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Effects of sulfur vulcanization system on cure characteristics, physical properties and thermal aging of epoxidized natural rubber

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Abstract

The epoxidized natural rubber (ENR) with 40 mol% epoxidation (ENR-40) was initially prepared via '*in situ*' epoxidation of concentrated natural rubber latex with formic acid (1M to isoprene unit) and hydrogen peroxide (0.75 M to isoprene unit) at 50ºC for 8 h. The as-prepared ENR-40 was then cured with three different sulfur vulcanization/curing systems, including conventional (CV), semi-efficiency (semi-EV) and efficiency (EV) systems using tetrabenzylthiuram disulphide (TBzTD) as a non-carcinogenic accelerator on a compression molding machine. The effects of sulfur to accelerator ratio on the cure characteristics, tensile properties (tensile strength, modulus at 300% strain (M300) and elongation at break), thermal aging, thermal stability and oil resistance were investigated. The results revealed that the EV system exhibited the longest scorch time (t_{s2}) and cure time (t_{90}) and the highest elongation at break (both before and after thermal aging), but the lowest crosslink density. The CV system had the highest crosslink density, tensile strength and M300 (both before and after thermal aging) and oil resistance, but the lowest thermal stability. Moreover, the semi-EV system exhibited the highest cure rate and thermal stability, but the lowest t_{s2}, t_{90} and elongation at break (both before and after thermal aging).

1. Introduction

In the rubber production, vulcanization/cure is one of the most essential processes to improve the strength and elasticity and reduce the sensitivity to temperature of rubber. At present, there are several curing processes using sulfur [1–12], peroxide [2,11], ultraviolet light [12], electron beam [2,13] and microwave [14]. Among them, sulfur vulcanization is the most economical and practical technique by heating and incorporating accelerator and activator. El-Nemr [2] reported that the sulfur vulcanization exhibited the higher tensile strength, tear strength, elongation at break and crosslink density than those of the peroxide vulcanization system due to the flexible and labile C-S-C linkages. Based on the ratios of accelerator-to-sulfur, the sulfur vulcanization can be classified into three systems namely conventional (CV), semi-efficient (semi-EV) and efficient (EV) systems with an accelerator-to-sulfur ratio of 0.1–0.6, 0.7–2.5 and 2.5–12, respectively [3]. By varying the ratio of accelerator-to-sulfur, the sulfidic linkages between the rubber chain were formed with various sulfur atoms (C-S-C, mono- sulfidic; C-S_2-C, di-sulfidic and C-S_x-C, poly-sulfidic, where x can vary 3 to 6) resulting in the different end used properties of rubber such as curing properties, mechanical properties, thermal stability and aging properties [8,9]. Generally, the vulcanized rubbers with CV system have high crosslink density which contains predominantly polysulfudic linkages resulting in good mechanical properties for products. In contrast, semi-EV and EV systems give enhanced

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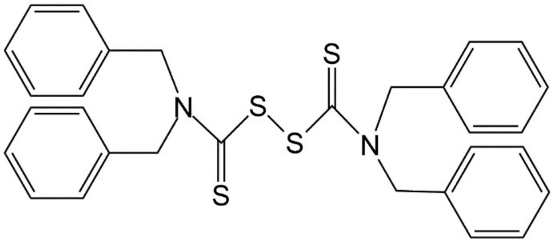
thermal properties due to forming mono- and disulfidic linkages, but at the expense of reducing mechanical properties compared to the vulcanized rubbers with CV system. This is caused by lower crosslink density [15,16]. Nitrosoamines have well known as common traditional accelerators in sulfur vulcanization such as tetramethylthiuramdisulfide (TMTD) and *N,N*-diisopropyl-2-benzo-thiazole sulfenamide (DIBS). However, these accelerators are considered to be possible human carcinogens [8,15,17]. According to the suspected carcinogenicity mentioned above, tetrabenzylthiuram disulphide (TBzTD, Scheme 1), a fast curing accelerator, was selected for using as a safe nitrosamine (non-carcinogenic) accelerator in this study to replace the TMTD. In this study, the sulfur vulcanization systems using TBzTD as an accelerator were comparatively investigated for epoxidized natural rubber (ENR) properties. The ENR can be synthesized through *in situ* performic epoxidation of natural rubber (NR) generated from hydrogen peroxide (H_2O_2) and formic acid (HCOOH) in the latex stage. The degree of epoxidation of NR controlled by the type and content of peracid, reaction temperature and reaction time can be indicated the properties of products such as hardness, elasticity, stability to non-polar solvent and oxidation and gas permeability. Normally, there are two degrees of commercial ENR having a 25 and 50 mol% epoxidation (ENR-25 and ENR-50, respectively). ENR-50 exhibits oil resistance similar to medium nitrile rubber and superior to chloroprene rubber, but becomes harder, low resilience and elasticity. In contrast, ENR-25 is a typical elastomer with less oil resistance [6–10]. Therefore, in this study the in-house prepared ENR with medium epoxidation degree (about 40 mol% epoxidation) was synthesized via *in situ* epoxidation from concentrated NR latex to obtain ENR with a higher oil resistance, but a comparable elasticity and strain crystallization to NR. To the best of our knowledge, use of the TBzTD as a safe accelerator for the in-house ENR 40 in sulfur vulcanization systems has never been reported. The effects of sulfur vulcanization system using TBzTD as a safe accelerator on the curing properties, tensile properties, thermal aging, thermal stability, oil resistance and morphology of the in-house prepared ENR 40 were investigated for comparison.



Scheme 1. Chemical structure of a tetrabenzylthiuram disulphide accelerator (TBzTD).

2. Experimental

2.1 Materials

Concentrated natural rubber latex (60% dry rubber content, DRC) and 10 wt% polyalcohol ethylene oxide condensate (Terric 16A–16) were obtained from Rubber Authority of Thailand (Thailand). Sulfur, zinc oxide (ZnO) and stearic acid were purchased from KIJ Paiboon Chemical Co. (Thailand). Tetrabenzylthiuram disulphide (TBzTD), a product of Performance Additive Co. (Italy), was supplied by Behn Meyer Chemical Co. (Thailand). Laboratory-grade 98 wt% formic acid (HCOOH), a product of Fisher Chemical Co. (UK), and 35 wt% hydrogen peroxide (H_2O_2), a product of Chem-Supply Pty Co. (Australia), were purchased from Myscience Co. (Thailand) and RCI Lab scan Co. (Thailand), respectively. Sodium carbonate (Na_2CO_3) was purchased from Merck Thailand Co. (Thailand), whereas commercial-grade (99.5%) methanol was purchased from RCI Lab scan Co. (Thailand). The standard oil for rubber (IRM 901 and IRM 903) was supplied by Chemical Innovation Co. (Thailand). All ingredients were used as received.

Table 1. Formulations used to prepare the ENRs.

Chemical	Formulation						
	1	2	3	4	5	6	7
NR latex (phr)	100	100	100	100	100	100	100
Terric 16A–16 (phr)	3	3	3	3	3	3	3
HCOOH (mol·g^{-1})	0.75	0.75	0.75	0.75	0.25	0.5	1
H_2O_2 (mol·g^{-1})	0.25	0.5	0.75	1	0.75	0.75	0.75

2.2 *In situ* epoxidation and characterization

The epoxidized natural rubber (ENR) was prepared by *in situ* performic epoxidation of NR using HCOOH and H_2O_2. The ENR was first diluted to 20% DRC with distilled water and stabilized with 3 parts by weight per hundred of rubber (phr) of Terric 16A−16 as a non-ionic surfactant at room temperature under stirring 1 h. Under continuous stirring, the diluted NR was stepwise fed with HCOOH within 10-15 min at 40ºC and then raised the temperature to 50ºC within 10 min before slow adding H_2O_2 within 5-10 min. The reaction was allowed to perform at 50ºC for various reaction times (4, 6, 8 and 10 h). The formulation recipe used for preparation of the ENRs is shown in Table 1. The as-prepared ENR was coagulated in methanol, thoroughly washed with distilled water, soaked in 10% of Na_2CO_3 solution and rinsed with distilled water again until neutral, finally dried at 60ºC for 48 h before characterization.

The functional groups analysis were performed using Fourier transform infrared (FT-IR) spectroscopy (Nicolet 6700-FTIR, USA) over a frequency range of 400–4000 cm^{-1}. The degree of epoxidation was determined as mol% epoxidation by calculation from equation 1 using data obtained from the characteristic FT-IR peaks at 870 and 835 cm^{-1} [6–8].

$$\text{Mol\% epoxidation} = [A_{870}/(A_{870} + A_{835})]\times 100 \quad (1)$$

where A_{870} and A_{835} are the absorbancies at wavenumbers 870 and 835 cm^{-1}, respectively.

2.3 Preparation of ENR compound and vulcanized ENR

The ENR compounds were prepared with three sulfur vulcanization systems (CV, semi-EV and EV systems) by mixing the dried ENR (100 phr) with the required amounts of ZnO (5 phr), stearic acid (2 phr), TBzTD (0.6-6 phr) and sulfur (0.5-2.5 phr), as shown in Table 2. The melt mixing was performed in an internal mixer (MX500-D75L90, Thailand) at 70°C and rotor speed at 30 rpm for 9 min. The samples were then sheeted on a two–roll mill (Lab Tech Engineering LRM-S-110, Thailand) at room temperature for 1 min.

The cure characteristics, in terms of scorch time (t_{s2}, min), cure time (t_{90}, min), minimum torque (M_L, dN·m), maximum torque (M_H, dN·m) and torque difference (Δ torque, M_H-M_L, dN·m) were determined at 150ºC according to ASTM D5289 using a moving die rheometer (MDR) (A0225-rheo Tech MD, USA). The cure rate index (CRI, min^{-1}) was then calculated from equation 2.

$$\text{CRI} = 100/(t_{90} - t_{s2}) \quad (2)$$

The compounded ENR was compressed and vulcanized into a 15×15×0.2 cm^3 sheet by compression molding (Lab Tech Engineering LP-S-50, Thailand) at 150ºC according to the respective t_{90}.

Table 2. The composition of the ENR compounds.

Chemical	Sulfur vulcanization system		
	CV	Semi-EV	EV
ZnO (phr)	5	5	5
Stearic acid (phr)	2	2	2
TBzTD (phr)	0.6	1	6
Sulfur (phr)	2.5	2	0.5

2.4 Testing and characterization of vulcanized ENR

The tensile properties of at least five specimens for each sulfur vulcanization system determined as tensile strength (TS, MPa), modulus at 300% strain (M300, MPa) and elongation at break (EB, %) were performed according to ISO 37 Type II using a universal testing machine (Instron, 5840 series single column systems, USA) with a 1 kN load cell and at a crosshead speed of 500 mm·min^{-1}.

The thermal aging of the vulcanized ENR was carried out in a universal oven (Model UF55, Germany) with air circulating system at 70ºC for 72 h according to ASTM D573 and then the specimens were cooled at room temperature for 16 h. The tensile properties of the thermal aged specimens were measured as mentioned above. The thermal aging resistance is expressed as the percentage retention in tensile properties calculated from equation 3 [8].

$$\text{Retention (\%)} = \frac{\text{Value after aging}}{\text{Value before aging}} \times 100 \quad (3)$$

The thermal degradation of the vulcanized ENR was measured by means of thermogravimetric analysis (TGA) on a thermogravimetric analyzer

(Mettler Toledo, TGA/SDTA 851^e, Switzerland) in an alumina pan under nitrogen atmosphere by heating the samples from 50 to 600ºC at 10ºC·min^{-1}. The temperature for initial degradation (T_{onset}, ºC), final degradation (T_{endset}, ºC), maximum degradation ($T_{\max}$, ºC) and the char residue (% char, %) were investigated.

The oil resistance of the vulcanized ENR was determined by measurement of the percentage volume change (ΔV, %) after immersion the samples in two standard types of oil, IRM 901 and IRM 903, at 100ºC for 72 h according to ASTM D471-79. Prior to immersion, the samples were weighed in both air and distilled water at room temperature. After immersion, the samples were then removed from the respective oils, cooled to room temperature and cleaned test oil for about 30 min. The samples were quickly dipped in acetone at room temperature and lightly wiped with filter paper to remove excess the oil from the surface before weighing again in both air and distilled water. The weights from the test were used for calculation the ΔV by using equation 4 [8].

$$\Delta V\,(\%) = [(M_3–M_4)–(M_1–M_2)]/(M_1–M_2)\times 100 \quad (4)$$

where M_1 and M_2 are the initial mass (g) of the sample in air and distilled water, respectively, and M_3 and M_4 are the mass (g) of the sample in air and distilled water after immersion the standard oil, respectively.

The morphology of tensile fractured surface was observed by a scanning electron microscope (SEM) (Jeol JSM-6480LV, Japan) at an accelerated voltage of 15 kV and a magnification of 1000×. The fractured surface was coated with a thin layer of gold to form a conductive layer before observation.

3. Results and discussion

3.1 Characterization of ENR

Figure 1 shows the FT-IR spectra of NR and ENR to confirm the successful epoxidation of NR. The FT-IR spectrum of NR (Figure 1(a)) has absorption peaks at 2850 (C–H stretching), 1650 (C=C stretching), 1450 (–CH_2– deformation), 1375 (C–H deformation of CH_2) and 835 (=C–H deformation) cm^{-1} which are the characteristic peaks of NR [6–8]. By contrast, FT-IR of the ENR (Figure 1 (b)) shows the additional band at 1240 and 870 cm^{-1} ascribed to the symmetric stretching and asymmetric stretching of epoxide ring (C–O–C), respectively [6–8]. This confirmed the formation of epoxide rings by the random reaction of performic acid with C=C bonds on the NR molecules.

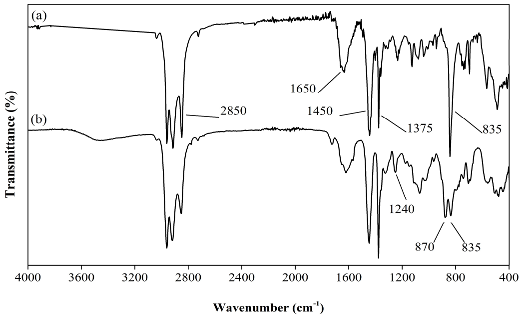


Figure 1. FT-IR spectra of the (a) NR and (b) ENR.

By varying reaction time and HCOOH:H_2O_2 ratios, the prepared ENRs exhibited various contents of mol% epoxidation as calculated from the equation 1 using data obtained from the characteristic FT-IR peaks (not shown here). The calculated mol% epoxidation of the prepared ENRs is shown in Figure 2. The results showed that mol% epoxidation increased with increasing the reaction time and the chemical (HCOOH and H_2O_2) concentrations, ranging from 26% to 54% due to the increased time for reaction and the increased performic acid content. With the balance of ENR properties including strain crystallization, elasticity and oil resistance, the ENR with medium mol% epoxidation (43 mol%), prepared from 1 M HCOOH and 0.75 M H_2O_2 (Formula 7) was used for further investigation its properties.

3.2 Cure characteristic

The cure characteristics, expressed in terms of t_{s2}, t_{90}, CRI, M_L, M_H and M_H–M_L, for vulcanized ENR in three sulfur vulcanization systems are listed in Table 3. The t_{s2} is a time that vulcanization begins, while t_{90} is the optimum vulcanization time. Among the three sulfur vulcanization systems, the EV system contained the highest accelerator concentration. However, the EV system showed unexpected results when the t_{s2} and t_{90} were the longest, while the CRI referred to the rate of vulcanization was the lowest. This is due to the bulky benzylthiuram substituents in the excess TBzTD accelerator that hinder the crosslink reaction [8]. On the other hand, the semi-EV system

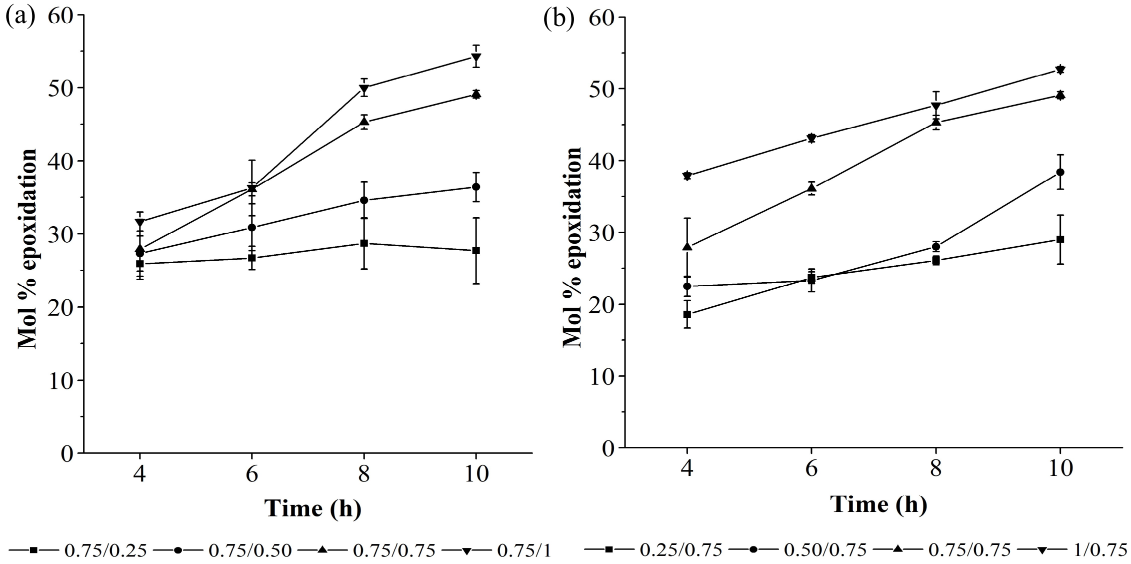


Figure 2. Mol% epoxidation of the in-house prepared ENRs: (a) formula 1, 2, 3, 4 and (b) formula 3, 5, 6, 7.

exhibited shorter t_{s2} and t_{90} than the CV system due to higher TBzTD concentration. Therefore, more crosslinks are formed in the short time caused the highest CRI. The types of sulfur vulcanization systems had no effect on the changes of M_L indicating to the similar uncured modulus and processing properties, while dependencies were observed for M_H and M_H–M_L. The highest M_H and M_H–M_L values were observed for the CV system which indicated to higher stiffness and crosslink density of the vulcanized ENR. This may be attributed to the higher loading of sulfur for crosslinking in the CV system. Higher the sulfur contents, more the crosslink density formed.

Table 3. Cure characteristics of the vulcanized ENR in different sulfur vulcanization systems.

Cure characteristic	Sulfur vulcanization system		
	CV	Semi-EV	EV
t_{s2} (min)	2.1	1.9	5.1
t_{90} (min)	4.5	3.3	7.2
CRI (min^{-1})	41.7	71.4	47.6
M_L (dN·m)	0.5	0.5	0.4
M_H (dN·m)	6.7	6.1	4.4
M_H–M_L (dN·m)	6.2	5.6	4

3.3 Tensile testing and thermal aging properties

The tensile properties both before and after thermal aging, in terms of the tensile strength (TS), modulus at 300% strain (M300) and elongation at break (EB) of the vulcanized ENR with three vulcanization systems are shown in Figure 3 and summarized in Table 4, including the percentage retention in the tensile properties. Before thermal aging, the vulcanized ENR with the CV system exhibited the highest TS and M300, followed by the semi-EV and EV systems. This is caused by the highest crosslink density of the CV system, follow by the semi-EV and EV systems (Table 3). By contrast, the lowest crosslink density of the EV system caused the highest EB. Although, the vulcanized ENR with the CV system exhibited a high crosslink density, it still had a high EB. This is suggested that the high flexibility of polysulfidic linkages formed mainly in the CV system can slide pass each other, increasing the free volume in the vulcanizate molecules. For the aged ENR vulcanizates, the TS and EB of all vulcanized ENR decreased, while the M300 increased. This is due to the crosslink scissions during thermal aging and the formation of new crosslinks into the stable networks affected these properties [18-20]. Moreover, the results showed that the vulcanized ENR with the CV system exhibited the lowest percentage retention in TS and EB, while the highest percentage retention was shown in the EV system. This is due to the fact that mono- and di-sulfidic linkages formed mainly in the EV system have higher thermal stability than polysulfidic linkages.

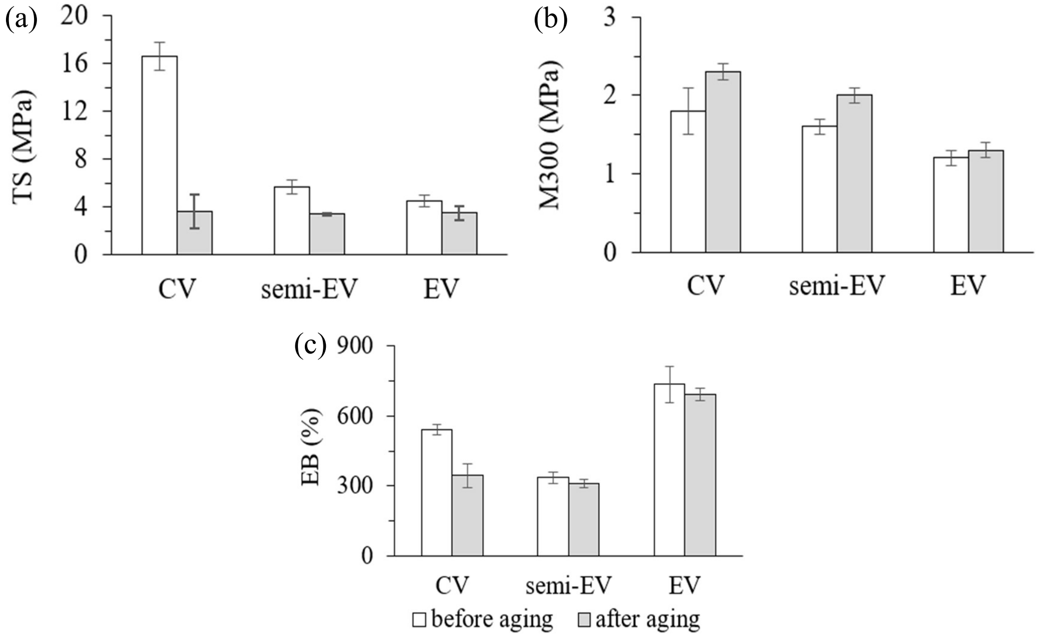


Figure 3. The (a) tensile strength (TS), (b) modulus at 300% strain (M300) and (c) elongation at break (EB) of the vulcanized ENR in different sulfur vulcanization systems before and after thermal aging.

Table 4. Tensile properties and %retention of the vulcanized ENR in different sulfur vulcanization systems.

Tensile propertie	**Sulfur vulcanization system**		
	CV	**Semi-EV**	**EV**
TS			
before aging (MPa)	16.6 ± 1.2	5.8 ± 0.6	4.6 ± 0.5
after aging (MPa)	3.6 ± 1.4	3.4 ± 0.1	3.5 ± 0.3
retention (%)	21.7	59.6	77.8
M300			
before aging (MPa)	1.8 ± 0.3	1.6 ± 0.1	1.2 ± 0.1
after aging (MPa)	2.3 ± 0.1	2.0 ± 0.1	1.3 ± 0.1
retention (%)	127.8	125	108.3
EB			
before aging (MPa)	540.8 ± 21.6	336 ± 23.7	735.5 ± 28.5
after aging (MPa)	344.2 ± 52.4	310 ± 18.2	692.7 ± 20.6
retention (%)	63.6	92.3	94.2

3.4 Thermal stability

The thermal stability in terms of T_{onset}, $T_{\text{end set}}$, $T_{\max}$ and %char of the vulcanized ENR with three vulcanization systems studied by TGA analysis are illustrated in Figure 4 and listed in Table 5. It can be observed that the vulcanized ENR with the CV and semi-EV systems exhibited single-stage degradation, except that the EV system revealed two-stage degradation. The first stage mainly involves the degradation of excess TBzTD, while the second stage mainly corresponds to the degradation of hydrocarbon molecules in vulcanized ENR. Moreover, the vulcanized ENR with the CV, semi-EV and EV systems showed T_{onset2} (353, 378 and 367.8°C, respectively), $T_{\text{end set2}}$ (443, 441.2 and 447.8ºC, respectively) and $T_{\max2}$ (405, 410.7 and 406.3°C, respectively). The obtained results obtained are in agreement with the thermal aging. That is, the CV system exhibited lower thermal stability compared to the semi-EV and EV systems caused by the higher content of polysulfidic linkages that had a lower thermal stability compared to the mono- and di-sulfidic linkages. Moreover, the semi-EV system samples possessed the highest thermal stability due to a high crosslink density and forming mostly mono- and di-sulfidic linkages. However, %char at 600ºC of the vulcanized ENR with the CV system was slightly higher than those of the vulcanized ENR with the semi-EV and EV systems. This is caused by the higher crosslink density as described above.

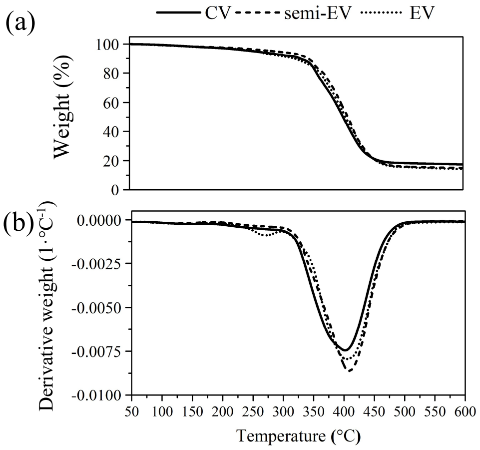


Figure 4. TGA (a) and DTG (b) curves of vulcanized ENR in different sulfur vulcanization systems.

3.5 Oil resistance

The percentage volume change (ΔV) of the vulcanized ENR with three vulcanization systems after being immersed in IRM 901 (low polar hydrocarbon oil; aniline point~124ºC) and IRM 903 (high polar hydrocarbon oil; aniline point~90ºC) at 100ºC for 72 h is illustrated in Figure 5. As can be seen, the vulcanized ENR with the CV system after immersion in both IRM 901 and IRM 903 exhibited the lowest ΔV (5.6% and 84.3%, respectively), followed by the semi-EV (6.7% and 84.6%, respectively) and EV (7.6% and 97%, respectively) systems, again due to the higher crosslink density that the penetration of oil into rubber matrix.

3.6 Morphology

Figure 6 displayed the SEM micrographs of the fractured surfaces of vulcanized ENR with three vulcanization systems resulting from the tensile testing. The vulcanized ENR with the CV and semi-EV systems displayed a smooth and continuous fractured surface. By contrast, the large grain boundaries were observed in the vulcanized ENR with the EV system indicating to the phase separation occurred by excess content of TBzTD.

Table 5. TGA-derived data for the vulcanized ENR in different sulfur vulcanization systems.

Sulfur vulcanization system	$T_{\text{onset 1}}$ (ºC)	$T_{\text{endset 1}}$ (ºC)	$T_{\text{max 1}}$ (ºC)	$T_{\text{onset 2}}$ (ºC)	$T_{\text{endset 2}}$ (ºC)	$T_{\text{max 2}}$ (ºC)	Char (%)
CV	-	-	-	353.0	443.0	405.0	17.4
semi-EV	-	-	-	378.0	441.2	410.7	15.0
EV	248.0	277.6	272.7	367.8	447.8	406.3	14.2

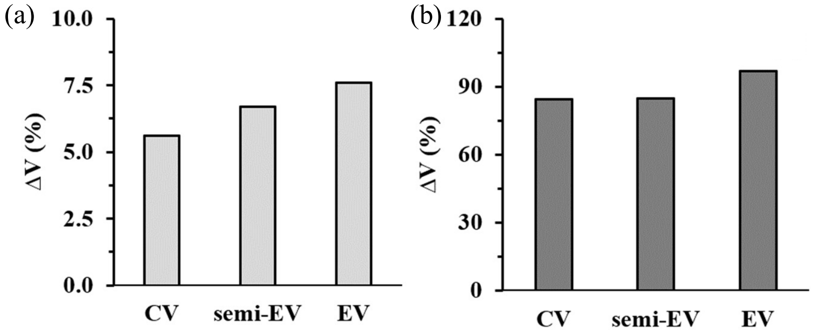


Figure 5. The percentage volume changes of the vulcanized ENR in different sulfur vulcanization systems after immersion: (a) IRM 901 and (b) IRM 903.

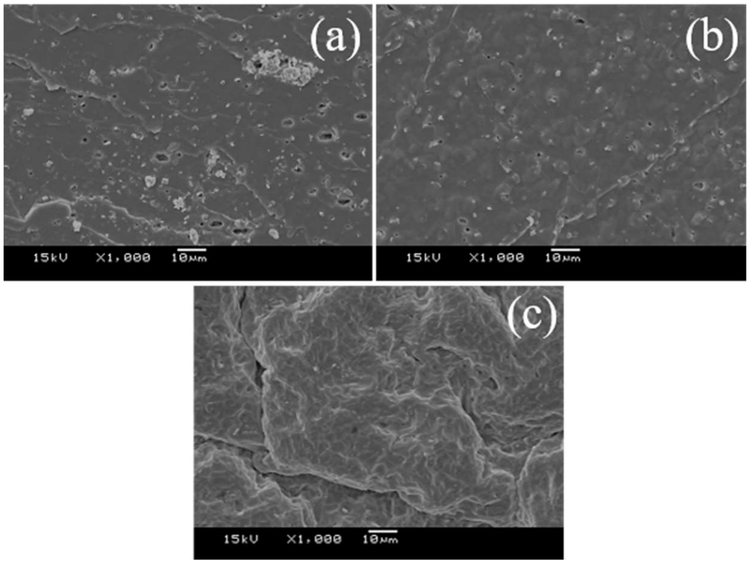


Figure 6. Representative SEM micrographs of the tensile fractured surface of the vulcanized ENR in (a) CV, (b) semi-EV and (c) EV systems.

4. Conclusions

The in-house prepared ENRs were successfully synthesized via *in situ* epoxidation of concentrated NR latex by performic acid obtained from the reaction between formic acid (HCOOH) and hydrogen peroxide (H_2O_2). The results showed that the increase in mol% epoxidation with the increasing the chemical (HCOOH and H_2O_2) concentrations and reaction time. From elasticity and oil resistance consideration, the ENR with 40 mol% epoxidation using a molar ratio of 1/0.75 HCOOH/H_2O_2 at 50°C for 8 h was chosen for further vulcanization with three vulcanization systems (CV, semi-EV and EV systems) using TBzTD as a non-carcinogenic accelerator. The results revealed that the types of sulfur vulcanization systems have significant influence on curing characteristic, mechanical properties, thermal aging, thermal stability and oil resistance of the vulcanized ENR. It was unexpected that the EV system possessed the longest t_{s2} and t_{90} due to the steric hindrance of the bulky groups in TBzTD. Moreover, it was noticed that before aging, the crosslink density determined the tensile properties and oil resistance of the vulcanized ENR. After aging, the properties, especially thermal properties depended on the sulfur vulcanization systems referred to the types of sulfidic linkages.

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