Hydrogenated Natural Rubber Blends: Aspect on Thermal Stability and Oxidative Behavior

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ABSTRACT: Hydrogenated natural rubber (HNR) prepared from natural rubber (NR) is a new sustainable elastomer with excellent thermal properties. This study reports on the effect of vulcanization system and blend ratio on the thermal and oxidative resistance of HNR/NR vulcanizates. The various HNR/NR ratios vulcanized by peroxide and sulfur donor system exhibited the highest retention of tensile strength after thermal aging due to the formation of zinc-dimethyldithiocarbamate (ZDMDC) which is an efficient antioxidant. The results from thermogravimetric analysis (TGA) indicated that the saturated structure of HNR had higher decomposition temperature and activation energy to enhance the thermal stability of HNR/NR vulcanizates. The initial and maximum decomposition temperatures of NR and HNR phases in vulcanizates were not affected by rubber blend ratio. This suggests that the decomposition pattern of HNR has no influence on another constituent. The increase in HNR content in the blends could retard the ozonolysis resulting in the surface cracking attacked by ozone. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1566–1575, 2009

Key words: thermal properties; thermogravimetric analysis (TGA), activation energy; hydrogenated natural rubber; ozone resistance

INTRODUCTION

Natural rubber (NR) is well known as a highly valuable biomaterial which has superior building tackiness, high strength and resilience, good tear resistance, and excellent dynamic properties.[1] However, NR can be deteriorated by sunlight, ozone, and oxygen because of its high unsaturation level.[2] Blending of two or more existing elastomers has been a commercial technique to achieve the new materials with desired properties. The incorporation of NR with a highly saturated elastomer such as ethylene–propylene diene rubber (EPDM) results in the significant improvement in the thermal and oxidative resistance of the rubber blend.[3,4] Because the cost of plastics and synthetic elastomers including EPDM is directly related to the price of petroleum which is the raw material for the polymerization, considerable interest has arisen to use NR or modified NR as a possible substitute for synthetic rubbers.[5]

To improve the properties, in terms of thermal and weathering resistance, of unsaturated elastomers such as styrene–butadiene rubber (SBR) and nitrile rubber (NBR), hydrogenation has been applied to reduce the unsaturation level of these diene-based elastomers to obtain greater stability against thermal and oxidative degradation.[6–8] Also, there have been many reports on the hydrogenation of NR by using catalytic and non-catalytic methods.[9–12] It has been shown that the structure of NR is changed from *cis*-1,4-polyisoprene to an alternating ethylene–propylene copolymer upon hydrogenation, which has higher thermal stability without affecting the inherent glass transition temperature of NR.[11–13] Although the kinetics of NR hydrogenation and thermal properties of hydrogenated NR (HNR) have been investigated, there are few literature reports on the measurement of any technological properties of HNR vulcanizates and rubber blends containing HNR. Inoue and Nishio[14] studied NR hydrogenation catalyzed by RhCl(PPh$_3$)$_3$ at 70–80°C and 100% hydrogenation was achieved within 96 h. For their HNR materials,

the mechanical properties of the HNR vulcanizates after aging were higher than NR and EPDM vulcanizates. In addition, the ozone and abrasion resistances of HNR vulcanizates were also higher than those of NR and EPDM. Therefore, HNR is expected to have use as a sustainable material for replacing the use of EPDM in the rubber blends containing diene-based elastomers. In our earlier work, the effect of the vulcanization system on the mechanical properties of HNR/NR blends was investigated.[15] The combination of peroxide and a sulfur donor vulcanization system resulted in the improved mechanical properties of the blends. It was believed that the peroxide possibly retarded the reactivity of the sulfur donor for curing NR in the blend to reduce the cure-rate mismatch due to the imbalance in unsaturation levels of the HNR and NR.

For product application, the HNR/NR blend is more desirable than the HNR due to the high mechanical properties of NR. However, the thermal and ozone stability of HNR/NR blends has not been reported. The objective of this present study is to investigate the effect of vulcanization systems and blend ratio on the thermal and ozone resistance of blends. To fully understand the environmental stability of blends at service conditions, thermogravimetric analysis (TGA) was employed to determine the upper temperature limit including the kinetic parameters and activation energy of the thermal decomposition.

EXPERIMENTAL

Materials

NR (STR-5L) was purchased from Romphotiyoke Co., Ltd. (Samutsakorn, Thailand). Reagent grade toluene and 3-chloropropionic acid (3-CPA) was obtained from Fischer Scientific Ltd. (Leicestershire, UK) and Fluka Chemie GmbH (Buchs, Switzerland), respectively. Oxygen-free hydrogen gas (99.99%) was supplied by Praxair Inc. (Samutprakarn, Thailand). The hydrogenation catalyst, OsHCl(CO)(O$_2$)(PCy$_3$)$_2$, was prepared in our laboratory following the procedure described elsewhere.[16,17] Stearic acid from Imperial Industrial Chemicals (Thailand) Co. Ltd. (Pathumthani, Thailand), zinc oxide and sulfur powder from Pan Innovation Ltd. (Bangkok, Thailand), N-cyclohexylbenzothiazole-2-sulfenamide (CBS) and tetramethylthiuram disulfide (TMTD) from Flexsys (Monsanto) (Cologne, Germany), and dicumyl peroxide (DCP) from Petch Thai Chemical Co. Ltd. (Bangkok, Thailand) were all commercial grade. EPDM of Nordel IP grade with 5.0 wt % diene content was obtained from DuPont Dow Elastomers (Wilmington, USA).

Hydrogenation of NR

The procedure for HNR preparation has been described in previous literatures.[11,15] A specific amount of NR (ca. 612.7 mM) dissolved in 1,200 mL of toluene with a small amount of 3-CPA (5 mM) was hydrogenated in a 2-L Parr reactor. OsHCl(CO)(O$_2$)(PCy$_3$)$_2$ used as a hydrogenation catalyst was weighed (ca. 105.8 μM) into a small glass bucket and placed in the catalyst addition port within the reactor head. After assembling the reactor and purging the system by using hydrogen gas to remove oxygen, heating was initiated and the system was stabilized at 140°C under an agitation speed of 600 rpm. The catalyst was then charged into the rubber solution using hydrogen pressure at 27.6 bar for 4 h to achieve >95% hydrogenation. The hydrogenated product was precipitated in ethanol and then dried under vacuum. The degree of hydrogenation was evaluated by ^{1}H-NMR-spectroscopy.

The molecular characterization of NR and HNR was performed on a gel permeation chromatograph (GPC) equipped with a Waters 1515 Programmable HPLC pump and a Waters 2414 refractive index detector. A Styragel® HR column (7.8 mm i.d. × 300 mm) was used for the measurement with 1 mL/min tetrahydrofuran as a mobile phase at 40°C. The quantity of injected rubber solution was 100 μL at a concentration of 0.1% (w/v). The results indicated that HNR with >95% hydrogenation had a molecular weight ($\overline{M_w}$) and polydispersity of 1.43 × 10^6 g/mol and 2.65, respectively. The $\overline{M_w}$ of HNR was lower than that of NR (1.76 × 10^6 g/mol) possibly due to the hydrogenation conditions operated under high reaction temperature and long reaction time resulting in the chain scission.

Preparation of HNR/NR vulcanizates

The formulation used for the preparation of the HNR/NR blends is given in Table I. The typical preparation of HNR/NR blends was described in previous literature.[15] To avoid the overcure effect of the NR phase, NR was blended with HNR using a two-roll mixing mill at room temperature. NR was masticated for 2 min before mixing with HNR. When the rubber blend was homogenized (ca. 5 min), the chemicals for vulcanization were added. The processing time after the addition of each component was ca. 2 min. The vulcanization systems applied for curing the blends were peroxide (PV) and two combination cure systems (CPV and EPV). The conventional vulcanization with peroxide (CPV) employed the use of peroxide and sulfur as the curatives; while the efficient vulcanization with peroxide (EPV) used peroxide and a sulfur donor (TMTD) as the vulcanizing agents. The information of cure

TABLE I
Compounding Recipe for HNR/NR Blends

Ingredients (phr)[a]	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	2	0 and 2	0 and 2
TMTD	–	–	1.5
Sulfur	–	3	–

[a] phr = parts per hundred of rubber by weight.

characteristics obtained from an oscillating disk rheometer (ODR, Techpro Model 121,105) at 150°C, such as minimum torque (ML), maximum torque (MH), scorch time (ts$_2$) and optimum cure time (tc$_{90}$) has been reported in the previous research work.[15]

Mechanical properties of HNR/NR vulcanizates before and after thermal aging

The tensile properties before and after thermal aging in air at 100°C for 22 ± 2 h of HNR/NR vulcanizates were investigated. The specimens were cut as a dumbbell shape using a die C according to the standard method ASTM D 412. The tensile properties of all vulcanized rubber samples were carried out on a Universal Testing Machine (LLOYD model LR5K) at 500 mm/min of cross-head speed. The elongation of specimens was detected from the extensometer. The average of three specimens was considered as the representative value.

Determination of crosslink density

The cross-linking efficiency of the specimens was evaluated in terms of crosslink density using an equilibrium solvent swelling test method. The specimens (10 × 10 × 2 mm^3) accurately weighted were immersed in toluene and allowed to swell in closed vessels for 7 days. Then, the surface of the swollen samples was quickly wiped and weighed (w_1). After drying at 40°C for 48 h, the dried rubber samples were weighed again (w_2) to determine the amount of absorbed toluene inside the samples. The volume fraction of polymer in the swollen specimens (υ) was calculated using eq. (1):

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

where δ_r and δ_s are the rubber and solvent densities, respectively.[18] The crosslink density of the specimens was calculated based on the 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 n is the number of elastically active chains per unit volume (mol/cm^3), V_0 is the molar volume of the solvent (106.3 cm^3/mol for toluene) and χ is the Flory-Huggins polymer–solvent interaction term (0.393 for NR-toluene).[19,20]

Thermal decomposition determined using TGA

The decomposition temperature and kinetics of thermal decomposition of NR, HNR (96.4% hydrogenation), and HNR/NR vulcanizates were determined. The analysis of thermogravimetric (TG) and derivative thermogravimetric (DTG) curves was performed on a Perkin–Elmer Pyris Diamond TG/DTA. Samples (3 ± 1 mg) was heated from 40 to 800°C at three heating rates of 2.5, 5, and 10°C/min under a dynamic nitrogen atmosphere flow of 50 mL/min. The initial (T_{id}) and final (T_f) decomposition temperatures was obtained from the intersection of two tangents at the initial and final stages of the decomposition, respectively. The maximum decomposition temperature at maximum weight-loss rate (T_p) was also recorded.

To study the overall kinetics of thermal decomposition, the Kissinger method (differential method) was applied to determine the activation energy (E_a) of the solid state reaction without a precise knowledge of any mechanism of thermal decomposition.[21,22] The Kissinger method proposed employs eq. (3):

$$\ln \frac{\beta}{T_p^2} = \ln \frac{AR}{E_a} + \ln\left[\ln\left(1 - \alpha_p\right)^{n-1}\right] + \frac{E_a}{RT_p} \quad (3)$$

where β is the heating rate, T_p and α_p are the absolute decomposition temperature and weight loss at the maximum weight-loss rate $(d\alpha/dt)_p$, respectively. R is the gas constant, A is the pre-exponential factor, and n is the reaction order. E_a was calculated from the slope of the straight line obtained from a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$.

Ozone resistance test

The test of ozone resistance of the vulcanized rubber samples followed the Physical Testing Standards of Rubbers developed by Nishi and Nagano.[23] The rubber specimens (1.5 × 8.0 × 0.2 cm^3) were submitted to a deformation of 20% under stress using a specimen holder maintained for a 48 h period in the

Rubber blends	Vulcanization System	DCP content (phr)	Crosslink density (mmol/cm^3)	Tensile strength (MPa)		Elongation at break (%)	
				Before aging	% Retention[a]	Before aging	% Retention
HNR/NR	PV	2	0.172	3.53 (0.60)[b]	18.4	361 (48)	27.1
	CPV	0	0.241	3.69 (0.51)	41.5	375 (19)	41.5
		2	0.274	2.53 (0.10)	53.8	292 (11)	40.7
	EPV	0	0.051	2.87 (0.05)	113	682 (58)	97.5
		2	0.104	7.54 (0.24)	98.5	1005 (14)	65.9
EPDM/NR	PV	2	0.271	4.66 (0.28)	72.3	462 (35)	92.1
	CPV	0	0.139	6.44 (0.14)	56.7	555 (17)	62.3
		2	0.341	3.98 (0.40)	91.0	386 (18)	78.5
	EPV	0	0.038	3.85 (0.09)	77.7	747 (26)	88.2
		2	0.044	8.74 (0.34)	85.2	657 (7)	96.1

Aging conditions: 100°C under air atmosphere for 22 ± 2 h
[a] %Retention = (Properties after aging/Properties before aging) × 100.
[b] The standard deviation is in a parenthesis.

absence of light and an ozone-free atmosphere. The stretched specimens were exposed to an ozone atmosphere of 50 pphm (part per hundred million) at 40°C for 24 h in an ozone cabinet (HAMPDEN, Northampton, England). The cracking traces on the rubber surfaces at a deformation of 20% stretch were examined by using a CCD camera.

RESULTS AND DISCUSSION

Thermal stability of HNR/NR vulcanizates

Effect of vulcanization system

The tensile strength (TS) and elongation at break (EB) of HNR/NR blends, at a 50/50 wt ratio with HNR > 95% hydrogenation, vulcanized by using various vulcanization systems are presented in terms of values before heat aging and the retention after heat aging as illustrated in Table II. For the incompatibility of HNR and NR in the blends due to the cure-rate mismatch effect resulting from the imbalance of unsaturation, the results indicated that an EPV system using 2 phr DCP was appropriate for curing HNR/NR blends to give the maximum TS and EB at 7.54 MPa and 1005%, respectively with 0.104 mmol/cm^3 of crosslink density. This phenomenon was also observed for the EPDM/NR blend cured using the EPV system at the same DCP content and rubber blend ratio. It was noted that the suitable crosslink density for the high tensile properties of rubber blends (50/50 wt ratio) containing the highly different unsaturation levels was in the range of 0.04–0.14 mmol/cm^3.

The performance on thermal resistance of HNR was compared with EPDM at the same blend composition. For EPDM/NR vulcanizates obtained from the conventional vulcanization without addition of

DCP, the mechanical properties retention of this blend were lower than that cured using peroxide; whereas, the blend cured by efficient vulcanization still retained the mechanical properties after thermal aging. This could be explained that the crosslink chains mainly generated in efficient vulcanization were monosulfidic linkages that had higher resistance to thermal-oxidative aging compared with polysulfidic crosslinks normally obtained from conventional vulcanization.[24] In addition, the carbon–carbon linkages in vulcanizates obtained from PV has highest bond energy (85 kcal/mol) resulting in the better thermal resistance than that from conventional vulcanization.[24–26] Conversely, the HNR/NR blends cured using the PV system showed the lowest retention mechanical properties (18.4% for TS and 27.1% for EB). It is possible that the residual Os complex remaining in the HNR might promote the oxidation of HNR/NR vulcanizates in the presence of peroxide. Some previous research reported that carbonyl osmium complexes had the potential to be a catalyst for oxidation of alkanes and alcohols with hydrogen peroxide.[27,28] Therefore, the EPDM/NR vulcanizates cured using the PV system exhibited a comparatively higher retention of mechanical properties (72.3% for TS and 92.1% for EB).

For the conventional vulcanization with peroxide (CPV), the retention of TS of HNR/NR and EPDM/NR blends was enhanced to 53.8% and 91%, respectively compared with the conventional vulcanization without the addition of DCP due to the rigid C—C bonds with high thermal resistance generated from peroxide in the network structure of vulcanizates. However, the TS and EB of vulcanizates obtained from CPV system were comparatively low. This could be explained in that the rigid C—C network chain produced from CPV system was easily

TABLE III
Effect of Blend Ratio on the Thermal Stability of HNR/NR (>95% Hydrogenation) and EPDM/NR Blends
Cured by EPV System Using 2 phr of DCP

Rubber blends	Blend Ratio	Crosslink Density (mmol/cm^3)	Tensile strength (MPa)		Elongation at break (%)	
			Before aging	%Retention[a]	Before aging	%Retention
NR	–	0.111	15.2 (0.53)[b]	63.2	717 (18.9)	96.4
HNR/NR	25/75	0.052	10.6 (0.57)	102	659 (25.3)	107
	50/50	0.104	7.54 (0.24)	98.6	1005 (13.6)	65.9
	75/25	0.116	3.52 (0.39)	129	715 (26.5)	102
	90/10	0.106	4.10 (0.35)	87.0	789 (34.4)	85.5
EPDM/NR	25/75	0.091	9.70 (0.41)	109	712 (15.9)	97.5
	50/50	0.044	8.74 (0.34)	85.2	657 (7.34)	96.1
	75/25	0.008	1.04 (0.05)	122	1084 (41.6)	99.5
	90/10	0.027	2.07 (0.17)	108	1048 (40.4)	91.9

Aging conditions: 100°C under air atmosphere for 22 ± 2 h.
[a] %Retention = (Properties after aging/Properties before ageing) × 100.
[b] The standard deviation is in a parenthesis.

damaged under an applied stress.[29] In addition, the combination of peroxide and sulfur in the CPV system decreased the optimum cure time of the HNR/NR and EPDM/HNR blends to possibly cause the prematurity of the NR phase resulting in the lower mechanical properties of the vulcanizates.[15]

For the efficient vulcanization with peroxide (EPV), the vulcanizates exhibited the highest TS and EB. The tensile strength of HNR/NR and EPDM/HNR after thermal aging was also retained at 98.5% and 85.2%, respectively. It is possible that the addition of peroxide in efficient vulcanization may retard the reactivity of the sulfur donor, TMTD, for curing NR in the blends.[15] Consequently, the cure-rate mismatch due to the imbalance in unsaturation levels of the HNR or EPDM and NR was reduced to give the better mechanical properties. Moreover, the use of a TMTD sulfurless cure system in the presence of ZnO gives stable crosslinks and produces the zinc-dimethyldithiocarbamate (ZDMDC) which is also an efficient antioxidant.[30] This may provide the good properties retention of both HNR/NR and EPDM/NR vulcanizates.

Effect of rubber blend ratios

The effect of blend ratio on mechanical properties of HNR/NR and EPDM/NR vulcanizates cured using the EPV system with 2 phr of DCP is shown in Table III. The crosslink density of EPDM/NR blends at all rubber blend ratios was lower than that of NR vulcanizates (0.11 mmol/cm^3) due to the incompatibility caused from the imbalance of unsaturation levels of rubbers in the blends. This led the reduction of mechanical properties of the blends when the content of EPDM was increased.

For the potential to retain the mechanical properties of the blends after heat aging, the results

showed that the percent retention of TS of HNR/NR and EPDM/NR blends at every blend ratio was higher than that of the NR vulcanizate (63.2%). However, NR vulcanizate could retain the EB value after heat aging. It is possible that the EPV system enhanced the thermal resistance of NR as well as the blends of NR and EPDM. For the HNR/NR vulcanizate at all blend ratios except for the 50/50 wt ratio, the good retention of EB after heat aging was found due to the combination of the saturated elastomer and the effect of EPV system which increased the thermal resistance of the rubber blends. At the critical blending composition (50/50 wt ratio) of HNR/NR vulcanizate, its EB value before heat aging was highest compared with the other blend ratios due to the co-continuous morphology, which caused a high strain as reported in our previous work.[15] However, it was observed that the percent retention of the EB of HNR/NR vulcanizate at 50/50 wt ratio was lowest (65.9%). This might be due to the co-continuous effect that caused the good dispersion of HNR containing residual Os catalyst into the NR phase. This could promote the oxidation of HNR/NR vulcanizates under thermal aging as described above resulting in a decrease in the retention of EB.

TGA and the activation energy of thermal decomposition

Unvulcanized rubbers

Thermal stability can be regarded as the ability to maintain the required properties of materials at a desired temperature. To study how the decomposition temperature is related to the structure of materials, TGA is widely used to determine the range of service temperature due to its simplicity to analyze the information obtained from a simple thermogram. The results of decomposition temperature of the

TABLE IV
Decomposition Temperatures, Maximum Weight-Loss Rate and Activation Energy of Thermal Decomposition Under N_2 Atmosphere of Unvulcanized Rubbers

Sample	Decomposition temperature (°C)[a]			$(d\alpha/dt)_p$[a] (%/min)	E_a (kJ/mol)
	T_{id}	T_p	T_f		
NR	358	384	410	18.2	179
HNR[b]	432	462	476	24.3	236
EPDM	454	472	483	33.4	193

[a] Recorded at 10°C/min of heating rate.
[b] 96.4% hydrogenation.

unvulcanized NR, EPDM, and HNR (96.4% hydrogenation) in the presence of a nitrogen atmosphere are given in Table IV and Figure 1. It indicated that the thermal decomposition of rubbers was an overall one-step reaction because the TG curve of the samples was one-step and provided smooth weight loss curves. The range of the decomposition temperature of NR was 358–410°C. It was also reported that the decomposition over this temperature range gave 39% isoprene, 13.2% dipentene, and small amounts of *p*-menthene.[31] Since hydrogenation can convert the weak π bond within NR to the stronger C—H σ bond, the initial, maximum and final decomposition temperatures of NR after hydrogenation increased ca. 74, 78, and 66°C, respectively. These decomposition temperatures of HNR were also close to that of EPDM.

Arrhenius activation energy (E_a) of pure gum NR, HNR, and EPDM calculated using the Kissinger method are obtained from the slope of the plot between $\ln(\beta/T_p^2)$ versus $1/T_p$ as shown in Figure 2. From Table IV, the E_a of HNR (236 kJ/mol) was significantly higher than that of NR (179 kJ/mol). This implies that HNR required more energy to break down the chemical bond due to the greater saturation in the structure. In addition, E_a of HNR was
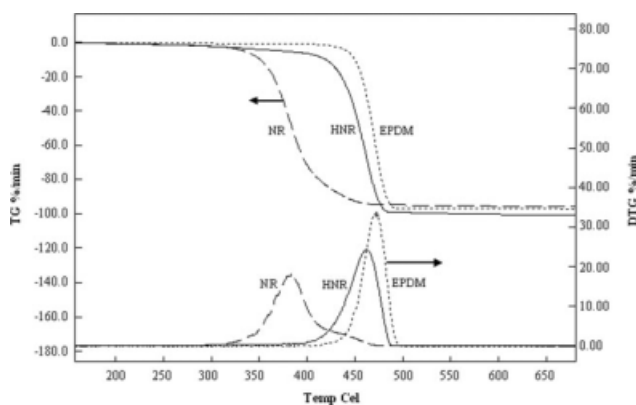
Figure 1 TG and DTG curves of NR, EPDM, and HNR (96.4% hydrogenation) at 10°C/min under nitrogen atmosphere.
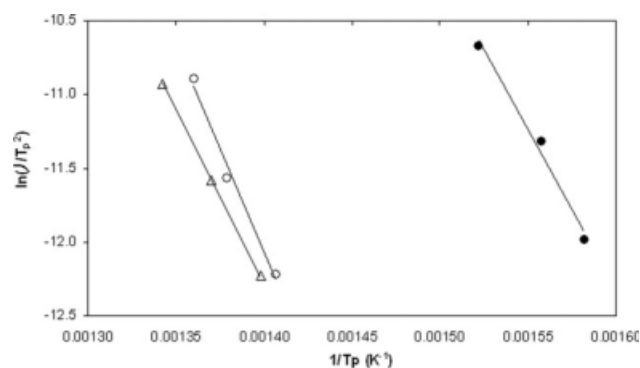
Figure 2 Plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ at various heating rates: (●) NR, (○) HNR (at 96.4% hydrogenation) and (△) EPDM.

also higher than that of EPDM (193 kJ/mol). This result can also be explained from the DTG curve shown in Figure 1. The maximum weight-loss rate of EPDM was highest compared with NR and HNR. It can be seen that EPDM was rapidly decomposed at a temperature above 472°C; although, the saturation backbone of EPDM provides the highest maximum decomposition temperature. It implies that HNR containing very small unsaturation portions (ca. 3.6%) in its backbone structure had the higher thermal resistance under an inert atmosphere than the pendent unsaturated carbon–carbon double bond of EPDM.

HNR/NR vulcanizates

The effect of blend ratio on the decomposition temperature and activation energy of thermal decomposition under an inert atmosphere of HNR/NR vulcanizates cured by EPV system using 2 phr of DCP are presented in Table V. The thermogravimetric curves of vulcanizates illustrated in Figure 3(a,b) show the two-stage decomposition pattern. From the DTG curve [Fig. 3(b)], the first stage of decomposition with a peak temperature around 381°C for various HNR/NR blends corresponded to the decomposition of the NR phase in the blends. The second stage of thermal decomposition occurred at a peak temperature around 463°C, which is attributed to the maximum decomposition temperature of HNR with >95% hydrogenation. The decomposition temperature at the initial stage and at 50% mass loss are plotted as a function of HNR content as shown in Figure 4. The dot line represents the calculated decomposition temperature at various blend ratios with no interaction between components in the blends. If the observed decomposition temperature at any blend ratio shows the positive or negative deviation from the dot line, this means that the interaction effect promotes the higher or lower thermal stability of the blends. The results showed that

TABLE V
Decomposition temperatures, Maximum Weight-Loss Rate and Activation Energy of Thermal Decomposition Under N_2 Atmosphere of HNR/NR Vulcanizates

HNR/NR (wt ratio)	NR phase			HNR phase[a]		
	Decomposition temperature (°C)[b]		$E_{a,NR}$ (kJ/mol)	Decomposition temperature (°C)[b]		$E_{a,HNR}$ (kJ/mol)
	$T_{id,NR}$	$T_{p,NR}$		$T_{id,HNR}$	$T_{p,HNR}$	
0/100	355	381	60.0	–	–	–
25/75	356	382	57.4	444	462	244
50/50	353	377	64.1	440	461	260
75/25	352	381	56.4	441	464	247
90/10	354	386	45.3	442	466	216

[a] >95% hydrogenation.
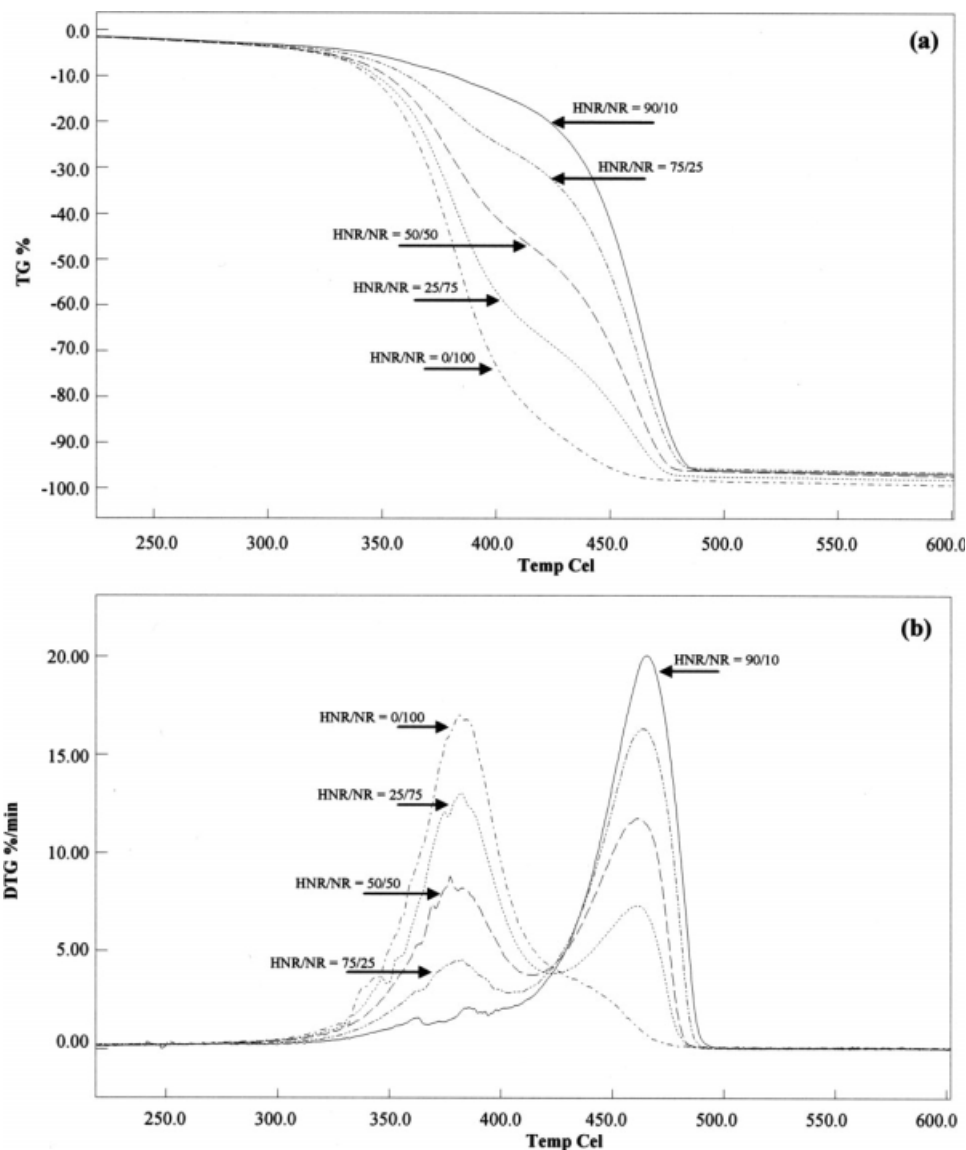[b] Recorded at 10°C/min of heating rate.

Figure 3 Thermogravimetric curves of HNR/NR vulcanizates at various blend ratios cured by EPV systems with 2 phr of DCP at heating rate of 10°C/min under nitrogen atmosphere: (a) TG and (b) DTG curves.
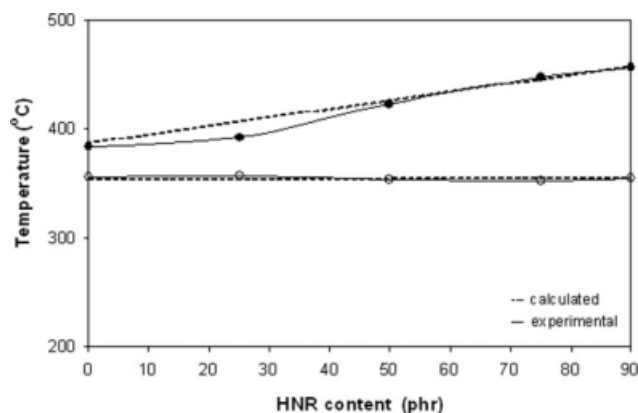
Figure 4 Effect of blend ratio on T_{id} and T_{50} values of HNR/NR vulcanizates: (○) T_{id} and (●) T_{50}.

the initial decomposition temperature (T_{id}) was not affected by the blend composition. This means that the addition of HNR did not change the T_{id} value of NR phase in the blends caused from an incompatibility effect of HNR and NR in the blends as shown by DTG curves in Figure 3(b). For the decomposition temperature at 50% mass loss (T_{50}), the results indicated that T_{50} increased with increasing HNR content. It could be explained that NR phase was partially decomposed at T_{50}. Consequently, HNR with the higher decomposition temperature compared to NR acted as the predominant phase to increase the thermal stability of the vulcanizates.

For the HNR/NR vulcanizates, the activation energy of thermal decomposition for the NR phase (45.3–64.1 kJ/mol) was lower than that of the HNR phase (216–260 kJ/mol) due to the large amount of unsaturation in the NR structure. Furthermore, E_a of the NR vulcanizate (60 kJ/mol) was lower compared to NR gum (179 kJ/mol) before vulcanization. It is possible that some byproducts obtained from vulcanization, unreacted ingredients in the vulcanizates and weak links in the rubber skeleton may accelerate the thermal decomposition.[32] It was also observed that the E_a of both NR and HNR phases in the vulcanizates tended to be decreased with increasing the HNR content possibly due to the residual Os catalyst in the HNR portion that might reduce the E_a value resulting in the ease of thermal decomposition. In addition, it was believed that the more incompatibility of the rubber phases induced the lower E_a of the blends. Thus, the HNR/NR at 50/50 wt ratio with higher compatibility compared with other blend ratios had the highest E_a in both phases of NR and HNR at 64 and 260 kJ/mol, respectively.

Ozone resistance of HNR/NR vulcanizates

The ozone resistance of polymer products becomes one of the important polymeric properties since the

atmospheric ozone concentration has gradually increased; especially, in industrialized areas. Because of the presence of carbon–carbon double bonds in the backbone structure, NR and many unsaturated rubbers are susceptible to degradation by ozone attack to form ozonides, which causes brittleness and macroscopic cracks on the surface of the rubber specimens.[2,33] It has been well known that the blending of NR with ozone inert rubbers such as ethylene/propylene rubber consequently provides a new material that has greater thermal and ozone resistance. Because HNR is also a saturated elastomer like EPDM, the effect of HNR on the ozone resistance of HNR/NR blends was investigated.

The effect of vulcanization systems on the ozone resistance of the HNR/NR specimens (50/50 wt ratio) is presented in Figure 5(a–c). The results showed that the cracking traces from ozonolysis did not appear on the surface of vulcanizate cured by peroxide after exposure to 50 pphm of ozone concentration at 40°C for 24 h [Fig. 5(a)]. This indicated that the peroxide vulcanization enhanced the resistance to ozonolysis for vulcanizates. It might be explained that some crosslinks possibly formed via the mechanism of vulcanization induced by interaction of the peroxide-derived free radical with the double bond of isoprene resulting the reduction of the C=C unsaturation in the blends as shown in eqs. (4)–(6).[24]

$$\text{peroxide} \longrightarrow 2R^* \tag{4}$$

$$\tag{5}$$

$$\tag{6}$$
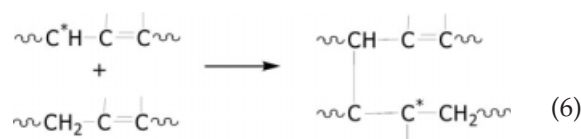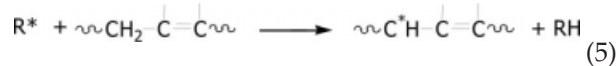
For the HNR/NR vulcanizate obtained from the CPV system [Fig. 5(b)], the more severe ozone cracks developed on the surface were appeared compared with the vulcanizate obtained from the EPV system [Fig. 5(c)]. It is possibly due to the antioxidant role of ZDMDC obtained from the reaction of zinc oxide and TMTD in EPV system.

For the effect of blend ratio of vulcanizates cured by the EPV system using 2 phr of DCP, the increase in the HNR content up to 90 phr could retard the initiation and propagation of surface cracking caused by ozone as shown in Figure 5(d). A similar behavior was also observed by Inoue and Nishio in that the ozone cracking on the surface of 100% HNR did not appear.[14] This implies that the blends containing higher HNR content resulted in a superior ozone resistance. On the other hand, the increase in the NR content led to more ozone cracking traces on
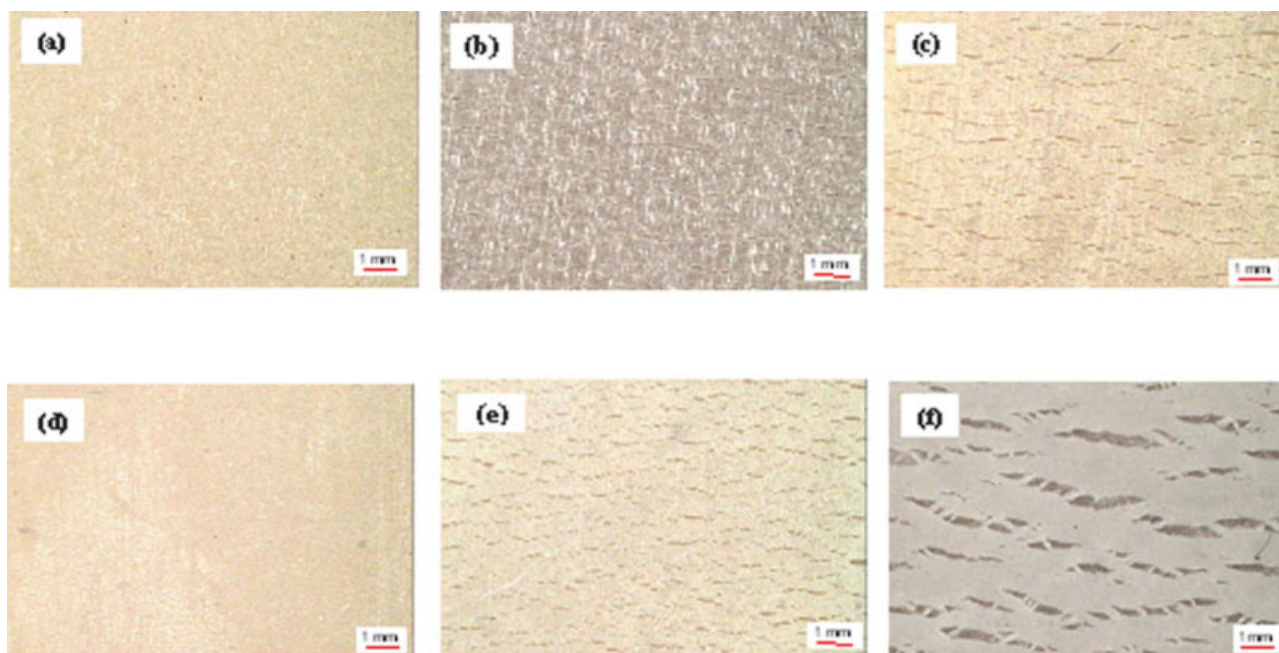
Figure 5 Stretched surface of HNR/NR vulcanizates (using 2 phr of DCP) after exposure to ozonised air of 50 pphm ozone concentration at 40°C for 24 h: (a) HNR/NR = 50/50 cured by PV, (b) HNR/NR = 50/50 cured by CPV, (c) HNR/NR = 50/50 cured by EPV, (d) HNR/NR = 90/10 cured by EPV, (e) HNR/NR = 75/25 cured by EPV, and (f) NR cured by CPV. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the surface of the specimens as shown in Figure 5(e,f). Numerous horizontal cracking lines on the surface of NR vulcanizates [Fig. 5(f)] appeared after exposure to 50 pphm of ozone at 40°C within 24 h. The possible reaction mechanism during ozonolysis of NR involves the formation of an intermediate carbonyl oxide which then further reacts to produce primary and secondary ozonides and various peroxidic species resulting in the scission products.[34]

CONCLUSIONS

This work reports on a study of thermal stability of HNR/NR blends in terms of mechanical properties and activation energy of thermal decomposition obtained from TGA. The results indicated that HNR had the potential to replace the use of EPDM for blending with NR to enhance the thermal resistance of vulcanizates. The EPV system was an appropriate vulcanization method for the blends containing different unsaturated elastomers. The HNR/NR and EPDM/NR vulcanizates using the EPV system retained the highest TS and EB before and after thermal aging due to the production of ZCMDC derived from TMTD and zinc oxide which is the efficient antioxidant. From TGA of unvulcanized rubbers, the greater saturation level of HNR resulted in the higher activation energy of thermal decomposition compared with NR. Therefore, HNR required more energy to break down the chemical bond in the

structure. For HNR/NR vulcanizates, the activation energy of the NR and HNR phases was decreased with increasing HNR content possibly due to the higher residual Os catalyst and the higher incompatibility of the rubber phases in the blends. However, the change of the blend ratio did not affect the initial and maximum decomposition temperatures of the HNR/NR vulcanizates; while the increase in HNR content in the blends resulted in the higher thermal decomposition at 50% mass loss. The observations from ozonolysis tests showed that the rubber blends containing the higher content of HNR could retard the initiation and propagation of surface cracking caused by ozone.

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