Available online at www.rsu.ac.th/rjas

Rangsit Journal of Arts and Sciences, January-June 2015 RJAS Vol. 5 No. 1, pp. 27-41

ISSN 2229-063X (Print)/ISSN 2392-554X (Online)

Effect of blend ratio on cure characteristics, mechanical properties, oil resistance, and ageing resistance of silica-filled ENR/NR blends

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Submitted 27 August 2014; accepted in final form 26 February 2015

Abstract

The effects of blend ratio on cure characteristics, mechanical properties, morphology, and the resistance to oil, thermal ageing, and ozone of blends based on epoxidized natural rubber (ENR) and natural rubber (NR) have been investigated in the presence of silica selected as a reinforcing filler due to its unique characteristic to interact with ENR. The blend composition was varied from 0 to 100%. The results indicate that the Mooney viscosity increased whereas cure time (t_{90}) decreased with an increase of ENR in the blend. Due to better filler dispersion and greater crosslink density, the silica-filled ENR exhibited slightly better tensile properties, compared to silica-filled NR. The maximum value of tensile properties was obtained for at 50/50 (wt/wt) of ENR/NR blend. The observed changes in the mechanical properties of the blends were correlated with phase morphology as attested to by scanning electron microscopy (SEM). The results reveal that the oil and ozone resistances of the ENR/NR blend were increased with increasing ENR content. However, the resistances to degradation from thermal ageing and abrasion showed a reverse behavior in their respective blends.

Keywords**:** *epoxidized natural rubber, blend, resistance, mechanical properties.*

บทคัดย่อ

บทความนี้ศึกษาอิทธิพลของอัตราส่วนยางผสมที่ประกอบด้วยยางธรรมชาติอิพ็อกซิไดซ์และยางธรรมชาติที่อัตราส่วนร้อยละ 0–100 โดยน้ำหนักของยางผสมต่อสมบัติการคงรูป สมบัติเชิงกล และความต้านทานน้ำมัน ความร้อนและโอโซน โดยใช้ซิลิกาเป็นสารตัวเติมเสริมแรงเนื่องจากสมบัติเข้ากันได้ดีกับยางธรรมชาติอิพ็อกซิไดซ์ จากการศึกษาพบว่าค่าความหนืดมูนี่มีค่าเพิ่มขึ้นขณะที่เวลาในการคงรูปลดลงเมื่อเพิ่มอัตราส่วนยางธรรมชาติอิพ็อกซิไดซ์ในยางผสม เนื่องจากการกระจายตัวและความหนาแน่นของการเกิดสารเชื่อมโยงที่ดี ยางธรรมชาติอิพ็อกซิไดซ์ผสมซิลิกามีสมบัติความต้านทานแรงดึงสูงกว่ายางธรรมชาติและค่าสูงที่สุดที่ร้อยละ 50 โดยน้ำหนักของยางผสม เมื่อสังเกตการเปลี่ยนแปลงสมบัติเชิงกลของยางผสมร่วมกับสัณฐานวิทยาของวัฏภาคซึ่งได้จากการทดสอบด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด ผลการทดลองแสดงให้เห็นว่าสมบัติด้านความต้านทานน้ำมันและโอโซนมีแนวโน้มเพิ่มขึ้นเมื่ออัตราส่วนยางธรรมชาติอิพ็อกซิไดซ์ในยางผสมเพิ่มขึ้น อย่างไรก็ตามสมบัติด้านความต้านทานการเสื่อมสภาพเนื่องจากความร้อนและความต้านทานการขัดสีมีแนวโน้มลดลงเมื่อเพิ่มอัตราส่วนยางธรรมชาติอิพ็อกซิไดซ์ในยางผสม

คำสำคัญ: *ยางธรรมชาติอิพ็อกซิไดซ์, ยางผสม, ความต้านทาน, สมบัติเชิงกล*

1. Introduction

Several methods can be used for developing new polymeric materials for commercial applications; among these are the synthesis of new polymers, copolymerization and blending of miscible polymers (George, Joseph, & Francis, 1986; Mousa, Ishiaku, & Ishak, 1998). Blending of miscible materials, resulting in a new product with properties that lie between those of the pure components is frequently used in the rubber industry to allow the user to access properties of the final blend that are not accessible from a single, commercially available polymer alone (Hess, Scott, & Callan, 1967; Marsh, Voet, Price, & Mullens, 1968; McDonald & Hess, 1977; Joseph, George, Francis, & Thomas, 1987). Generally, physical properties of polymer blends are controlled by many factors including the nature of polymers, blend composition, and blending conditions (Thomas & Groeninckx, 1999; Varghese, Bhagawan, Rao, & Thomas, 1995). Natural rubber (NR), a renewable resource, consists almost entirely of cis-polyisoprene and has numerous advantages for a wide range of applications. It possesses excellent characteristics such as high tensile and tear strengths due to its ability to crystallize upon stretching. The elasticity and dynamic properties of NR are also excellent. However, due to the unsaturation in its high cis-1,4-polyisoprene structure, NR is highly susceptible to degradation by thermal ageing and ozone attack. In addition, oil resistance of NR is relatively poor, as a result of its non-polar character (Fernandes, Visconte, & Nunes, 2011). To gain desired properties of final product properties such as hydrocarbon oil, heat, and weathering resistances, NR has been blended with many polymers, including SBR (styrene butadiene rubber) (Shan et al., 2011; Mansilla, Silva, Salgueiro, Marzocca, & Somoza, 2012; Poh, Ismail, Quah, & Chin, 2001), nitrile rubber (NBR) (Kader, Kim, Kaang, & Nah, 2005; Nah, 2002; Nah, Han, Jo, Kim, & Chang, 2002), and epoxidized natural rubber (ENR) (Mansilla et al., 2012; Ismail & Poh, 2000; Arroyo, Lopezmanchado, Valentin, & Carretero, 2007; Bandyopadhyay, Thakur, Pradhan, & Bhowmick, 2010). ENR is a modified natural rubber having properties resembling those of synthetic rubbers rather than natural rubber (Ng & Gan, 1981). ENR vulcanizates exhibit good oil resistance, low gas permeability, improved wet grip and rolling resistance, coupled with high strength (Gelling, 1985; Baker, Gelling, & Newell, 1985). For example, a 50 mol% ENR is comparable in oil resistance to a medium nitrile rubber (NBR) and has air permeability similar to butyl rubber (Lee, Kim, & Kim, 1997). Many blends based on ENR and other polymers, like NR, chloroprene rubber (CR), polypropylene (PP), poly (vinyl chloride) (PVC), and SBR have been reported in the literature. Poh, Ismail, and Quah (2001) studied the fatigue, resilience and hardness properties of natural rubber/epoxidized natural rubber (SMR L/ENR 25) and natural rubber/styrene-butadiene rubber (SMR L/SBR) blends with a blend ratio from 0 to 100% rubber. Ismail and Leong (2001) investigated a comparison of cure characteristics and mechanical properties of NR/CR and ENR/CR blends and also reported on the effect of temperature on curing characteristics of the blends. Mousa et al. (1998) studied dynamically vulcanized PVC/ENR thermoplastic elastomers (TPEs) prepared with a Brabender the plasticorder coupled with a mixing attachment by melt mixing. They reported excellent mechanical behavior of the PVC/ENR TPEs even after immersing the samples in oil at 100°C, which provides a good indication of the oil resistance of the materials. The morphology, miscibility, mechanical, and viscoelastic behavior of NBR/ENR blends, (Mathai & Thomas, 2005) the cure characteristics and mechanical properties of carbon black filled styrene-butadiene rubber (SBR)/ENR blends, (Nasir & Choo, 1989) differential scanning calorimetry study of natural rubber NR/ENR blend, (Ng & Chee, 1989) the effect of blend ratio on the Mooney scorch time of ENR/NR and ENR/SBR blends (Poh & Wong, 1998; Poh & Khok, 2000) and the tensile properties of ENR/NR and ENR50/SBR blends (Poh & Jalaluddin, 2000) were also studied.

In the present study, the effect of blend ratio on properties of silica-filled ENR/NR blend was investigated. The mechanical properties as well as the resistance to thermal ageing, oil and ozone of the blends were examined.

2. Experimental

2.1 Materials

Epoxidized Natural Rubber containing 50 mol % epoxidation (ENR 50) was supplied by Muang Mai Guthrie Public Co., Ltd. (Thailand). Natural rubber (NR, STR 5L) was obtained from Thailand by Union Rubber Products Corp. Ltd. Sulfur (S_8, Chemmin Co. Ltd., Thailand), N-cyclohexy l-2-benzothiazole-2-sulphenamide and tetramethylthiuramdisulphide (CBS and TMTD, Flexsys Co. Ltd., Germany), zinc oxide (activator, Gradmann, Thailand), stearic acid (activator, P. T. Cisadaneraya Chemical, Indonesia), Poly(ethylene glycol) (PEG, Brand Co., Ltd.) and precipitated silica (Hi-Sil 233 with specific surface area of 165 m^2/g) supplied by PPG-Siam Silica Co., Ltd., Thailand were of commercial grade and used as received.

2.2 Preparation of vulcanizates

The compound formulation is given in Table 1. The rubber compounds were prepared using a laboratory-sized two-roll mill (Kodaira Seisakusho Co., Ltd., Tokyo, Japan).

NR and ENR were masticated for 3 min, followed by addition of activators (ZnO and stearic acid), filler (silica), PEG, and accelerators (CBS and

TMTD), respectively. Compounding was completed by the addition of sulfur at 70°C for 3 min.

Before the processing, the optimum cure time, t_{90} was determined on the basis of the results of cure characteristics using a rheometer. Each rubber compound was compression molded at 150°C with a force of 17.5 MPa using a hydraulic press (Power Drive System Co., Ltd., Thailand) according to their respective cure time, t_{90}, determined with a rheometer. Vulcanizates were conditioned for 24 h before testing.

Table 1 The formulation of silica-filled ENR/NR blends for effect of blend ratio

Ingredient	**Loading (parts per hundred of rubber, phr)**				
Epoxidized natural rubber (ENR)	100	75	50	25	0
Natural rubber (NR)	0	25	50	75	100
Zinc Oxide	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0
Silica	40	40	40	40	40
CBS	1.6	1.6	1.6	1.6	1.6
TMTD	0.3	0.3	0.3	0.3	0.3
PEG	3.0	3.0	3.0	3.0	3.0
Sulphur	2.5	2.5	2.5	2.5	2.5

2.3 Cure characteristics

The mooney viscosity (ML1+4 at 100°C) was determined by using a Mooney viscometer (TECH-PRO, Cuyahoga Falls, Ohio, USA). The testing procedure was conducted according to the method described in ISO 289-1. Cure characteristics were studied using the rheometer (TECH-PRO, Cuyahoga Falls, Ohio, USA) according to ISO 3414 for 30 min at 150°C.

2.4 Mechanical properties

Tensile properties were determined on an Instron universal testing machine (model 4466; Instron Corp., Canton, MA) using C-type Dumbbell-specimen, according to ASTM D412. An abrasion test was carried out according to B.S. 903 Part A9 on a Wallace Test Instrument (England).

2.5 Oil resistance and swelling behavior

Oil resistance was determined in terms of tensile properties after immersion and swelling behavior was reported by measurement of the change in volume. The cured specimens to be tested were immersed in IRM 901 and IRM 903 oils 100°C for 72 h. When the specificed time was reached, the test specimens were removed from the oil and wiped with tissue paper to remove the excess oil from the surface. Finally, changes in volume and tensile properties of the specimens were measured according to ASTM D471-06.

2.6 Accelerated thermal ageing

Tensile specimens were aged at 100°C for 72 h in an air-circulating ageing oven and the tensile properties of the aged samples were determined according to ASTM D573 (1994). Tensile tests (ASTM D412-99) were carried out on tensile dumbbell test specimens after ageing to estimate thermal ageing resistance.

2.7 Ozone ageing

Ozone ageing studies under static conditions were conducted according to ISO 1431/1-1980 (E) using a Hampden (Model 1008-AH, Northampton, England) ozone test chamber at 40°C. Ozone concentration in the chamber was adjusted to 50 parts per hundred million (pphm). The ozonised oxygen generated in the ozoniser by a UV quartz lamp was collected in a separate chamber in which the sample was exposed. The ozone cracks were thereafter determined. Photographs were taken using an optical microscope Carl Zeiss Stemi 2000 C (WerkGöttingen, Germany) with magnification of 0.

2.8 Scanning electron microscopy

Scanning electron microscopic studies of the compound tensile fracture surfaces were carried out on gold-coated samples using a Joel Microscope (model JSM 5600 LV; Tokyo, Japan) at a magnification of 3,000.

3. Results and discussion

The dependence of the Mooney viscosity on blend ratio is illustrated in Figure 1. As can be seen, the mooney viscosity of the ENR/NR blend increased continuously with increasing ENR content in the blends. The results reveal that rich NR possessed the lowest viscosity whereas rich ENR possessed the highest viscosity. Apart from the higher molecular weight of NR, the poor filler dispersion also contributed to the low viscosity of silica-filled NR. As silica is highly polar filler whereas NR is considered to be a non-polar elastomer, the rubber-filler interaction is therefore relatively low. The improvement in the rubber-filler compatibility by the addition of ENR not only caused a better dispersion of the silica particles in the rubber matrix with an increase of the interphase but also increased the rubber-filler interactions and decreased the agglomeration of filler particles. The degree of filler dispersion in rich ENR was therefore higher than that in rich NR. According to all these factors, the increase in viscosity might be attributable to the chemical interaction between the epoxide group in the ENR and sianol groups on the silica surface. Therefore, Mooney viscosity progressively increased as ENR content in the blend increased.

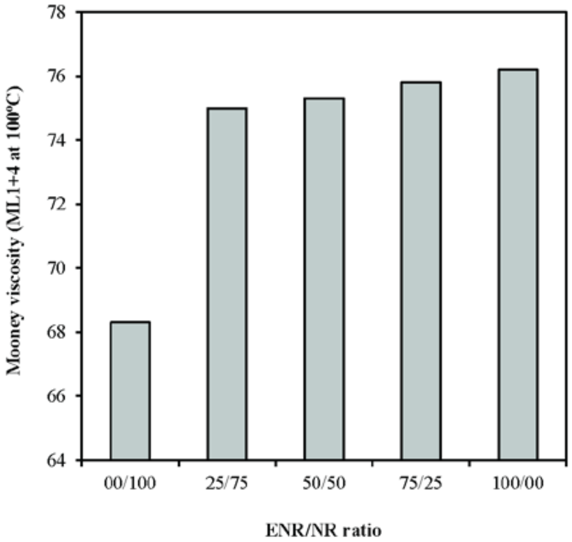


Figure 1 The Mooney viscosity of silica-filled ENR/NR compound in various blends ratio

The cure characteristics of the studied materials, expressed in terms of optimum cure time, t_{90}, were compiled and are shown in Figure 2. It can be seen that rich ENR had a significantly shorter optimum cure time, compared to rich NR. The optimum cure time decreased with an increase in the ENR content. The shorter cure time observed in rich ENR was due to the limited availability of crosslink sites obtained from an acid-catalyzed epoxy ring-opening reaction by sulfoxide and sulfenic acid from oxidation of the sulphur during the vulcanization process (Poh, Chen, & Ding, 1996; Lee et al., 1997), which might have led to ether crosslinks vulcanization by sulphur alone was faster and more efficient for ENR than for NR since isolated double bonds reacted more rapidly than contiguous double bonds (Gelling & Morrison, 1985; Ooi, Ismail, & Bakar, 2014). Similar observations were reported by Poh et al. (Poh et al, 2001) for the cure and tear properties of ENR 25/SMR L and ENR 50/SMR L blends. Longer cure times were found for rich NR. This is due to higher chemical interaction between molecules of rubber and filler via polar functional groups. ENR with its strong polar group produced a stronger filler-rubber interaction between the epoxide and silanol groups enhancing the curing reaction, compared with less polar rubber such as NR. NR has a poor filler-rubber interaction leaving the free silanol groups on the silica surface which can absorb some accelerators (Sengloyluan, Sahakaro, Dierkes, & Noordermeer, 2014) and/or can form an activator zinc-complex (Sombatsompop, Thongsang, Markpin, & Wimolmala, 2004), resulting in retardation of the vulcanization process.

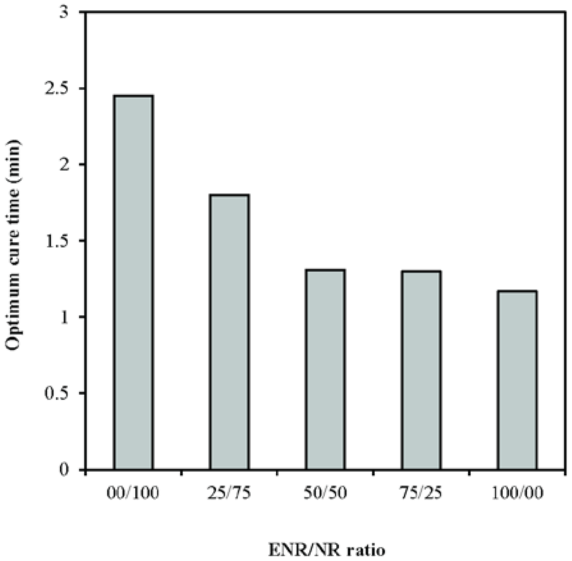


Figure 2 Optimum cure time (T_{90}) of silica-filled ENR/NR compound in various blends ratio

3.1 Tensile properties

The tensile properties the ENR/NR blend before ageing are shown in Figure 3. For the ENR/NR blend, the tensile properties were seen to increase marginally with an increase of the blend ratio up to 50/50 (wt/wt) and then those values slightly decreased. A positive deviation of tensile strength from the ideal was observed, suggesting that synergism had occurred and the maximum valves of tensile properties were obtained at 50% of ENR. This may be due to the synergistic effect obtained with miscible or partially compatible blends. When one component in the blend was in excess, as in the 25/75 or 75/25 ENR/NR blends, the rubber vulcanizates showed a progressing decrease in tensile strength when compared with a 50/50 blend ratio because the interaction between the two rubbers was no longer sufficient to withstand the applied stress. This behavior has also been reported by Poh and Khok (2000). It can be seen that the silica-filled ENR vulcanizate showed slightly higher tensile properties compared to the silica-filled NR vulcanizate because higher chemical interaction between the epoxide groups in the ENR molecules and the polar functional groups on the silica surface led to better filler dispersion, thus a higher tensile strength should be observed in ENR.

Modulus at 100% elongation which followed the same trend as the tensile result is shown in Figure 3. For the unaged blend, again a positive deviation from ideality was observed due to the miscibility of each other in the blend, as was previously discussed from the tensile measurements. The maximum value of the modulus at 100% elongation also occurred at 50% ENR, similar to that reported in the case of tensile strength. Expectedly, as seen in Figure 3, the modulus at 100% elongation of all blends did not significantly change. It was found that rich NR exhibited lower modulus than that of rich ENR. With the incorporation of ENR, the modulus at 100% elongation increased probably because of polymer-polymer or polymer-filler interactions. According to Gelling and Morrison (1985), the isolated double bonds in ENR enhanced the formation of intra-molecular sulphide linkages. Consequently the crosslink rate increased which restricted the flexibility of the rubber chains and produced stiffer rubber compounds resulting in a substantial increase in modulus.

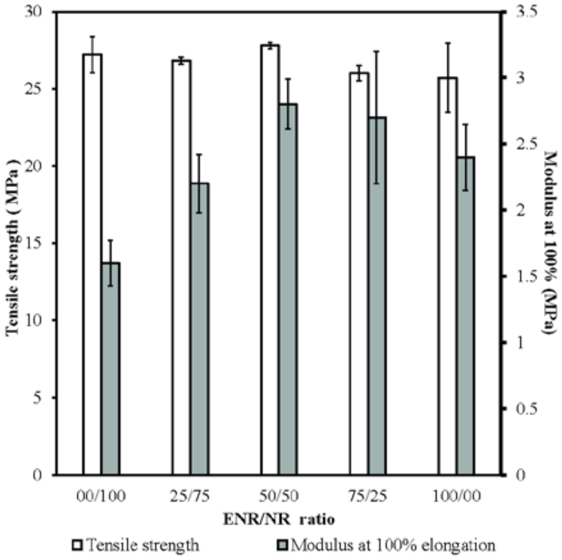
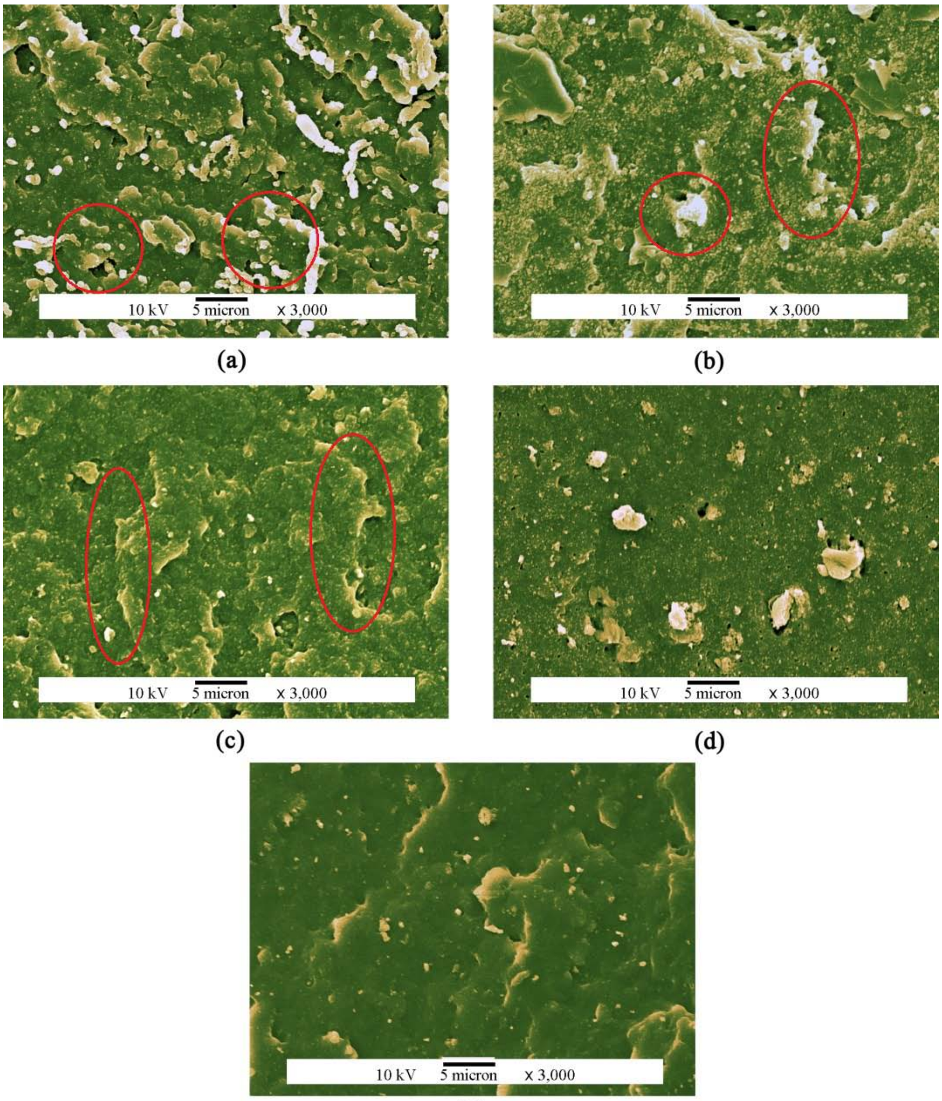


Figure 3 Tensile strength and modulus at 100% elongation of silica-filled ENR/NR compound in various blends ratio

3.2 Morphology

The differences in the results of tensile strength of the blends can be explained from scanning electron microscopy (SEM) micrographs of the fracture surface at various blend ratios, which are shown Figure 4. Figure 4(a) shows a SEM micrograph of the fracture surface of silica-filled NR vulcanizate; the dispersed particles of the pure NR were a cluster type, the dispersed particles were generally large and the shape of particles was irregular. The dispersion of filler in the rubber matrix was not continuous as a result of filler agglomeration and some voids (void defect) were present due to a lack of interfacial interaction between the filler and rubber matrix, which thus led to a poor filler dispersion and which thus decreased the tensile strength. However, the rough surface with stress whitening is a typical feature of ductile failure; which indicates the high tensile strength of the silica-filled NR vulcanizate. Compared to the silica-filled ENR, the fracture surface of the silica filled ENR vulcanizate was smooth, which resulted in brittle failure and hence an enhancement in the stiffness. The presence of the oxirane groups led to a polar-polar interaction between the silica and ENR matrix as discussed earlier. Agglomeration of silica was therefore difficult and as a result uniform dispersion was observed as shown in Figure 4(e). The heterogeneity of the system was confirmed from the SEM micrographs given in Figure 4(b) and 4(d). For the fracture surface of the filled ENR/NR blends [Figure 4(b-d)], the minor phase was dispersed as a the major continuous phase as shown in Figure 4(b) for 25/75 ENR/NR blend and an uniform dispersion became difficult and the particles were loosely packed, whereas for the 75/25 ENR/NR blend [Figure 4(d)], a flake-like structure was filled with pores and showed pullouts at its fracture surface. This indicated that the two rubbers had low miscibility with each other when one component in the blend was in excess. However, the fracture surface of the 50/50 ENR/NR blend [Figure 4(c)] showed a co-continuous morphology, where the phase was continuous and more homogenous phase dispersion and rough surface with stress whitening occurred. There was a good interfacial interaction between the filler and the matrix, resulting in the highest tensile properties. The dispersed particles became uniform and showed an excellent structure arrangement. The rubbers reinforce each other when subjected to tensile stress, as reflected by a higher tensile strength of the blend. The SEM micrographs shown in Figure 4 confirm that the presence of the oxirane groups which provided an interfacial interaction between filler and rubber matrix, thus resulting in better filler dispersion. These morphological features contributed to differences in the behavior shown by a variation of the blend ratio.



(a) (b) (c) (d) (e)

Figure 4 SEM micrographs of fracture surface of silica-filled ENR/NR vulcanizate in various blends ratio. (a) 0/100; (b) 25/75; (c) 50/50; (d) 75/25; (e) 100/0

3.3 Oil resistance and thermal ageing properties

The changes in properties after oil immersion could be used as an indicator of the resistance to oil which is one of the key characteristics in the final selection of the rubber to be used, especially in automotive, industrial and seal applications. Figure 5 shows the changes in volume of ENR/NR blends after being immersed in a low polar hydrocarbon oil having a high aniline point at 123.8°C (IRM 901) and in a more polar hydrocarbon oil having a lower aniline point at 89.5°C (IRM 903). It can be seen that ENR, a high polar rubber, contributes to an improvement in the oil resistance of the NR vulcanizate (Ngudsuntear et al., 2014). The filler-rubber interaction caused limitations in the ease of penetration of oil into the rubber chains. When the NR content in the blend increased, volume changes increased markedly. This is due to its similar hydrocarbon structure to NR and oil. However, ENR with a strong molecular polarity, in the more polar hydrocarbon oil (IRM 903), showed a larger change in volume than in the low polar hydrocarbon oil (IRM 901) because of high penetration of more polar hydrocarbon oil.

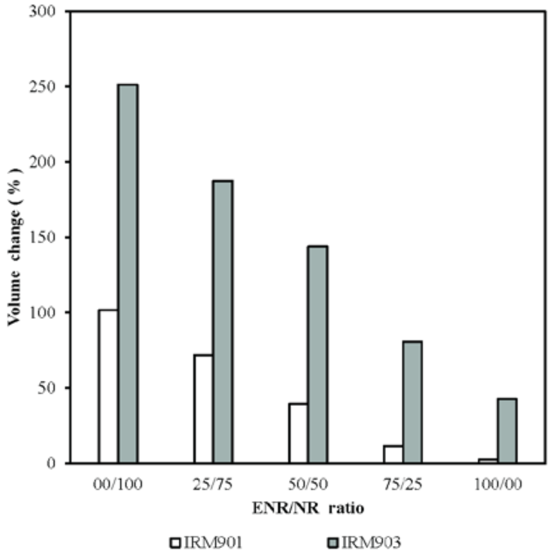


Figure 5 Volume change of silica-filled ENR/NR vulcanizate in various blends ratio after oil immersion at 100°C for 72 h

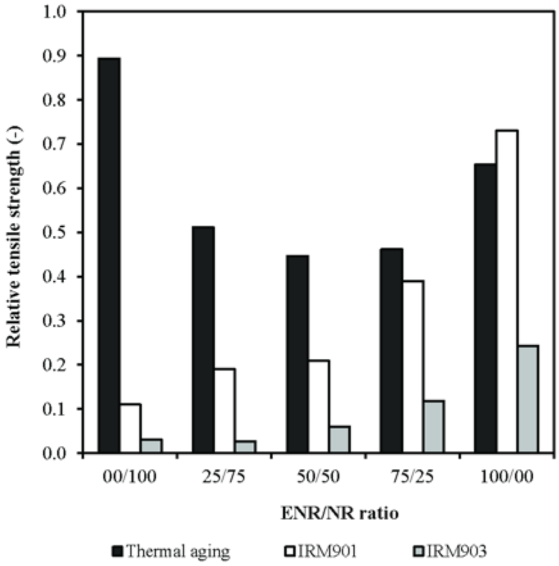


Figure 6 Relative tensile strength of silica-filled ENR/NR vulcanizate in various blends ratio

The effect of blend ratio on ageing resistance which is represented in terms of the relative value, the ratios of properties after ageing to those before ageing, were used as indicators for determining ageing resistance. The relative properties are more than 1, which indicated a high ageing resistance. The result of oil resistance based on the changes in tensile strength after oil immersion at 100°C for 72 h are presented in Figure 6. It is evident that tensile strength of all blends decreased after oil immersion because the relative tensile strength is less than 1. The relative tensile strength trends after immersion in both IRM 901 and IRM 903 oil were similar. As expected, the lowest relative tensile strength was found for rich NR and the highest relative tensile strength was found for rich ENR. NR is known to have poor oil resistance. Epoxidation has brought about substantial improvement in oil resistance. Tensile resistance of all the blends decreased with an increasing blend ratio of NR. This is due to more oil penetration into the blends and consequently during testing failure occurred at lower strength. However, at a similar blend ratio, blends after being immersed in IRM 901 oil exhibited higher relative tensile strength than in IRM 903 oil. ENR is a polar rubber due to the presence of the oxirane groups and the oil resistance was expected to increase with an increase in polarity.

Since natural rubber possesses high levels of unsaturation in the polymer backbone, the degradation of NR is promoted by exposure of NR to high temperature, oxygen, ozone, ultraviolet light, moisture, radiation and chemical agents. Multiple exposures, such as a combination of moisture and heat or oxygen and light can often result in accelerated deterioration. The decrease in tensile strength after thermal ageing was due to the breakdown of the crosslinks, mainly the polysulphidic ones. This decrease in crosslinks would therefore cause a drop in tensile strength of the aged blends. In order to obtain a quantitative representation of the severity of the effect of thermal ageing on the tensile strength, a plot of the relative tensile strength was carried out as shown in Figure 6. After thermal ageing at 100°C for 72 h, regardless of the blend ratio, ageing at high temperature led to a reduction of tensile strength (the relative tensile strength was less than 1). For the aged blends, the relative tensile strength decreased with increasing ENR content up to 50% by weight and then increased with a further increase in ENR content. Unlike oil resistance, silica-filled NR possessed higher relative tensile strength, compared to silica-filled ENR. The effects of thermal ageing are more significant in the case of ENR compared to NR. Poh and Lee (1994) reported thermal oxidation of the double bonds of NR occurred to form oxidative products which mainly consisted of hydroperoxide, hydroxyl and carbonyl compounds. In the case of ENR, thermal oxidation occurred not only of the double bonds, but also involved a epoxide ring-opening reaction to yield oxidative products having similar functional groups as that of NR. As the double bonds in NR were less reactive to thermal oxidative degradation, NR was more resistant to thermal ageing than ENR as can be seen from the higher relative tensile strength. The results of the present study agreed with the results of Chuayjuljit, Yaowsang, Na-Ranong, and Potiyaraj (2006) who reported the effects of ageing were more significant in the case of ENR as compared with NR. This probably is due to the fact that double bonds in the ENR molecular chains were activated by the neighboring epoxide groups. The poor ageing of sulphur vulcanizates of ENR was due to an acid-catalyzed ring-opening reaction of the epoxide groups with the formation of ether crosslinks. The acids were produced by the thermal decomposition of oxidized sulphides.

The effect of blend ratio on the relative modulus at 100% elongation strains after oil immersion and thermal ageing are shown in Figure 7. Also, the relative modulus increased progressively with increasing ENR content in the blends. It can be seen that the change (positive or negative) in modulus of all blends was observed after oil immersion. Blends with larger ENR content exhibited higher relative modulus. As the amount of the epoxide group increased, the mobility of the polymer chains decreased. Consequently, less oil penetrated into the rubber matrix and the elasticity of the rubber chains was reduced at higher relative modulus. However, at a similar blend ratio, ENR/NR blends after oil IRM 901 immersion exhibited higher relative modulus than the similar blends after oil IRM 903 immersion. ENR 50 is a polar rubber due to the presence of the oxirane groups and in the more polar hydrocarbon oil (IRM 903), it was found to exhibit a larger change in volume than in oil IRM 901, thus reducing its stiffness properties.

The modulus of all blends was relatively sensitive to thermal ageing, compared with the change in oil, as shown in Figure 7. It is known that rubber is prone to thermal oxidation leading to molecular chain-scission and thus a reduction in elasticity. The Young’s modulus for all of the silica-filled blends with different blend ratio shifted to a higher value after accelerated heat ageing tests indicating thermal degradation of the rubber matrixes in the blends (the relative Young’s modulus is more than 1). These increases are generally attributed to an increase in the stiffness of the rubber matrix brought about by a reduction in the elasticity of the rubber chains. The effects of ageing were more significant in the case of ENR as compared to NR. This probably was due to the fact that thermal oxidation occurred not only of the double bonds, but also involved epoxide ring-opening reactions to yield oxidative products, resulting in a relatively larger modulus for ENR as explained earlier. It can be seen that as the amount of ENR increased up to 50% by weight, the relative modulus significantly increased. For the blend with ENR >50% by weight, the relative modulus at 100% elongation decreased. The observed trend suggests epoxidized natural rubber has improved resistance to hydrocarbon oils, an improvement over the ageing limitations of natural rubber, whereas, the reverse was true for thermal ageing.

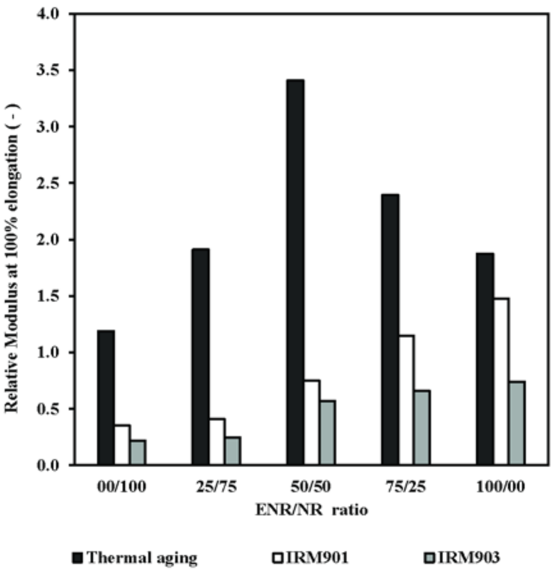


Figure 7 Relative modulus at 100% elongation of silica-filled ENR/NR vulcanizate in various blends ratio

3.4 Ozone resistances

The investigation of ozone cracks at the surface of the specimens could be used as an indicator of ozone resistance of the rubber vulcanizates, as was shown in Figure 8. Obviously, the photographs clearly showed that no critical cracks were form in the ENR vulcanizate even after exposing to 50 pphm of ozone concentration for 72 hours. This is probably due to the presence of a chemical interaction such as a crosslink and furthermore the presence of ENR might contribute to higher polymer-polymer or polymer-filler interactions prohibiting the growth of ozone cracks initiated in the rubber matrix. Consequently, ozone resistance of ENR arose from the lower reactivity of the double bonds to ozone attack.

However, for NR in which its double bonds were highly reactive to ozone attack, the fracture process was much faster, and this might allow matrix tearing to take place. Hence, the ozone cracks developed were large, deep, and wide in rich NR and 25/75 and 50/50 ENR/NR blends. Shorter cracks were also found in the 75/25 ENR/NR blend and the cracks found in this blend were less severe, compared to rich NR. The ozone ageing studies showed that a high ENR content in the blend was effective in modifying the weak NR from ozone attack.

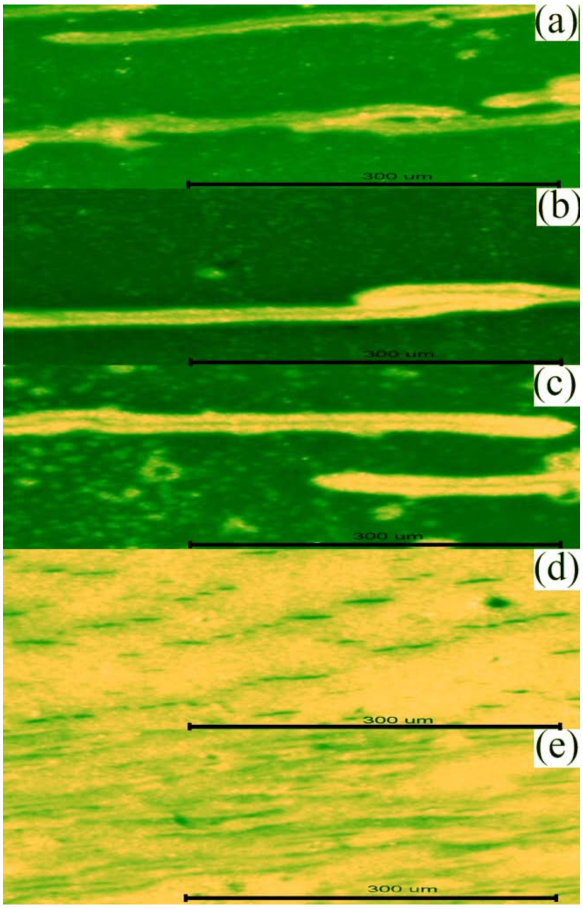


Figure 8 photograph of the ozone cracks at the surface of silica-filled ENR/NR vulcanizate in various blends ratio. (a) 0/100; (b) 25/75; (c) 50/50; (d) 75/25; (e) 100/0

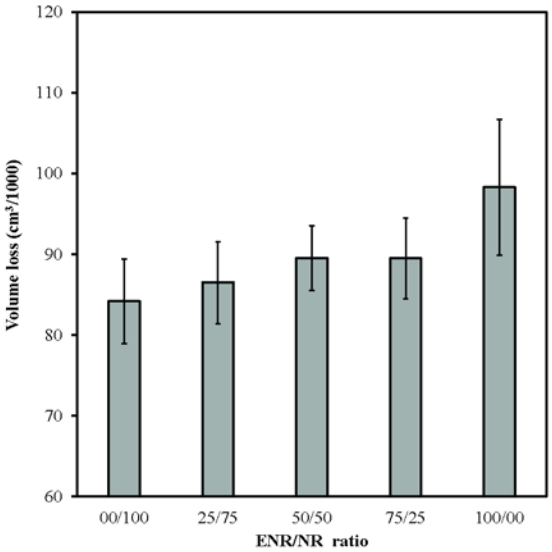


Figure 9 Volume loss of silica-filled ENR/NR vulcanizate in various blends ratio

3.5 Abrasion resistance

The abrasion resistance of a solid body is defined as its ability to withstand the progressive removal of material from it surface, as the result of mechanical action of a rubbing, scraping, or erosive nature. The effect of the ENR/NR blend ratio on abrasion resistance is as show in Figure 9. The volume losses increase with increasing ENR content in the blends. The increase in volume losses results from a reduction in difference torque (M_H-M_L) due to a greater acidity of the silica acceleration on the cure rate of ENR, whereas the NR vulcanizate showed better resistance to abrasion compared to the ENR vulcanizates because increasing the NR content in the blend gave rise to a softer silica-filled vulcanizate. Therefore, the rich NR rubber blend showed a better resistance to abrasion.

4. Conclusion

The cure characteristics and physiomechanical properties of silica-filled ENR/NR blends were investigated with special attention given to the effect of blend ratio. In addition to the mechanical properties, attention was also given to the resistance to oil, thermal ageing, and ozone of the blends. It was found that vulcanization was accelerated in the presence of ENR content in the blends. Increasing ENR content in the silica-filled ENR/NR blend gave rise to an increase in Mooney viscosity; however, cure time showed a reverse behavior for their respective blends. The faster cure found in silica-filled ENR was thought to arise from an additional crosslinks obtained from an epoxide ring-opening reaction via ether crosslinks and the chemical reaction between epoxide groups of ENR and the silanol groups on the silica surface, thus resulting in an increase in the crosslink density, high degree of reinforcement, and high mechanical properties such as tensile strength and Young's modulus. The tensile properties of the vulcanizate containing a rich ENR content in the blend was superior to that of the vulcanizate rich in NR content. The maximum value of tensile properties was obtained at 50/50 (wt/wt) of an ENR/NR blend and was correlated with the phase morphology. Resistance to oil and ozone attack of the rubber blend was mainly governed by polar functional groups in the rubber matrix as well as the silica. It is found that increasing the ENR content in the silica-filled ENR/NR blend led to an improvement in oil and ozone resistance, probably due to the improved silica dispersion in the rubber matrix and higher crosslink density (via ether crosslinks), with a reduction in resistance to degradation from thermal ageing and abrasion. ENR obtained by epoxidation of 1,4-polyisoprene is an intermediate material for value-added natural rubber. Above all, the results of this study have shown that the oil and ozone resistances of NR were improved by blending NR with ENR. In addition, there were improvements in the rheological and mechanical properties of the vulcanizate with blends of ENR.

5. Acknowledgements

Financial support of this research by the Rangsit Research Institute, Rangsit University is gratefully acknowledged.

6. References

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