

The Fraction of Effective Sulfur Crosslinking in SBR Vulcanizates

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Modulus measurements on SBR vulcanizates at high sulfur percentages indicate that less than 0.20 of the combined sulfur is effective as crosslinks after vulcanization.

Recipes containing sulfur in amounts ranging between 6 and 34 wt.-% were prepared from a single bale of SBR-1000 copolymer. The rubber was used as received and contained all of the fatty acids, soap, antioxidant and other nonpolymer materials normally present in commercial polymer. Butyraldehyde amine accelerator¹ was mixed with the rubber in the proportion of 4 parts by weight of accelerator for each 100 parts of rubber (4 pphr), and then sulfur was added to the indicated percentage by weight of each final mixture. All of the mixing operations were done on a two-roll rubber mixing mill without precautions against oxygen pickup. There was some loss of sulfur, amounting to between 0.1 and 0.2% of the recipe during the mixing and subsequent vulcanizing operations.

Slabs of each mixture approximately 2 mm. thick were vulcanized 2 hrs. at 165°C. in a steel mold. The temperature of vulcanization was chosen by vulcanizing $\frac{1}{4}$ in. (6.35 mm.) thick slabs of the high sulfur mixtures and selecting a temperature approximately 5°C. below that which resulted in a runaway exotherm evidenced by decomposition and gassing during vulcanization. The time of vulcanization at this temperature was arbitrarily taken as 4 times the time necessary to produce maximum tensile strength in the high-sulfur recipes.

The moles of sulfur atoms per cubic centimeter in each mixture shown in Table I was calculated from the amount in the original recipe and from the density, known losses during mixing and vulcanization being disregarded. Most of the sulfur is combined with the rubber, although experience shows² that a minimum of 0.1% remains uncombined even in recipes containing less than one atom of sulfur per mole of unsaturation and that recipes containing higher ratios of sulfur commonly are found to have several per cent of uncombined sulfur even after protracted vulcanization.

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Calculation of vulcanizable unsaturation shows that approximately 29% sulfur in the recipe would be required to provide one sulfur atom for each butadiene unsaturation in the polymer.

The butyraldehyde amine type of acceleration which we used has been previously shown³ to be very effective in promoting the vulcanization of ebonites, and the presence of amines during the sulfuration of olefins has been shown to result^{4,5} in saturated products, mostly mono- and disulfides. A preponderance of monosulfide products is formed as a result of the reaction of sulfur with symmetrical disubstituted olefins similar in structure to polybutadiene. Trisubstituted olefins similar to polyisoprene are more favorable to the formation of disulfide products.⁵

TABLE I

Sulfur in recipe, %	Sulfur, moles cm. ⁻³ × 10 ⁻³	Density <i>d</i>	3 <i>G</i> × 10 ⁸ at 110°C.	<i>c</i> , moles cm. ⁻³ × 10 ⁻³	Fraction of sulfur atoms effective in cross-linking	<i>T</i> _i at 3 <i>G</i> = 10 ⁹ , °C.
6	1.9	0.99	0.473	0.25	0.13	-35
8	2.5	1.01	0.469	0.25	0.10	-26
12	3.9	1.05	0.667	0.35	0.09	-5
16	5.4	1.09	1.04	0.54	0.10	+24
20	7.0	1.13	1.38	0.72	0.10	+47
22	7.9	1.15	1.61	0.84	0.11	+57
24	8.7	1.16	2.08	1.1	0.12	+68
26	9.5	1.18	2.44	1.3	0.13	+86
			at 150°C.			
34	13	1.23	5.46	2.6	0.20	+127

Shear modulus was determined on a Gehman apparatus⁶ modified to take a specimen 6.35 mm. (0.250 in.) wide and 63.5 mm. (2.50 in.) long. The specimen thicknesses used were between 1.5 and 2.0 mm. and were measured to within 0.025 mm.

The specimens were twisted with a distance of 38.18 mm. (1.50 in.) between grips and the angular distortion was read after 10 sec. under stress. Wires with torsional constants in the neighborhood of 2.000 g.-cm./angular degree were used for measurements in the glassy modulus and transition range. Wires with torsional constants near 0.125 g.-cm./angular degree were used for measurements in the transition and rubbery modulus range. The modulus curves obtained in this manner coincided in the transition region and composites were used to provide the data shown in Figure 1. We plot 3*G*(10), thrice the shear modulus measured after 10 sec.

The shape and slope of the modulus-temperature curves we have obtained are typical of crosslinked amorphous polymers. There is a consistent displacement of the curves toward higher temperatures as the percentage of sulfur in the recipes is increased. We define *T*_i as the tempera-

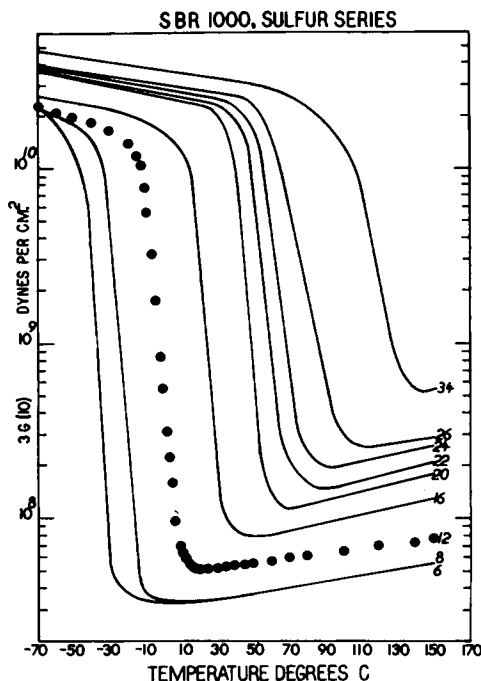


Fig. 1. The data for all of the recipes except the 12% sulfur mixture are shown as curves, for clarity of presentation. The individual data points are plotted for the 12% recipe to indicate the spacing of the measurements and the precision obtained.

ture at which $3G(10)$ is equal to 10^9 dynes/cm.² There is a linear relationship between T_i and the percentage of sulfur, as shown in Figure 2.

The modulus values in Table I and for use in eq. (1) below were determined at 110°C. (except for the 34% recipe, which did not undergo complete transition to the rubbery state at temperatures below 140°C.). The temperature 110°C. was chosen arbitrarily because it is the lowest temperature in the range of *rubbery* modulus common to all of the mixtures below 34% sulfur. 150°C. was used for the 34% sulfur recipe because, although it is well above the lowest temperature at which the mixture can be vulcanized, it is close to the minimum temperature at which the modulus curve enters the region of rubbery behavior.

The degree of crosslinking achieved after vulcanization of these mixtures was calculated from eq. (1):⁷

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

where G is the rubbery shear modulus, n is the number of chains per unit volume, c is the moles of crosslinks per cubic centimeter (assuming 4 chains terminate at each crosslink), R is the gas constant, and T is the absolute temperature. The front factor⁷ is assumed to be equal to unity for this case.

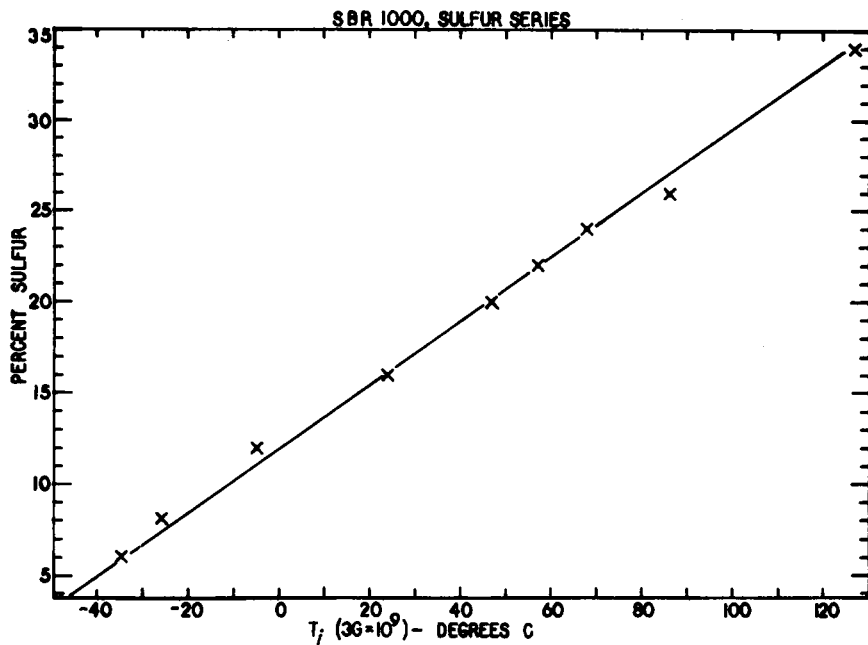


Figure 2.

Values of c obtained from eq. (1) are shown in Table I. Also shown is the ratio of c to the moles of sulfur atoms per cubic centimeter.

The fact that only 0.09 to 0.20 of the sulfur atoms present contribute to effective crosslinks, even under conditions conducive to the formation of monosulfide products, lends support to the conclusions of Bateman et al.⁸ and Bloomfield⁹ that prolonged vulcanization (of natural rubber) tends to result in a high percentage of cyclic structures. The possibility of significant amounts of polysulfide crosslinks is not ruled out, but it appears more reasonable for us to attribute the low fraction of crosslinks, which we obtained under conditions favorable to monosulfide formation, to combination of the major portion of the sulfur to modify the chain by cyclization, leaving only minor amounts of sulfur combined in links between chains.

References

1. Du Pont 808.
2. Scott, J. R., *J. Rubber Research*, **13**, 27 (1944); *Rubber Chem. Technol.*, **17**, 724 (1944).
3. Fisher, D. G., R. G. Newton, R. H. Norman, and J. R. Scott, *J. Rubber Research*, **17**, 161 (1948).
4. Moore, C. G., and R. W. Saville, *J. Chem. Soc.*, **1954**, 2082, 2089; *Rubber Chem. Technol.*, **28**, 92, 102 (1955).
5. Glazebrook, R. W., and R. W. Saville, *J. Chem. Soc.*, 2094 (1954); *Rubber Chem. Technol.*, **28**, 109 (1955).
6. "Tentative method of measuring low temperature stiffening of rubber and rubber-like materials by means of a torsional wire apparatus," *ASTM D-1053-58T*, Am. Soc.

Testing Mater., Philadelphia, Pa.; Gehman, S. D., D. E. Woodford, and C. S. Wilkinson, *Ind. Eng. Chem.*, **39**, 1108 (1947).

7. Tobolsky, A. V., *Properties and Structure of Polymers*, Wiley, New York, 1960, pp. 88-97.

8. Bateman, L. C., R. W. Glazebrook, C. G. Moore, and R. W. Saville, *Proc. Third Rubber Technol. Conf.*, London, 298 (1954), publ. 1956.

9. Bloomfield, G. F., *J. Soc. Chem. Ind.*, **63**, 66 (1949).

Synopsis

Shear modulus measurements as a function of temperature have been made for SBR vulcanized with sulfur in amounts between 6 and 34% of the recipe. The shape of the modulus-temperature curves are typical of crosslinked amorphous polymers and there is a consistent displacement of the curves toward higher temperatures as the percentage of sulfur in the mixture is increased. The rubbery plateau modulus also increases with increasing sulfur, and from its magnitude the concentration of crosslinks is computed. The ratio of crosslinks to total sulfur atoms is below 0.20 in all cases. The results lend support to the conclusions of Bateman and of Bloomfield that a high proportion of cyclic structures is formed during sulfur vulcanization.

Résumé

On a effectué des mesures de module de cisaillement en fonction de la température pour du SBR vulcanisé au soufre dans des proportions de 6 et 34% du poids total. La forme des courbes module-température sont typiques de polymères amorphes ramifiés et on a un déplacement des courbes vers des températures plus élevées lorsque le pourcentage de soufre augmente dans le mélange. Le module du plateau caoutchouteux augmente également avec une augmentation de soufre, et à partir de sa grandeur on peut évaluer la concentration de soufre ramifié. Le rapport d'atomes de soufre ramifié au soufre total est dans tous les cas en-dessous de 0.20. Les résultats tendent à soutenir les conclusions de Bateman et Bloomfield suivant lesquelles on forme une forte proportion de structures cycliques pendant la vulcanisation au soufre.

Zusammenfassung

Der Schubmodul von schwefelvulkanisiertem SBR (Schwefelmenge zwischen 6 und 34 Prozent des Rezepts) wurde in Abhängigkeit von der Temperatur gemessen. Die Gestalt der Modul-Temperaturkurve ist typisch für vernetzte amorphe Polymere und mit steigendem Schwefelgehalt in der Mischung tritt eine systematische Verschiebung der Kurven gegen höhere Temperaturen ein. Der Modul im Kautschukplateau nimmt ebenfalls mit steigender Schwefelmenge zu und aus seiner Grösse wird die Vernetzungskonzentration berechnet. Das Verhältnis Vernetzungen zu gesamten Schwefelatomen liegt in allen Fällen unterhalb 0,20. Die Ergebnisse bilden eine Stütze für die Ansicht von Bateman und Bloomfield, dass während der Schwefelvulkanisation ein hoher Anteil zyklischer Strukturen gebildet wird.

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