

## The Fraction of Effective Sulfur Crosslinking in High Sulfur-Natural Rubber Vulcanizers

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Modulus measurements on natural rubber vulcanizates at high sulfur percentages indicate that the fraction of combined sulfur which is effective as crosslinks after vulcanization is lower than in SBR-1000 mixtures.

In previous work,<sup>1</sup> SBR-1000 copolymer recipes containing 6-34% sulfur were found to contain crosslinks amounting to less than 0.20 of the sulfur combined during vulcanization. We have now found that the amount of combined sulfur which is effective as crosslinks in natural rubber mixtures containing 2-34% sulfur does not exceed 0.07, even though the butyraldehyde amine type of accelerator which we used has been shown to be particularly effective as a promoter of sulfur combination during the vulcanization of hard rubber recipes.<sup>2</sup>

Natural rubber recipes were prepared from material cut from the interior of a single bale of No. 1 ribbed smoked sheets. The rubber was blended thoroughly on a two-roll rubber mixing mill, and phenyl- $\beta$ -naphthylamine in the proportion of 1 part by weight for each 100 parts of rubber was added to insure antioxidant protection during the ensuing mixing operations. Butyraldehyde amine accelerator (du Pont Accelerator 808) was mixed into the antioxidant-rubber mixture in the proportion of 4 parts accelerator to 100 parts of the mixture. Sulfur was then added to the indicated percentage by weight of each final mixture. Losses of sulfur during mixing and vulcanizing amounted to between 0.1 and 0.2%, as in the previous work.

Slabs of each mixture approximately 2 mm. thick were vulcanized 2 hr. at 165°C. in a steel mold, and shear modulus at 10 sec.<sup>3</sup> was determined by the modified Gehman procedure previously described.<sup>1</sup>

The unsaturation in the original rubber was determined, after extraction for 65 hr. with acetone in a Soxhlet apparatus, by dissolving the dried residue in *p*-dichlorobenzene and titrating with iodine monochloride in carbon tetrachloride according to the method of Kemp and Peters.<sup>4</sup> The calculated value of the vulcanizable unsaturation in the antioxidant-

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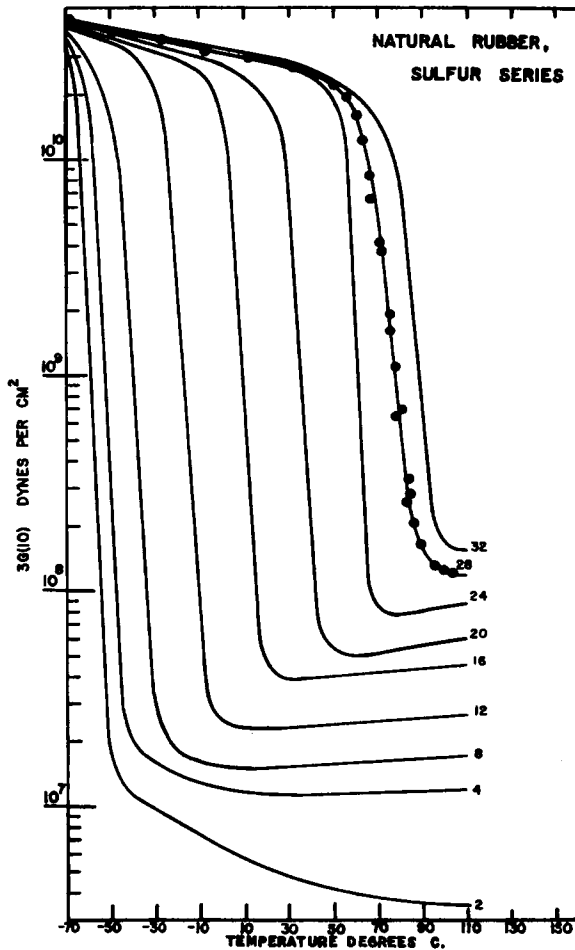


Figure 1.

accelerator-rubber mixture based on these measurements was found to be 87.7% of the theoretical value deduced from the structure of polyisoprene. This is equivalent to 29.25% sulfur required in the recipe to provide one sulfur atom for each isoprene unsaturation in the polymer, and is only insignificantly higher than the 29.1% sulfur previously calculated for our SBR mixtures. Direct comparisons of the two systems on a recipe percentage basis are thus facilitated.

The shape and slope of the modulus-temperature curves in Figure 1 are similar to those of the SBR mixtures and are typical of those for cross-linked amorphous polymers. They all show a glassy region, a transition region, and a rubbery plateau region. The transition region is displaced towards higher temperatures, and the rubbery plateau modulus increases as the percentage of sulfur in the recipes, and therefore the concentration

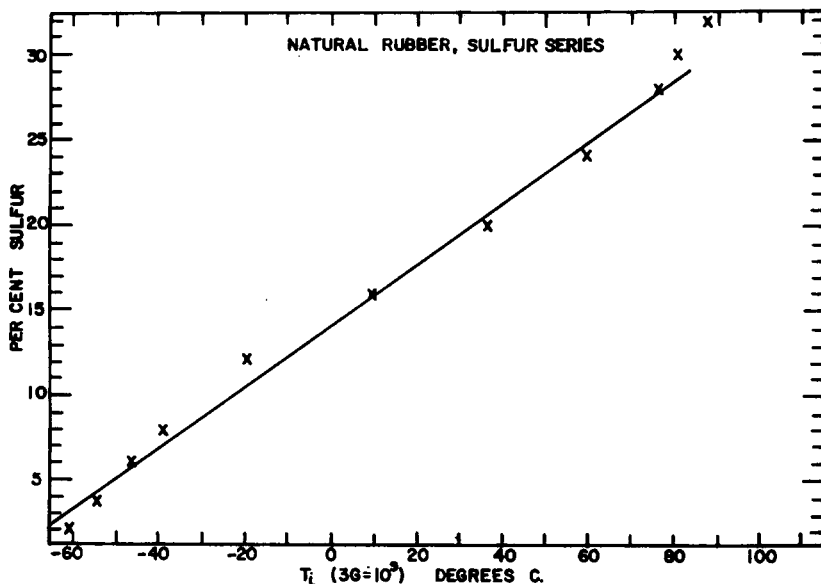


Figure 2.

of crosslinks, is increased. This is the same general pattern found for SBR. Others<sup>5</sup> have recently reported that this pattern is also found in natural rubber vulcanized with dicumyl peroxide or by means of an electron beam.

$T_i$  is defined as the temperature at which  $3G(10) = 10^9$  dynes/cm.<sup>2</sup>. It is reasonable to expect that progressive chemical combination of polyisoprene with sulfur should lead to substances having progressively higher  $T_i$  or  $T_g$  values, because of the increasing solubility parameter of the sulfur containing compositions.

The slope of the plot of  $T_i$  against per cent sulfur shown in Figure 2 is the same as the slope found for SBR-1000 mixtures but is displaced downscale on the temperature axis by slightly less than 12°C. This agrees well with the 10–15°C. difference<sup>6</sup> in the glass transition temperatures of the unvulcanized polymers of natural rubber and SBR found by expansivity measurements.

The molar concentration of sulfur atoms per unit volume in each mixture shown in Table I was calculated from the amount in the original recipe and from the density of the vulcanized material. The small losses during mixing and vulcanization were disregarded. The concentration of crosslinking after vulcanization was calculated from eq. (1),<sup>3</sup> and from the measured rubbery plateau modulus:

$$G = nRT = 2cRT \quad (1)$$

where  $G$  is the shear modulus in the rubbery plateau region,  $n$  is the number of chains per unit volume,  $c$  is the moles of crosslinks per unit volume (cubic centimeter) (assuming four network chains terminate at each crosslink),

TABLE I

Sulfur in recipe, %	Sulfur $\times 10^{-3}$ , moles/cm. <sup>3</sup>	Density $d$ , g./cm. <sup>3</sup>	$3G$ $\times 10^3$ at 110°C.	$c$ $\times 10^{-3}$ , moles/cm. <sup>3</sup>	Fraction of sulfur atoms effective in crosslinking	Slope at $T_i$ $\Delta \log(3G) / \Delta T$	$T_i$ , °C. at $3G = 10^9$
2	0.58	0.93	0.036	0.019	0.033	0.23	-60
4	1.2	0.94	0.12	0.063	0.052	0.24	-54
6	1.8	0.96	0.14	0.073	0.041	0.25	-46
8	2.4	0.98	0.17	0.089	0.037	0.17	-39
12	3.8	1.02	0.27	0.14	0.037	0.14	-19
16	5.3	1.06	0.44	0.23	0.043	0.15	10
20	6.9	1.10	0.56	0.29	0.042	0.15	37
24	8.5	1.13	0.85	0.44	0.052	0.22	60
28	10	1.16	1.2	0.63	0.063	0.09	77
30	11	1.17	1.3	0.68	0.062	0.07	81
32	12	1.19	1.5	0.78	0.065	0.11	88
34	13	1.20	1.5	0.78	0.060	0.09	90

$R$  is the gas constant, and  $T$  is the absolute temperature. The front factor<sup>3</sup> is assumed to be equal to unity for this case.

The modulus values in Table I were determined at 110°C. for all of the mixtures. This temperature is in the region of the rubbery plateau modulus for all of the compositions studied. It is also sufficiently low to avoid all but negligible effects of reversion and other degradative reactions which become important at high temperatures, especially with compositions containing high amounts of sulfur. Table I shows that the fraction of sulfur atoms effective in crosslinking was less than 0.07 for all of the compositions. This of course refers only to the particular type of curing recipe which we used. The fact that the fraction of combined sulfur which is effective to produce crosslinks in natural rubber is very small, even smaller than in SBR, lends further support to the conclusions<sup>7,8</sup> that prolonged vulcanization with large amounts of sulfur tends to result in a high percentage of cyclic structures. It may well also relate with the findings of Saville et al.,<sup>9,10</sup> who showed that although sulfur tends to form a preponderance of monosulfide products by reaction with symmetrical disubstituted olefins similar in structure to polybutadiene, disulfides are more likely to result from reactions between sulfur and trisubstituted olefins similar to polyisoprene.

The obvious conclusions from this are that cyclization is the primary cause of the low sulfur efficiency in crosslinking both natural and SBR synthetic rubber and that, in the case of natural rubber, polysulfide formation may further reduce the ratio of crosslinks formed per atom of sulfur combined.

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## Synopsis

Shear modulus measurements as a function of temperature for smoked sheet natural rubber vulcanized with sulfur in amounts between 2 and 34% show the crosslinking efficiency of sulfur to be much lower in natural rubber than in SBR-1000, at least for the particular curing recipe here used. The ratio of crosslinks to total sulfur atoms computed from the rubbery plateau modulus is below 0.07 for all of the natural rubber mixtures. Ratios up to 0.20 were found in SBR mixtures. The shape and slope of the modulus-temperature curves of natural rubber vulcanizates are similar to those of SBR mixtures and are typical of crosslinked amorphous polymers. Consistent displacement of the curves toward higher temperatures and higher rubber modulus as the percentage of sulfur in the recipes is increased also follows the same general pattern found for SBR. Cyclization is concluded to be the primary cause of the low sulfur efficiency in crosslinking both polymers, although polysulfide formation in natural rubber may further reduce the ratio of crosslinks formed per atom of sulfur combined.

## Résumé

On a effectué des mesures de module de tension en fonction de la température sur des feuilles formées de caoutchouc naturel vulcanisé au soufre dont la proportion variait de 2 à 34%. Ces mesures ont montré que l'efficacité de pontage du soufre est beaucoup plus faible dans le caoutchouc naturel que dans le SBR-1000, à tout le moins dans les conditions particulières de vulcanisation employées ici. Le rapport des ponts en nombre total d'atomes de surface calculé à partir du module du plateau caoutchouteux est inférieur à 0.07 pour l'ensemble des mélanges de caoutchouc naturel. Des rapports supérieurs à 0.20 ont été trouvés dans des mélanges de SBR. La forme et la pente des courbes module-température de caoutchouc naturel vulcanisé sont analogues à celles de mélanges de SBR et sont typiques de polymères amorphes pontés. On constate un déplacement régulier des courbes à des températures plus élevées et à un module plus grand lorsque le pourcentage de soufre dans les formules est augmenté et ce déplacement suit également de même schéma général trouvé pour le SBR. On conclut qu'une cyclisation est la cause première de la basse efficacité du soufre dans le pontage des polymères bien que la formation de polysulfure dans le caoutchouc naturel peut diminuer ultérieurement le rapport des ponts formés par atome de soufre combiné.

### Zusammenfassung

Messungen des Schubmoduls in Abhängigkeit von der Temperatur an Smoked-Sheet-Naturkautschuk-Schwefelvulkanisaten mit 2 bis 34 Prozent Schwefel zeigen, dass zumindest für das spezielle verwendete Vulkanisationsrezept die Vernetzungswirkung von Schwefel in Naturkautschuk viel niedriger ist als in SBR-1000. Das aus dem Modul im Kautschukplateau berechnete Verhältnis der Zahl der Vernetzungen zur Gesamtzahl der Schwefelatome liegt für alle Naturkautschukmischungen unterhalb 0,07. In SBR-Mischungen traten Verhältnisse bis zu 0,20 auf. Gestalt und Neigung der Modul-Temperaturkurven von Naturkautschukvulkanisaten sind denjenigen von SBR-Mischungen ähnlich und für vernetzte, amorphe Polymere typisch. Die Verschiebung der Kurven gegen höhere Temperatur und höheren Kautschukmodul mit zunehmendem Prozentgehalt an Schwefel im Rezept folgt ebenfalls dem gleichen allgemeinen Verhalten wie bei SBR. Die Zyklisierung scheint die primäre Ursache für die geringe Vernetzungswirkung des Schwefels bei beiden Polymeren zu sein; bei Naturkautschuk kann die Anzahl der pro begundenes Schwefelatom gebildeten Vernetzungen durch Polysulfidbildung weiter herabgesetzt werden.

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