Mechanical Properties of Deproteinized Natural Rubber in Comparison with Synthetic *cis*-1, 4 Polyisoprene Vulcanizates: Gum and Black-Filled Vulcanizates

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ABSTRACT: Gum and black-filled vulcanizates having various crosslink densities were prepared from 2 types of rubber, namely, deproteinized natural rubber (DPNR) and synthetic *cis*-1, 4 polyisoprene vulcanizates (IR). Their mechanical properties, such as tensile strength, tear strength, abrasion loss, and heat buildup resistance, at various crosslink densities as well as at similar optimum crosslink density were compared. For both gum and black-filled systems, IR possessed a higher crosslink density than that of DPNR at a fixed curative content. Tensile and tear strength of all vulcanizates passed through a maximum with increasing crosslink density. For gum vulcanizates, tensile and tear strengths of DPNR and IR below the maximum were not much different. However, IR had a narrower tear strength peak relative to DPNR. At a comparable optimum crosslink density, DPNR exhibited higher tensile strength and crack growth resistance than IR. For black-filled vulcanizates, tensile and tear strengths, and heat buildup resistance of DPNR and IR at a given crosslink density were similar. The results revealed that the properties of gum samples were more dependent upon crosslink density than the black-filled ones because the reinforcement by carbon black overshadowed the intrinsic properties of the rubbers. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1139–1144, 2005

Key words: natural rubber; synthetic *cis*-1, 4 polyisoprene; crosslink density; mechanical properties

INTRODUCTION

It has been reported that proteins naturally existing in natural rubber latex (NRL) can cause allergy to some people using natural rubber (NR) products.[1,2] However, the treatment of NRL with a proteolytic enzyme for preparing a deproteinized natural rubber (DPNR) is shown to effectively reduce the antigenic protein content.[2] Therefore, DPNR might be used as an alternative raw material for producing low allergen NR products if its properties attain the requirement. Generally, the strength of crystallizable polymers is known to be governed by their crystallizability during stretching, which is in turn influenced by the crosslinking magnitude. The strength of rubber usually passes through a maximum with crosslink density and then decreases steadily as crosslink density increases.[3,4] However, the range of crosslinking to achieve the optimum properties of different rubbers is not the same.[5] The range of modulus, which is directly related to crosslink density, to obtain the maximum tensile strength of synthetic *cis*-1,4-polyisoprene (IR) is narrower than that of NR.[6] Earlier investigators also found that the tensile strength and green strength of NR are not changed by deproteinization with a proteolytic enzyme and surfactant but they decrease dramatically after transesterification.[7–9] This implies that the crystallization behavior of NR is not originally promoted by proteins but by fatty acids.[10] In addition, it is reported that DPNR crystallizes much faster than IR although their chemical constitution is closely alike. This result has been explained to be due to the presence of nucleating impurities and the more perfect microstructure of DPNR.[11] Although several past studies have been carried out to investigate the properties of DPNR and IR in various conditions, the effect of crosslink density on their mechanical properties has not been compared. Furthermore, several researchers have shown that carbon black, widely used as a reinforcing filler, can also promote crystallization in NR during stretching.[12–14] Studies of cut growth in gum and black-filled NR vulcanizates have demonstrated that a tightly crosslinked gum NR vulcanizate incapable of strain-induced crystallization may be induced to

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do so by carbon black.[15,16] Thus, it is of interest to investigate the effect of crosslink density on the mechanical properties of DPNR and IR for both gum and black-filled systems. The dependence of the properties on crosslink density of each vulcanizate is also discussed.

EXPERIMENTAL

Preparation of NR samples

High ammonia (HA) concentrated latex (*Hevea brasiliensis* latex), purchased from 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 proteolytic enzyme was added into 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 thin film and dried at room temperature for 2 days. Consequently, a DPNR sample was obtained. An ordinary NR sample used for comparative purposes was prepared by casting the HA concentrated latex on glass plates, where it was left to dry at room temperature (~ 30°C) for 2 days. The nitrogen content, which is an indication of the amount of proteins, was determined by the micro-Kjeldahl method to be 0.35% and 0.02% by weight for the ordinary NR and DPNR, respectively. Synthetic *cis*-1,4 polyisoprene (JSR IR2200) was used as purchased.

Preparation of compounds

All compounds had the same composition, except for the amounts of curatives (sulfur and *N*-*tert*-butyl-2-benzothiazolesulfenamide (TBBS)), which were varied to prepare the samples of different crosslink densities. The compound contained (in phr): rubber, 100; stearic acid, 1.8; ZnO, 3.5; polymerized 2, 2, 4-trimethyl-1,2-dihydroquinoline (TMQ), 1.0; N-(isopropyl)-N′-phenyl-*p*-phenylenediamine (I-PPD), 1.5; wax, 1.0; and N-(cyclohexylthio) phthalimide (PVI), 0.1. The ratio of sulfur to TBBS is about 2.32 in all cases. The rubbers used were DPNR, IR, or ordinary NR. For black-filled compounds, 50 phr of carbon black (N 330) were added. All ingredients, except the curatives, were mixed with rubbers in a water-cooled 500 mL internal mixer using a rotor speed of 40 rpm and a fill factor of 0.7. 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. Then, the curatives were added and mixed for 5 min more. Finally, 10 end-roll passes were made before sheeting off.

Preparation of cured samples

Cure time of the rubber compounds was determined at 140°C with an oscillating disc rheometer (ODR), in accordance with ASTM D 2084–88. About 10 g of rubber compound were used with a 1° arc. The cure time was the time at which the rheometer torque increased to 100% of the total torque change on the cure curve.

Determination of crosslink density

The crosslink densities of cured samples were measured by the swelling method. The thickness and weight of sample 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 swelling ratio (Q) was calculated: $Q = 100 \times (W_s - W_u)/W_u$, where W_s and W_u are weights of the swollen and unswollen samples. For black-filled samples, W_s and W_u are weights of the swollen and unswollen samples, not including the weight of the carbon black because only the rubber would swell in the solvent. The reciprocal swell value, 1/Q, was used as crosslink density.[17] The value of crosslink density was the average of three specimens.

Mechanical properties measurements

Compression molded sheets having thickness about 1.2 mm were used for tear and tensile testing. Tensile and tear properties of the specimens were measured according to ASTM D 412–89a and ASTM D 624–98, respectively. The measurement was carried out by using Instron Universal Tester Model 4301. The crosshead rate was 500 mm/min with an initial clamp separation of 65 mm. The value of tear and tensile properties were averaged of 3–5 specimens.

Hardness, abrasion, heat buildup, and crack growth resistance of the vulcanizates were measured, in accordance with ASTM D 2240–97 (Durometer Hardness tester, Type A; Zwick), DIN 53,516 (Zwick abrasion tester 6102), ASTM D 623–78 (Goodrich Flexometer), and ASTM D 813–95 (Wallace De Mattia flexing machine), respectively.

RESULTS AND DISCUSSION

The mechanical properties of the vulcanizates at various crosslink densities

Gum and black-filled DPNR, and IR vulcanizates having various crosslink densities, were prepared by varying the curative contents. In this experiment, the gum vulcanizate containing light crosslink density was not prepared because its strain exceeded the limitation of the current universal tester. The relationship between the curative content and crosslink density of various vulcanizates is presented in Figure 1. The first letter of a designation denotes *g*um, G, or *f*illed, F, while the second letter represents *D*PNR, D, or *I*R, I. It

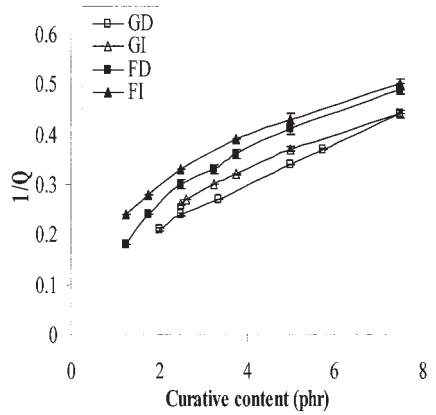

Figure 1 Correlation between crosslink density and curative content of various vulcanizates.

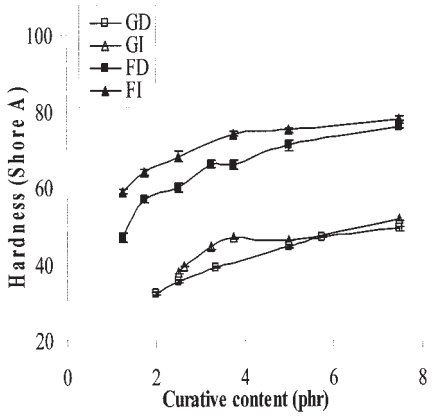

Figure 3 Hardness versus curative content for both gum and black-filled DPNR and IR vulcanizates.

can be seen that crosslink densities of all vulcanizates increased with increasing the amount of curatives. In addition, the black-filled vulcanizates possessed a higher crosslink density than did the gum vulcanizates due to the additional interaction between the rubber and carbon black. At a given curative content, IR yielded vulcanizates with higher crosslink density than did DPNR for both gum and black-filled samples. The reason for having higher crosslinking of IR than DPNR is still not clear but it may result from some additives added into the IR during manufacturing. Therefore, a greater curative content is required for DPNR to achieve the same degree of crosslink density as IR. However, crosslink densities of GD and GI became similar at a very high curative content. This seems to be the same with FD and FI.

Figures 2 and 3 relate 100% modulus and hardness to curative content for both gum and black samples. At a fixed curative content, the lower stiffness as a result of a lower extent of crosslink density of DPNR compared to IR was observed, though the modulus of the gum samples (GD and GI) at a fixed curative content was insignificantly different.

Tensile strength and tear strength versus crosslink density of gum and black-filled DPNR and IR vulcanizates are depicted in Figures 4 and 5, respectively. Both tensile and tear strength of all vulcanizates increased up to a maximum and then declined as crosslink density increased. It is well established that the strength of crystallizable elastomers depends on their crystallizability during stretching. Therefore, the results indicate that the crystallizability of these elastomers passed through a maximum with crosslink density. As described in a previous study,[15] chain orientation during stretching will occur when an appropriate degree of crosslinking exists, but the structural regularity needed for crystallization will be hindered if crosslink junctions are dense. The results also indicate that tensile strength as high as that of the black-filled DPNR could be obtained from gum DPNR when it had appropriate crosslink density. This can be seen in Figure 4, that tensile strength at maximum of GD was higher than GI but comparable to that of FD

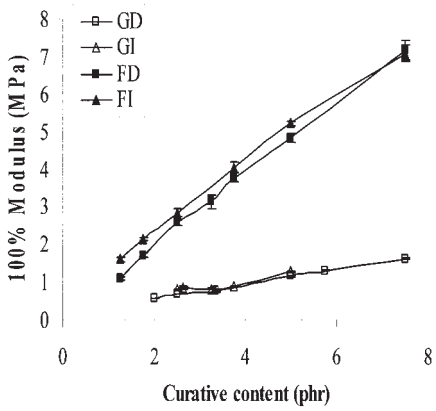

Figure 2 100% modulus versus curative content for both gum and black-filled DPNR and IR vulcanizates.

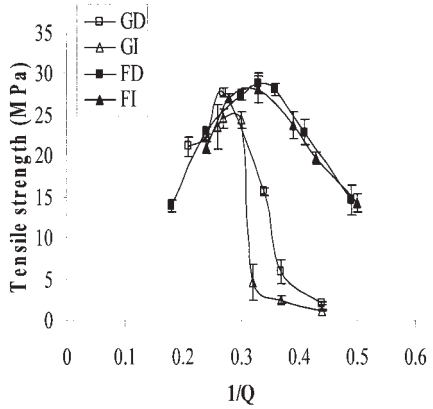

Figure 4 Tensile strength as a function of crosslink density for both gum and black-filled DPNR and IR vulcanizates.

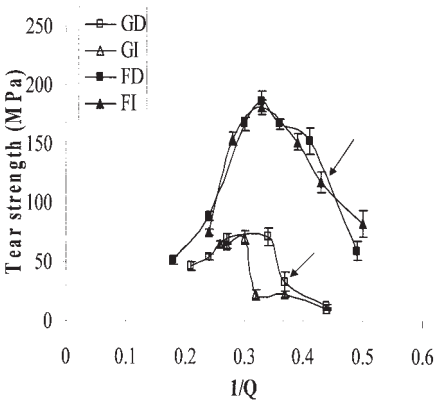

Figure 5 Tear strength as a function of crosslink density for both gum and black-filled DPNR and IR vulcanizates.

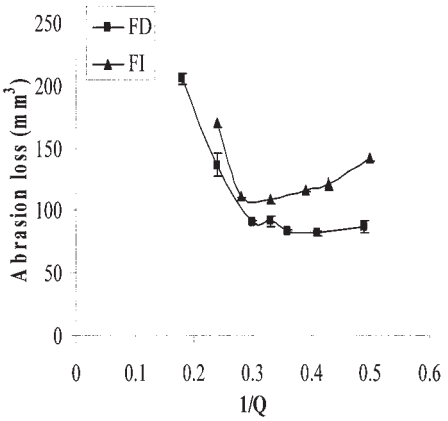

Figure 6 Abrasion loss as a function of crosslink density of FD and FI.

and FI. In addition, the maximum tear strength of GD, shown in Figure 5, was comparable to GI but much lower than that of the black samples. This means carbon black serves the function of reinforcing filler for this property. After the maximum, both tensile and tear strength of the black samples did not drop as much as that of the gum samples. The results clearly indicated the lesser dependence of strength upon the changes in crosslink density of the black vulcanizates. In other words, it is revealed that reinforcement by carbon black obscured the inherent property of the rubber. For gum samples, the abrupt decrease of tear strength occurred in GI at a lower crosslink density than that of GD, resulting in a narrower maximum peak of GI relative to GD. This might be attributed to the differences in their crystallizability under tension. The results again indicate that the strength of GI was more dependent on the crosslink density than that of GD. Apparently, the appropriate crosslink density to achieve optimum strength of GI and GD was different. Bruzzone and coworkers also presented the narrower modulus range to obtain the maximum tensile strength of IR compared to that of the ordinary NR.[6] In addition, Flory and coworkers reported that an amorphous styrene butadiene rubber has a sharper maximum and the maximum occurs at a much lower crosslinking than NR.[4] Moreover, it can be seen in Figures 3 and 4 that tensile and tear strength of tightly crosslinked black samples were not as low as that of the tightly crosslinked gum samples (as indicated by arrows) because carbon black acts as a reinforcing filler and promotes the crystallization in the black samples. Additionally, the results imply that the tightly crosslinked gum samples did not crystallize before the failure took place.

Abrasion loss and heat buildup values of FD and FI as a function of crosslinking are illustrated in Figures 6 and 7, respectively. Basically, abrasion resistance and heat buildup resistance are inversely proportional to the abrasion loss and heat buildup values, respectively. In this experiment, only the abrasion and heat buildup resistance of the black samples were determined since the gum vulcanizates bounced during abrading, resulting in an inaccuracy of abrasion loss value, and they normally did not contribute much heat under dynamic force. Both FD and FI showed the decrease in abrasion loss and heat buildup values with increasing crosslinking and then they became almost constant. At these constant regions, FD exhibited the superior abrasion resistance to that of FI while their heat buildup resistance at a given crosslink density was not significantly different. Although it is shown that hardness is an important factor affecting the abrasion resistance,[18] these results confirmed that hardness was not the only prime factor controlling abrasion resistance. As shown in Figures 3 and 6, the hardness of the black samples tended to increase with increasing crosslink density while the abrasion loss became finally almost constant. It has been reported in other experiments that the frictional coefficient of the samples might be the primary factor determining abrasion resistance.[19,20]

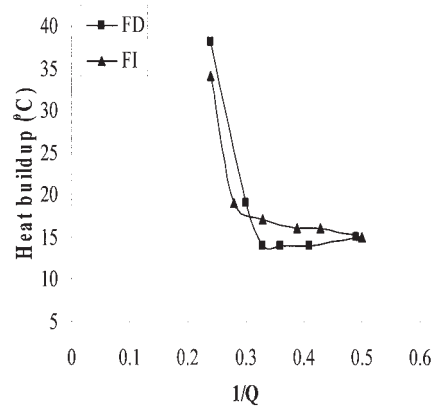

Figure 7 Heat buildup as a function of crosslink density of FD and FI.

TABLE I
Mechanical Properties of Gum Vulcanizates at Similar Optimum Crosslink Density

Properties	GD	GI	GN
Crosslink density (1/Q)	0.27	0.27	0.27
100% Modulus (MPa)	0.75 ± 0.02	0.85 ± 0.03	0.77 ± 0.01
300% Modulus (MPa)	1.62 ± 0.07	2.02 ± 0.05	1.65 ± 0.03
Hardness (Shore A)	39 ± 0	40 ± 0	40 ± 0
Tensile strength (MPa)	27.7 ± 0.6	24.6 ± 1.2	28.0 ± 1.7
Tear strength (N/mm)	70 ± 4	64 ± 2	63 ± 4
Crack length at 50 kcycles (mm)	6.8 ± 0.0	8.5 ± 0.3	7.2 ± 0.2

Mechanical properties of gum vulcanizates at similar optimum crosslink density

The mechanical properties of gum vulcanizates having similar optimum crosslink density are compared to eliminate the effect of crosslinking variation. In this experiment, GD and GI were prepared to have crosslink density of 0.27 because their tensile strength was maximum at this region, as shown in Figure 1. Their mechanical properties are displayed in Table I. The mechanical properties of the ordinary NR or GN, having crosslink density of 0.27, were also determined for comparative purposes. At equal crosslink density, the hardness of all gum vulcanizates was comparable while there was a slight difference in their moduli. GD showed the comparable 100 and 300% moduli to those of GN but lower than those of GI.

It was found that tensile strength of GI was rather lower than GD and GN. This may be due to the lower crystallizability of GI compared to the others. However, tear strength of all gum vulcanizates was not markedly different. The length of crack growth at 50 kcycles of gum vulcanizates was also measured. GD showed similar crack growth resistance to that of GN but greater than that of GI. Although all samples had similar crosslink density and hardness, the modulus of GD was comparable to GN but slightly less than that of GI. It seems that modulus plays a role in determining crack growth resistance of the vulcanizates. As described in a previous study,[8] the vulcanizate having lower modulus would yield the higher crack growth resistance. Since GD had the lowest modulus, the lowest load was needed to deform it to the same level as GI vulcanizates. Thus, stress concentration at the crack tip of GD was the lowest. As a result, crack propagation in GD was lower than GI.

Mechanical properties of black-filled vulcanizates at similar optimum crosslink density

Same as the gum samples, the crosslink density yielding maximum tensile strength for both FD and FI was selected from Figure 1 to prepare the samples with similar optimum crosslinking. Here, FD and FI were prepared to have crosslink densities of about 0.33, and their mechanical properties are compared in Table II. Likewise, the mechanical properties of black-filled ordinary NR designated as FN were also determined for the comparison. It appears that hardness and tensile strength of all black samples were comparable, whereas 100 and 300% moduli of FI were rather lower than those of FD and FN. Tear strength and heat buildup of FD were not very different from those of FI and FN. Abrasion resistance of FD was similar to FN but obviously superior to that of FI even though their hardness were comparable. As mentioned previously, although hardness is reported to be an important factor for determining abrasion resistance, it is not the only factor controlling the abrasion resistance of the vulcanizates. In contrast to abrasion resistance, the crack growth resistance of FD was comparable to that

TABLE II
Mechanical Properties of Black-Filled Vulcanizates at Similar Optimum Crosslink Density

Properties	FD	FI	FN
Crosslink density (1/Q)	0.33	0.33	0.34
Hardness (Shore A)	66 ± 1	68 ± 1	66 ± 2
100% Modulus (MPa)	3.12 ± 0.17	2.84 ± 0.10	3.19 ± 0.13
300% Modulus (MPa)	15.7 ± 0.5	13.3 ± 0.4	15.7 ± 0.5
Tensile strength (MPa)	28.8 ± 1.2	28.8 ± 1.7	28.6 ± 0.6
Tear strength (N/mm)	186 ± 9	181 ± 6	193 ± 10
Heat build up (°C)	14 ± 1	17 ± 1	15 ± 1
Abrasion loss (mm)	91 ± 5	109 ± 3	98 ± 2
Crack length at 24 kcycles (mm)	18.0 ± 0.8	13.7 ± 0.9	19.3 ± 1.5

of FN but clearly lower than FI. The lower crack growth resistance of FD seemed to result from its higher modulus as described above.

CONCLUSIONS

DPNR needed a higher amount of curatives to achieve the same level of crosslink density as that of IR for both gum and black-filled systems. Tear strength of GI was more dependent on the crosslink density than that of GD. This can be seen by an abrupt drop in tear strength at lower crosslink density and a narrower range of crosslinking to achieve the optimum tear strength of GI relative to GD. On the contrary, tensile and tear strengths of FD and FI were not markedly different at various crosslink densities due to the reinforcing effect by carbon black, which overshadowed the inherent property of each rubber. For both gum and black-filled systems, most mechanical properties at the similar optimum crosslink density of DPNR were comparable to those of IR and the ordinary NR except that the crack growth resistance of FD was inferior to that of FI due to the lower 100% modulus of FI. However, one can improve the crack growth resistance of FD without much drop in strength by preparing FD with a little lower crosslinking.

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