Cure Characteristics and Mechanical Properties of Hydrogenated Natural Rubber/Natural Rubber Blends

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ABSTRACT: The cure characteristics and mechanical properties of blends consisting of hydrogenated natural rubber (HNR) and natural rubber (NR) blends were investigated. The HNR/NR blends at 50/50 wt ratio were vulcanized using various cure systems: peroxide vulcanization, conventional vulcanization with peroxide, and efficient vulcanization with peroxide. The HNR/NR vulcanizates cured by the combination of peroxide and sulfur donor (tetramethylthiuram disulfide, TMTD) in the efficient vulcanization with peroxide exhibited the best mechanical properties. It was also found that the hydrogenation level of HNR did not affect the tensile strength of the vulcanizates. The tensile strength of the blends decreased with increasing HNR content because of the higher incompatibility to cause the noncoherency behavior between NR and HNR. However, the HNR/NR vulcanizate at 50/50 wt ratio showed the maximum ultimate elongation corresponding to a co-continuous morphology as attested to by scanning electron micrographs. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2813–2821, 2009

Key words: vulcanization; mechanical properties; blending; natural rubber; hydrogenated natural rubber

INTRODUCTION

Natural rubber (NR) is the one of important materials that can be used in various industries for the following reasons: superior building tackiness, high strength and resilience, good tear resistance, and excellent dynamic properties.[1] Because of its high degree of carbon–carbon double bond, NR is deteriorated when it is exposed to sunlight, ozone, and oxygen.[2] Hydrogenation has been applied for reducing the unsaturation level providing greater stability against thermal and oxidative degradation.[3] With almost complete saturation, the backbone structure of NR was changed from *cis*-1,4-polyisoprene to an alternating ethylene-propylene copolymer.[4] It has been shown that its initial and maximum decomposition temperatures were close to those of ethylene–propylene–diene rubber (EPDM) with 9.5% diene content.[5] Since hydrogenated natural rubber (HNR) is prepared from NR, which is a sustainable polymer resource, it would be expected to possibly replace the use of EPDM as its price is dependent on the crude oil.

The blending of NR with a highly saturated elastomer such as EPDM is the usual technique to improve the aging resistance of NR. However, the mechanical performance of this blend is poor due to the difference in the unsaturation level between these components, which causes incompatibility and cure-rate mismatch.[6] Many attempts have been made to improve the compatibility of NR/EPDM blends by using compatibilizers. The maleic anhydride modified EPDM (MA-EPDM) and mercapto-modified EPDM (EPDMSH) have been prepared as compatibilizers for NR and EPDM rubbers to obtain improved mechanical properties.[7,8] Moreover, the addition of a third polymeric component such as polybutadiene, chlorinated rubber, chlorosulfonated PE, and polyvinyl chloride has been shown to enhance the compatibility of the NR/EPDM blends.[9]

Besides the use of compatibilizers, the selection of crosslink network types also significantly influences the mechanical properties of the vulcanizates.[10] Generally, there are two main types of rubber vulcanization: peroxide and sulfur vulcanization.[11] The peroxide vulcanization is applied for highly saturated elastomers such as ethylene-propylene rubber (EPR), ethylene-vinyl acetate copolymers (EVA), and silicone rubber.[12] The accelerated sulfur vulcanization, which

is classified as conventional vulcanization (CV) and efficient vulcanization (EV) is usually appropriate for unsaturated rubbers such as NR, polybutadiene (PB), nitrile rubber (NBR), and styrene-butadiene rubber (SBR).[4] Some researchers have studied the effect of the combination of sulfur and peroxide vulcanization on the rubber blends containing two polymeric materials with different unsaturation levels. Tobing[2] reported that a cure system consisting of sulfur and peroxide curatives, catalyzed by mercaptobenzothiazole disulfide (MBTS) and diphenylguanidine (DPG), exhibited a two-fold improvement in the tensile strength of the NR/EPDM vulcanizates with excellent thermal and ozone resistance without the addition of any antioxidant. Nair et al.[13] studied the effect of cure systems on the mechanical properties of EPDM/SBR. It was also found that the rubber blends vulcanized by a sulfur-peroxide cure system showed better stress-strain behavior, tensile strength and elongation at break including tear strength. Radhakrishnan et al.[14] also observed that the sulfur-peroxide cure system gave the shortest cure time for SBR/poly(ethylene-co-vinyl acetate) blends. In addition, the combination of sulfur and peroxide vulcanization could be employed for the blends consisting of rubbers with dissimilar polarity. It was found that the tear strength of SBR/NBR vulcanizates cured by sulfur-peroxide vulcanization was higher than that cured by only peroxide vulcanization.[15]

The aim of this work was to prepare and characterize the HNR/NR blends vulcanized by using peroxide as a co-crosslinking agent in the conventional (CV) and efficient (EV) vulcanizations. The cure characteristics and mechanical properties such as tensile strength, ultimate elongation, and hardness were investigated.

EXPERIMENTAL

Materials

NR (STR-5L) was purchased from Romphotiyoke (Samutsakorn, Thailand). Toluene provided from Fischer Scientific (Leicestershire, UK) was reagent grade and was used as received. 3-Chloropropionic acid (3-CPA) was obtained from Fluka Chemie GmbH (Buchs, Switzerland). The 99.99% oxygen-free hydrogen gas was supplied by Praxair. (Samutprakarn, Thailand). $OsHCl(CO)(O_2)(PCy_3)_2$ used as catalyst for hydrogenation was prepared in our laboratory following the procedure described by Esteruelas et al.[16,17]

The rubber chemicals for the vulcanization process such as stearic acid from Imperial Industrial Chemicals (Thailand) (Pathumthani, Thailand), zinc oxide and sulfur powder from Pan Innovation (Bangkok, Thailand), N-cyclohexylbenzothiazole-2-sulfenamide (CBS) and tetramethylthiuram disulfide (TMTD) from Flexsys (Monsanto) (Cologne, Germany) and dicumyl peroxide (DCP) from Petch Thai Chemical (Bangkok, Thailand) were all commercial grade. Ethylene-propylene rubber (EPDM) of Nordel IP grade (5.0 wt % diene content) obtained from DuPont Dow Elastomers (Wilmington, DE) was used for the properties comparison.

Preparation of HNR

The hydrogenation of NR was carried out in a 2-L Parr reactor. A specific amount of NR ($\sim$ 612.7 mM) was dissolved in 1,200 mL of toluene in the dark. The small amount of 3-CPA (5 mM) was added into the rubber solution to enhance the hydrogenation rate as described in the previous report.[5] The catalyst was weighed ($\sim$ 105.8 μM) into a small glass bucket, and placed in the catalyst addition port within the reactor head. After assembling the reactor, the system was purged by passing hydrogen gas at 14 bar through the rubber solution for 45 min with a 600 rpm of agitation speed. Heating was then initiated and stabilized at 140°C. The catalyst was charged into the rubber solution using hydrogen pressure at 27.6 bar for 1–4 h depending on the desired hydrogenation level. The hydrogenated product was isolated by precipitation in ethanol and then dried under vacuum. The degree of hydrogenation was evaluated by ^{1}H-NMR-spectroscopy.

The molecular weights and polydispersity of NR and HNR were analyzed by using gel permeation chromatography (GPC) consisting of Waters 1515 Programmable HPLC pump and Waters 2414 refractive index detector. Tetrahydrofuran (THF) was used as mobile phase at a flow rate of 1 mL/min. It was found that the molecular weight ($\overline{Mw}$) of NR was 1.76×10^6 g/mol with polydispersity of 3.50; while HNR (>95% hydrogenation) had $\overline{Mw}$ and polydispersity as 1.43×10^6 g/mol and 2.65, respectively.

Preparation of rubber blends and vulcanizates

The preparation of HNR/NR blends was performed using a two-roll mixing mill at room temperature to avoid the overcure of NR in the rubber blends. NR was masticated for 2 min and then HNR was subsequently added. After the homogenization of the rubber blend ($\sim$ 5 min), the chemicals for vulcanization were added. The processing time after each component addition was $\sim$ 2 min. The compound recipes for blending are given in Table I. For the blends of HNR (>95% hydrogenation) and NR at 50/50 wt ratio, the three vulcanization systems such as peroxide (PV) and combination cure systems: conventional vulcanization with peroxide (CPV) and efficient vulcanization with peroxide (EPV) were employed. The

TABLE I
Formulation of Vulcanization Systems

Ingredients (phr)	Vulcanization systems		
	PV	CPV	EPV
HNR/NR	50/50	50/50	0/100, 25/75, 50/50, 75/25, and 90/10
EPDM/NR	–	–	0/100, 25/75, 50/50, 75/25, and 90/10
Zinc oxide	–	3	3
Stearic acid	–	1.5	1.5
CBS	–	0.7	0.7
DCP	1 and 2	1 and 2	1 and 2
TMTD	–	–	1.5
Sulfur	–	3	–

phr, parts per hundred of rubber by weight.

rheometric characteristics of blends such as minimum torque (ML), maximum torque (MH), scorch time (ts$_2$), and optimum cure time (tc$_{90}$) were measured by using an Oscillating Disk Rheometer (ODR, Techpro Model 121105) at 150°C. Subsequently, the blends were vulcanized in an electrically heated compression mold at 150°C at the optimum cure time.

Crosslink density determination

For the crosslink density of vulcanizates, the specimens (10 × 10 × 2 mm^3) were accurately weighed (w) and then immersed in toluene in closed vessels for a week. After wiping the surface of the specimens, they were quickly weighed (w_1) and dried at 40°C for 48 h and weighed again (w_2). The volume fraction of the specimens was calculated by eq. (1):

$$v = \frac{w_2(\delta_r)^{-1}}{w_2(\delta_r)^{-1} + (w_1 - w_2)(\delta_s)^{-1}} \quad (1)$$

where v is the volume fraction of polymer in the swollen mass, δ_r and δ_s are the rubber and solvent densities, respectively.[8] The crosslink density of the specimens was calculated following Flory-Rhener equation [eq. (2)]:

$$-\left[\ln(1-v) + v + \chi v^2\right] = V_0 n\left[v^{1/3} - \frac{v}{2}\right] \quad (2)$$

where V_0 is the molar volume of the solvent (106 cm^3/mol for toluene) and χ is the Flory-Huggins polymer-solvent interaction term (0.39 for toluene).[18]

Mechanical properties and morphology analysis of vulcanizates

The mechanical properties in terms of tensile strength, ultimate elongation, and hardness of vulcanizates were evaluated. The tensile properties of all vulcanized rubber samples were examined following ASTM D 412 using a dumbbell-shape specimen. A Universal Testing Machine (LLOYD model LR5K) was used at 500 mm/min of the cross-head speed. The average of three specimens was considered as the representative value. The shore hardness measurement of the specimens was measured according to ASTM D 2240 using a type A Durometer.

To investigate the morphology of the samples, the tensile fracture surfaces of rubber blends were characterized using scanning electron microscopy (SEM). The fracture surfaces after tensile testing were cut and stitched on a SEM stub using double-sided tape. The samples were then sputter-coated with gold and examined using an electron microscope, JEOL model JSM-6480 LV, operated at 15 kV.

RESULTS AND DISCUSSION

Cure characteristics

The rheometric characteristics of the HNR/NR blends are presented in Tables II, III, and Figure 1. The coding of rubber compounds in Tables II and III represents the vulcanization system, DCP content, and wt ratio of the rubber blend. For example, the blend vulcanized by the EPV system is designated as EP$_2$H$_{50}$ where EP is the efficient vulcanization with peroxide, and its subscript indicates the content of DCP in units of phr. H means HNR with higher 95% degree of hydrogenation and its subscript shows the weight percentage of HNR in the blend; while EPDM used for the comparison of mechanical properties is represented by E. For example, EP$_2$E$_{25}$ implies an EPDM/NR blend with a 25/75 wt ratio vulcanized by EPV system using 2 phr of DCP.

The effect of the vulcanization systems on the cure behavior of HNR/NR blends at a wt ratio of 50/50 is presented in Table II. The minimum and maximum torques of blends from three vulcanization systems increased with increasing DCP content because

TABLE II
Effect of Vulcanization Systems and Hydrogenation Level of HNR on Cure Characteristics of HNR/NR Blends at 50/50 wt Ratio

Sample code	Minimum torque (ML, dNm)	Maximum torque (MH, dNm)	Scorch time (ts$_2$, min)	Optimum cure time (tc$_{90}$, min)
P$_1$H$_{50}$	9.83	51.2	2.75	24.2
P$_2$H$_{50}$	10.9	76.4	1.96	22.1
CP$_0$H$_{50}$[a]	5.50	81.0	6.15	10.8
CP$_1$H$_{50}$	6.04	85.4	3.29	10.2
CP$_2$H$_{50}$	6.88	89.5	2.50	9.71
EP$_0$H$_{50}$[b]	6.55	54.8	4.29	9.79
EP$_1$H$_{50}$	6.88	61.4	3.04	12.2
EP$_2$H$_{50}$	9.74	65.3	2.67	14.9
EP$_2$H$_{50\ (83\%)}$[c]	8.98	61.1	3.13	17.2
EP$_2$H$_{50\ (75\%)}$	8.73	47.9	2.96	20.2
EP$_2$H$_0$ (NR)	5.29	47.7	3.25	20.2

[a] CV system.
[b] EV system.
[c] The hydrogenation level is in a parenthesis.

the rigid C—C crosslinking structure obtained from peroxide vulcanization promoted the higher resistance to the rheometric torque.[14] The rheograph for the HNR/NR blends cured by various vulcanization systems containing 2 phr of DCP is shown in Figure 1(a). The vulcanizates obtained from the CPV system exhibited a comparatively higher maximum torque due to the combination of C—C and polysulfidic crosslinking which possibly produces the high crosslink density. Whereas, the short chains of the C—C bond from pure peroxide and monosulfidic linkage generated from TMTD in EPV system showed the lower value according to the limitation of chain orientation that caused the low rheometric torque resistance. The scorch time (ts$_2$) of blends for all vulcanization systems tended to decrease with an increasing amount of peroxide. For both peroxide and CPV systems, the optimum cure time (tc$_{90}$) of blends was also reduced when the DCP content increased. Similar results were also observed by

Manix[19] which showed that the rate of NR vulcanization accelerated by CBS could be enhanced in the presence of DCP. However, the rheometric results indicated that vulcanization by the EPV system required a longer tc$_{90}$. It could be explained by using the possible reaction postulated by Das et al.[20] The cumyloxy radicals (P*) generated by the thermal dissociation of DCP react with the rubber chain to produce the effective crosslinking site (R*) as shown in eqs. (3) and (4). Some portion of DCP and R* was sacrificed by directly combining with thiuram radicals dissociated from TMTD as shown in eqs. (5)–(7).
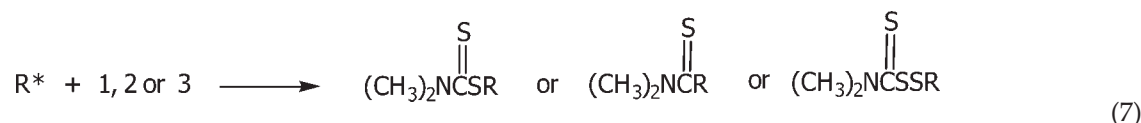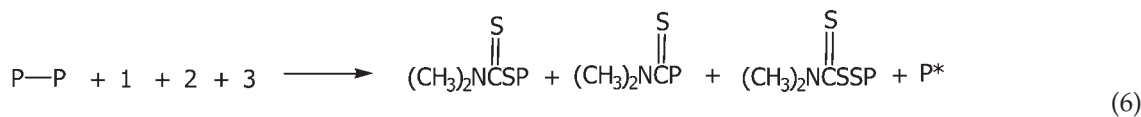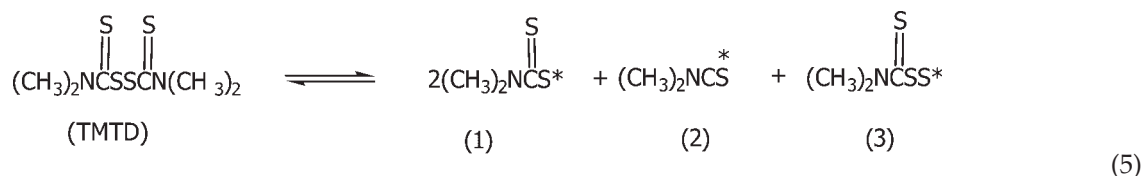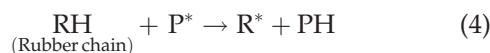
$$P{-}P \rightleftharpoons 2P^* \quad (DCP) \tag{3}$$

$$\underset{\text{(Rubber chain)}}{RH} + P^* \rightarrow R^* + PH \tag{4}$$

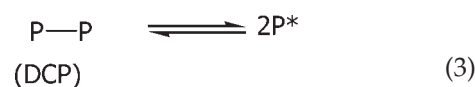$$\tag{5}$$

$$\tag{6}$$

$$\tag{7}$$

TABLE III
Effect of HNR and EPDM Contents on the Cure Characteristics of Blends[a]

Blend ratio	Sample code	Minimum Torque (ML, dNm)	Maximum Torque (MH, dNm)	Scorch time (ts$_2$, min)	Optimum cure time (tc$_{90}$, min)
NR	EP$_2$H$_0$	5.29	47.7	3.25	20.2
HNR/NR	EP$_2$H$_{25}$	4.87	65.0	3.17	17.8
	EP$_2$H$_{50}$	9.74	65.3	2.67	14.9
	EP$_2$H$_{75}$	10.7	68.7	2.58	12.7
	EP$_2$H$_{90}$	38.6	70.3	2.88	17.0
EPDM/NR	EP$_2$E$_{25}$	4.95	41.3	3.63	19.3
	EP$_2$E$_{50}$	8.90	40.2	3.08	19.9
	EP$_2$E$_{75}$	9.40	34.2	4.25	22.4
	EP$_2$E$_{90}$	11.1	39.6	5.00	24.2

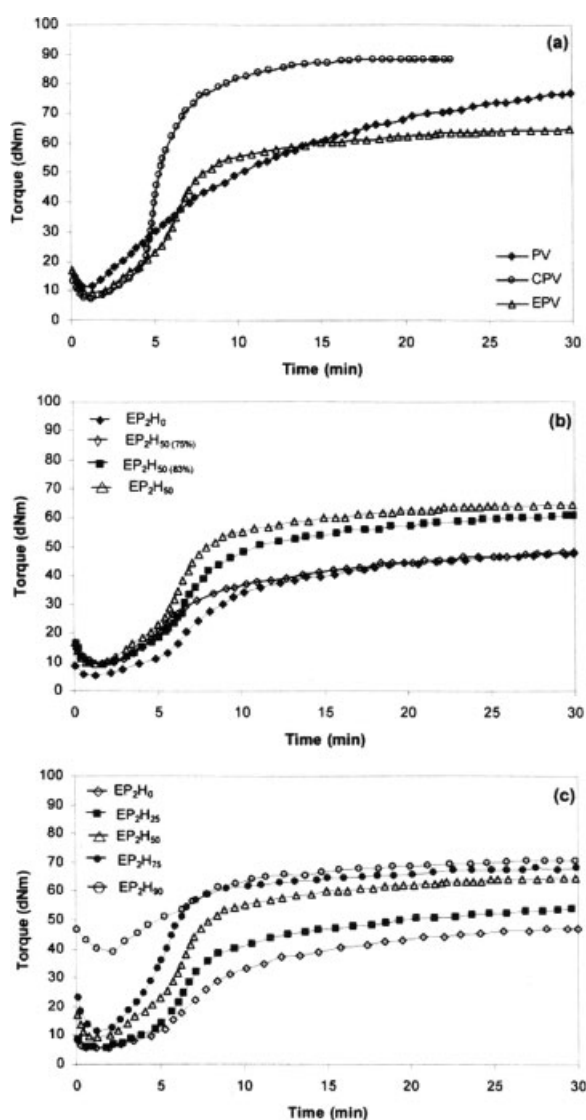[a] Blends cured by EPV system using 2 phr of DCP.

Figure 1 Rheographs of HNR/NR blends: (a) Effect of vulcanization systems with 2 phr of DCP at 50/50 wt ratio of HNR/NR (>95% hydrogenation); (b) Effect of hydrogenation level of HNR vulcanized by EPV system using 2 phr of DCP at 50/50 wt ratio of HNR/NR and (c) Effect of HNR/NR blend ratio with >95% hydrogenation vulcanized by EPV system using 2 phr of DCP.

The cure behavior of the blends containing HNR at various hydrogenation levels obtained from the EPV system is shown in Figure 1(b). The minimum and maximum torques of HNR/NR blends was higher than that of the NR vulcanizates (EP$_2$H$_0$) due to the less flexibility of the saturated chain of HNR. The HNR/NR blends also showed the decrease in tc$_{90}$ when the level of hydrogenation in the blends increased. This implied that the lower content of C=C in the blends induced the higher rate of vulcanization. For the effect of blend ratio (Table III), the tc$_{90}$ also decreased with increasing HNR content from 25 to 75 parts in blends; while, the tc$_{90}$ of EPDM/NR blends cured by the same vulcanization system tended to be increased with increasing EPDM content. Similar results were also observed for EPDM/SBR blends.[13] It is possible that the remaining unsaturation C=C in the backbone structure of HNR has a higher reactivity for vulcanization than that of EPDM. From Figure 1(c), the EP$_2$H$_{90}$ with a small amount of NR had a comparatively long tc$_{90}$ (17 min) and the highest minimum torque. It can be explained that the small portion of NR in the blend was prematured by both TMTD and DCP; whereas the predominant HNR phase was subsequently cured by only DCP. Therefore, this blend with high HNR content had the highest minimum torque and required longer tc$_{90}$ to complete the vulcanization. Similar results were also observed in blends cured by peroxide vulcanization (P$_1$H$_{50}$ and P$_2$H$_{50}$) as presented in the Table II.

Mechanical properties of NR/HNR blends

Effect of vulcanization systems and hydrogenation levels

The mechanical properties of HNR/NR blends at 50/50 wt ratio containing > 95% hydrogenation vulcanized by various cure systems are presented in Table IV. Without the addition of DCP, the vulcanizates obtained from the conventional vulcanization

TABLE IV
Effect of Cure Systems and Hydrogenation Level on the Mechanical Properties of HNR/NR Blends at 50/50 wt Ratio

Sample code	Tensile strength (MPa)	Ultimate elongation (%)	Hardness	Crosslink density ($\times 10^4$ mol/cm^3)
P_1H_{50}	4.19 (0.2)	565 (17)	33.5 (0.5)	0.57 (0.03)
P_2H_{50}	3.53 (0.6)	361 (48)	43.5 (0.4)	1.72 (0.01)
CP_0H_{50}	3.69 (0.5)	375 (19)	46.2 (0.4)	2.41 (0.06)
CP_1H_{50}	2.40 (0.2)	328 (20)	43.6 (0.3)	2.57 (0.11)
CP_2H_{50}	2.53 (0.1)	292 (11)	45.4 (1.0)	2.74 (0.14)
EP_0H_{50}	2.87 (0.1)	682 (58)	40.2 (0.3)	0.51 (0.00)
EP_1H_{50}	6.80 (0.1)	1150 (12)	42.7 (0.6)	0.67 (0.04)
EP_2H_{50}	7.54 (0.2)	1005 (14)	44.7 (0.6)	1.04 (0.03)
$EP_2H_{50\ (83\%)}$	8.91 (1.1)	715 (59)	39.4 (1.0)	1.34 (0.05)
$EP_2H_{50\ (75\%)}$	7.99 (0.1)	716 (25)	36.5 (0.7)	1.29 (0.09)
EP_2H_0 (NR)	15.2 (0.5)	717 (39)	34.0 (0.0)	1.11 (0.05)

Standard deviation values are given in the parenthesis.

(CP_0H_{50}) had the higher tensile strength and hardness than that cured by the efficient vulcanization (EP_0H_{50}). It can be explained that the vulcanizates cured by the conventional vulcanization normally have higher crosslink density than that cured by the efficient vulcanization. Thus, the samples vulcanized by the conventional system exhibited higher tensile strength with lower ultimate elongation. Rattanasom et al.[10] reported a similar behavior for NR/tire tread reclaimed rubber blends. However, the tensile strength of vulcanizates cured by conventional or efficient vulcanization was very low due to the cure-rate mismatch effect resulting from the imbalance of unsaturation of these rubbers as described in the previous work.[6] For the addition of only DCP, the samples (P_1H_{50}, P_2H_{50}) also exhibited lower tensile strength and breaking strain as the network structure of vulcanizates cured by DCP has rigid C—C bonds, which are easily damaged under an applied stress.[14]

When DCP was added as the co-curative in CPV and EPV systems, the vulcanizates cured by the EPV system (EP_1H_{50} and EP_2H_{50}) showed higher tensile strength and ultimate elongation than the ones cured with the CPV system. The stress-strain behavior of vulcanizates cured by PV, CPV, and EPV systems using 2 phr of DCP is illustrated in Figure 2. The initial modulus of HNR/NR vulcanizates cured by CPV system was slightly higher than those cured by other vulcanization system due to the higher crosslink density generated from both sulfur and DCP in the NR phase of the blends. However, the vulcanizate cured by EPV clearly exhibited the soft and tough behavior with higher stress and ultimate elongation than that cured by PV and CPV. It can be explained that the cure rate obtained from sulfur vulcanization of the unsaturated elastomer is normally faster than that of the saturated elastomer. Therefore, the addition of DCP in efficient vulcaniza-

tion may retard the reactivity of TMTD for curing NR and decrease the crosslink density of the blend as described earlier. Consequently, the cure-rate mismatch due to the imbalance in unsaturation levels of the HNR and NR was reduced to give better mechanical properties. Whereas, the addition of DCP in the conventional vulcanization (CP_1H_{50} and CP_2H_{50}) decreased the optimum cure time of the blends as shown in Table III. This may cause the prematurity of NR to result in the lower tensile properties of vulcanizates. A possible schematic representation of the network crosslink obtained from various vulcanization systems is given in Figure 3.

For the effect of the hydrogenation level of HNR, the tensile strength of HNR/NR vulcanizates was not significantly affected by the change of the hydrogenation level of HNR (Table IV). It might be related to the glass transition temperature (T_g) of rubbers. From the previous works, the glass transition temperature of NR (ca. $-63°C$) was not significantly changed with an increasing level of hydrogenation
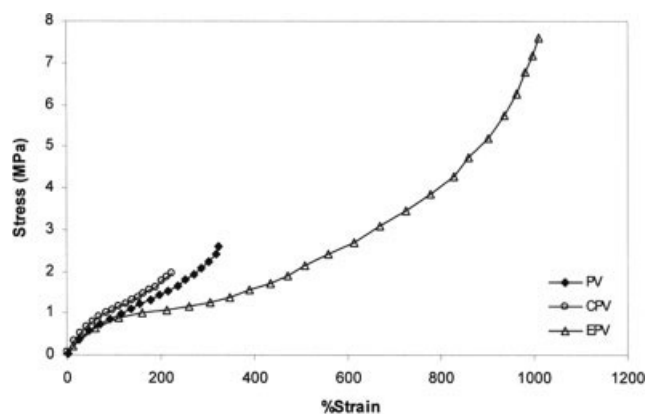

Figure 2 Stress-strain behaviors of HNR/NR vulcanizates cured by various vulcanization systems using 2 phr of DCP.
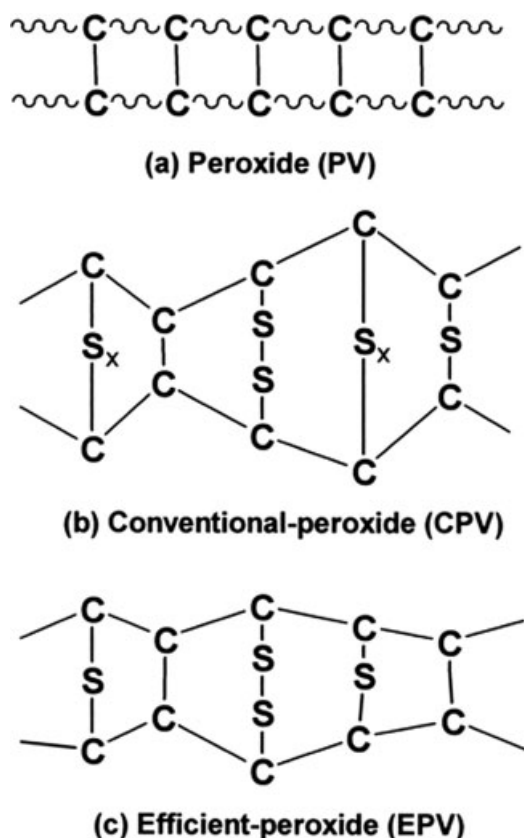
(a) Peroxide (PV)

(b) Conventional-peroxide (CPV)

(c) Efficient-peroxide (EPV)

Figure 3 A possible schematic representation of network crosslink obtained from various vulcanization systems.

from 38 to 100% ($T_g \approx -63°C$ to $-60°C$).[5,21] Thus, the HNR product still has a high rubbery property, which retains the same tensile strength at any hydrogenation level. However, it was found that the HNR/NR blends with > 95% hydrogenation at 50/50 wt ratio cured by EPV system exhibited the highest ultimate elongation due to the low crosslink density. Thus, the HNR/NR blend at this ratio was the soft and tough material at any hydrogenation level. This phenomenon will be explained by SEM micrograph in a later section of this article. For the hardness property, it was found that the hardness of the vulcanizates tends to increase with increasing level of the hydrogenation of HNR due to the reduction of the flexible C=C bonds in the blends.

Effect of rubber blend ratio

The mechanical properties of vulcanizates at various contents of HNR (>95% hydrogenation) in the blends were investigated. The results of HNR/NR blends were also compared with that of EPDM/NR vulcanizates as shown in Figure 4. From Figure 4(a), the tensile strength of HNR/NR vulcanizates decreased when the HNR content increased similar

to the increase in EPDM content in EPDM/NR blends. This suggests that both HNR and EPDM are incompatible with NR due to the imbalance in the unsaturation level; although, T_g of HNR is closer to that of NR than EPDM ($T_g = -43°C$). However, the addition of peroxide as the co-curative with the sulfur donor in the efficient vulcanization can improve the mechanical properties of the blends consisting of two dissimilar elastomers by possibly reducing the effect of cure-rate mismatch as described earlier. Therefore, the EPV system gave tensile strengths of
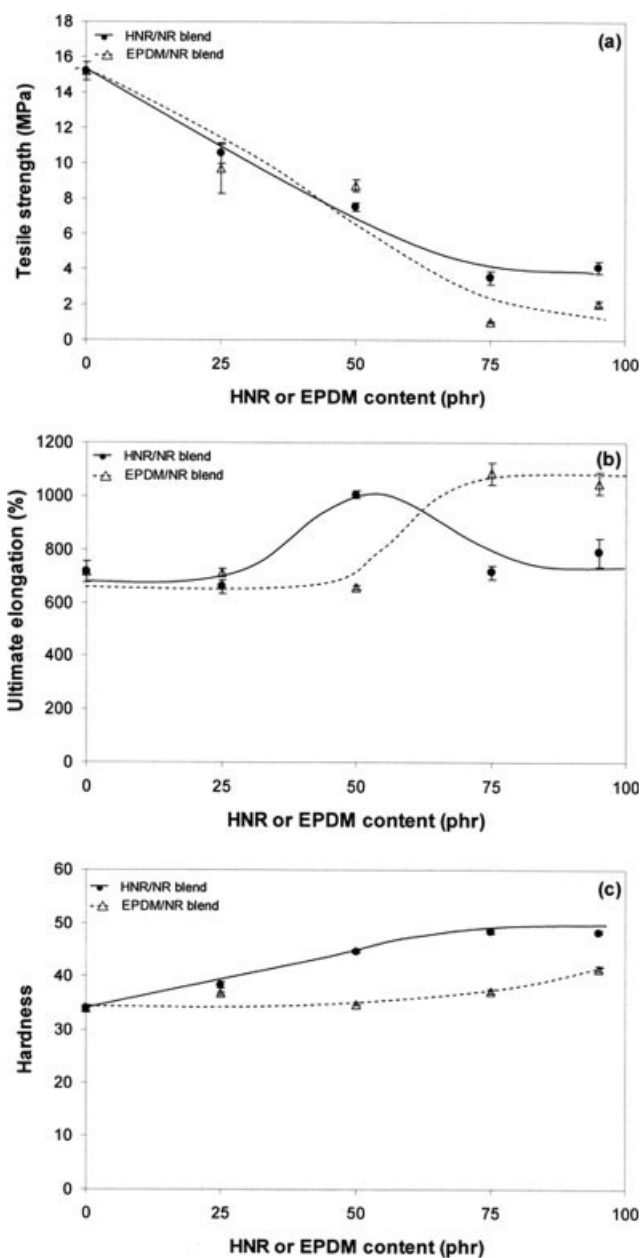

Figure 4 Effect of rubber blend ratios on the mechanical properties of vulcanizates cured by EPV system using 2 phr of DCP: (a) Tensile strength; (b) Ultimate elongation, and (c) Hardness.
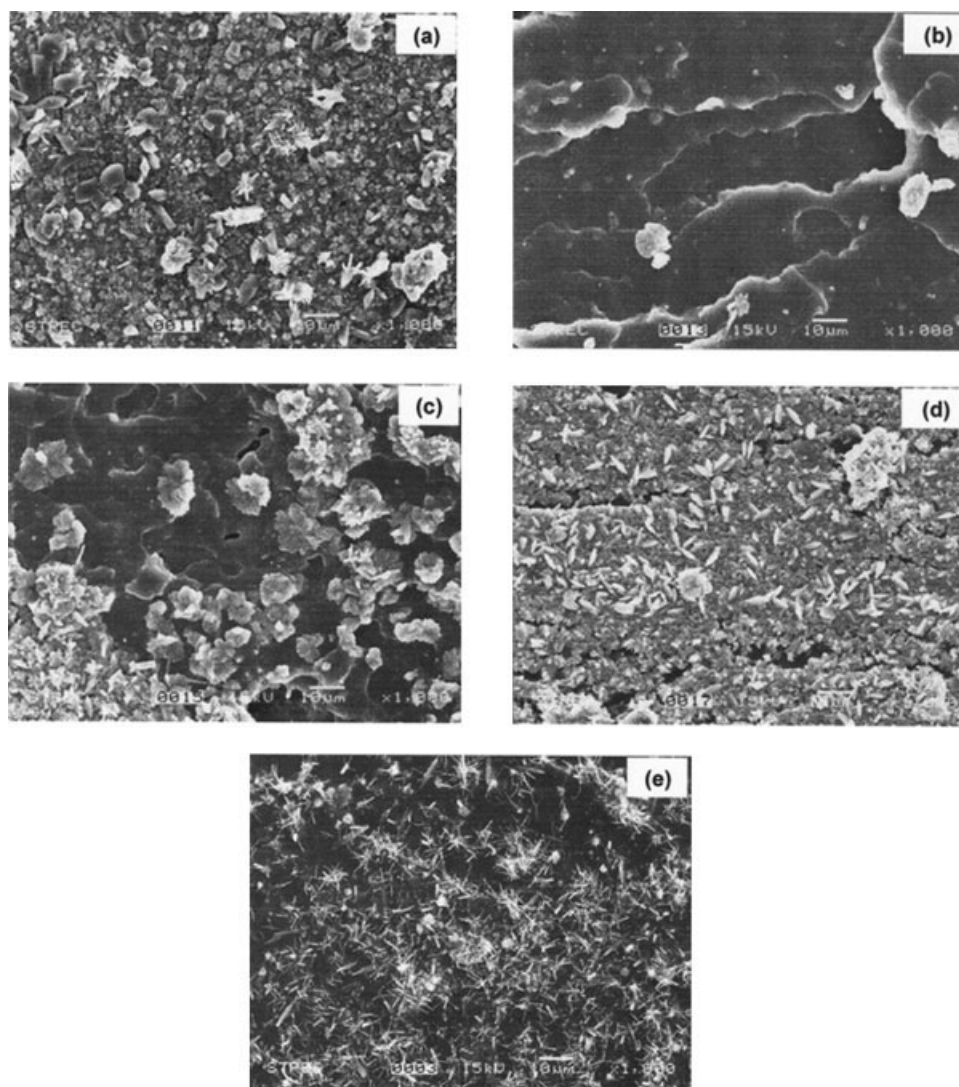
Figure 5 Scanning electron micrograph of tensile fracture surface of vulcanizates at various rubber blend ratios cured by EPV system using 2 phr of DCP: (a) HNR/NR = 25/75; (b) HNR/NR = 50/50; (c) HNR/NR = 75/25; (d) HNR/NR = 90/10, and (e) EPDM/NR = 50/50 (×1000 Magnification).

the HNR/NR and EPDM/NR vulcanizates as high as the vulcanizates containing bis(diisopropyl)thiophosphoryl disulfide (DIPDIS) as a coupling agent accelerator in the two-stage vulcanization of EPDM/NR blends.[6]

Figure 4(b) shows the effect of HNR and EPDM content on the ultimate elongation of the vulcanizates. The HNR/NR vulcanizates at 50/50 wt ratio had a maximum ultimate elongation at ∼ 1000%. It can be explained that the vulcanizates exhibited a synergistic effect due to the compatibility of the different morphology of HNR and NR at a ratio of 50/50. This result was also confirmed by the SEM micrograph discussed in following section. When HNR loading in the blends was increased to 75 and 90 phr, the ultimate elongation decreased and leveled off at ∼ 750% due to the higher incompatibility involving the phase separation. For EPDM/NR

vulcanizates, the elongation at break of the vulcanizate increased with increasing EPDM content and then leveled off at EPDM content higher than 75 phr. This might be due to the loss of crosslinking density which results in the low tensile strength and high ultimate elongation at high EPDM content.

The hardness of HNR/NR vulcanizates compared with EPDM/NR vulcanizates is illustrated in Figure 4(c). The hardness of both vulcanizates tends to increase with an increasing amount of saturation of the elastomers in the blends. Thus, the more flexible NR replaced by the less flexible HNR or EPDM resulted in the higher hardness of rubber vulcanizates.

Morphology of HNR/NR vulcanizates

The tensile fracture surface of vulcanizates visualized by using SEM technique is shown in Figure 5.

At a 25/75 wt ratio of HNR/NR vulcanizates [Fig. 5(a)], the morphology of the fracture surface shows uniform globular shape of NR, which is the domain phase at this blend composition. However, it was observed that the small particles of HNR were dispersed in the NR phase. This could result in the reduction of tensile strength. For the HNR/NR blend at 50/50 wt ratio, the SEM micrograph suggests the morphology of the continuous phase with homogeneity that resulted in the enhancement of the ultimate elongation. Hussen et al.[22] reported that a hydrogenated acrylonitrile-butadiene rubber (HNBR)/NBR blend at 50/50 wt ratio also exhibited the co-continuous morphology which resulted in an increase in stress at high strains. On comparing with the EPDM/NR blend at a 50/50 wt ratio as shown in Figure 5(e), incompatibility between two dissimilar elastomers was observed. Thus, the ultimate elongation of the EPDM/NR blend was lower than that of the HNR/NR blend at the same composition. When the HNR loading was increased to 75 and 90 phr as shown in Figure 5(c,d), SEM micrographs indicate the noncoherency between NR and HNR. Thus, the non-homogeneous fracture surface confirmed the poorer mechanical properties of HNR/NR vulcanizates at high loading of HNR.

CONCLUSIONS

In this work, the appropriate vulcanization for HNR/NR blends was the EPV system, which involved a combination of peroxide and the sulfur donor, TMTD as the curatives for the efficient vulcanization. The HNR/NR vulcanizates at 50/50 wt ratio cured by this vulcanization system exhibited improved mechanical properties. The addition of DCP in the efficient vulcanization possibly retarded the reactivity of TMTD for curing NR in the blend; consequently, the cure-rate mismatch due to the imbalance in unsaturation levels of the HNR and NR was reduced. For the effect of hydrogenation level of HNR in HNR/NR blends, the increase in hydrogenation level did not affect the tensile strength of the vulcanizates, but the hardness of samples increased with increasing hydrogenation level due to the reduction of the flexible C=C in the blends. For the effect of rubber blend ratio, an increase in the amount of HNR or EPDM in the blends caused a reduction of tensile strength; while,

the hardness of vulcanizates increased. For the SEM micrograph of the HNR/NR blend at 50/50 wt ratio, the co-continuous morphology supported the maximum value of ultimate elongation. A HNR content of 75 and 90 phr in the blends resulted in poorer mechanical properties because of the higher incompatibility between the two dissimilar saturation levels of these elastomers.

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