# **Structure Properties of Purified Natural Rubber**

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ABSTRACT: Purified natural rubber (PNR) is natural rubber (NR) from which most of the nonrubber constituents are removed by repeated centrifugation. The study of PNR is of interest for two reasons. First, it has been reported that deproteinized natural rubber exhibited improved dynamic mechanical properties including heat buildup and flex-cracking resistance. However, the explanations for the observed improvement have not been given. Second, NR uncontaminated by nonrubber substances (mainly proteins and lipids) might be more suitable for medical applications than normal NR, which contains potential allergy-causing compounds, e.g., proteins. The present work was carried out with dual objectives: to understand the effect of nonrubber constituents on the network structures and properties of NR vulcanizates and to make the first assessment of the mechanical properties of the prepared PNR vulcanizates. The vulcanization system used was N-cyclohexylbenzothaizole-2-sulphenamide (CBS)-accelerated sulfur vulcanization system. Both the efficient vulcanization (EV) and conventional vulcanization (CV) systems were studied. It was found that vulcanization of PNR was strongly inhibited compared with normal NR, indicating significant influences of nonrubber compounds. For unfilled PNR, their tensile and tear properties were generally smaller than those of NR containing nonrubber constituents (WNR). PNR vulcanizates were also softer than WNR vulcanizates. Vulcanized PNR, however, exhibited distinct superiority in flex-cracking resistance than its WNR counterpart. Analysis of the network structures of the vulcanizates studied showed that for the EV system, the type of crosslinks [polysulfidic  $(S_x)$ , disulfidic  $(S_2)$ , and monosulfidic (S)] in PNR vulcanizates were more evenly distributed than in WNR samples. The %  $S_x$ ,  $S_2$ , and S crosslinks were respectively 36.4, 25.0, and 38.7 in PNR samples compared with 6.6, 29.7, and 64.1 in WNR samples. For the CV vulcanization system, the differences in sulfur crosslink type were not as great but the tendency toward the formation of shorter sulfur crosslinks persisted in PNR vulcanizates. The more uniformly distribution of sulfur crosslink type was thought to be responsible for the observed superiority in flex-cracking resistance of PNR vulcanizates. For carbon black-filled PNR vulcanizates, similar trends existed with respect to their properties. Properties of PNR vulcanizates were generally lower than those of WNR vulcanizates, particularly when the CV vulcanization system was employed. The EV vulcanization system gave PNR properties comparable to those of WNR samples except for heat buildup where PNR showed better properties. Flex-cracking resistances of CB-filled PNR vulcanizates, however, still maintained their superiority over those of WNR counterparts of similar crosslink density. It was concluded, therefore, that the improved dynamic properties of filled PNR vulcanizates over those of normal NR are also likely to be due to more balanced formation of sulfidic crosslinks of different lengths, thus better cyclic loadbearing properties. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1495-1504, 2000

**Key words:** purified natural rubber (PNR); carbon black-filled PNR; network structure; nonrubber constituents; physical properties

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# INTRODUCTION

Purified natural rubber (PNR) is natural rubber (NR) from which most of the nonrubber constituents are removed by repeated centrifugation. The study of PNR is of interest for two reasons. First, it has been reported that deproteinized natural rubber exhibited improved dynamic mechanical properties including heat buildup and flex-cracking resistance.<sup>1</sup> However, the explanations for the observed improvement have not been given. Second, NR uncontaminated by nonrubber substances (mainly proteins and lipids) might be more suitable for medical applications than normal NR, which contains potential allergy-causing compounds, e.g., proteins. Applications of NR for medical products such as catheter tubing are of interest as NR possesses superior strength and elasticity to those of synthetic rubber and plastics.

The present work was carried out with dual objectives: to understand the effect of nonrubber constituents on the network structures and properties of NR vulcanizates, and to make a first assessment of the mechanical properties of the prepared PNR. The vulcanization system used was N-cyclohexylbenzothaizole-2-sulphenamide (CBS)-accelerated sulfur vulcanization system. Both the efficient vulcanization (EV) and conventional vulcanization (CV) systems were studied.

# **EXPERIMENTAL**

#### **Preparation of NR Samples**

## Whole NR (WNR)

WNR was prepared by casting fresh NR latex into thin film. The latex was left to dry at room temperature (ca.  $30^{\circ}$ C) for 24 h, then ovendried at  $50^{\circ}$ C for further 24 h. The nitrogen content, which is a measure of proteins present in NR, was determined by micro-Kjeldahl method to be 0.59% by weight of the rubber.

### **Purified NR**

PNR was prepared by repeated centrifugation of fresh NR latex using sodium dodecyl sulfate as dispersant. Centrifugation was carried out 4 times at the speed of 8000 rpm for 90 min. The final centrifuged latex was then casted into thin film and dried under similar conditions as with the preparation of WNR. The nitrogen content of PNR prepared was determined to be 0.09% by weight of the rubber.

# Preparation of Vulcanized NR Samples

WNR and PNR samples were vulcanized by accelerated sulfur vulcanization system. Both conventional vulcanization (CV) system and efficient vulcanization (EV) system were studied. The compound formulations used are given in Table I.

# **Vulcanization Characteristics**

The vulcanization characteristics of the rubber compounds studied were determined by using an oscillating disk rheometer (ODR) (Monsanto 100S) at 155°C.

Scorch time was taken as the time at which the rheometer torque rises 2 units from the minimum torque  $(T_2)$ .

Optimum cure time was taken as the time at which the rheometer torque increases to 90% of the total torque change following curing of rubber.

Unfilled Compound Formulation			Filled Compound Formulation			
Ingredient	CV	EV	Ingredient	CV	EV	
NR	100	100	NR	100	100	
ZnO	5	5	ZnO	5	5	
Stearic acid	2	2	Stearic acid	1	1	
Sulfur	3	1	Carbon black	40	40	
CBS	0.8	5	(N330)			
			Sulfur	2	0.5	
			CBS	0.5	2.5	

Table I Compound Formulations of NR Samples Studied

Reagent	Condition	Action
Propane-2-thiol (0.4 <i>M</i> ) Piperidine (0.4 <i>M</i> ) in n-hexane	25°C, 2h	Polysulfides are cleaved with di- and monosulfides remaining intact
nexane-1-tinoi (LM)	25 0,401	leaving only monosulfides

Table IIReagents and Conditions Used to Selectively Cleave Sulfide Crosslinks for CrosslinkType Determination

#### **Physical Property Measurement**

#### **Tensile Properties**

Tensile properties of PNR and WNR vulcanizates were measured according to ASTM D-412 using Instron Universal Tester Model 4301. The rate of extension was 500 mm/min.

# **Dynamic Fatigue Properties**

Dynamic fatigue properties of the vulcanized NR samples studied were measured according to ASTM D-813 using the Wallace De Mattia flexing machine.

#### Heat Buildup

Heat buildup of vulcanized PNR and WNR samples were measured by using Goodrich Flexometer following ASTM D-623 method of measurement.

#### Abrasion Resistance

Abrasion resistances of NR vulcanizates were measured according to DIN 53516 method using Zwick Abrasion Tester 6102.

# Determination of Network Structures of NR Vulcanizates

#### **Determination of Crosslink Density**

The crosslink densities of unfilled NR vulcanizates were determined from stress–strain measurements followed by the applications of Mooney–Rivlin equation [eq. (1)] and eq. (2). The molecular weights between crosslinks  $(M_c)$  were finally obtained.

$$F = 2(C_1 + C_2 \lambda^{-1})(\lambda - \lambda^{-2})$$
(1)

$$C_1 = \frac{\rho RT}{2M_c} \tag{2}$$

where *F* is the force required to extend the rubber sample to a given extension ratio  $(\lambda)$ ,  $\rho$  the density of the rubber sample, *R* the gas constant, and *T* the absolute temperature.

The crosslink densities of filled NR vulcanizates were measured by equilibrium solvent (cyclohexane) swelling method. The crosslink density ( $\nu$ ) or  $M_c$  was determined from modified Flory–Rehner equation .

$$\nu = \frac{1}{2} M_c = \frac{-[\ln(1 - V_2) + V_2 + \chi V_2]}{2\rho_r V_0 (V_2^{1/3} - V_2/2)}$$
(3)

where  $V_2$  is the volume fraction rubber,  $V_0$  the molar volume of solvent,  $\rho_r$  the density of the rubber sample, and  $\chi$  the polymer-solvent interaction parameter.

The values of the constant used in the above calculation were  $V_0 = 108 \text{ cm}^3/\text{mole}$  and  $\chi = 0.399$ .

#### Determination of Type of Sulfur Crosslinks

The types of sulfur crosslinks in the vulcanizate network were characterized by the chemical probe method used by Saville and Watson.<sup>2</sup>

In this method, the crosslink densities before and after the rubber samples are treated with chemical reagents that selectively cleave polysulfidic and disulfidic linkages were determined. Table II gives the reagents and conditions used.

The crosslink densities were measured by the stress–strain method as described above.

Details of the experimental procedure are given elsewhere.  $^{1}$ 

# **RESULTS AND DISCUSSION**

# Structure and Properties of Unfilled PNR Vulcanizates

#### **Vulcanization Characteristics**

Figure 1(a) and (b) shows vulcanization curves of PNR and WNR compounds as obtained from os-







**Figure 1** Sulfur vulcanization curves of PNR and WNR compounds vulcanized by the CV system (a) and the EV system (b).

cillating disk rheometer (ODR); those of the conventional vulcanization (CV) system are shown in Figure 1(a) whereas Figure 1(b) shows the results for the efficient vulcanization (EV) system. The calculated scorch times ( $T_2$ ) and optimum vulcanization times ( $T_{90}$ ) are given in Table III.

From Figure 1(a) and (b), it is apparent that nonrubber constituents have large effects on the curing of NR. PNR exhibited long delay in vulcanization compared with WNR, resulting in much longer vulcanization times shown by PNR. However, slopes of the vulcanization curves of PNR and WNR are approximately the same, for both the CV and EV systems. Therefore, the results obtained indicated that nonrubber substances participate in reactions that lead to initiation of vulcanization but once the vulcanization is initiated, the rate of vulcanization appears to be unaffected by nonrubber compounds. Thus, nonrubber substances might participate in the formation of vulcanization reaction intermediates. Among the nonrubber compounds that have been attributed as natural accelerators for sulfur vulcanization of NR are choline and ethanolamine<sup>3,4</sup> and amino acids,<sup>5</sup> all are nitrogenous compounds which either occur naturally in fresh latex or are formed as the result of putrefaction, heating or other decomposition processes.

# Network Structure of PNR Vulcanizates

Although the effects of nonrubber constituents of NR on properties of NR vulcanizates have been well documented,<sup>5</sup> the corresponding effects on network structure of NR vulcanizates have not been reported. The present study undertook analyses of network structures of sulfur-vulcanized PNR and WNR samples. Comparison between the network structures of these two NR samples thus would give information on the effects of nonrubber compounds on network structure of NR vulcanizates. The results obtained are shown in Table IV.

From Table IV, where the crosslink densities and the relative amounts of different types of sulfur crosslinks of NR vulcanizates cured by CV and EV systems are given, it can be seen that for the CV system, the distribution of poly-, di-, and monosulfidic crosslinks of PNR are the same as those of WNR, i.e., 20-30% of disulfidic crosslink and 70-80% of polysulfidic crosslink. No monosulfidic linkage was detected for the CV system irrespective of the presence or absence of nonrubber constituents. Therefore, it appears that nonrubber constituents show no effect on the type and amount of sulfur crosslinks formed in NR vulcanized by CV system. However, the total number of crosslinks formed appeared to be smaller in the PNR sample. Thus, apart from taking part in the formation of sulfurating agents, nonrubber constituents might also have a role to play in increasing the overall efficiency of vulcanization of NR.

Table IIIVulcanization Characteristics of PNRand WNR Compounds

	Scorch 7 (m	$\begin{array}{l} \text{fime } (t_2) \\ \text{in} \end{array}$	Cure Time (t <sub>90</sub> ) (min)		
Sample	CV System	EV System	CV System	EV System	
PNR WNR	$\begin{array}{c} 4.9\\ 2.3\end{array}$	7.1 $2.5$	9.0 6.0	11.0 $7.5$	

	CV System				EV System			
Sample	$(2M_c)^{-1} \times 10^{-5}$	$\% S_x$	$\% S_2$	% S	$(2M_c)^{-1} \times 10^{-5}$	$\% S_x$	$\% S_2$	% S
WNR PNR	$\begin{array}{c} 6.91 \\ 5.56 \end{array}$	$\begin{array}{c} 80.0\\71.0\end{array}$	$\begin{array}{c} 20.5\\ 29.1 \end{array}$	_	$\begin{array}{c} 6.52 \\ 6.31 \end{array}$	$\begin{array}{c} 6.6\\ 36.4\end{array}$	$\begin{array}{c} 29.7\\ 25.0\end{array}$	$\begin{array}{c} 64.1\\ 38.7\end{array}$

Table IV Network Structures of WNR and PNR Vulcanizates

For NR cured by EV system, Table IV shows that nonrubber constituents of NR have interesting effect on the network structures. It will be seen that while WNR sample contains mainly the monosulfidic crosslink (60-70%), some disulfidic crosslinks (25-30%) and small quantity of polysulfidic crosslinks (5-8%), as is already well known, the sample from which nonrubber substances were removed (PNR) shows the formation of approximately equal amounts of mono-, di-, and polysulfidic crosslinks, i.e., 30-40% of each type of crosslink. The crosslink density, however, appeared to be unaffected by nonrubber substances present. This is in slight contrast to the results obtained for the CV system.

Although the effect of nonrubber substances in speeding the vulcanization process of NR have been repeatedly reported,<sup>5,6</sup> no explanation has been made of the possible roles of nonrubber substances in the vulcanization mechanism. It is not the aim of the present work to elucidate the mechanism of sulfur vulcanization involving nonrubber compounds. Further study is obviously required to understand the present observation. However, the following explanation might be given.

Morrison and Porter<sup>7</sup> believed that the type of vulcanizate network formed is the results of competition between two reactions, viz. desulfuration (reaction 1) and thermal decomposition of polysul-fidic crosslink (reaction 2):







If the concentration in the rubber of zinc accelerator thiolate complexes (I) is high, the polysulfides crosslinks will be desulfurated rapidly to stable monosulfides (normal of EV system). If the zinc complexes are present in low concentration or are insufficiently soluble, desulfuration is slow and the polysulfide crosslinks suffer thermal decomposition, leading to extensive modification of the main chains (normal of CV system). For the present observation, the structure of the zinc-accelerator complexes formed in the absence of certain nonrubber compounds might be different from those formed when nonrubber substances are present in the rubber sample. As a result, desulfuration occurs more slowly than normally is the case. Therefore, the concentration of monosulfidic formed will be smaller and the quantity of the initial polysulfidic crosslink remains comparatively higher. The overall results are equal concentration of each type of sulfidic linkage.

#### **Properties of PNR Vulcanizates**

Physical properties of PNR vulcanizates cured by the CV and EV systems are presented in Table V. The properties of WNR vulcanizates are also given in comparison. The flex-cracking resistances of both kinds of NR samples are shown in Figure 2(a) and (b).

The results obtained showed that tensile strength, elongation at break, tear strength, and hardness of the vulcanizates cured by CV system are higher than those of the EV system for both PNR and WNR samples. Since the CV and EV system vulcanizates contained essentially the same crosslink density (see Table IV), the better properties of the CV system vulcanizate should be

Sample WNR PNR	Conventional Vulcanization System							
	Tensile Strength (MPa)	100% Modulus (MPa)	300% Modulus (MPa)	Elongation at Break (%)	Tear Strength (KN/m)	Hardness (Shore A)		
	$\begin{array}{c} 29.7\\ 27.1 \end{array}$	1.0 0.8	2.6 1.8	735 782	$\begin{array}{c} 67.7\\56.3\end{array}$	$\begin{array}{c} 47.6\\ 40.5\end{array}$		
	Efficient Vulcanization System							
Sample	Tensile Strength (MPa)	100% Modulus (MPa)	300% Modulus (MPa)	Elongation at Break (%)	Tear Strength (KN/m)	Hardness (Shore A)		
WNR PNR	21.7 20.5	0.8 0.7	$\begin{array}{c} 2.2\\ 1.7\end{array}$	627 690	45.1 38.7	43.5 40.2		

Table V Physical Properties of NR Vulcanizates

due to higher concentrations of the longer polysulfidic crosslinks in these rubber samples than in the EV-cured samples.





**Figure 2** Flex-cracking properties of PNR and WNR vulcanizates vulcanized by the EV system (a) and the CV system (b).

Comparison of the properties of PNR and WNR samples within the same system of vulcanization revealed that tensile properties and tear strengths are not very different, although properties of the samples from which the nonrubber substances were removed are rather smaller. The crosslink densities of PNR samples, in both types of vulcanization system, appeared to be on the low side. This might explain the marginally poorer properties of PNR samples. PNR sample showed tendency to be softer than WNR sample. This can be seen from the values of hardness, 100% modulus and 300% modulus.

In contrast to tensile and tear properties, the flex-cracking properties of NR vulcanizates, cured by EV or CV systems, appeared to be affected by nonrubber constituents. This is clearly seen in Figure 2(a) where the flex-cracking properties of PNR and WNR samples vulcanized by EV system are shown. The flex-cracking resistance of PNR samples are obviously superior to those of WNR samples. The improved flex-cracking properties of PNR samples may be due to uniform distribution of sulfidic crosslink types in these rubber samples, as already observed compared to the WNR samples. It is possible to imagine that the stress input to the rubber could be more evenly shared out by the crosslinks existed. The energy dissipated following subjection of the rubber samples to dynamic force could, therefore, be smaller. As the results, both heat buildup and crack growth are lower.

Figure 2(b) shows improved flex-cracking properties of CV vulcanizates of PNR samples com-

	Scorch 7	Fime (t <sub>2</sub> )	Cure Time $(t_{90})$		
	(m	in)	(min)		
Sample	CV	EV	CV	EV	
	System	System	System	System	
PNR WNR	$\begin{array}{c} 3.6\\ 1.4\end{array}$	$\begin{array}{c} 2.4 \\ 1.0 \end{array}$	10.0 8.0	8.4 4.8	

Table VIVulcanization Characteristics ofCarbon Black-Filled PNR and WNR Compounds

pared with WNR samples. The differences between the two rubber samples in this case, however, are much less than in the EV-vulcanized system. The slight improvement in flex-cracking resistance of PNR sample might be the result of increased concentration of disulfidic crosslink observed for these NR samples (see Table IV).

# Structure and Properties of Carbon Black-Filled PNR Vulcanizates

#### **Vulcanization Characteristics**

The vulcanization characteristics of carbon blackfilled PNR were assessed in comparison with WNR. The results obtained shown in Table VI reveal that PNR compounds exhibited long delay in scorch times and cure times compared with WNR compounds, similar to the behavior of their corresponding rubber gums. The same explanation, i.e., the absence of proteinaceous natural accelerator for sulfur vulcanization in PNR samples, may again be given here.

#### **Network Structure**

For carbon black-filled NR vulcanizates, the types of sulfur crosslinks contained within the samples could not be determined without complication as in the case of gum vulcanizates. Therefore, only the crosslink densities were characterized. The results attained are presented in Table VII.

From Table VII, it can be seen that for the CV system, the crosslink density of PNR sample is lower than that of its WNR counterpart, confirming the less efficient curing of NR when the non-rubber constituents were absent. However, when the accelerator/sulfur ratio was increased as in the EV system, the vulcanization efficiency of PNR could be increased, so that its crosslink density became comparable with that of WNR.

#### **Properties of Vulcanizates**

The physical properties of PNR vulcanizates studied together with those of WNR samples were tensile properties, abrasion resistance, dynamic heat buildup and dynamic flex-cracking properties. The results obtained are given in Table VIII.

From the results presented, it can be seen that 100 and 300% moduli of PNR vulcanizate cured by the CV system are much lower than those of the corresponding WNR vulcanizates. For the EVcured system, the moduli of PNR vulcanizates are closer to those of WNR samples. The crosslink density data reported in Table VII show that the smaller moduli exhibited by PNR vulcanizates are due to their lower crosslink density compared with those of WNR vulcanizates. For the EV system in which the vulcanization is more efficient, PNR could crosslink almost as well as could WNR. Therefore, it exhibited comparable level of moduli as those of WNR samples.

For tensile strength, the value for PNR that was cured by the CV system is only about half that of WNR, but when the EV system was used, PNR achieved the same level of tensile strength as WNR. For elongation at break, both types of NR samples showed almost the same values, although those of PNR vulcanizates appeared to be rather smaller.

Other properties studied were abrasion resistance, dynamic heat buildup, and flex-cracking resistance. The results of Table VIII show slightly poorer abrasion resistances of PNR compared with those of WNR. The PNR sample that was efficiently cured (EV system) exhibited better abrasion resistance than did the CV-cured sample.

For heat buildup, the EV-cured PNR vulcanizate showed better value than that of WNR vulcanizate, but the corresponding PNR sample that was vulcanized by the CV system exhibited much poorer heat buildup than the WNR counterpart. It is not clear why heat buildup of the CV-cured

Table	VII	Cros	slink	Density	of	Carbon	Black-
Filled	PNR	and	WNR	Vulcani	zat	tes	

	Crosslink Density (mole/g) $\times$ 10 <sup>-4</sup>				
Sample	CV System	EV System			
PNR	1.68	1.50			
WNR	3.77	1.83			

Sample WNR PNR	Conventional Vulcanization System								
	Tensile Strength (MPa)	100% Modulus (MPa)	300% Modulus (MPa)	Elongation at Break (%)	Abrasion Loss (mm <sup>3</sup> )	Heat Buildup (°C)			
	$\begin{array}{cccc} 22.8 & 2.5 \\ 12.5 & 1.3 \end{array}$		$\begin{array}{c} 11.7\\ 6.3\end{array}$	482 458	227 264	$\begin{array}{c} 25.1\\ 59.0\end{array}$			
		Efficient Vulcanization System							
Sample	Tensile Strength (MPa)	100% Modulus (MPa)	300% Modulus (MPa)	Elongation at Break (%)	Abrasion Loss (mm <sup>3</sup> )	Heat Buildup (°C)			
WNR PNR	$\begin{array}{c} 21.2\\ 21.3 \end{array}$	$\begin{array}{c} 1.5\\ 1.4\end{array}$	7.5 7.7	574 $534$	279 282	$\begin{array}{c} 30.7\\ 27.9\end{array}$			

Table VIII Physical Properties of Carbon Black-Filled NR Vulcanizates

PNR sample should be much worse than that of the equivalent WNR vulcanizate. Suspected undercure of the PNR sample used was believed to be the responsible reason. The lower heat buildup displayed by the EV-cured PNR vulcanizate might be explained on the basis of the more evenly distribution of the three types of sulfur crosslinks formed—viz. polysulfidic, disulfidic, and monosulfidic linkages—as previously found in gum vulcanizate. Of course, an assumption is made here that the nature of sulfur crosslinks formed is unchanged when carbon black is present.

The flex-cracking resistances of PNR and WNR vulcanizates are compared in Figure 3(a) and (b) for the CV-cured system and the EV-cured system, respectively. The results obtained again showed the superiority of flex-cracking resistance of filled PNR vulcanizates over those of WNR vulcanizates. The reason for better performances of PNR vulcanizates has previously been attributed to the more balanced number of different sulfur crosslink type (section on structure and properties of unfilled PNR vulcanizates). However, a look at the values of crosslink density shows that the crosslink densities of PNR vulcanizates are smaller than those of the corresponding WNR samples. Therefore, it might be argued that the improved flex-cracking resistances of PNR samples are due to higher flexibility of the rubber molecules in those samples as the result of lower extent of crosslink. The relationship between crack growth property and crosslink density of PNR and WNR samples were then studied.

The data obtained are presented in Figure 4(a–f) for the test made at different frequencies.

It can be seen from Figure 4 that crack growths of PNR vulcanizates are lower than those of WNR



**Figure 3** Flex-cracking properties of carbon blackfilled PNR and WNR vulcanizates vulcanized by the CV system (a) and the EV system (b).



**Figure 4** Relationships between crack-growth and crosslink density of PNR and WNR vulcanizates at various cycles of measurement: (a) 2000, (b) 4000, (c) 10,000, (d) 16,000, (e) 21,000, and (f) 27,000.

counterparts for all crosslink densities and flexing cycles studied. Thus, at comparable crosslink density, PNR samples showed smaller crack growth than did WNR samples. This implies that crosslink density is not the factor or at least is not the only factor that is responsible for improved flex-cracking resistance of PNR vulcanizates. Thus, the hypothesis that improved flex-cracking resistance, and also heat buildup, of PNR vulcanizates over those of WNR vulcanizates are due to more uniform distribution of polysulfidic, disulfidic, and monosulfidic crosslinks in the rubber network structure should gain more weight.

#### **CONCLUSIONS**

PNR, whether filled or unfilled with carbon black, exhibited slower cure by sulfur vulcanization system than its WNR counterpart. The network structures of the vulcanizates formed are also different, which reflect the influences of nonrubber substances present in NR. The crosslink densities of PNR vulcanizates were generally lower than those of the corresponding WNR, for the same amount of curing agent used. The extents of differences in the crosslink density depend on the type of sulfur vulcanization system used. The EV system appeared to be more efficient in vulcanizing PNR than the CV system. A more significant finding of the present study was that the network structure of PNR vulcanizate that was vulcanized by using an EV system and CBS as accelerator is different from that of its WNR counterpart. The three types of sulfidic crosslinks formed-viz. polysulfidic, disulfidic, and monosulfidic crosslinks—were more evenly distributed in the PNR sample than in WNR sample. This is in contrast to the biased formation of high concentration of monosulfidic crosslink found in normal NR (contains nonrubber compounds), which is cured by the EV system. Such a structure is believed to impart better flex-cracking properties and heat buildup to the PNR vulcanizate compared with NR which contains nonrubber constituents (WNR). However, the general properties of PNR vulcanizates, including tensile properties and abrasion resistance, were observed to be on the

low side relative to its corresponding WNR vulcanizates. These were true for both gum and carbon black-filled vulcanizates.

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