Thermoplastic Natural Rubber Based on Polyamide-12: Influence of Blending Technique and Type of Rubber on Temperature Scanning Stress Relaxation and Other Related Properties

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ABSTRACT: Thermoplastic natural rubber based on polyamide-12 (PA-12) blend was prepared by melt blending technique. Influence of blending techniques (i.e., simple blend and dynamic vulcanization) and types of natural rubber (i.e., unmodified natural rubber (NR) and epoxidized natural rubber (ENR)) on properties of the blends were investigated. It was found that the simple blends with the proportion of rubber ∼ 60 wt % exhibited cocontinuous phase structure while the dynamically cured blends showed dispersed morphology. Furthermore, the blend of ENR exhibited superior mechanical properties, stress relaxation behavior, and fine grain morphology than those of the blend of the unmodified NR. This is attributed to chemical interaction between oxirane groups in ENR molecules and polar functional groups in PA-12 molecules which caused higher interfacial adhesion. It was also found that the dynamic vulcanization caused enhancement of strength and hardness properties. Temperature scanning stress relaxation measurement revealed improvement of stress relaxation properties and thermal resistance of the dynamically cured ENR/PA-12 blend. This is attributed to synergistic effects of dynamic vulcanization of ENR and chemical reaction of the ENR and PA-12 molecules. Furthermore, the dynamically cured ENR/PA-12 blend exhibited smaller rubber particles dispersed in the PA-12 matrix. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 805–814, 2011

Key words: thermoplastic natural rubber; simple blend; polyamide-12; epoxidized natural rubber; stress relaxation

INTRODUCTION

Blending of polymer is an effective way to obtain desirable combination properties of materials that could not be achieved from a single component. Therefore, preparation of miscible blends with unique properties different from the parent polymer pairs has been one of the main routes to search for new materials. However, immiscible blends or partly compatible blends with some degree of interfacial interaction have also been another route which has been used to prepare thermoplastic elastomers (TPEs) materials based on rubber and thermoplastic blends. The TPEs are materials which exhibit functional properties of conventional thermoset rubber, but they can be processed and re-cycled using thermoplastic fabricating technique. There are various categories of TPE materials. These include styrenic block copolymer, multi-block copolymers (i.e., copolyesters, thermoplastic polyurethanes, and thermoplastic polyamides), and thermoplastic/elastomer blends and alloys (i.e., thermoplastic polyolefins and thermoplastic vulcanizates). In this work, attention has been paid to prepare the TPE based on blending of thermoplastic and elastomeric material.

Two types of blending techniques have been generally used to prepare the TPEs: simple blend and dynamic vulcanization (DV) techniques. The first technique is concerned with blending rubber and thermoplastic materials under high shear and temperature without incorporation of curatives. The final morphology of the TPE material is cocontinuous structure with dual continuous phases of rubber and plastic. The latter technique (i.e., DV), the curatives are incorporated during mixing operation of rubber and plastic under high mechanical shearing

condition at high temperature. The rubber and plastic blends are first forced to form cocontinuous structure before adding the curatives. Viscosity is abruptly increased after incorporation of the curatives which thereafter generated very high shear and elongational flow fields. This results in breaking up of the rubber phase to be smaller particles and eventually becomes micron size particles which disperse in the thermoplastic matrix or droplet morphology. After, the stability of the droplets, the thermoplastic vulcanizates (TPVs) or dynamic vulcanizates (DVs) are obtained.

Interest in preparation of thermoplastic elastomer based on natural rubber (NR) and thermoplastic blends [i.e., thermoplastic natural rubbers (TPNRs)] has been increased recently. Apart from raw NR, the modified form of NR has also been used to prepare the TPNRs. Epoxidized natural rubber (ENR) is one of the most frequent used modified NR by blending with various types of thermoplastics.[1–4] This is because ENR exhibits various excellent properties that include oil resistance, gas impermeability, good wet grip, and high damping characteristics. Also, ENR has been used to improve blend compatibility by blending with polar thermoplastics.[5–7]

Blending of nylon and rubber has been studied by focusing on improvement of impact properties for various types of nylon.[8] Therefore, the toughness of rigid nylon material was improved by proper blending with small amounts of rubber.[9] Furthermore, TPVs based on nylon-6/EPDM blends have also been prepared.[10,11] With suitable compatibilization and crosslinking system of the rubber phase, up to 60 wt % rubber was dispersed in the nylon-6 matrix with great improvement of mechanical properties.[9] According to the available literatures, most of the research works related to nylon and rubber blends have been focused on blending of nylon with high melting temperature and high heat resistant rubbers, such as EPDM, NBR, CIIR, and BIIR.[12–15] Polyamide-12 is considered as one of the lowest melting temperature (i.e., 175°C) and water-absorbing polyamide. It exhibits excellent resistance toward solvents, abrasion and fatigue, as well as exhibits good melt processability. Therefore, blending of natural rubber and NR derivatives is favored because the melt is less subjected to oxidative degradation. To increase polarity and blend compatibilization, the modified NR, such as epoxidized natural rubber (ENR) and maleated natural rubber (MNR) are alternative blend components for blending with nylon material. Functionalized synthetic rubbers have also been used to prepare reactive blending of rubber and nylon. Epoxy functionalized rubbers are one of successful example.[16–21] This is attributed to chemical interaction between the epoxy groups and the functional groups of nylons (i.e., —NH$_2$, —COOH,

—NH—CO—). The reactive blending of nylon-6 and acrylate rubber (ACM) was also reported.[16] The advantages of the TPE materials based on ENR/PA-12 blend are higher service temperature and oil resistant as well as low gas permeability. Therefore, they are suitable to apply in automotive and other related industries which require these superior properties.

This research work was aimed to prepare natural rubber and PA-12 blends by simple blend and dynamic vulcanization technique. Effect of two types of natural rubber (i.e., ENR and unmodified NR) and blending techniques on the properties of the blends were investigated.

EXPERIMENTAL

Materials

Two types of natural rubber used in this study: air dried sheet (ADS), manufactured by a local factory operated by Khuan Pan Tae Farmer Cooperation (Phattalung, Thailand) and epoxidized natural rubber (ENR) with 50 mol % epoxide and ML$_{1 + 4}$(100°C) = 70, manufactured by Muangmaiguthrie (Suratthani, Thailand). Heat stabilized and nonreinforced injection molding grade PA-12, Grilamid L20G was used as the thermoplastic blend component. It was manufactured by EMS-Grivory GmbH, Gross-Umstadt, Germany. Melting temperature and MFI of this grade of PA-12 are 178°C and 125 g/10 min (5 kg, 275°C), respectively. Di-(2-*tert*-butylperoxyisopropyl) benzene (Peroxan BIB-40 MB, on silica carrier, with active peroxide content of 40 wt %) was used as peroxide curing agent, manufactured by Pergan GmbH, Bocholt, Germany. Triallyl cyanurate (TAC) with active agent content of 50 wt % was used as a coagent for peroxide cured system, manufactured by Rhein Chemie Rheinau GmbH, Mannheim, Germany. The zinc oxide manufactured by Lanxess, Leverkusen, Germany and stearic acid manufactured by Unichema International B.V., Gauda, Netherlands, respectively. The polyphenolic antioxidant additive, Wingstay-L used as an antioxidant, manufactured by Eliokem, OH.

Preparation of natural rubber/PA-12 blends

Simple blend technique

Polyamide-12 was first dried at 40°C for 24 h. It was then blended with natural rubber at a fixed blend ratio of NR/PA-12 = 60/40 wt %. The natural rubber was first mixed with polyphenolic antioxidant (i.e., Wingstay L) in the internal mixer using a Haake Rheocord 600 laboratory internal mixer (Thermo Electron, Karlsruhe, Germany) at 80°C and a rotor speed of 40 rpm for 4 min before removing

TABLE I
Compounding Formulations

Ingredients	Dynamic vulcanization (phr)	Simple blend (phr)
Rubber (ENR or NR)	100	100
ZnO	5.0	–
Stearic acid	1.0	–
Wingstay-L	1.0	1.0
TAC (50% active)	2.0	–
Di-(2-tert-butylperoxyisopropyl) benzene (40% active)	2.0	–

from the mixing chamber. The mix was then added into the chamber at 160°C. The rotor speed was set at 80 rpm for 1 min before increasing to 150 rpm for another 1 min. After reaching a temperature of ∼ 170°C, PA-12 component was added. The temperature the material was gradually increased to 185–195°C due to frictional heat. The rotor speed was then decreased to 60 rpm to reduce the mixing temperature and continued mixing for another 7 min with the total mixing time of 9 min. The blend product was removed from the mixer, cooled down to room temperature and pelleticized for fabrication and characterization.

Dynamic vulcanization technique

Polyamide-12 was also dried at 40°C for 24 h and blended with natural rubber at a fixed blend ratio of NR/PA-12 = 60/40 wt %. Two-step mixing process was performed. The first step was compounding of natural rubber at 80°C and a rotor speed of 40 rpm for 10 min, as a formulation shown in Table I and the step of adding components into a mixing chamber shown in Table II. The rubber was masticated for 1 min (ENR) and 3 min (NR). Activators (i.e., ZnO and stearic acid) and antioxidant (i.e., Wingstay-L) was then incorporated and mixing was continued for 2 min. The coagent of peroxide cured system (i.e., triallyl cyanurate) was then added with continue mixing for 1 min. Di-(2-*tert*-butylperoxyisopropyl) benzene (i.e., Peroxan BIB-40 MB) was finally mixed until total mixing time of 10 min. The rubber compound was then removed from the mixer and cooled down to room temperature to avoid scorch of the material. In the second step, rubber compound was incorporated into the mixing chamber with temperature of 160°C and a rotor speed of 80 rpm. The rubber compound was then mixed for 1 min before increasing the rotor speed to 150 rpm for another 1 min. PA-12 component was then added after reaching the temperature of ∼ 170°C. The temperature of the material was then increased to 190–210°C due to frictional heat and dynamic vulcaniza-

tion. The rotor speed was then decreased to 60 rpm and continued mixing for another 10 min with the total mixing time is 12 min. The blend product was dumped from the mixer, cooled down to room temperature and pelleticized.

Tensile and hardness tests

The dumbbell shaped specimens were prepared by thermoplastic injection molding machine (The BOY 22, BOY Machines, PA) for tensile measurement. Tensile test was performed at 23°C ± 2°C according to ISO 527 using a Zwick Z 1545 tensile testing machine (Zwick GmbH, Ulm) at a fixed speed of 500 mm min^{-1}. Indentation hardness was tested by durometer Shore A and Shore D according to ISO 868 using a hardness testing machine (Frank GmbH, Germany).

Temperature scanning stress relaxation (TSSR)

The TSSR measurement of rubber/PA-12 blends was performed using Brabender GmbH (Duisburg, Germany). The instrument consists of an electrical heating chamber where the sample is placed between two clamps which are connected to a linear drive unit to apply a certain uniaxial extension to the sample. High quality signal amplifier in combination with a high resolution AD-converter is used to detect and digitize analog signals of the high-resolution force transducer and the thermocouple which are digitized and transferred to a personal computer. A special software program is used to treat and evaluate data as well as to control the machine system.

The TSSR measurement provides the force-temperature curves, which the certain characteristic, such as T_{10}, T_{50}, T_{90} and the rubber index (RI) are calculated. The temperature T_x stands for the temperature at which the force F has decreased about x% with

TABLE II
Step of Adding Components into a Mixing Chamber

Mixing time (min)	Dynamic vulcanization (phr)	Simple blend (phr)
0	Rubber[a]	Rubber[a]
1	TAC	Wingstay-L
2	ZnO + Stearic acid + Wingstay-L	
3		
4		Dump
5	Di-(2-tert-butylperoxyisopropyl) benzene	
6		
7		
8		
9		
10	Dump	

[a]ENR or NR (NR was masticated 3 min before compounding).

respect to the initial force F_0, while the RI is a measure of the rubber-like behavior of the material. It is calculated based on the area under the force-temperature curves according to the relation below[22,23]:

$$\mathrm{RI} = \frac{\int_{T_0}^{T_{90}} F(T)/F_0 dT}{T_{90} - T_0} \tag{1}$$

where $F(T)$ is the force at testing temperature T and F_0 is the initial force determined at a starting temperature (T_0). The temperature T_{90} is the temperature at which the force F has decreased about 90% with respect to the initial force (F_0).

To elucidate the force-temperature dependency of the TPV material compared with the conventional thermoset rubber. The TSSR measurement was performed on model materials (i.e., EPDM/PP TPV and EPDM vulcanizate) which have been widely studied than that of the natural rubber based materials. The EPDM was compounded using the formulation and blending conditions the same as in the ENR/PA-12 TPV, as described in Dynamic Vulcanization Technique section.

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR)

Interfacial reactions between polar functional groups in ENR and PA-12 molecules in dynamically cured ENR/PA-12 and NR/PA-12 blends were identified by ATR-FTIR. The samples were first dissolved in mixed solvents of phenol/xylene (40/60 w/v) to separate the PA-12 phase. Ethanol was incorporated to precipitate the remained rubber fraction. The process was repeated to make sure that all un-reacted PA-12 was removed. The extracted rubber was then dried in a hot air oven at 40°C for at least 24 h. ATR-FTIR was then used to analysis using a Nicolet ATR-FTIR spectrophotometer at 4 cm^{-1} resolution and 32 scans.

Morphological characterization

Morphological characterization was performed using Leo scanning electron microscope, model VP 1450, manufactured by Leo, Cambridge, UK. Injection molded samples of the blends were first cryogenic cracked in liquid nitrogen to avoid any possibility of phase deformation. The rubber phase was preferable dissolved by extraction with toluene in the simple blend samples. However, in dynamically cured blends, it was not possible to extract the vulcanized rubber phase. Therefore, PA-12 phase was preferentially extracted by immersing the fractured surface into a mixture of 40/60 w/v % phenol/xylene. The extracted samples were then dried in vacuum oven at 40°C for 24 h. The dried surfaces were then
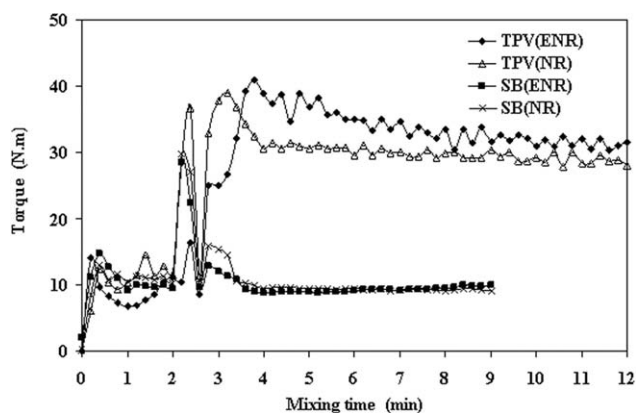

Figure 1 Relationship between mixing torque and time of 60/40 rubber/PA-12 blends using unmodified NR (ADS) and ENR (TPV = thermoplastic vulcanizates based on dynamic vulcanization and SB = simple blend).

gold-coated and examined by scanning electron microscope.

RESULTS AND DISCUSSION

Mixing torques

Figure 1 shows mixing torques of the simple blends and dynamic vulcanization based on blending of unmodified NR (ADS)/PA-12 and ENR/PA-12 with a fixed blend ratio = 60/40. It can be seen that different types of rubbers and blending techniques gave different mixing torque-time curves. First peaks of the mixing torque at $\sim$ 0.5 min are related to increasing of viscosity of the rubber compounds after incorporation into a mixing chamber. The second peaks at a mixing time of $\sim$ 2 min related to the viscosity of the blends after incorporation of PA-12 into the mixing chamber. It is seen that the mixing torque of the simple blend slightly decreased after reaching the second peak which thereafter reached a plateau region at a mixing time of $\sim$ 4 min. However, in the dynamic vulcanization, abruptly increasing trend of torque was observed after the second peak (i.e., at $\sim$ 2.5 min) because of crosslinking reaction of the rubber phase. It is noted that the difference in torque of dynamic vulcanization of NR and ENR can be originated by differences in molecular weight and viscosity of the rubber phase, thermal energy released by the crosslinking reaction, and levels of the polarity of the rubber phase. The mixing torque reached the maximum values and become marginal decreasing trend at a mixing time longer than 5 min. It is also seen that the simple blend of ENR/PA-12 exhibited marginally higher mixing torque at the end of mixing process than that of the simple blend of NR/PA-12. This might be attributed to higher viscosity of the blend based on ENR because of chemical interaction between oxirane groups in ENR

TABLE III
Curing Properties of ENR and NR Compounds at 190°C

Compounds	t_{s2} (min)	t_{90} (min)
ENR	1.92	7.75
NR	1.12	7.73

molecules and polar functional groups in PA-12 molecules. Furthermore, it is clear that the dynamically cured ENR/PA-12 blend exhibited higher final mixing torque than that of the NR/PA-12 blend. This is due to synergistic effect of dynamic vulcanization and chemical interaction between polar functional groups of ENR and PA-12 molecules. The height of the third peak of mixing torque (i.e., at ~ 4 min) is related to the crosslink density of the rubber phase. It is also seen that the dynamically cured NR/PA-12 blend reached the maximum torque (i.e., at the third peak) faster than the dynamically cured ENR/PA-12 blend. This is elucidated by curing properties of ENR and NR (ADS) compounds with peroxide curing system, as shown in Table III. It can be seen that the NR compound exhibited slight shorter scorch time (t_{s2}) and cure time (t_{90}). As a consequence, faster cure of the NR compound caused shorter time to reach the maximum torque (i.e., at the third peak).

Figure 2 shows mixing temperature versus time. It is seen that the mixing temperature decreased after incorporating of rubber compounds. The temperature thereafter slight increased with increasing mixing time until 2 min when the PA-12 was incorporated. Decreasing trend of temperature was again observed due to the initial temperature of the PA-12. Temperature of dynamic vulcanization blend was then abruptly increased with increasing time due to exothermic crosslinking reaction of the rubber phase. However, only marginal increasing trend of temper-

Figure 3 Stress–strain curves of 60/40 rubber/PA-12 blends using unmodified NR (ADS) and ENR (TPV = thermoplastic vulcanizates based on dynamic vulcanization and SB = simple blend).

ature was observed in the simple blend. Therefore, dynamic vulcanization generated higher mixing temperature than that of the simple blend. Additionally, dynamic vulcanization of ENR/PA-12 blend exhibited higher mixing temperature at the final mixing process (i.e., at ~ 202°C) than that of the NR/PA-12 blend (i.e., ~ 190°C). This may be attributed to higher frictional heat generated from higher viscosity due to chemical interaction between the polar functional groups of ENR and PA-12 molecules in the blend system.

Mechanical properties

Figure 3 shows stress–strain curves of dynamically cured rubber/PA-12 compared with the simple blend. It can be seen that the dynamically cured rubber/PA-12 blends exhibited higher Young's modulus (i.e., slope at initial part of the curves) than that of the simple blend. This reflects higher stiffness of the

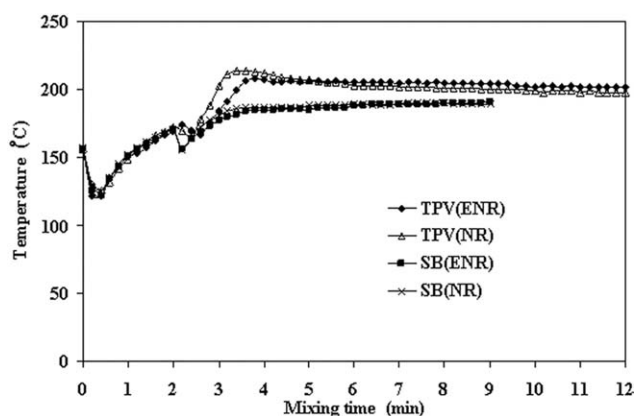**Figure 2** Relationship between mixing temperature and time of 60/40 rubber/PA-12 blends using unmodified NR (ADS) and ENR (TPV = thermoplastic vulcanizates based on dynamic vulcanization and SB = simple blend).

Figure 4 Tensile strength and elongation at break of 60/40 rubber/PA-12 blends using unmodified NR (ADS) and ENR (TPV = thermoplastic vulcanizates based on dynamic vulcanization and SB = simple blend).
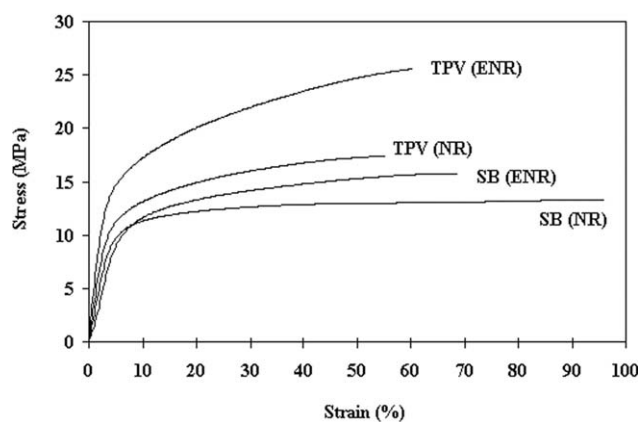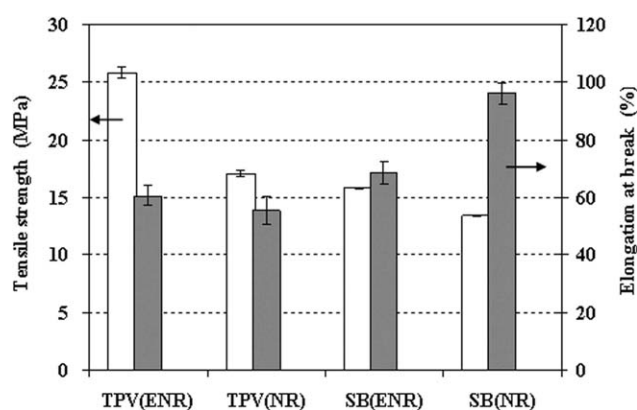
Scheme 1 Possible grafting reaction of epoxide groups in ENR molecules and acid-end groups of PA-12 molecules at the interface.

TPVs materials. Furthermore, the dynamically cured materials showed higher tensile strength but lower elongation at break, as shown in Figure 4. This confirms that the dynamic vulcanization improved stiffness and strength properties of the blends. Furthermore, it is seen that the dynamically cured ENR/PA-12 blend exhibited higher tensile strength than that of the TPV based on NR/PA-12 blend. This might be attributed to chemical interaction between epoxide rings in the ENR molecules and polar functional groups in the PA-12 molecules. This caused chemical reactions between epoxide groups in the ENR molecules and amino, acid and amide groups (i.e., $-NH_2$, $-COOH$, $-NH-CO-$, respectively) in the PA-12 molecules.[16,19] As a consequence, formation of *in situ* graft copolymerization of the ENR and PA-12 molecules occurred at the interface, as a propose reaction mechanism shown in Scheme 1. This causes decreasing of the interfacial tension but increasing interfacial force between the phases. As a result, smaller vulcanized ENR domains were finely dispersed in the PA-12 matrix.

FT-IR technique was used to elucidate the formation of graft copolymer of ENR and PA-12 molecules, as shown in Figure 5. It is noted that the free (i.e., unreacted) PA-12 phases were previously separated by solvent extraction technique. In Figure 5(a), It is seen that the IR spectrum of extracted ENR/PA-12 TPV based in dynamic vulcanization technique showed characteristic bands of ENR (i.e., 870 and 833 cm^{-1} which are assigned to symmetric $-C-H$ stretching of oxirane ring and to $=CH-$ out of plane bending, respectively) and PA-12 (i.e., 3295, 1642, and 1544 cm^{-1} which are assigned to $-NH$ stretching and, $-C-O$ stretching vibration and $-NH$ bending vibra-

tion, respectively). This proves the occurrence of *in situ* graft copolymerization of ENR and PA-12. The same experimental treatment and FTIR characterization were performed on dynamically cured NR/PA-12 blends but the characteristic bands of graft copolymer were not observed. That is, the characteristic bands of PA-12 in the extracted NR/PA-12 TPV in Figure 5(b) were not observed.

In Figure 4, it is also seen that the dynamically cured rubber/PA-12 gave lower elongation at break than those of the simple blend. These may result from substantial increasing of crosslink density that restricts the extension or chain movement of the specimens. Also, different in morphological properties might be another reason. That is, the simple blend material consist of dual continuous phases or cocontinuous phase morphology, while the dynamically cured blends contain droplets of vulcanized rubber dispersed in the PA-12 matrix, as will be described in morphological properties section. Therefore, the rubber phase of the simple blend is capable of elongated with higher extensibility as a continuous matrix rather than the droplets in the case of the dynamically cured blends.

Hardness properties of rubber/PA-12 blends are shown in Figure 6. It is seen that the dynamically cured blends gave higher hardness properties (i.e., > 90 Shore A) than those of the simple blends. Furthermore, the hardness properties of dynamically cured blends could be clearly distinguished by durometer Shore D. That is, no significant difference of hardness Shore A between the dynamically cured ENR/PA-12 and ENR/PA-12 blends. On the other hand, the hardness of the simple blend could be distinctly identified by the durometer Shore A. In Figure 6, it is also seen that the dynamically cured ENR/PA-12

Figure 5 Infrared spectra for pure ENR, PA-12 and the extracted 60/40 ENR/PA-12 and NR/PA-12 blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 Hardness of 60/40 rubber/PA-12 blends using unmodified NR (ADS) and ENR (TPV = thermoplastic vulcanizates based on dynamic vulcanization and SB = simple blend).
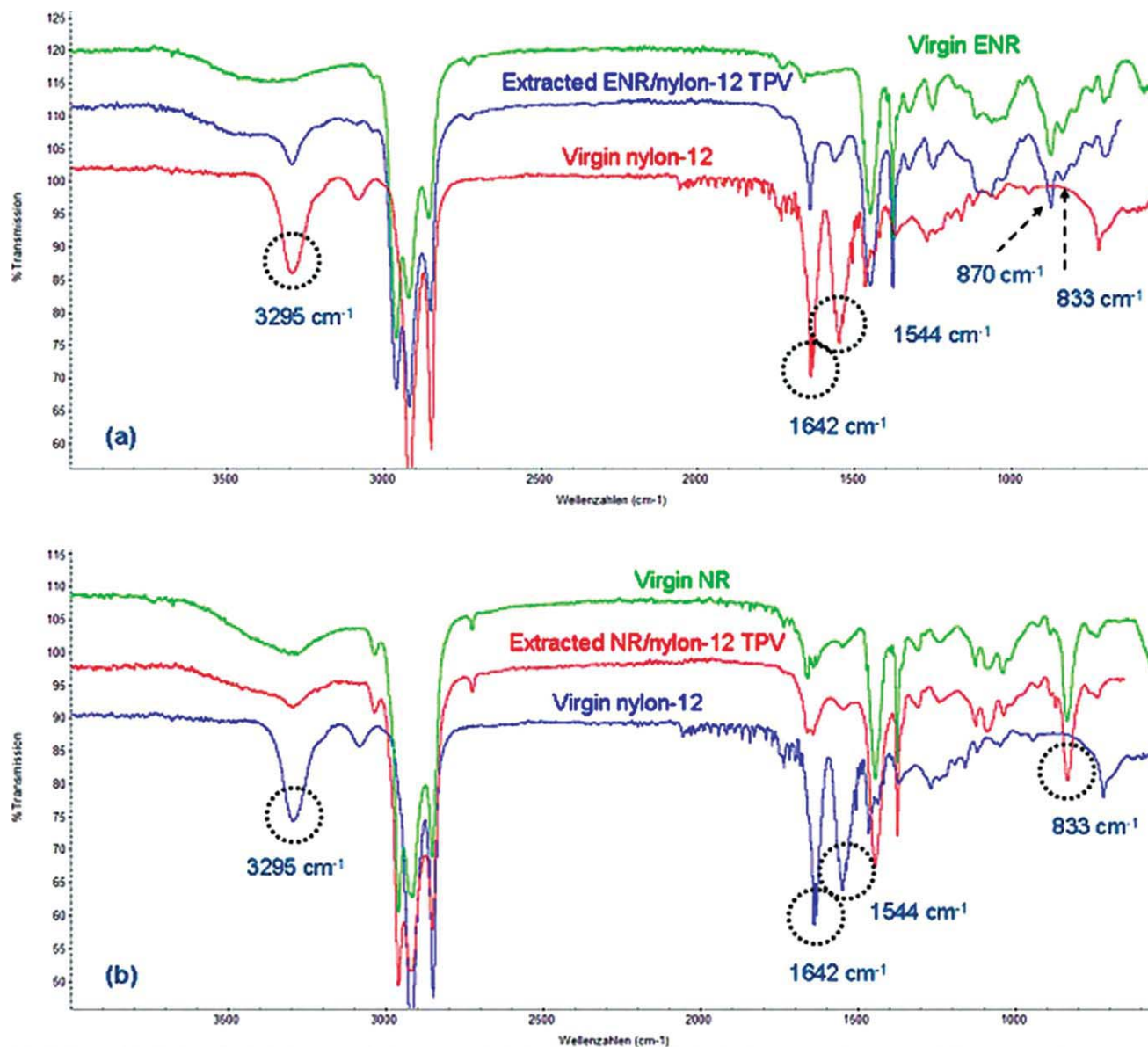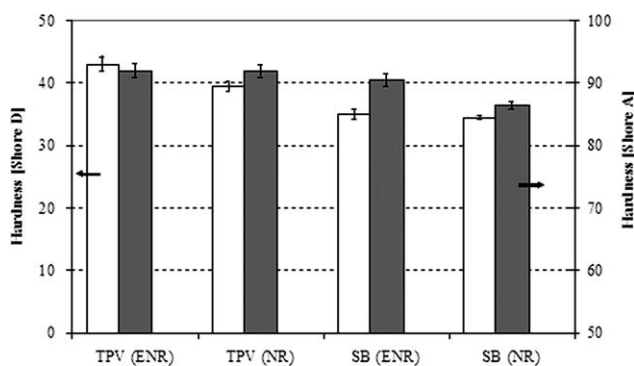
blend exhibited higher hardness Shore D than that of the NR/PA-12 blend. This may be due to higher chemical interaction at the interface of ENR and PA-12 phases. It is noted that hardness is a macroscopic property which is as a coadjuvant in the discussion of interaction between phases. To clarify the existence of chemical interaction between the phases, FTIR results (Fig. 5) were used together with the smaller phase sizes were observed in the ENR blends, as discuss in Morphological Properties section.

TSSR measurement

The TSSR has been developed recently to characterize thermomechanical behavior of thermoplastic elastomer materials.[22,23] During the TSSR measurement, a constant
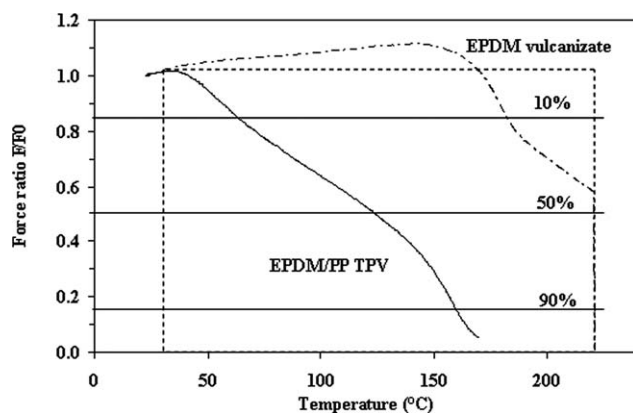
Figure 7 Normalized force-temperature curves of EPDM vulcanizate and dynamically cured EPDM/PP blend (i.e., TPV) from TSSR measurement.

Figure 8 Normalized force-temperature curve of 60/40 rubber/PA-12 blends using unmodified NR (ADS) and ENR (TPV = thermoplastic vulcanizates based on dynamic vulcanization and SB = simple blend).

tensile strain of 50% was applied to dumbbell test pieces (Type 5A, ISO527) where they were preconditioned at 55°C for 1 h. Most of the short time relaxation processes occurred during this period. After the sample reached the quasi-equilibrium state, the system was heated at a constant heating rate of 2 K min^{-1} until the completion of stress relaxation process or failure of the sample. The force-temperature curves are the results of the TSSR measurement. They contain information relating to thermomechanical behavior of the samples. The TSSR tests of the EPDM/PP TPV and EPDM vulcanizate were performed a constant tensile strain of 50% and preconditioned at 23°C for 2 h before heating the samples at a constant heating rate of 2 K min^{-1}.

Figure 7 shows the early test results of the model materials, conventional vulcanized EPDM, and dynamically cured EPDM/PP blends. It is seen that, at the early stage, the force slight increased with increasing temperature due to the entropy effect. The slope of the increased force corresponds to the crosslink density of the rubber network. It is also seen that increasing temperature caused stress relaxation, which thereafter overshadowed the entropy effect. Hence, abrupt decreasing trend of force (i.e., stress relaxation) approaching to zero was observed. Thermo-oxidative reaction is one of the main parameter causing the severe stress relaxation. Furthermore, in Figure 7, it is clear that the thermomechanical behavior of thermoplastic elastomer is significantly different compared with the rubber vulcanizate. That is, the force marginally increased over a narrow range of temperatures in the TPE (i.e., dynamically cured EPDM/PP blend) but abruptly increased with wider temperature ranges were observed in the EPDM vulcanizates.

Figure 8 shows normalized force-temperature curves of 60/40 rubber/PA-12 blends using unmodified NR (i.e., ADS) and ENR with two different blending techniques. It is seen that the force-temperature curves are similar to the curve of a model
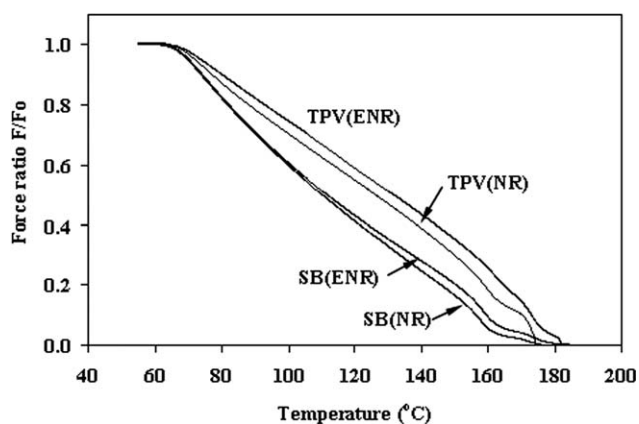
dynamically cured EPDM/PP in Figure 7. It is seen that the dynamically cured blend exhibited higher force-temperature curve than those of the simple blend. That is, the dynamically cured ENR/PA-12 and NR/PA-12 blends exhibited the preeminent relaxation behavior curves while the simple blend (i.e., un-crosslinked sample) exhibited stronger stress decreased. This behavior was expected because the dynamic vulcanization is typically caused enhancement of the stress relaxation.[24] Therefore, dynamic vulcanization gave higher area underneath of the normalized force-temperature curves. Consequently, higher initial force (F_0), rubber index (RI), and T_x values were observed in the dynamically cured blends, as shown in Table IV. This indicates an improvement of elastomeric behavior.[23] Moreover, the dynamic vulcanization also caused an improvement of thermal resistance of the blend, as observed from a strong increase in T_{10}, T_{50}, and T_{90} in dynamically cured ENR/PA-12 and NR/PA-12 blends.

In Figure 8 and Table IV, it is also seen that the dynamically cured ENR/PA-12 blend showed greater relaxation behavior, thermal resistance (i.e., T_{10}, T_{50}, and T_{90}), and elastomeric nature (i.e., RI) than that of the dynamically cured NR/PA-12 blend. Additionally, the ENR/PA-12 simple blend also showed marginally higher normalized force-temperature curve than that of the simple blend based on NR/PA-12. This is attributed to chemical interaction between oxirane groups in ENR molecules and polar

TABLE IV
TSSR Results of 60/40 Rubber/Nylon-12 Blends

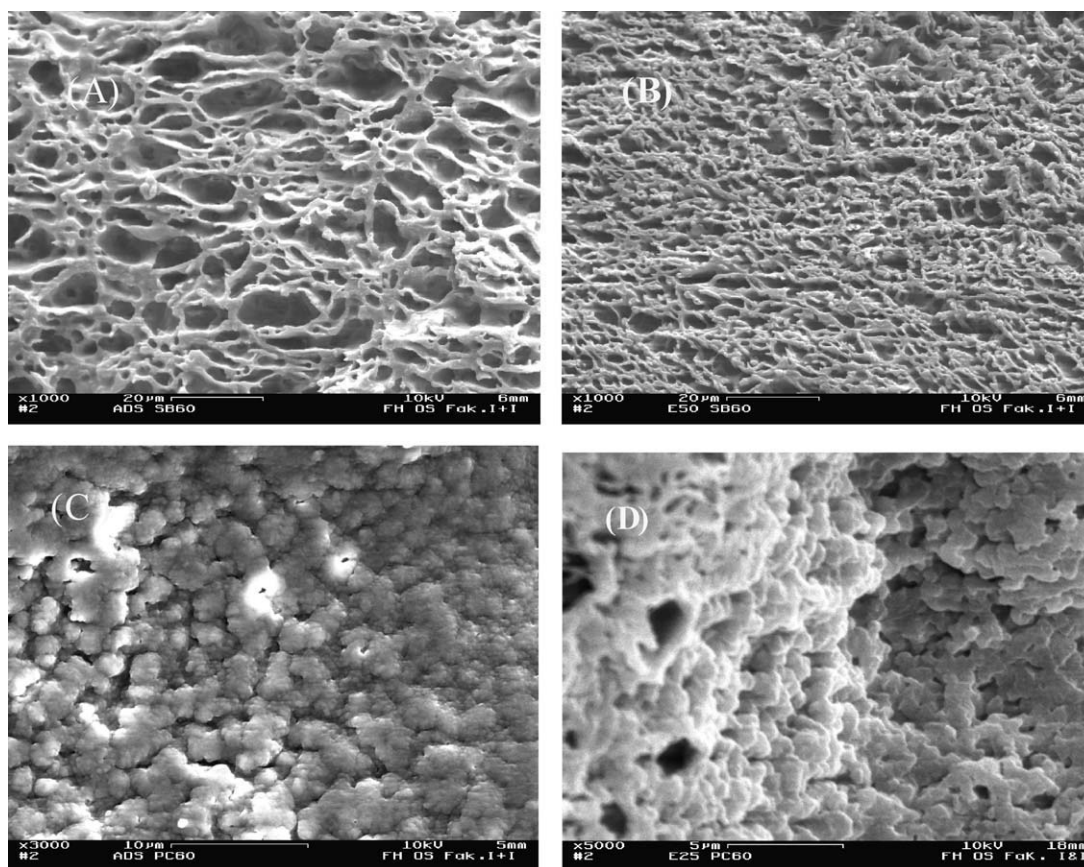| Samples	F_0 (MPa)	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	RI
TPV(ENR)	7.62	80.2	131.7	173.1	0.63
TPV(NR)	5.52	77.0	126.0	170.1	0.60
SB(ENR)	3.72	74.2	111.7	159.6	0.58
SB(NR)	3.93	73.9	110.3	156.5	0.57

Figure 9 SEM micrographs of 60/40 rubber/PA-12 blends using unmodified NR (ADS) and ENR: (A) NR/PA-12 simple blend, (B) ENR/PA-12 simple blend (×1000), (C) NR/PA-12 TPV and (D) ENR/PA-12 TPV (×3000).

functional groups in PA-12 molecules (i.e., as a proposed reaction shown in Scheme 1). As a result, higher compatibility between ENR and PA-12 caused improvement of the stress relaxation, thermal resistance and elastomeric nature of the blends. Therefore, it is concluded that the dynamic vulcanization caused higher normalized force-temperature curves (Fig. 8) and mixing torques (Fig. 1) than that of the simple blend. In addition, the ENR/PA-12 simple blend exhibited slight higher normalized force-temperature curve and the mixing torque than that of the simple blend of NR/PA-12.

Morphological properties

High resolution SEM micrographs of 60/40 rubber/ PA-12 blends with two different types of rubber and blending techniques are shown in Figure 9. Toluene was used to etch the rubber phase of cryogenic fracture surfaces of the simple blend. Therefore, the rubber phase was removed as cavitations with the remained PA-12 phase, as shown in Figure 9. It is seen that the cocontinuous structure with dual continuous phases was observed in the simple blend which proves the characteristic of thermoplastic elas-

tomer materials. As might be expected, the simple blend based on blending of ENR/PA-12 exhibited finer grain morphology compared with the NR/PA-12 blend. This is due to compatibilization effect between oxirane groups in ENR molecules and polar functional groups in PA-12 molecules, which led to improvement of tensile strength (Fig. 4), stress relaxation behavior and thermal resistance (Fig. 8).

The PA-12 phase at the cryogenic cracked surfaces of dynamically cured blends was extracted by a mixture of phenol/xylene. This caused undissolved vulcanized rubber particles adhered at the surface, as shown in Figure 9. It is also seen that the dynamically cured ENR/PA-12 blends provided smaller vulcanized rubber particles dispersed in the PA-12 matrix than that of the dynamically cured NR/PA-12 blends. These might be attributed to the combination effects of dynamic vulcanization and reactive blending of ENR and PA-12. As a consequence, smaller rubber particles dispersed in PA-12 matrix was observed in the dynamically cured ENR/PA-12 blends. This led to higher tensile strength (Fig. 4), hardness (Fig. 6), stress relaxation behavior, and thermal properties (Fig. 8) of dynamically cured ENR/PA-12 blend.

CONCLUSION

Effects of blending techniques (i.e., simple and dynamic vulcanization) and types of rubber (NR (ADS) and ENR) on mechanical properties, stress relaxation behavior, and morphological properties of rubber/PA-12 blend were investigated. It was found that ENR caused improvement of various properties of the 60/40 rubber/PA-12 blends due to chemical interaction between oxirane ring in ENR molecules and polar functional groups in PA-12 molecules. Moreover, dynamic vulcanization showed stronger influence causing superior properties of the blends compared with the simple blend. Additionally, the dynamic vulcanization also caused improvement of stress relaxation properties and thermal resistance. The synergistic effects of dynamic vulcanization of ENR phase and reaction between ENR and PA-12 molecules gave the material with superior properties.

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