Effect of Blend Ratio on Cure Characteristics, Mechanical Properties, and Aging Resistance of Silica-filled ENR/SBR Blends

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A R T I C L E I N F O	A B S T R A C T
	The effects of blend ratio on cure characteristics, tensile properties and the resistance to oil and thermal aging of epoxidized natural rubber (ENR) blended with styrene butadiene rubber (SBR) was investigated in the presence of silica selected as a reinforcing filler due to its unique characteristic to interact with ENR. The composition of ENR and SBR was varied from 0 to 100%. The results indicate that the Mooney viscosity and cure time, t_{c90} decreased with an increase of ENR in the blends. The silica-filled ENR exhibited higher tensile properties and high crosslink density compared to silica-filled SBR. The oil and thermal aging resistance of the ENR/SBR blend were increased with increasing ENR content. 2014 INT TRANS J ENG MANAG SCI TECH.

1. Introduction

The blending of two or more polymers by physical or chemical means may improve a variety of physical and chemical properties of the constituent polymers (Jovanovic *et al.*, 2013). The blending of rubbers plays an important role in enhancing the physical properties of

the final vulcanized product. The rubber blends are frequently used in the rubber industry to obtain the best combination of compound properties, processability, and cost. Natural rubber (NR) is a renewable and sustainable material, which has various good properties, such as high tensile strength, high elongation, and outstanding resilience, lending itself to be used in various applications. NR is an unsaturated polymer that consists of mainly of cis-1,4-polyisoprene. It nevertheless has some drawbacks such as poor oil resistance due to its nonpolar nature; high sensitivity to heat, oxygen, and ozone due to its reactive double bonds. A variety of synthetic counterparts are made to meet some specific requirements such as for high temperature applications or for oil-in contact products. To extend the use of NR, a variety of modification methods can be used to partly or completely alter the NR structure to enhance its properties to meet some specific requirements. The modification of NR via epoxidation reaction is probably the most common method used to prepare a product that has some improved properties than those of the unmodified one. Epoxidation of NR is the reaction of the carbon double bond with an active oxygen atom to yield a three membered ring structure containing oxygen. Reduction of the unsaturated unit or converting part of the carbon double bond of NR would improve its oil resistances and oxidative properties. Epoxidized natural rubber (ENR) containing 50% mole epoxidation (ENR50) has similar oil resistance to medium nitrile rubber and has properties which resemble those of synthetic rubbers, whereas the tensile properties are near those of NR because the ENR50 still has some remaining carbon double bonds but suffers from poor ozone resistance and heat aging properties (Chuayjuljit *et al*., 2006; Ismail *et al*., 2000). SBR, nonpolar synthetic rubber, describes families of synthetic rubbers derived from styrene and butadiene. It has good abrasion resistance and thermal aging properties (Goyanes *et al*., 2008). The ENR/SBR blend should be beneficial for improved thermal and oxidative stability.

The main aim of this work was to study the effect of blend ratio on cure characteristics, mechanical properties, and aging resistance of silica-filled ENR/SBR rubber blends over a range of blend ratios. The aging property studies are of interest for thermal aging at 100°C for 72 h and two types of oil, namely low polarity oil and high polarity oil at room temperature for 72 h.

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2. Research Methodology

2.1 Materials

High ammonia natural rubber latex (dry rubber content, DRC = 60%) was purchased from Thai Hua Rubber PCL., Rayong, Thailand. The latex is composed almost entirely of cis-1,4-polyisoprene. 98% formic acid was produced by Merck. 50% hydrogen peroxide (commercial grade), Teric 16A16, Methanol, and Sodium carbonate were purchased from GSP products Co., LTD., Thailand. Styrene butadiene rubber (SBR-1502) rubber was produced by BST Elastomers co., Ltd., Rayong, Thailand. Zinc Oxide (white seal) was purchased from Thai lysaght Co., Ltd., Thailand. Silica (TOKUSIL 233) was produced by Tokuyama Asia Pacific Pte., Ltd., Singapore. Benzothiazy l-2-cyclohexylsulfenamide (CBS, Monflex) was produced by MONFLEX PTE., Ltd., Singapore. Polyethylene glycol (PEG-4000) was purchased from Imperial industrial chemicals Co., Ltd., Thailand. Tetramethyl thiumram disulfide (TMTD) was purchased from Vessel Chemical Co., Ltd., Thailand. Wingstay-L and sulphur were purchased from GSP products Co., LTD., Thailand.

2.2 Preparation of *in-situ* epoxidized natural rubber

The formulation of ENR is shown in Table 1 Initially, ENR was prepared from dilute natural rubber latex (60% to 20% DRC with distilled water), 10% Teric16A16, as nonionic surfactant, was added to a 1 liter three-necked flask reactor, in which a controlled speed stirrer was mounted. The latex was stirred for 1 h, before a given amount of formic acid and hydrogen peroxide were slowly dropped into the reactor respectively using a peristaltic pump for a controlled addition rate. The latex was continuous stirred at 300 rpm for 6 h. A water bath was used to maintain the temperature at 50ºC. After the reaction, the ENR latex was coagulated by ethanol and the coagulum was washed repeatedly and dried thoroughly. ^{1}H-NMR spectra were recorded on a Bruker 300 MHz spectrometer and the conversion was determined as mol % epoxide by calculation using equation (1)

$$\text{mol \% epoxide} = \frac{I_{2.7}}{I_{2.7} + I_{5.1}} \times 100\% \quad \frac{I_{2.7}}{I_{2.7} + I_{5.1}} \times 100\%$$

$$(1),$$

where I is the intensity of the ^{1}H-NMR signals and the subscripts represent a value of the chemical shift.

Table 1: Formulation used for epoxidized natural rubber

Ingredients	
NR latex (20% DRC)	1.7 mole
Teric 16A16	2 phr[*]
98% Formic acid	0.39 mole
50% H_2O_2	1.3 mole

[*]phr = parts per hundred rubber

2.3 Compounding of ENR/SBR blends

ENR was prepared by the above method providing about 43% mole epoxidation. A ENR/SBR rubber blend compounded via conventional vulcanization (C.V.) using a two-roll mill with various chemicals, according to the formulations for rubber compounds is shown in Table 2 The SBR was masticated first on a two-roll mill by passing it through the rolls many times and then added ENR. After that, ZnO, stearic acid, and accelerator were added and mixed for 3 min. with a rolling bank and cut on each side. Then sulphur was added and mixed for 2 min. The mixing was completed by the addition of sulphur at 70°C for 3 min. Compounded rubbers were left overnight at room temperature. In advance of the processing, the optimum cure time (t_{c90}) was determined on the basis of the results of curing characteristics using a rheometer (TECH-PRO, Cuyahoga Falls, Ohio, USA) according to ISO-3414 for 30 min at 160°C. Each rubber compound was compression molded at 160°C and t_{c90} min using a hydraulic press.

Table 2: Formulations for rubber compound

Ingredients	phr
ENR	100-0
SBR	0-100
Zinc oxide	5
Stearic acid	2
Silica (TOKUSIL233)	40
PEG4000	3
Wingstay-L	2
CBS	1.6
TMTD	0.3
Sulphur	2.5

2.4 Tensile properties and aging properties

The tensile properties of blended vulcanizates were determined using a universal testing machine (Model 5565; Instron Corp., Canton, MA) with a crosshead speed of 500 mm/min

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and a 500 N load cell. The specimens were dumbbell shaped. The test specimens were aged for 72 h with hot air at 100°C and oil resistance was determined in accordance with the method described by ASTM D471-06. The specimens to be tested were immersed in hydrocarbon oils at room temperature for 72hr. Oils used in this testing were, IRM 901 as low polarity oil and IRM 903 as high polarity oil. When the specified test time was reached, the test specimens were removed from the oil and wiped with tissue paper to remove the excess oil from the surface before properties testing.

2.5 Estimation of crosslink density

The estimation of crosslink density of rubber blends from the stress-stain data was used the relationship of $\sigma/(\lambda-\lambda^{-2})$ which respect to $1/\lambda$ according to equation (2), which is of the Mooney-Rivlin equation.

$$\frac{\sigma}{\lambda - \lambda^{-2}} = 2C_1 + \frac{2C_2}{\lambda} \tag{2}$$

where the constants C_1 and C_2 can be obtained. $2C_1$ represents the y-axis intercept of the curve whereas $2C_2$ represents the slope of the curve. From the plot, a linear trend is observed and the physically effective crosslink density (η_{PHY}) can thus be determined. Using the value of the y-axis intercept, the physically effective crosslink density is calculated by equation (3) with R, the gas constant (8.314 J.mole^{-1}K^{-1}) and T, the absolute temperature (273.15 K).

$$\eta_{PHY} = \frac{C_1}{RT} \tag{3}$$
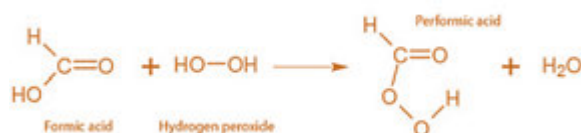
2.6 Morphorogy of the blend

The morphology of the NR and ENR latex was examined using a JEM-1220 transmission electron micro-scope (TEM) with a magnification of 3,000 and 80 kV. A thorough understanding of blend morphology is important because the properties of polymer blends are strongly dependent upon it. A scanning electron microscopic (SEM) Model JEOL-5600LV; Tokyo, Japan was used to observe the tensile specimens fractured surface at a magnification of 3,000. The samples were mounted on aluminum stubs and sputter coated with a thin layer of gold to avoid electrostatic charging during examination.
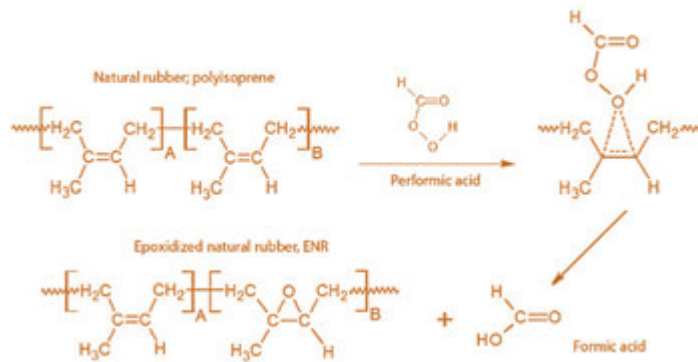
3. Results and Discussion

The in situ epoxidation of the NR latex (Figure 1) using hydrogen peroxide and formic acid also yields epoxidized natural rubber (ENR). The characteristics of the ENR latex were analyzed based on proton nuclear magnetic resonance (^{1}H-NMR). The unsaturated methine protons of cis-1,4-isoprene units appeared at 1.68, 2.05, and 5.1 ppm, respectively. The characteristic peaks for olefinic and oxirane methine protons in the ^{1}H-NMR spectrums appear at 5.1 and 2.7 respectively. The results reveal that the increasing signals at 2.7, is a result of the increment of the epoxide group as shown in Figure 2. In Figure 3, the morphology of NR and the ENR latex were examined by transmission electron microscopy (TEM). The particles of NR and ENR are spherical and have a smooth surface and darker areas at the center represent the NR core regions, which contain the carbon double bonds stained with OsO$_4$, (Figure 3a) and the lighter color areas in Figure 3b show domains which indicate the region of lower carbon double bonds concentration. The observed proton NMR signals and TEM micrograph can be qualitatively used to confirm that the NR was epoxidized.
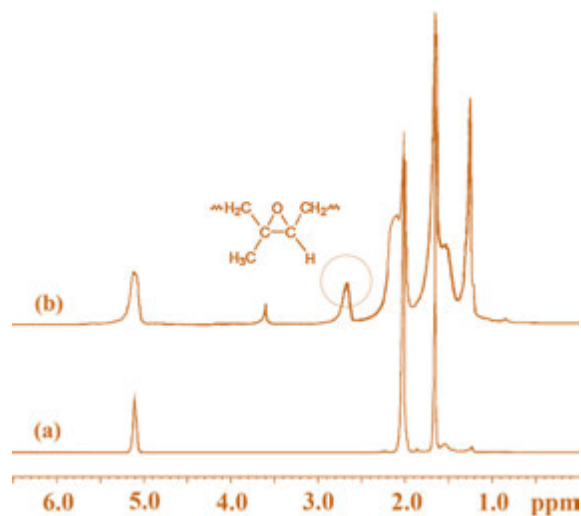
3.1 Processability and Cure characteristics

The result of the Mooney viscosity of ENR/SBR rubber blends is shown in Figure 4. With the increment of SBR, the value of the Mooney viscosity of ENR/SBR rubber blend increased with increasing SBR content due to the reduction of its bulkiness, which is attributed to the restriction of molecular chain movement. This resulted in an increase in the Mooney viscosity of the compound rubber blends. The optimum cure time is the time for the vulcanization reaction required to obtain optimum physical properties. It can be seen that each compound exhibits different cure characteristics, which is attributed to the fact that each type of rubber possesses difference properties, such as structure, polarity, and compatibility.

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**Figure 1:** The *in-situ* epoxidation of NR employing hydrogen peroxide and formic acid.

Figure 2: ^{1}H-NMR spectra for (a) NR, and (b) ENR containing 43% epoxide group.

Figure 5 shows the variation of optimum cure time of the SBR/ENR blend with blend ratio. It can be seen that t_{c90} decreases with increasing ENR composition in the blend. Owing to the activation of an adjacent double bond by the epoxide group (Sadequl et al., 1998), the optimum cure time for ENR is shorter than that of SBR. The reduction of t_{c90} with increasing ENR composition in the blend is more significant. This may be due to chain opening of the epoxy group on ENR (rubber-rubber interaction) which participated in the vulcanization reaction leading to a low cure time of the blends having high ENR content (Hakim *et al.*, 2009).
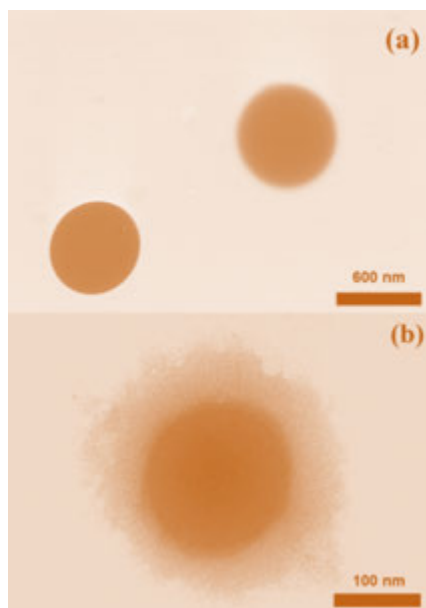
Figure 3: TEM micrograph at 80,000× (a) NR (b) ENR.
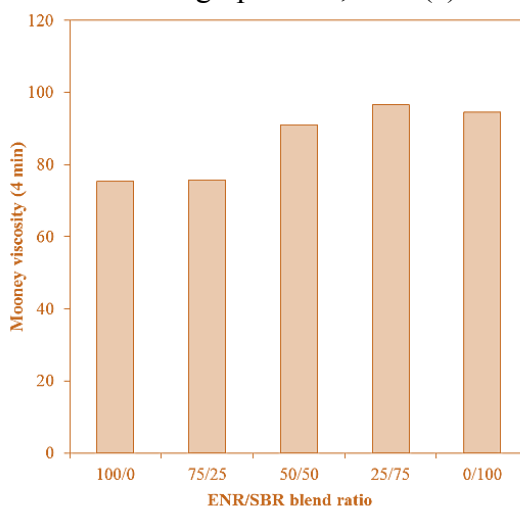

Figure 4: Mooney viscosity ENR/SBR blends.

3.2 Tensile properties and Crosslink density

The tensile instrument provided values of the tensile strength and tensile modulus. Figure 6 shows the tensile properties of vulcanizates of ENR/SBR blend. The tensile strength of high ENR blend ratio is higher than the low ENR blend ratio due to the remaining strain-induced crystallinity of ENR (Chuayjuljit *et al*., 2006). On the other hand, it can be seen that the silica filler distribution in rubber matrix is affected significantly by the difference in polarity between the ENR and SBR. This may be attributed to a higher filler-rubber interaction between the epoxide groups in ENR and the hydroxyls on the silica surface (Poh *et al*., 2002) which provided an improvement in the rubber-filler interaction (Manna *et al*., 1998) and led to a better distribution of filler in the rubber matrix; thus a higher tensile strength should be

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observed in high ENR blend ratio when compared with that of high SBR blend ratio.

In Figure 6, it can be seen that the tensile modulus increased with increasing ENR content in the rubber blends. This is an indication of the rubber stiffness for high content of ENR due to the filler-rubber interactions. The data from stress-strain measurements for rubber films was used to construct plots of $\sigma/(\lambda-\lambda^{-2})$ against $1/\lambda$ to obtain the values of the elastic constants and estimation of crosslink density. The crosslink density is expressed in terms of moles of effective network chains per cubic centimeter of rubber as shown in Figure 7. It can be seen that the crosslink density increases as the ENR increase, resulting in high tensile strength.
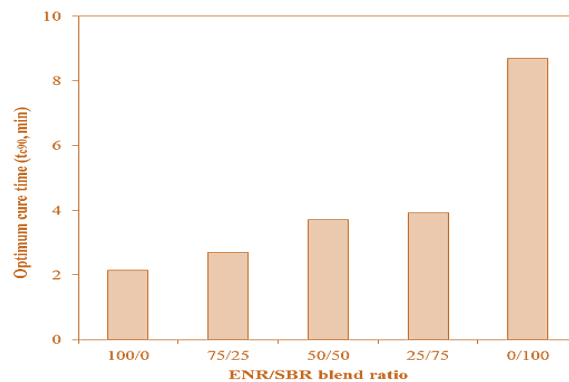
Figure 5: Optimum cure time of ENR/SBR blends.
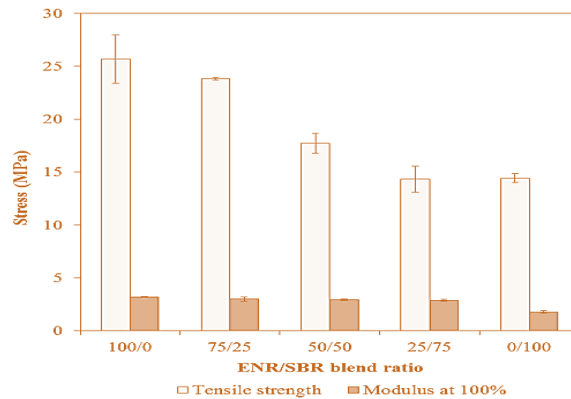
Figure 6: Tensile properties of ENR/SBR blends.
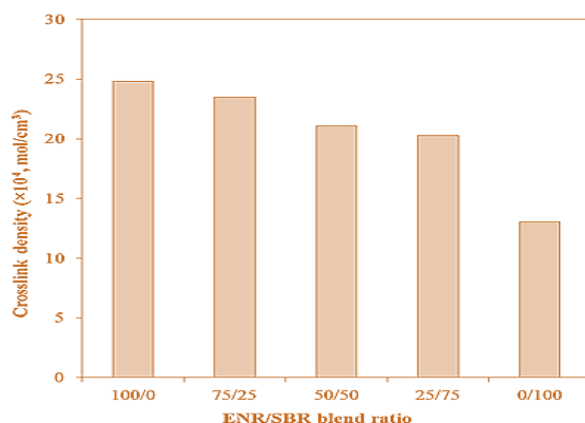
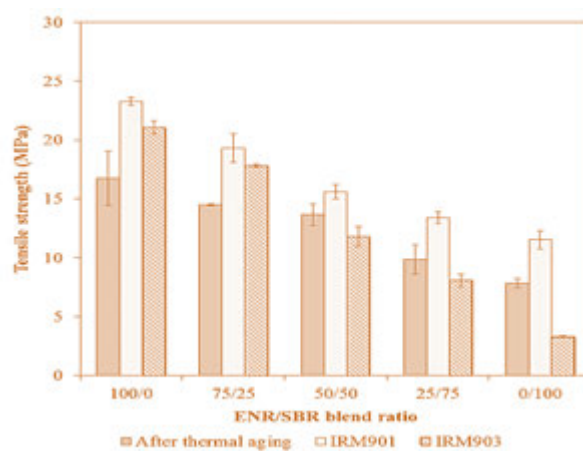**Figure 7:** Crosslink density of ENR/SBR blends.

3.3 Thermal aging and oil resistance

The thermal aging and oil resistance results are presented as tensile properties. The thermal aging properties measurement at 100°C for 72 h is presented in Figure 8. It can be seen that the results of tensile strength are increased with increasing ENR; the lowest tensile strength was found for rich SBR and the highest tensile strength was found for rich ENR. This is due to the good filler-rubber and rubber-rubber interaction of ENR, whereas the tensile strength decreased compared with before aging. It can be seen that the lower of tensile strength after aging is due to thermal aging. Rubbers undergoing oxidation reactions resulted in chain scission or oxidative breakdown. For the case of oil resistance, it can be seen that tensile strength increased with increasing ENR because the small amount of unsaturated in ENR reduced the elasticity of the rubber chains leading to a rigid rubber material and better interaction of silica in the polar rubber matrix, which consequently resulted in less oil penetration into the rubber matrices. This also implies that the presence of polarity of the rubber plays a significant role in providing a good filler-rubber interaction which resisted the penetration of the oil into the gaps between the rubber chains.

Figure 9 shows the results of 100% Modulus of rubber vulcanizate, which indicates the stiffness of the material. It can be seen that the Modulus increased with increasing ENR due to chain scission or oxidative breakdown with oxygen while aging. This resulted in the generation of rubber macro-radicals, which formed rubber chains with some degree of branching. Thus the vulcanizates would become stiffer resulting in higher Modulus. In the case of oil immersion, the results show a similar trend of on oil immersion of tensile strength.

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3.4 Morphology of blend

Morphology is a major factor of rubber blends, which determines the extent to which the blends are compatible. It is well known that the phase structure of the blend is influenced by several factors, including the surface characteristics, blend ratio, viscosity of each component and compounding process. The morphology of the rubber blend before aging tensile fracture surface at a magnification of 3000 is shown in Figure 10. After the polymer was stretched with high stress, it can be observed that the fracture had white fibrils on the surface, which is a typical feature in ductile failure. The ENR vulcanizate had a high amount of white fibrils and a rough surface, which is an indication of a higher tensile strength than observed for the SBR vulcanizates. This is due to high dispersion of silica in ENR matrix. In the case of SBR, the agglomeration of silica in the blend matrix occurred and smooth surface without white fibrils and many small pores indicated that the interaction between the silica and rubber was poor leading to the low values for the tensile properties. The morphology of the ENR/SBR blend with a 50/50 ratio is shown in Figure 10b; it can be seen that the small amount of white fibrils and many tiny holes are present. This implies that ENR/SBR blends are immiscible which may be due to the difference of polarity in each rubber component.

Figure 8: Tensile strength of ENR/SBR blends after aging.
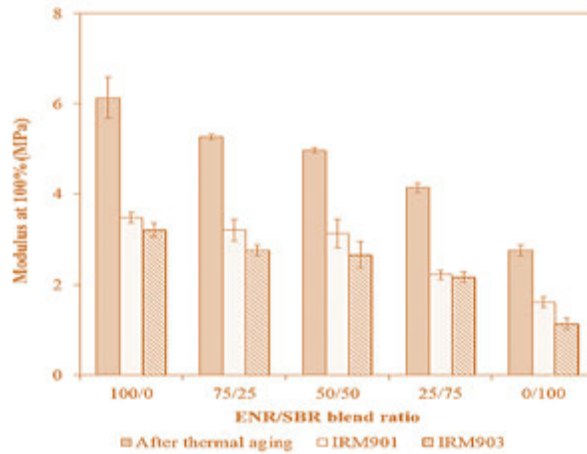
Figure 9: Modulus at 100% of ENR/SBR blends after aging.
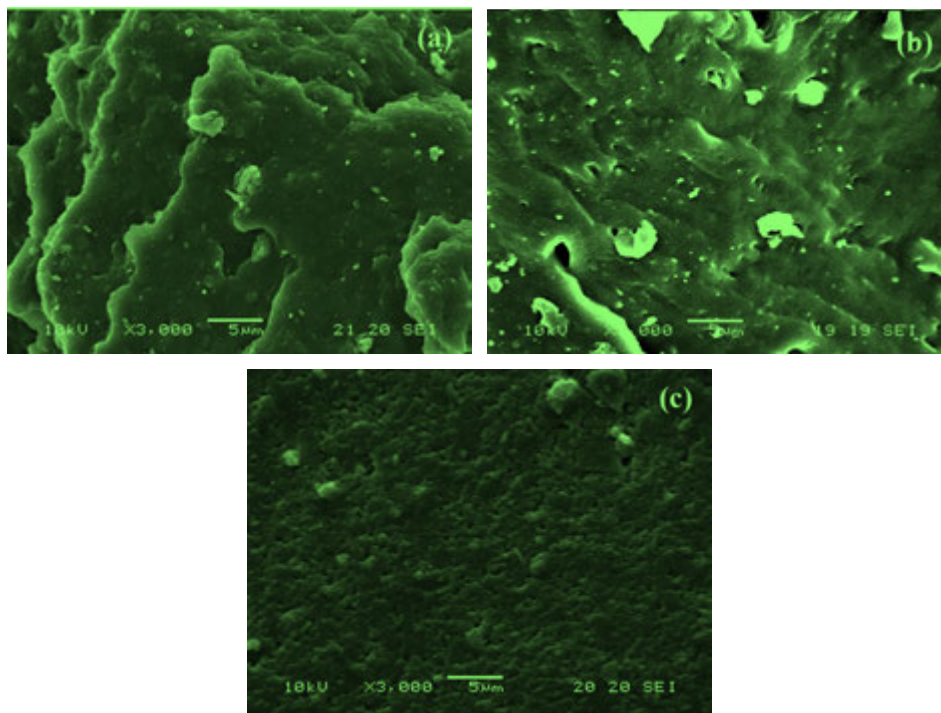
Figure 10: Crosslink density of ENR/SBR blends.

4. Conclusion

The effect of blend ratio on cure characteristics and physico-mechanical properties of silica-filled ENR/SBR blends were investigated. Mooney viscosity decreased with an increase in ENR content in the blends, whereas vulcanization was accelerated in the presence of ENR content in the blends. The tensile properties of the vulcanizate were increased with increasing ENR content in the rubber blends. In addition to the mechanical properties, attention was also given to the resistance to thermal aging and oil on the blends. Resistance to thermal aging and oil of the rubber blend was mainly governed by polar functional groups in the rubber matrix

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as well as the silica. It is found that increasing ENR content in the silica-filled ENR/SBR blend led to an improvement in thermal aging and oil resistance, probably due to the improved silica dispersion in the rubber matrix.

5. Acknowledgements

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