60 wt %. This may be attributed to poor elongational characteristics of the PMMA used in this work. That is, it exhibits very low elongation at break, which is only 2–5% of its original length.

Hardness

Figure 5 shows the hardness trends of the TPVs prepared from 50/50 ENR/PMMA blends using various types of the ENRs. The hardness values of the TPVs were quite high. This is because of the nature of typical PMMA, which is a hard and rigid material. Furthermore, the hardness increased with increasing levels of epoxide groups in the ENRs. Increasing chemical interactions between the ENR molecules and between ENR and PMMA phases may lead to higher tensile and hardness properties for the TPVs. Increasing the quantity of ENRs in the ENR/PMMA blends resulted in decreasing levels of hardness, as shown in Figure 6. This may be attributed to the higher elastomeric properties of the TPVs from increasing the softer ENR phase. The TPVs therefore exhibited greater elastomeric properties such as elongation (Fig.

4) but smaller stiffness and hardness properties with increasing levels of ENRs.

Morphological studies

The etched cryogenic fracture surfaces of the TPVs based on 60/40 ENR/PMMA blends using various types of ENRs are shown in Figure 7. The thermoplastic phase was preferentially extracted using methyl ethyl ketone/acetone. As a result, the PMMA was dissolved at an elevated temperature and left holes on the surfaces. The two-phase morphology is obvious. Smaller dispersed rubber phases were observed for the TPVs based on ENR-20 [Fig. 7(B)] and ENR-50 [Fig. 7(E)]. This corresponds to higher tensile strength for these two types of TPVs (Fig. 3). The other types of ENRs exhibited similar sized rubber particles dispersed in the PMMA matrix. The SEM micrographs of the TPVs from ENR-30/PMMA blends with various blend ratios are shown in Figure 8. Note that the size of the rubber domains decreased with increasing contents of the PMMA in the blends. This develops lower interfacial tension and higher interfacial forces of the blends. As a result, higher tensile (Fig. 3) and hardness (Fig. 6) properties were observed.

Swelling behavior

Figure 9 shows the degree of swelling for the TPVs based on 50/50 ENR/PMMA blends using various types of ENRs. Abrupt decreasing trends of swelling occurred upon increasing the level of epoxide groups of ENRs. Therefore, increasing polarity because of the increasing contents of the epoxide groups resulted in lower swelling capacity of the TPVs in a nonpolar solvent (diesel oil). However, a very high degree of swelling was observed in the mixed solvent, 50%

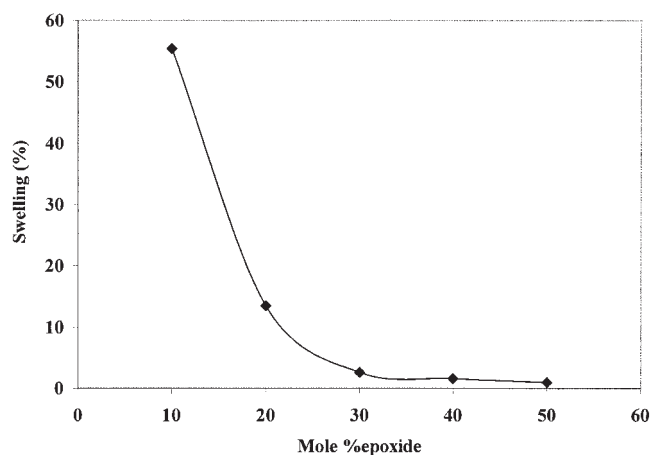


Figure 9 The swelling behavior in diesel oil of TPVs based on 50/50 ENR/PMMA blends using ENRs with various levels of epoxide groups.

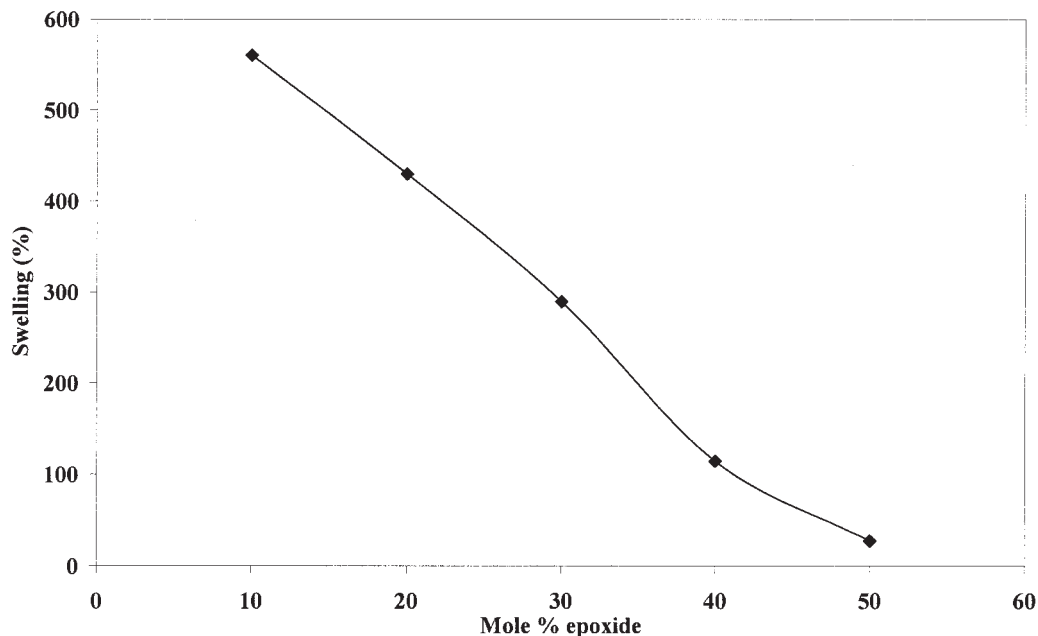


Figure 10 The swelling behavior in toluene/isooctane of TPVs based on 50/50 ENR/PMMA blends using ENRs with various levels of epoxide groups.

(v/v) toluene/isooctane, as shown in Figure 10. This may be attributed to the high solubility of PMMA in toluene. The close values of the Hildebrand solubility parameters for these two materials are obvious: $18.00 \text{ (MPa)}^{1/2}$ for PMMA and $18.30 \text{ (MPa)}^{1/2}$ for toluene.³¹ A decreasing trend of swelling was also observed for the TPVs with ENRs with higher levels of epoxide groups. Therefore, swelling in toluene/isooctane also

decreased with the increasing polarity of the blend systems.

Figure 11 shows the swelling behavior of TPVs based on ENR-30/PMMA blends with various contents of ENR-30 in diesel oil. The swelling decreased with an increasing quantity of ENR-30 in the blends. This may be attributed to the increasing degree of polarity. Therefore, the diesel oil, which is a nonpolar

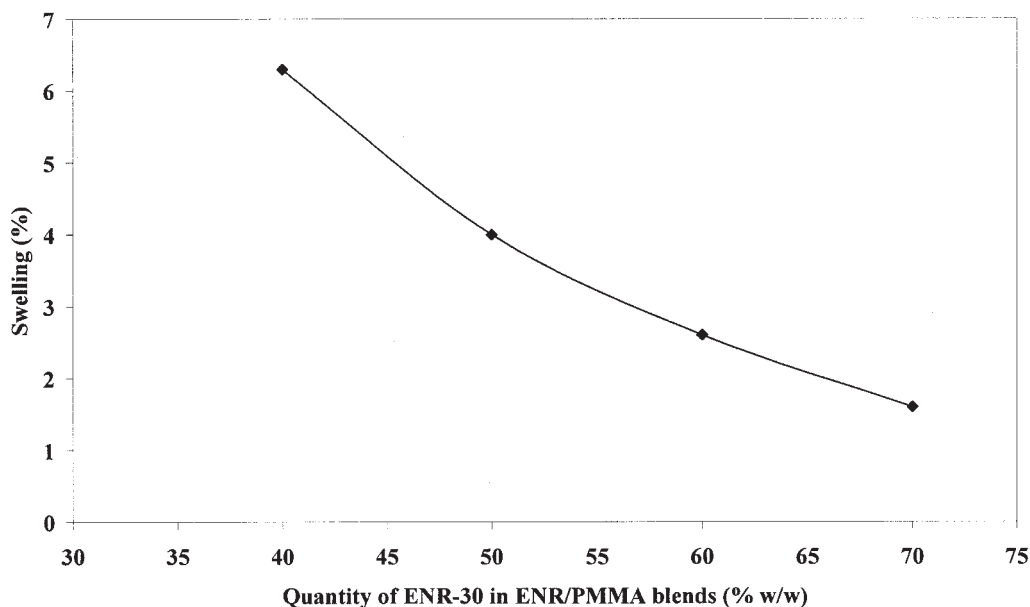


Figure 11 The swelling behavior in diesel oil of TPVs based on ENR-30/PMMA blends with various levels of ENR-30.

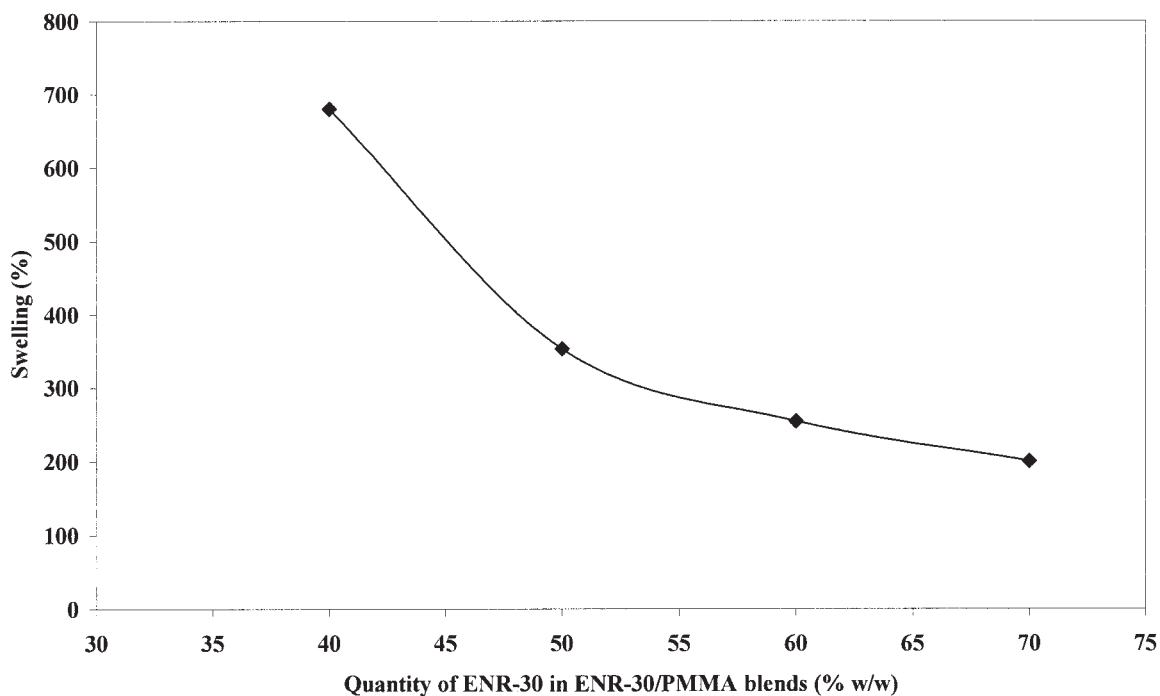


Figure 12 The swelling behavior in toluene/isooctane of TPVs based on ENR-30/PMMA blends with various levels of ENR-30.

solvent, exhibited lower swelling in the blend systems with higher polarity. The decreasing trend of swelling was also observed for toluene/isooctane, as shown in Figure 12. However, a higher degree of swelling was observed in the latter case as compared to the diesel oil results, because of the solubility of PMMA in toluene. It is therefore concluded that various types of TPVs exhibited a higher degree of solvent resistance to diesel oil than to toluene/isooctane.

Thermal degradation

The thermal degradation of the TPVs was investigated using thermogravimetric analysis. Figure 13 shows the thermograms for various types of ENRs blended with PMMA at 50/50 ENR/PMMA. It can be seen that the degradation of the TPVs based on ENR-10 was started and completed at the lowest temperature, whereas ENR-50 exhibited the highest temperature. Therefore, the starting T_d of the various types of TPVs from ENRs/PMMA blends is ordered as follows: ENR-10 < ENR-20 < ENR-30 < ENR-40 < ENR-50. Comparisons of the thermograms for the TPVs based on the ENR-30 blended with various contents of PMMA are shown in Figure 14. The blend formulation with a lower content of ENR-30 exhibited a lower starting T_d . The results agree with the influence of the various types and contents of ENRs in the blends on the thermal degradation of the TPE based on a simple

blend of ENR/PMMA described in our previous work.²² The T_d values of the TPVs were determined from the main weight loss obtained from the differential thermogravimetry curves (not shown). The results are given in Figures 15 and 16. We found that the T_d increases upon increasing the level of epoxide groups in the ENR molecules and increasing the amounts of ENRs in the blends. For the polymer blends and TPVs, the thermal degradation depends on the morphological characteristics and the extent of the interaction between different phases in the blends. From the SEM micrographs, we concluded that the TPVs based on ENR/PMMA blends have two-phase morphologies with partly miscible blends. The extent of interaction depends on the concentration of the polar functional groups in the ENR and PMMA molecules. Therefore, the increasing trend of the T_d corresponds to the increasing degree of chemical interaction between the different phases.

CONCLUSIONS

ENRs with 10, 20, 30, 40, and 50 mol % epoxide groups were successfully used to prepare TPVs based on ENR/PMMA blends using a dynamic vulcanization process. Various concentrations of the blend components and various types of ENRs were used in the blend formulations. We found that the mixing torque increased with the increase of epoxide groups in the

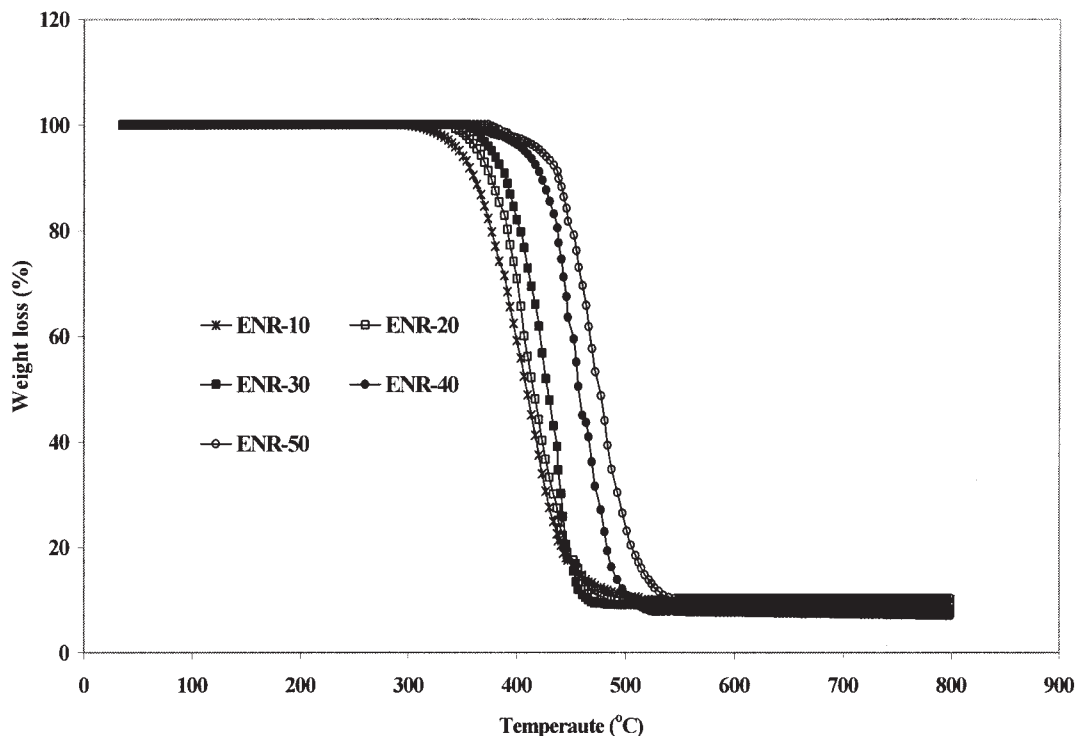


Figure 13 TGA thermograms of TPVs based on 50/50 ENR/PMMA blends with various types of ENRs.

ENRs and the contents of ENR in the blend formulation. This was a result of increasing chemical interaction between polar groups for each blend component. We also found that the TPVs with ENR-20 exhibited a high ultimate tensile strength because of strain-induced crystallization. The ENR-30 TPV exhibited lower tensile strength than ENR-20 because of more irregularity in the molecules. Increasing the levels of epoxide groups to >30 mol % caused an increasing trend of the tensile strength because of an increasing level of chemical interaction between molecules and phases. The ultimate elongation of the TPVs decreased with increasing levels of epoxide groups but increased with increasing contents of ENR. However, increasing

levels of ENRs caused a decreasing trend in the hardness. Two morphology phases were observed in the SEM micrographs with a small elastomeric domain (i.e., vulcanized ENR) dispersed in the PMMA matrix. The TPVs with ENR-20 and ENR-50 exhibited smaller dispersed rubber particles than those of other types of ENRs. Furthermore, the size of the rubber domains decreased with increasing contents of PMMA in the blends. The swelling behavior of the TPVs was investigated. It was found that TPVs exhibited a very high degree of swelling in toluene/isooctane but showed

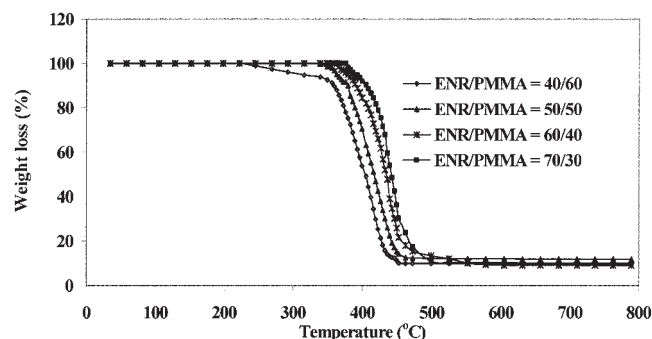


Figure 14 TGA thermograms of TPVs based on ENR-30/PMMA blends with various blend ratios.

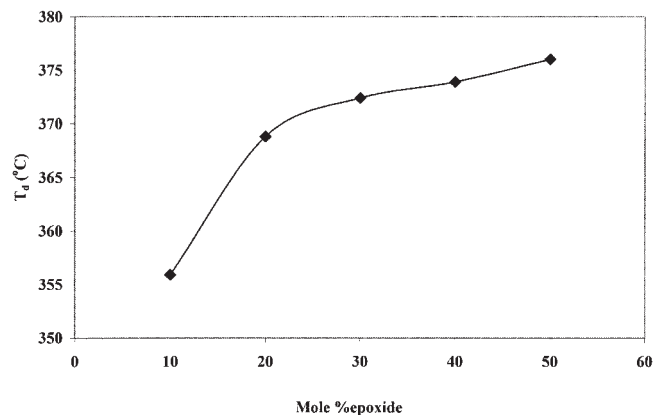


Figure 15 The decomposition temperature of TPVs based on 50/50 ENR/PMMA blends with various levels of epoxide groups.

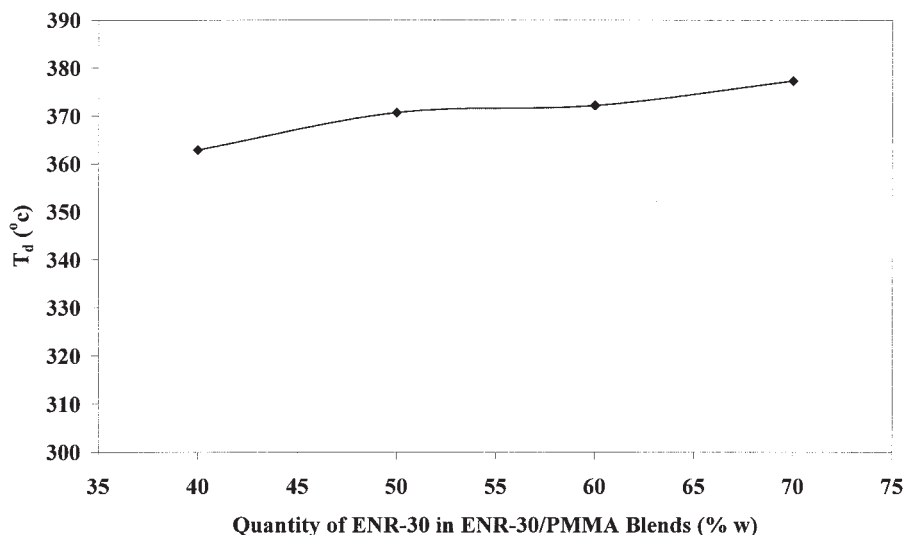


Figure 16 The decomposition temperature of TPVs based on ENR-30/PMMA blends with various blend ratios.

low values in diesel oil. Furthermore, the swelling decreased with increasing contents of the ENRs in the blends and the levels of epoxide groups of the ENRs. This was a result of an increasing degree of polarity of the blends. The thermal degradation of the TPVs was also investigated. We found that the decomposition temperature of the TPVs increased with the contents of ENRs in the blends and the levels of epoxide mole percentage of the ENR molecules. This may be the result of the increasing trend of chemical interactions between different phases of the blends.

The authors gratefully acknowledge financial support from the Thailand Research Fund. The second author (A.T.) also gratefully acknowledges a special scholarship granted by the Faculty of Science and Technology, Prince of Songkla University, Thailand

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