

# EFFECT OF VULCANIZATION SYSTEMS AND CROSSLINK DENSITY ON TENSILE PROPERTIES AND NETWORK STRUCTURES OF NATURAL RUBBER

Nabil Hayeemasae<sup>a,b</sup>, Kamaruddin Waesateh<sup>c</sup>, Siriwat Soontaranon<sup>d</sup>, Abdulhakim Masa<sup>e\*</sup>

<sup>a</sup>Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani Campus, Pattani, 94000, Thailand

<sup>b</sup>Research Unit of Advanced Elastomeric Materials and Innovations for BCG Economy (AEMI), Faculty of Science and Technology, Prince of Songkla University, Pattani Campus, Pattani, 94000, Thailand

<sup>c</sup>Islamic Sciences Demonstration School, Faculty of Islamic Sciences, Prince of Songkla University, Pattani Campus, Pattani, 94000, Thailand

<sup>d</sup>Synchrotron Light Research Institute, Muang District, Nakhon Ratchasima, 30000, Thailand

<sup>e</sup>Rubber Engineering & Technology Program, International College, Prince of Songkla University, Hat Yai, Songkhla, 90110, Thailand

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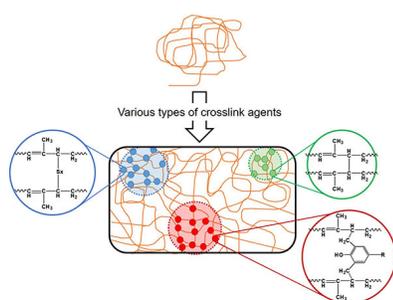
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\*Corresponding author  
abdulhakim.m@psu.ac.th

## Graphical abstract



## Abstract

The mechanical properties of natural rubber (NR) vulcanizate depend strongly on several factors, i.e., vulcanization systems and crosslink density. These two parameters are originally from the formulation design of the vulcanizate. To focus more on such details, influences of three different vulcanization systems (sulfur, peroxide, and phenolic resin) with variations in their crosslink densities were studied by focusing on the change of curing properties, crosslink densities, mechanical properties and network structures of the NR vulcanizates. The crosslink density of various vulcanization systems increased with increasing curing promoters, as revealed by temperature scanning stress relaxation measurement. The tensile modulus at 100% strain increased with increasing crosslink density in all systems but the tensile strength varied with the vulcanization systems and degree of crosslink density. At the same crosslink level, the greatest tensile strength was obtained when the sulfur was used as a crosslinker, which was 100% greater than those obtained from peroxide and 200% over phenolic systems. In comparison to the phenolic resin system, sulfur and peroxide crosslink systems had a more uniform distribution of the crosslink network structure. The size of the network structure was found to be independent of the tensile strength. The peroxide system had the most uniform distribution of the crosslink network structure.

Keywords: Natural rubber, Vulcanization systems, Crosslink densities, Network structure, Microstructure

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## 1.0 INTRODUCTION

Natural rubber (NR) is used extensively in various applications due to its excellent properties such as excellent elastic properties, high mechanical strength, good resilience, and damping behavior [1]. However, the NR has never been used as product unless it is vulcanized. By vulcanization, the properties of NR can be enhanced [2].

Vulcanization is chemical reaction where the three-dimensional (3D) linkages between rubber chains are formed, converting the rubber from viscoelastic materials to elastic materials. The vulcanization reaction is usually done at high temperatures in the presence of the vulcanizing agent. Various types of crosslink agents have been employed to vulcanize rubber compounds. Among them, sulfur, peroxides, and phenolic resin systems are of the most widely used for crosslinking the rubbers.

It is well-accepted that the network structures formed in the rubber depend on several factors, including, the curing system and degree of crosslink density [3-11]. The hardness and tensile modulus of rubber are generally enhanced linearly with the increasing crosslink density in all crosslink systems. The tensile strength increased until maximum value, then decreased while the thermal properties varied with type and crosslink density levels.

However, most studies only focused on individual crosslink systems in particular on the mechanical, thermal, and dynamics properties. Only a few studies have conducted comparative studies on the physical and microstructures of different systems [12,13]. Osaka *et al.* [12] investigated the effects of various amounts of peroxide and phenolic resin systems on the mechanical properties of hydrogenated acrylonitrile-butadiene rubber (HNBR). They found that the elastic modulus and the strain at break of the phenolic resin system were higher than those of the peroxide crosslinked HNBR due to the more stiffness and rigidity of the crosslink junctions initiated by phenolic resin. In addition to the lower crosslink density of phenolic resin, the more homogeneity in the network structure also facilitates the longer elongation. Ikeda *et al.* [13] comparatively studied the changes in mechanical properties and strain-induced crystallization behavior of peroxide and sulfur crosslinked NR. They found that the crystallization behaviors of both systems are different, depending on crosslink systems. The formation of network structure in the sulfur system was more complicated and less homogeneous. Although these reports provided much useful information, the effect of different crosslink agents on properties enhancement and microstructural change was still not entirely understood.

To gain more understanding of the influence of vulcanization systems and crosslink densities on the variation of mechanical properties and network structure formation in the rubber matrix, a comparative study of NR crosslinked with different

vulcanizing agents, i.e., sulfur, peroxide, and phenolic resin was conducted. The effect of these three vulcanization systems and their crosslink densities on curing behaviors, mechanical characteristics, and microstructures of the obtained NR vulcanizates were discussed.

## 2.0 METHODOLOGY

### Materials

NR used was Standard Thai Rubber (grade STR5L), purchased from Chalong Concentrated Natural Rubber Latex Industry Co., Ltd., Songkhla, Thailand. Stearic acid and zinc oxide (ZnO) used as an activator for sulfur vulcanization systems were supplied by Global Chemical Co. Ltd., Samut Prakarn, Thailand, and Imperial Chemical Co. Ltd., Pathumthani, Thailand. N-cyclohexyl-benzothiazyl-sulphenamide (CBS), used as an accelerator, was purchased from Flexsys America L.P., West Virginia, USA. Sulfur (S) was produced by Siam Chemical Co., Ltd., Samut Prakan, Thailand. Dicumyl peroxide (DCP) crosslinker was manufactured by Wouzhou International Co., Ltd., China. Triallyl isocyanurate (TAIC) supplied by Aldrich (USA) was used as a co-crosslink agent for the peroxide crosslink system. Resole-type phenolic resin crosslink agent (HRJ-10518) and stannous chloride ( $\text{SnCl}_2$ ), a catalyst for phenolic resin system supplied by Schenectady International, Inc., NY, USA, and KemAus, Australia, respectively.

### Sample Preparation

NR compounds containing different vulcanization systems, namely, sulfur, peroxide, and phenolic resin, were prepared by using a laboratory-size internal mixer. Three variations for each vulcanization system were employed to gain the vulcanizates with different crosslink densities. The list of all chemical names and contents is displayed in Table 1. It should be noted that the stearic acid and ZnO were not included in the formulation of peroxide and phenolic resin systems due to they were an activator only for the sulfur vulcanization system. Before adding curing chemicals (S+CBS, DCP+TAIC, and HRJ-10518+ $\text{SnCl}_2$ ), the NR with and without stearic acid and ZnO were initially mixed for 3 minutes. The overall mixing time was held constant at 5 min for all rubber formulations. The resultant rubber compounds were tested for their curing characteristics before compression-molding at 160 °C following their respective curing times. The amount of S, DCP, and HRJ-10518 crosslink agents were fixed at 1, 1, and 5 parts per hundred parts of rubber (phr), respectively. At the same time, the curing promoters, CBS for sulfur, TAIC for peroxide and  $\text{SnCl}_2$  for phenolic were varied to gain the vulcanizates with different crosslink densities. The sample crosslinked with sulfur, peroxide, and phenolic resin systems were noted as S: CBS, P: TAIC, and Ph:  $\text{SnCl}_2$ , respectively.

**Table 1** Compound formulations for NR with different crosslink agents

Ingredient	Quantity (phr)		
	S: CBS	P: TAIC	Ph: SnCl <sub>2</sub>
NR	100	100	100
Stearic acid	1	-	-
ZnO	3	-	-
S	1	-	-
CBS	1, 2, 3	-	-
DCP	-	1	-
TAIC	-	1, 2, 3	-
Phenolic resin	-	-	5
SnCl <sub>2</sub>	-	-	2, 3, 4

### Curing Characteristics

The curing properties, namely scorch time ( $T_{S1}$ ) and torque difference ( $M_H - M_L$ ) of the rubber compounds were investigated using a moving die rheometer (Montech MDR 3000 BASIC, Germany) at 160 °C.

### Measurement of Crosslink Density

The crosslink density ( $\nu$ ) of various rubber vulcanizates was estimated through the temperature scanning stress relaxation (TSSR) (Brabender, Duisburg, Germany). The NR specimens were placed and stretched for 50% in the heating chamber at a temperature of about 23 °C. After 2 h, a non-isothermal test was performed with a heating rate of 2 °C/min until the specimens were damaged.

The  $\nu$  was estimated from the initial part of the normalized force curve according to the following correlations:[14]

$$\sigma = \nu RT(\lambda - \lambda^{-2}) \quad (1)$$

$$\nu = \kappa/R(\lambda - \lambda^{-2}) \quad (2)$$

$$\kappa = \sigma/T \quad (3)$$

where,  $R$  is the universal gas constant,  $\lambda$  is the strain ratio,  $\sigma$  is mechanical stress and  $T$  is absolute temperature.

### Measurement of Tensile Properties

The tensile properties of NR vulcanizates were determined by using a universal tensile testing machine (LLOYD Instruments, LR5K Plus, UK). Dumbbell shaped test specimens were cut and tested at room temperature with crosshead speed of 500 mm/min according to ISO 37. Five replicates were done for each type of sample in the tensile test.

### Observation of Microstructural Changes

Microstructural changes, i.e., size and distribution of crosslinked network structures were investigated using

small angle X-ray scattering (SAXS) measurement. The SAXS measurements were performed at Beamline 1.3W, the Siam Photon Laboratory, Synchrotron Light Research Institute (SLRI), Nakhon-Ratchasima, Thailand. The data was collected during stretching at room temperature. All data were normalized and corrected by using SAXSIT 4.40 data processing software. Three replications were performed for each sample, and the data close to average was reported.

## 3.0 RESULTS AND DISCUSSION

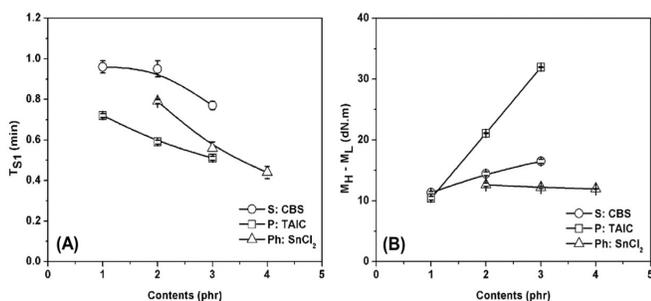
### Curing Characteristics

Variations of vulcanization systems and curing promoter content on the curing characteristics of the NR vulcanizates are shown in Figures 1(A) and (B). The  $T_{S1}$ , an initial formation of 3D networks between rubber chains, decreased with increasing curing promoters in all cases, indicating that the vulcanization reaction initiated faster with the presence of curing promoters. The  $T_{S1}$  was reduced from 0.96 min to 0.77 min in the sulfur system, 0.72 min to 0.51 min for the peroxide system, and 0.79 min to 0.44 min in the phenolic resin system. This reduction was attributed to increasing curing promoters resulting in a more significant number of reactive species for initiating and propagating the crosslink reaction, accelerating the formation of 3D links between rubber chains.

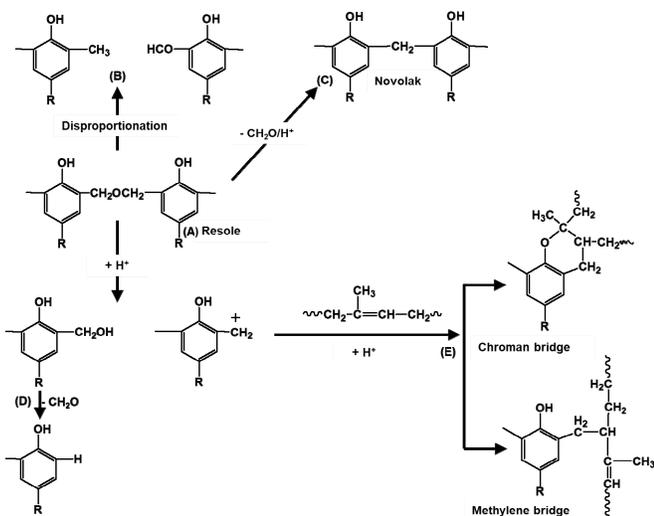
The  $M_H - M_L$ , an indication of crosslink density, was also shown to be enhanced by the increased addition of curing promoters in sulfur and peroxide systems. In contrast, the phenolic resin system showed the opposite trend. The increase of  $M_H - M_L$  revealed that the addition of crosslink promoters enhanced the crosslink density of rubber compounds containing sulfur and peroxide agents. In the case of the sulfur system, the  $M_H - M_L$  changed from 11.33 dN.m. to 16.51 dN.m. with an increasing amount of accelerator (CBS) due to an increase in the number of active sulfurating agents that were available for crosslinking reaction [5]. The increased TAIC contents in the peroxide system caused an increment of torque different from 10.43 dN.m. to 31.96 dN.m. due to the TAIC generating higher reactive sites for propagating crosslinking reactions. The TAIC co-agents are often used to enhance the crosslinking reaction capacity of the peroxide-based crosslink system, resulting in the crosslink density improvement in the vulcanizate [15-17].

In contradiction, the  $M_H - M_L$  of the rubber compounds with phenolic resin system was slightly decreased from 12.61 dN.m to 11.95 dN.m with increasing SnCl<sub>2</sub> contents, suggesting the reduction of crosslink density. The slight decrease was probably attributed to the competitive formation of non-reactive species, reducing the active sites for crosslinking reaction, as seen in Figure 2 (B - D).

According to the previous reports [18-19], the ether bridge and hydroxymethyl end groups of the resole type phenolic resin (Figure 2 (A)) are degraded under the acidic catalyst ( $\text{SnCl}_2$ ) condition, forming the benzylic cations. These cations are then attached to the rubber chains through methylene bridge and chroman linkages (Figure 2 (E)). However, the degradation of hydroxymethyl end groups also yielded unreactive species such as the transformation of dimethylene ether bridge to methyl ( $-\text{CH}_3$ ) or aldehyde ( $-\text{CHO}$ ) (Figure 2 (B)), novolac type resin (Figure 2 (C)) and H- atom end groups (Figure 2(D)). These unreactive groups would hamper the crosslinking reaction.



**Figure 1** Curing characteristics of the NR vulcanizates with variation of vulcanization systems and crosslink densities; (A) scorch time, TS1 and (B) torque difference,  $M_H - M_L$

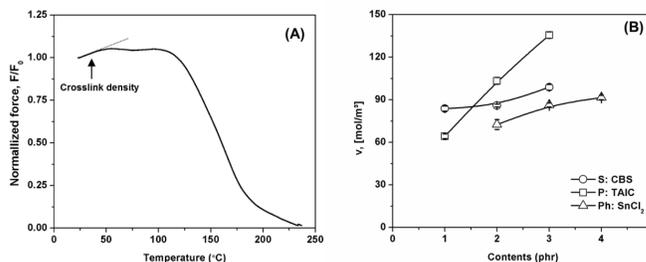


**Figure 2** Illustration of crosslink reaction of phenolic system with rubber

### Crosslink Density

The crosslink density of the NR vulcanizates with variation of curing systems and crosslinking levels are shown in Figure 3. It was seen that the crosslink density of various systems increased with increasing curing promoters. For the sulfur and peroxide systems, the enhancement of crosslink density was simply due

to the increased reactive site for initiating and propagating the crosslink reaction. As a result, the crosslink density of rubber vulcanizates was improved from  $83.78 \text{ mol/m}^3$  to  $98.82 \text{ mol/m}^3$ , and  $64.27 \text{ mol/m}^3$  to  $135.62 \text{ mol/m}^3$  for sulfur and peroxide systems, respectively. However, contradictory results were seen from rheometer and TSSR in case of phenolic resin cure system. The crosslink density results gained from rheometer showed a slight decrease trend (from  $12.61 \text{ dN.m}$  to  $11.95 \text{ dN.m}$ ) with increasing curing promoter. In contrast, the crosslink density obtained from TSSR measurement increased from  $72.58 \text{ mol/m}^3$  to  $91.57 \text{ mol/m}^3$ . The difference can be explained as follow; since the rheometer test was performed at a higher temperature ( $160 \text{ }^\circ\text{C}$ ), thus the torque obtained would be related to only the chemical crosslinks [20-22.]. In the case of TSSR measurement, the crosslink density was estimated from the initial part of the normalized force curve (Figure 3 (A)), which was at a much lower temperature (below  $50 \text{ }^\circ\text{C}$ ) than that of the rheometer. Thus, the effect of physical crosslinks, i.e., chain entanglements, was surely included in the obtained results in addition to the chemical crosslinks [23]. It is also assumed that the polymerized phenolic molecules such as novolac tend to aggregate to form phenolic resin domains, which can act as additional crosslinks and/ or fillers in the rubber matrix, restricting the movement of rubber molecules. Consequently, the overall crosslink density of the NR crosslinked with the phenolic resin was increased under TSSR measurement. Although the crosslink densities estimated from the rheometer and the TSSR were different, the results showed good agreement of crosslink densities ranking (peroxide > sulfur > phenolic).

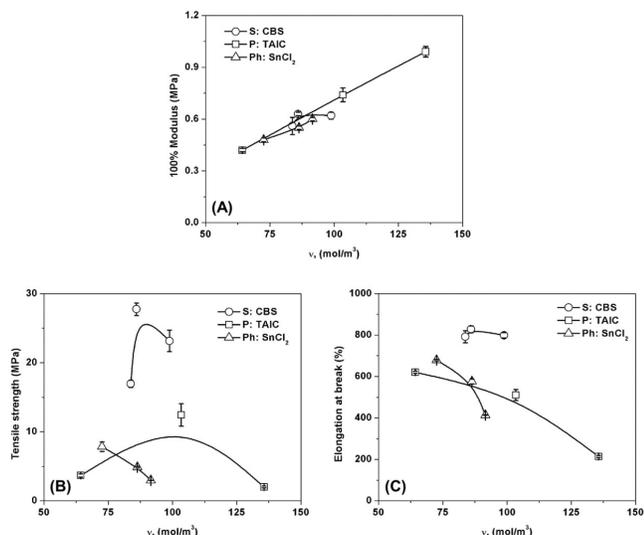


**Figure 3** (A) Plot of normalized force vs temperature and (B) crosslink density of the NR vulcanizates with variation of vulcanization systems and crosslink densities

### Tensile Properties

Tensile properties such as 100% modulus, tensile strength and elongation at break of various crosslinked NR samples are shown in Figure 4. In all cases, the 100% modulus increased with increasing crosslink density (Figure 4 (A)) due to the enhancement of stiffness and corresponding crosslink density [6, 24]. The 100% modulus was changed from  $0.56 \text{ MPa}$  to  $0.63 \text{ MPa}$  in sulfur,  $0.42 \text{ MPa}$  to  $0.99 \text{ MPa}$

in peroxide, and 0.48 MPa to 0.60 MPa in phenolic resin systems, depending on crosslink densities. At the same value of crosslink densities ranging from 75 to 85 mol/m<sup>3</sup>, the 100% modulus values of all vulcanization systems displayed slightly different, depending on the type of crosslink formation. The rigidity and flexibility of network structure formed by different vulcanization systems would be responsible for this variation. The results suggest that the modulus at low strain was assigned the type of bonding formation such as C-C, C-Sx-C and C-Ph-C bonds. Short and rigid C-C bonds showed greater modulus improvement at low strains.



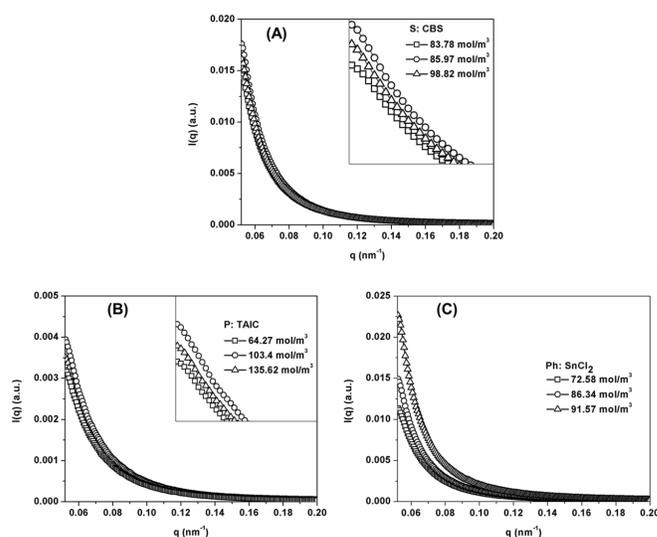
**Figure 4** Tensile properties of the NR vulcanizates with variation of vulcanization systems and crosslink densities; (A) 100% modulus, (B) tensile strength, and (C) elongation at break

On the other hand, the tensile strength of the vulcanizates showed variation, depending on the vulcanization systems and crosslink densities. The tensile strength of the sulfur system was maximized (27.76 MPa that was 100% and 200% greater than peroxide and phenolic systems, respectively) when the ratio of S:CBS was equal to 1:2, corresponding to the degree of crosslink density of about 85.97 mol/m<sup>3</sup>. The peroxide vulcanization system showed an optimum value of tensile strength at 12.45 MPa where the crosslink densities were 103.4 mol/m<sup>3</sup>, assigning to the ratio of DCP:TAIC of 1:2. However, the phenolic system did not display an optimum value within the tested range (Figure 4 (B)). The decrease of the tensile strength after the optimum value was attributed to the excessive crosslink density, which restricted the mobility and orientation of rubber chains during stretching. Consequently, the tensile strength decreased. [5,25]. As a result of increasing curing promoters, the decrement of elongation at break values was found in all samples (Figure 4 (C)) due to the increased restriction of chain mobility resulting from the enhancement of crosslink density [5]. The elongation at break of the sulfur system

reduced slightly from 828% to 792%, 621% to 214% in peroxide, and 679% to 414% in the phenolic resin system. Based on this result, the sulfur system provides the highest tensile strength with the greatest extensibility.

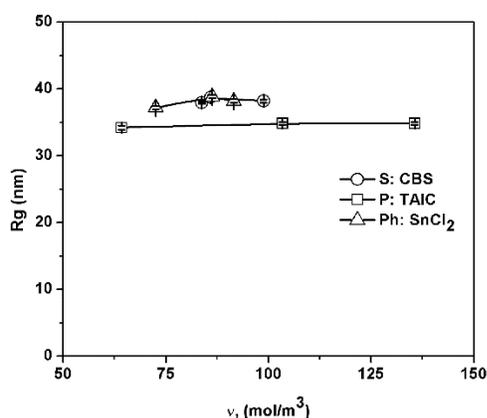
### Microstructural Changes

Figure 5 shows a plot of the scattering intensity at  $q$ ,  $I(q)$ , and scattering vector ( $q$ ) of the samples with different vulcanization systems and crosslink densities. The  $q$  is defined as  $q = (4\pi/\lambda) \sin\theta$ , where  $\lambda$  and  $2\theta$  are the wavelength and scattering angle. The intensity of all samples showed an upturn in the small  $q$  region due to the heterogeneous network structure that occurred during the crosslinking reaction [7,12]. The characteristic peak intensity of the phenolic system crosslinked NR (Figure 5 (A-C)) was higher than those of the sulfur and peroxide systems, indicating that higher heterogeneity crosslink network structure formed in the phenolic vulcanization systems [12]. Such heterogeneous distribution also increases with an increasing amount of SnCl<sub>2</sub>. As a result of the increasing heterogeneity of the crosslink network structure, the tensile strength decreased accordingly. In the sulfur and peroxide systems, the scattering intensity profiles were lower than that of the phenolic one, and the peroxide system showed the lowest. Thus, the heterogeneous network structure formed during the crosslinking reaction obtained in this study can be ranked as phenolic > sulfur > peroxide. The less homogeneous network structure of the sulfur system compared to the peroxide was consistent with the previous report [13]. In addition, the scattering profiles were independent of the curing promoter contents (i.e., CBS and TAIC) in the case of sulfur and peroxide, with only a slight increase of intensity with a variation of crosslink density.

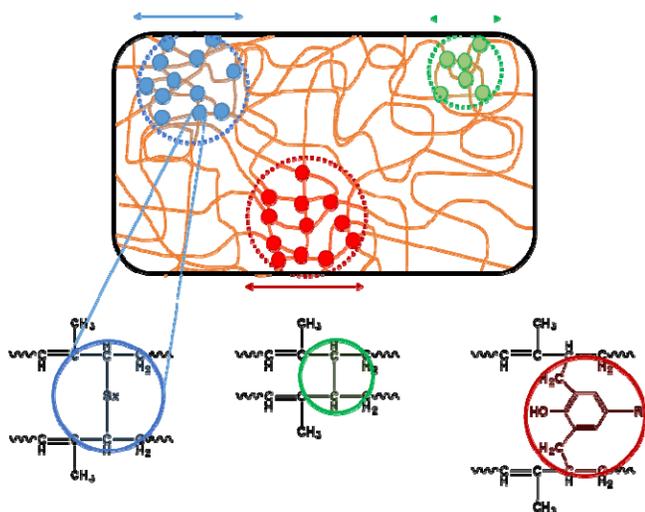


**Figure 5** Plot of intensity,  $I(q)$  with scattering vector,  $q$  (nm<sup>-1</sup>) of the NR vulcanizates with variation of vulcanization systems and crosslink densities: (A) sulfur, (B) peroxide, and (C) phenolic systems

Figure 6 shows the correlation of radius gyration (or size of crosslink network structure) with a variation of crosslink density. Increased crosslink density did not affect the size of the crosslink network structure formed during the vulcanization reaction since the change was negligible. However, the vulcanization system was found to be the major parameter affecting the size of the crosslink network structure. The size of the crosslink network structure was the smallest when the vulcanizing agent was the peroxide system. The  $R_g$  size obtained from peroxide system varied from 35.01 nm to 35.37 nm. The sulfur and phenolic system showed a comparable size of crosslink network structure (from 38.57 nm to 39.23 nm in sulfur and 38.02 nm to 39.39 nm in the phenolic resin system). The smallest size of  $R_g$  in peroxide crosslinked NR was probably attributed to the small size of C-C bonds formation between rubber chains as illustrated in Figure 7



**Figure 6** Relationship of radius gyration ( $R_g$ ) with crosslink density ( $v$ ) of the NR vulcanizates with variation of vulcanization systems and crosslink densities



**Figure 7** Illustration of various crosslink network structure

In contrast, the C-Sx-C bonds in sulfur system and methylene bridge and/or chromann ring in the phenolic system provided larger  $R_g$ . The larger crosslink network size of the sulfur system was attributed to the sulfur system containing domains of high crosslink density value embedded in the rubbery network matrix [13]. By contrast, the rigidity and large size of the methylene bridge/ chromann ring formed in the phenolic system were assumed to give a huge size of crosslink network structure.

## 4.0 CONCLUSION

The effect of vulcanization systems and crosslink densities on tensile properties and microstructure of NR was studied. The crosslink density of various vulcanization systems increased with increasing curing promoters (CBS, TAIC, and  $\text{SnCl}_2$  for sulfur, peroxide, and phenolic systems, respectively), as estimated from TSSR measurement. The tensile modulus at 100% strain increased with crosslink density, but the tensile strength depends on the vulcanization systems and crosslink density levels. The sulfur vulcanization system obtained the highest tensile strength at the same crosslink density, which was more than 100% greater than those obtained from peroxide and 200% over phenolic systems. Compared to the phenolic system, the sulfur and peroxide systems provided significantly homogeneous distribution of crosslink network structure formed during crosslink reaction, which might result from the greater tensile properties of these two systems. The sulfur crosslink system was determined to be the best systems for NR based on the variation and results from this study.

## Acknowledgment

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