Crack Growth and Abrasion Resistance of Carbon Black-Filled Purified Natural Rubber Vulcanizates

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ABSTRACT: The influence of parameters contributing to rubber stiffness, including, crosslink density, hardness, and modulus, on the crack growth and abrasion resistance of carbon black-filled purified natural rubber (PNR) vulcanizates as well as a whole natural rubber (WNR) vulcanizate counterpart or a control were elucidated. In addition, the tensile properties of PNR and WNR were also determined. PNR containing the same curative level as that of the control had lower stiffness and exhibited superior crack growth resistance. The results revealed that the improved crack growth resistance of PNR, compared to the control, was due to its lower crosslink density, hardness, and modulus. In addition, the tensile strength and abrasion resistance of PNR vulcanizates were not as sensitive as the crack growth resistance to the changes of their stiffness. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1793–1796, 2003

Key words: modulus; crosslinking; hardness

INTRODUCTION

Natural rubber (NR) is widely used in various applications such as tires, hoses, thread, and gloves due to its outstanding mechanical properties. Recently, some NR products, especially gloves, are of concern because they contain nonrubber constituents, for example, proteins which can cause a Type I allergic reaction.[1] Using proteolytic enzymatic treatment followed by repeated centrifugation of NR latex, most nonrubber substances, especially proteins, are effectively removed.[2] As a consequence, purified natural rubber (PNR) is obtained. It has been reported that nitrogeneous compounds occurring naturally in fresh latex or formed as the result of heating, that is, choline, ethanolamine, and basic amino acids, act as natural activators for sulfur vulcanization.[3,4] In addition, many researchers found that the removal of nonrubber substances from NR gives rise to NR with a slower cure compared to that of whole natural rubber (WNR).[5–7] Moreover, the resulting PNR vulcanizate has a lower crosslink density than that of the corresponding WNR.[7] This indicates that nonrubber substances, participating in the vulcanization reaction, can be eliminated by enzymatic treatment followed by repeated centrifugation. Furthermore, it was found that PNR vulcanizate exhibits better crack growth resistance than that of WNR.[7] Little work has been done to explain the observed improvement in the mechanical property of PNR vulcanizate. However, one claim is that the improved crack growth resistance of filled PNR vulcanizates results from a more even distribution of the three types of sulfidic crosslinks.[7] On the other hand, it is well known that crosslink density strongly affects the mechanical properties of the vulcanizates. Thus, the objective of this research was to elucidate the influence of parameters pertaining to rubber stiffness, that is, crosslink density, modulus, and hardness, on the mechanical properties of carbon black-filled PNR vulcanizate. Factors involving the improved crack growth resistance of PNR vulcanizate is also discussed.

EXPERIMENTAL

Preparation of NR samples

High ammonia (HA) concentrated latex (*Hevea brasiliensis* latex), purchased from the Thai Latex Co., Ltd. (Rayong, Thailand), was diluted to 30% dry rubber content using 0.5% w/v sodium dodecyl sulfate solution. About 0.04% w/v of a proteolytic enzyme was added to the diluted latex. Subsequently, the mixture was incubated at 37°C for 15 h. The mixture was then centrifuged twice at the speed of 13,000 rpm for 30 min. The obtained rubber cream fraction was cast into a thin film and dried at room temperature for 2 days. Consequently, the PNR sample was obtained. For preparation of the WNR sample, the HA concentrated

TABLE I
Compound Formulations

Ingredient	Amount (phr)			
	WNR-I	PNR-I	PNR-A1	PNR-A3
WNR	100	—	—	—
PNR	—	100	100	100
Carbon black (N330)	50	50	50	50
Stearic acid	1.80	1.80	1.80	1.80
ZnO	3.50	3.50	3.50	3.50
6-PPD[a]	1.50	1.50	1.50	1.50
TMQ[b]	1.00	1.00	1.00	1.00
Microcrystalline wax	1.00	1.00	1.00	1.00
PVI[c]	0.10	0.10	0.10	0.10
Sulfur	1.75	1.75	2.10	2.30
TBBS[d]	0.75	0.75	0.90	0.99

[a] N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine.
[b] Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline.
[c] N-(Cyclohexylthio)phthalimide.
[d] N-tert-Butyl-2-benzothiazolesulfenamide.

latex was cast onto the glass plates and left to dry at room temperature (ca. 30°C) for 2 days. Next, the nitrogen content, which is an indication of the amount of proteins present in the PNR and WNR samples, was determined by the semimicro-Kjeldahl method.

Preparation of compounds

Compound formulations are given in Table I. WNR-I and PNR-I had the same composition and WNR-I was used as the control. PNR-A1 and PNR-A3 contained the same composition as that of the control and PNR-I, except for the curative levels, which were varied to prepare the vulcanizates with either a similar modulus or crosslink density to that of the control. In this study, PNR-A1 showed a similar modulus to that of the control, whereas PNR-A3 exhibited a comparable crosslink density and hardness to the control. In addition, the ratio of sulfur to N-tert-butyl-2-benzothiazolesulfenamide (TBBS) was about 2.32–2.33 in all formulations.

The compounds were prepared in a water-cooled 500-mL internal mixer using a rotor speed of 40 rpm and a fill factor of 0.8. The total mixing time in the internal mixer was 8 min. After dumping, the compound was further mixed on a two-roll mill for 1 min and 10 end-roll passes were made before sheeting off.

Preparation of cured NR samples

The cure characteristics of the PNR and WNR compounds were determined at 140°C with an oscillating disc rheometer (ODR), in accordance with ASTM D 2084-88. About 10 g of the rubber compound was used with a 1° arc. The cure time was the time to reach maximum torque on the cure curve.

Determination of crosslink density

The crosslink densities of the NR samples were measured by the swelling method. The thickness and weight of the samples used were about 1.2 mm and 0.8 g, respectively. The sample was immersed in 80 mL of toluene in the dark for 1 week at room temperature. The crosslink density was calculated using the Flory–Rehner equation[8–11]:

$$\rho_c = -\frac{1}{2V_s}\frac{\ln(1 - V_r) + V_r + \chi_1(V_r)^2}{(V_r)^{1/3} - \dfrac{V_r}{2}} \quad (1)$$

where ρ_c is crosslink density (mol/m^3); V_s, the molar volume of toluene (106.9 cm^3/mol at 25°C); and χ_1, the interaction parameter (0.42 for black-filled NR), and V_r can be determined from eq. (2):

$$\frac{V_r^0}{V_r} = 1 - [3c(1 - V_r^{0\,1/3}) + V_r^0 - 1]\frac{\phi}{1 - \phi} \quad (2)$$

where V_r^0 is the rubber fraction in the swollen gel; c, the parameter for the carbon–rubber interaction (1.17); and ϕ, the volume fraction of carbon black.

Mechanical properties measurements

For tensile testing, dumbbell specimens about 1.2 mm thick were cut from compression-molded sheets along the milling direction, using a type C die. The tensile properties of the specimens were measured according to ASTM D 412-89a, using an Instron universal tester Model 4301. The crosshead rate was 50 mm/min with an initial clamp separation of 65 mm. The tensile properties shown in Table IV were averaged over three to four specimens. The hardness, crack growth, and abrasion resistance of NR vulcanizates were measured, in accordance with ASTM D 2240-97 (using a Durometer hardness tester, Type A; Zwick), ASTM D813-95 (using a Wallace De Mattia flexing machine), and DIN 53516 (using a Zwick abrasion tester 6102), respectively.

RESULTS AND DISCUSSION

Nitrogen content

Table II presents the nitrogen content of PNR and WNR. The nitrogen content of PNR was only 0.02% by

TABLE II
Nitrogen Content of WNR and PNR

Sample	Nitrogen content (% by weight of rubber)
WNR	0.276 ± 0.019
PNR	0.022 ± 0.006

TABLE III
Crosslink Density and Hardness of WNR and PNR Vulcanizates

Vulcanizate	Crosslink density (mol/m^3)	Hardness (Shore A)
WNR-I	170.8 ± 2.4	65.5 ± 1.3
PNR-I	128.5 ± 1.3	57.0 ± 1.0
PNR-A1	153.8 ± 2.1	62.1 ± 0.9
PNR-A3	172.7 ± 0.8	64.1 ± 0.9

weight of the rubber or 12.5 times lower than that of the WNR counterpart. Compared to a previous study,[7] PNR was prepared by repeated centrifugation without enzymatic treatment; the nitrogen content was determined to be 0.09% by weight of the rubber. This indicates that enzymatic treatment followed by repeated centrifugation could effectively remove non-rubber substances including proteins from NR latex.

Stiffness of carbon black-filled NR vulcanizates

Parameters contributing to vulcanizate stiffness, that is, crosslink density, hardness, and 100% modulus, are presented in Tables III and IV. PNR-I possessed a lower crosslink density, hardness, and modulus than those of WNR-I or the control, prepared from the same formulation. This is due to the nitrogeneous compounds, acting as natural activators for sulfur vulcanization, in PNR were leached out in the process of PNR preparation.[3,4] The present results are consistent with the previous study.[7] When curative levels were increased to prepare PNR-A1 and PNR-A3 vulcanizates, the stiffness of the vulcanizates increased. However, PNR-A1 still had a rather lower crosslink density and hardness than those of the control, while their moduli were comparable. On the other hand, PNR-A3 exhibited a similar crosslink density and hardness to those of the control but its modulus was slightly greater. These observations are surprising since the extent of the hardness and modulus of a vulcanizate generally depends upon its degree of crosslinking. When crosslink density increases, the hardness and modulus also increase.[12] It is not clear why the vulcanizates having comparable crosslink densities did not

TABLE IV
Tensile Properties of WNR and PNR Vulcanizates

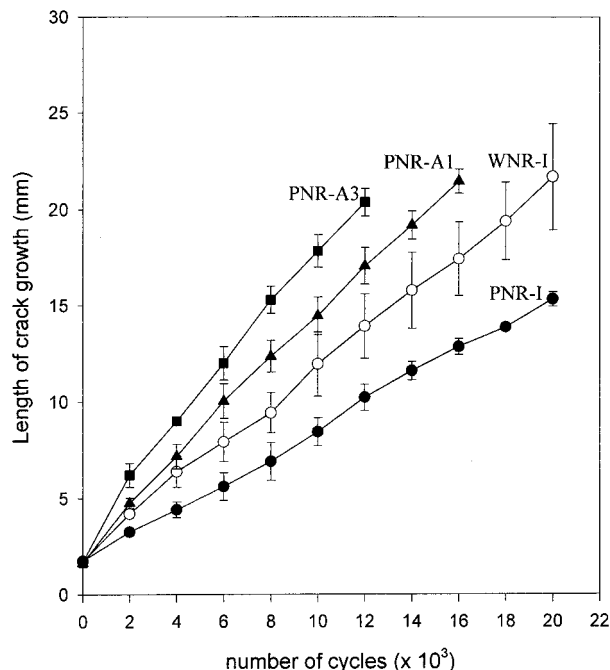| Vulcanizate	Tensile properties		
	100% modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
WNR-I	3.72 ± 0.22	28.9 ± 0.4	415 ± 21
PNR-I	2.80 ± 0.16	28.1 ± 0.1	435 ± 16
PNR-A1	3.73 ± 0.14	27.6 ± 0.7	386 ± 13
PNR-A3	4.15 ± 0.09	28.4 ± 0.4	377 ± 8

Figure 1 Length of crack growth of WNR and PNR vulcanizates at various cycles.

exhibit a similar hardness and modulus. However, it is interesting to explore the difference in such parameters of PNR-A1 and PNR-A3 on their mechanical properties and it will be discussed in the next sections.

Tensile properties

The tensile properties of the vulcanizates are shown in Table IV. PNR-I exhibited the highest elongation at break, followed by that of the control (WNR-I), PNR-A1, and PNR-A3. The tensile strength of PNR-I was comparable to the control and other vulcanizates although it had the lowest modulus. The previous study also presented that the tensile strength of NR was not changed by deproteinization with a proteolytic enzyme and surfactant,[13] but it was dramatically reduced after transesterification, due to the decomposition of the chemical crosslinks of phospholipids linked to fatty acid groups.[14] On the other hand, it is well known that crystallization behavior strongly affects the strength of the rubber vulcanizates. In addition, it has been demonstrated that the crystallization behavior of NR at −25°C is not primarily promoted by proteins, but by fatty acids.[15] Since fatty acids were not removed from the PNR used in this experiment, the comparable strength of all vulcanizates, therefore, might be due to their similar crystallization behaviors.

Crack growth resistance

Figure 1 demonstrates the length of crack growth at various cycles of the WNR and PNR vulcanizates. The length of crack growth at zero cycle resulted from

TABLE V
Volume Loss of WNR and PNR Vulcanizates

Vulcanizate	Volume loss (mm^3)
WNR-I	98.7 ± 2.6
PNR-I	123.7 ± 2.2
PNR-A1	104.5 ± 1.3
PNR-A3	101.3 ± 2.8

piercing the specimen with a tool before testing. PNR-I had the highest crack growth resistance, followed by WNR-I, PNR-A, and PNR-A3. Since PNR-I had the lowest crosslink density, hardness, and modulus, the lowest load was needed to deform it to the same level as that of other vulcanizates. Thus, the stress concentration at the crack tip of PNR-I was the lowest. As a result, crack propagation in PNR-I was slower than that of other vulcanizates at a certain cycle. Compared to the control, PNR-A1, with a rather lower crosslink density and hardness (see Table III) but similar modulus (see Table IV), exhibited lower crack growth resistance. In addition, PNR-A3, having a slightly higher modulus than that of the control (see Table IV), yielded lower crack growth resistance although their crosslink density and hardness were similar (see Table III). The results indicate that the improved crack growth resistance of PNR-I compared to the control was caused by its lower crosslink density, hardness, and modulus. Mun and Oon reported that the dilution of latex with water tends to leach out the natural antioxidants, thus reducing the aging resistance of rubbers.[16] Since the preparation of PNR involved both dilution and centrifugation of the latex, more of its natural antioxidants must be removed than with WNR. Therefore, a poorer crack growth resistance of PNR-A1 than that of the control, although their moduli were comparable, might be attributed to the susceptibility of PNR to degrade faster than WNR under repeated loading.

Abrasion resistance

The abrasion resistance of WNR and PNR vulcanizates, expressed as volume loss, is shown in Table V. The higher volume loss infers the lower abrasion resistance of the vulcanizate. The results indicated that PNR-I exhibited the lowest abrasion resistance, whereas the abrasion resistances of the control, PNR-A1, and PNR-A3 were not significantly different. The lowest abrasion resistance of PNR-I corresponded to its lowest crosslink density, hardness, and modulus (see Tables III and IV). Compared to the control, PNR-A1, having a similar modulus but somewhat lower crosslink density and hardness, exhibited slightly lower abrasion resistance. In addition, PNR-A3, with a little higher modulus but comparable crosslink density and hardness, showed similar abrasion resistance

to that of the control. Therefore, the present results demonstrate that abrasion resistance is more dependent on the hardness and crosslink density than on the modulus. Thavamani and Bhowmick also reported that abrasion resistance is contingent upon the hardness of the vulcanizate.[17]

CONCLUSIONS

For the conditions used in this study, the PNR vulcanizate possessed similar tensile strength to the corresponding WNR vulcanizate or to the control, whereas its abrasion resistance and crack growth resistance were lower than those of the control. The results revealed that the improved crack growth resistance of the PNR vulcanizate compared to the control resulted from a lower stiffness. Furthermore, it was found that parameters pertaining to the stiffness of the vulcanizates, such as crosslink density, hardness, and modulus, dramatically affected the crack growth resistance of the PNR vulcanizates. On the contrary, the differences in the stiffness of the PNR vulcanizates did not remarkably influence their tensile strength and abrasion resistance as much as it did their crack growth resistance.

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