

Fraction of Effective Sulfur Crosslinking in Polybutadiene Rubber Vulcanizates

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Synopsis

Shear modulus measurements as a function of temperature for the high *cis*- and high *trans*-isomers of 1,4-polybutadiene, vulcanized with sulfur in amounts between 2 and 44% of the recipe, show the crosslinking efficiency of sulfur in these systems to be slightly lower than in SBR-1000, but higher than in natural rubber. Two distinct modes of mechanical behavior are noted with these stereo regular rubbers. There is pronounced crystalline behavior at low degrees of vulcanization. After crystallinity has been destroyed by increased crosslinking, both polymers behave as typical cross-linked amorphous materials. Additional evidence is found to support the conclusion that polymer structure, as well as chemical reactivity, plays an important role in the chemistry of vulcanization.

Modulus measurements on high-*cis*- and high-*trans*-polybutadiene vulcanizates indicate that, at high sulfur percentages, the fraction of sulfur which combines to form effective crosslinks is only slightly lower than in SBR-1000 mixtures vulcanized under corresponding conditions of time and temperature. In previous work^{1,2} the number of effective crosslinks in natural rubber mixtures vulcanized with 2-34% sulfur was found to be much lower than in SBR-1000 mixtures containing corresponding percentages of sulfur.

Recipes were prepared from *cis*-1,4- and *trans*-1,4-polybutadiene by adding butyraldehyde amine accelerator (du Pont Accelerator 808) in the proportion of 4 parts accelerator to 100 parts rubber and then blending thoroughly on a two-roll rubber mixing mill. Sulfur was then added to a portion of the accelerator-rubber mixture and blended in thoroughly to obtain a recipe containing 50% sulfur by weight. Recipes containing lower percentages of sulfur were obtained as needed for molding by blending the 50% sulfur mixture with a quantity of accelerator-rubber mixture sufficient to reduce the sulfur content of the blend to the desired amount. Losses of sulfur during mixing and vulcanizing amounted to less than 0.2% of the amount added.

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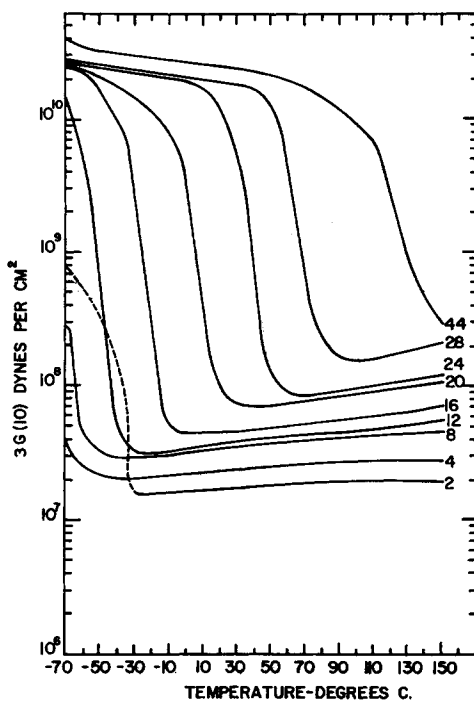


Fig. 1. *cis*-1,4-Polybutadiene modulus-temperature curves for recipes containing 2-44% sulfur showing (—) amorphous behavior and (---) crystalline behavior.

Slabs of each mixture, except the zero sulfur *trans*-polybutadiene, approximately 2 mm. thick, were vulcanized 2 hr. at 165°C. in a steel mold. The time of vulcanization was arbitrarily taken as four times the time necessary to produce maximum tensile strength in the high sulfur recipes. This was done to ensure combination of the maximum proportion of the sulfur contained in each recipe.

The *trans*-polybutadiene specimens without sulfur were molded by heating the polymer for 10 min. at 165°C. in the mold used for the other specimens, applying pressure to form the material into a slab, and then cooling under pressure to 25°C. in 10 min. The vulcanized slabs were cooled to room temperature on a wooden plank in still air. The times for cooling to below 30°C. were approximately 15 min. All of the specimens were stored at ambient temperatures in the range 22-27°C. until tested.

Shear modulus at 10 sec. was determined by the modified Gehman procedure previously described.^{1,3,4}

The polybutadiene rubbers used were supplied by the Phillips Petroleum Company and contained approximately 93% *trans*-1,4- and 95% *cis*-1,4-polybutadiene, respectively.⁵ The unsaturation of the polybutadienes was not determined because the previous work with both SBR and natural rubber indicated that sulfur combination during vulcanization continued

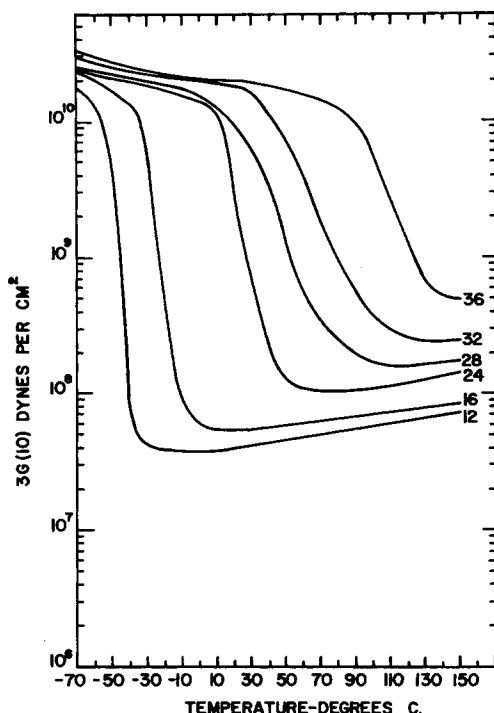


Fig. 2. *trans*-1,4-Polybutadiene modulus-temperature curves for recipes containing 12-36% sulfur, showing typical amorphous behavior.

beyond the stoichiometric ratio of one sulfur atom for each unsaturated site in the polymer. A very rough estimate of the unsaturation was therefore all that was required in order to allow us to include mixtures of sufficiently high sulfur content so that an excess would be present and probably uncombined in some of the recipes after vulcanization. This afforded assurance that both polymers were investigated up to the limits of useful sulfur combination.

Chemical measurements were not made to determine the combined sulfur because in the work with natural rubber and with SBR we found that in recipes containing up to 28% added sulfur, although nearly all of the sulfur was chemically combined during vulcanization, the fraction which was effective in producing crosslinks was very small in comparison to the total amount combined.

The shape and slope of the modulus temperature curves in Figure 1 for *cis*-1,4-polybutadiene and in Figure 2 for *trans*-1,4-polybutadiene, (except for the dashed portion of the curve for the 2% sulfur-*cis*-polybutadiene mixture) are all typical of the behavior of crosslinked amorphous polymers. They show a glassy region, a transition region, and a rubbery plateau region. The transition region, as with SBR and natural rubber mixtures, is displaced towards higher temperatures, and the rubbery

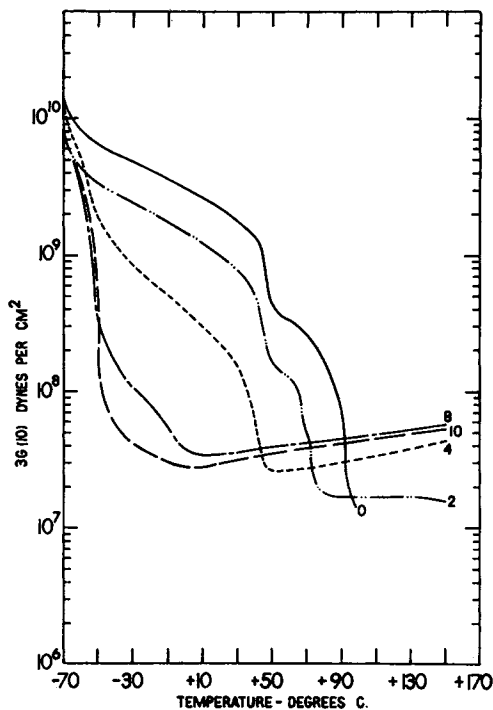


Fig. 3. *trans*-1,4-Polybutadiene modulus-temperature curves for recipes containing 0-10% sulfur, showing crystalline and semicrystalline behavior.

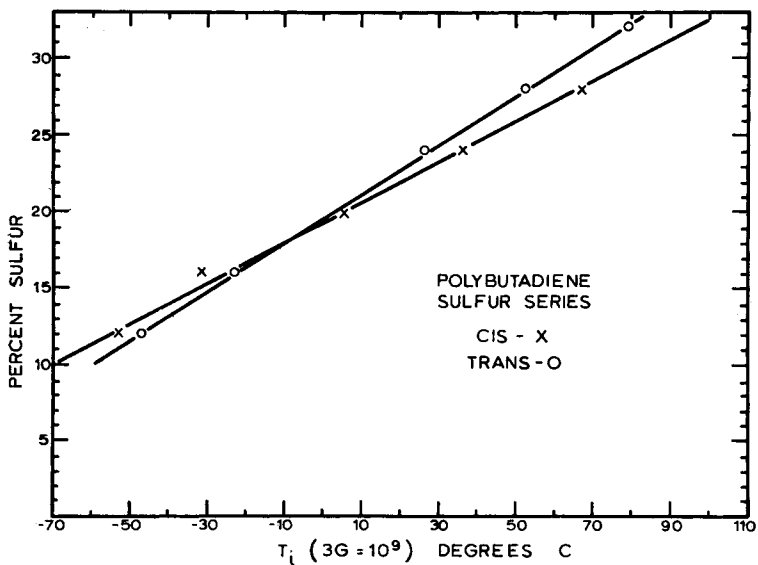


Fig. 4. Comparison of *cis*- and *trans*-polybutadiene isomers showing change in T_g with increase of sulfur for recipes characterized by amorphous behavior.

plateau modulus increases as the percentages of sulfur in the recipes, and therefore the concentration of crosslinks, is increased.

The anomalous location of the curve for the 2% sulfur-*cis*-polybutadiene mixture below -30°C . conforms to the pattern found for the *trans*-polybutadiene mixtures in Figure 3. The crystalline transitions which occur near -30°C . for *cis*-polybutadiene and at $+44^{\circ}\text{C}$. and just below 90°C . for *trans*-polybutadiene are displaced downscale on the temperature axis and the magnitudes of the transitions are also decreased as crystallinity diminishes in proportion to the degree of crosslinking introduced into the polymer.

Unfortunately we were not successful in preparing specimens of acceptable quality for tests on *cis*-polybutadiene mixtures containing less than 2% sulfur, but the displacement of crystalline transition temperature which occurs between 2 and 4% sulfur is unmistakable. The series of *trans*-polybutadiene mixtures in Figure 3 show this effect even more clearly. Here it is possible to follow the gradual suppression of the crystalline transitions until, in the 12% sulfur recipe, all evidence of crystalline behavior has disappeared. All of the mixtures, except the zero sulfur *trans*-polybutadiene, show a rubbery plateau region which increases in level proportionately to the degree of crosslinking produced by sulfur combination during vulcanization. The mixtures containing 12% or more of sulfur also give evidence of a glassy region above $3G = 10^{10}$ dynes/cm.².

T_i , the temperature at which $3G(10) = 10^9$ dynes/cm.², will be defined only for the completely amorphous polymers, i.e., those recipes which contain 10% sulfur or more. T_i increases with increasing amounts of sulfur in a linear fashion for both polymers, as shown in Figure 4. This increase is due to increasing cohesive energy density and also due to cyclization.^{1,2}

The total molar concentration of sulfur atoms present per unit volume in each mixture was calculated from the amount in the original recipes without regard for the small losses during mixing and vulcanization, and from the density of the specimens determined by displacement of water (or of methanol for the specimens having densities less than unity). The concentration of crosslinks after vulcanization was calculated from the measured rubbery plateau shear modulus:⁶

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

where G is the shear modulus in the rubbery plateau region, n is the number of chains per unit volume, c is the number of crosslinks per unit volume (cubic centimeter), R is the gas constant, and T is the absolute temperature. The assumption is made that four network chains terminate at each crosslink. The front factor⁶ is assumed to be unity for this case. The effects of chain entanglements and chain ends were not considered because they could not be measured. We believe that their effect is relatively small at high degrees of crosslinking.

Values of c , obtained from eq. (1), are shown in Table I for *cis*-1,4-polybutadiene and in Table II for *trans*-1,4-polybutadiene. Also shown is the ratio of c to the moles of sulfur atoms per cubic centimeter. The 32% and 36% sulfur, *trans*-polybutadiene recipes did not reach rubbery modulus at 110°C. and were therefore measured at 150°C.

Although the ratio of c to the moles of sulfur atoms per cubic centimeter for both polybutadienes is slightly lower than for SBR, it is appreciably higher than in natural rubber² and is therefore in accordance with the prediction^{7,8} that polybutadiene is more likely to yield monosulfide products

TABLE I
cis-1,4-Polybutadiene

Sulfur, % of recipe	Sulfur $\times 10^{-3}$, mole/cm. ³	Density d , g./cm. ³	$3G \times 10^8$ at 110°C., dyne/cm. ²	$c \times 10^{-3}$, mole/cm. ³	Fraction of sulfur atoms effective in crosslinking	T_i at $3G = 10^9$, °C.
2	0.58	0.929	0.19	0.10	0.17	*
4	1.2	0.946	0.28	0.14	0.12	*
8	2.4	0.980	0.43	0.22	0.09	*
12	3.8	1.02	0.49	0.26	0.07	-53
16	5.3	1.06	0.62	0.32	0.06	-32
20	6.8	1.10	0.95	0.50	0.07	5
24	8.5	1.14	1.03	0.53	0.06	37
28	10	1.17	1.56	0.82	0.08	67
44	18	1.30	62.8	^b	—	129

* Below -70°C., therefore not measured.

^b The 44% sulfur recipe did not reach a rubbery modulus level within the range of temperature measured, therefore the moles of crosslinking per cubic centimeter cannot be calculated from these data.

TABLE II
trans-1,4-Polybutadiene

Sulfur, % of recipe	Sulfur $\times 10^{-3}$, mole/cm. ³	Density d , g./cm. ³	$3G \times 10^8$ at 110°C., dyne/cm. ²	$c \times 10^{-3}$, mole/cm. ³	Fraction of sulfur atoms effective in crosslinking	T_i at $3G = 10^9$, °C.
0	0	0.967	*	0	0	44
2	0.58	0.958	0.17	0.09	0.15	21
4	1.2	0.956	0.36	0.19	0.16	-34
8	2.4	0.969	0.47	0.25	0.12	-58
10	3.1	0.985	0.46	0.24	0.08	-53
12	3.8	1.01	0.61	0.32	0.08	-47
16	5.2	1.05	0.71	0.37	0.07	-23
24	8.5	1.13	1.19	0.62	0.07	26
28	10	1.17	1.67	0.87	0.09	52
32	12	1.20	2.40 ^b	1.14	0.10	79
36	14	1.24	5.00 ^b	2.37	0.15	125

* Specimens broke at temperatures below 110°C.

^b $3G \times 10^8$ at 150°C.

than is natural or synthetic polyisoprene. Polybutadiene homopolymers and butadiene-styrene copolymers are thus capable of yielding more crosslinks per mole of sulfur combined during vulcanization than are the corresponding isoprene polymers. Much of the sulfur which is ineffective in producing crosslinks in each of these cases very probably combines intramolecularly to form cyclized structures.^{1,2}

TABLE III

Sulfur, % of recipe	$c \times 10^{-3}$, mole/cm. ⁻³				Fraction of sulfur atoms effective in crosslinking			
	SBR	Natural rubber	Polybutadiene		SBR	Natural rubber	Polybutadiene	
			<i>cis</i>	<i>trans</i>			<i>cis</i>	<i>trans</i>
2	—	0.019	0.10	0.09	—	0.03	0.17	0.15
4	—	0.063	0.14	0.19	—	0.05	0.12	0.16
8	0.25	0.089	0.22	0.25	0.10	0.04	0.09	0.12
12	0.35	0.14	0.26	0.32	0.09	0.04	0.07	0.08
16	0.54	0.23	0.32	0.37	0.10	0.04	0.06	0.07
20	0.72	0.29	0.50	—	0.10	0.04	0.07	—
24	1.1	0.44	0.53	0.62	0.12	0.05	0.06	0.07
28	—	0.63	0.82	0.87	—	0.06	0.08	0.09

Table III compares the number of crosslinks per mole and the fraction of sulfur atoms effective in crosslinking for SBR, natural rubber, and *cis*- and *trans*-polybutadienes.

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References

1. Meltzer, T. H., W. J. Dermody, and A. V. Tobolsky, *J. Appl. Polymer Sci.*, **7**, 1487 (1963); *Rubber Chem. Technol.*, **37**, 221 (1964).
2. Meltzer, T. H., W. J. Dermody, and A. V. Tobolsky, *J. Appl. Polymer Sci.*, **7**, 1493 (1963); *Rubber Chem. Technol.*, **37**, 225 (1964).
3. *ASTM Standards*, American Society for Testing Materials, Philadelphia, 1958, ASTM D-1053-58T.
4. Gehman, S. D., D. E. Woodford, and C. S. Wilkinson, *Ind. Eng. Chem.*, **39**, 1108 (1947).
5. Lang, E. Z., Phillips Petroleum Co., private communication.
6. Tobolsky, A. V., *Properties and Structure of Polymers*, Wiley, New York, 1960, pp. 88-97.
7. Moore, C. G., and R. W. Saville, *J. Chem. Soc.*, **1954**, 2082, 2089; *Rubber Chem. Technol.*, **28**, 92, 102 (1955).
8. Glazebrook, R. W., and R. W. Saville, *J. Chem. Soc.*, **1954**, 2094; *Rubber Chem. Technol.*, **28**, 109 (1955).

Résumé

Des mesures du module de cisaillement en fonction de la température effectuées sur des hauts polymères de cis- et trans-1,4-butadiène, vulcanisés au soufre dans les rapports situés entre 2 et 44% de l'échantillon, montrent que l'efficacité de pontage au soufre est sensiblement plus faible dans ces systèmes, que dans le SBR-1000, mais plus élevée que dans le caoutchouc naturel. On remarque deux types distincts de comportement mécanique de ces caoutchoucs stéréoréguliers. À des degrés de vulcanisation peu élevés on relève un comportement cristallin prononcé. Après destruction de la cristallinité par augmentation du pontage, chaque polymère se comporte typiquement comme des matériaux amorphes pontés. Nous croyons pouvoir suggérer que la structure du polymère, ainsi que la réactivité chimique, pourraient jouer un rôle important dans la chimie de la vulcanisation.

Zusammenfassung

Schubmodulmessungen als Funktion der Temperatur an mit Schwefel in Mengen zwischen 2 und 44% des Rezeptes vulkanisierten hochgradigen cis- und trans-Isomeren von 1,4-Polybutadien zeigen, dass die Vernetzungswirksamkeit des Schwefels in diesen Systemen etwas niedriger als in SBR-1000, jedoch höher als in Naturkautschuk ist. Zwei verschiedene Arten des mechanischen Verhaltens werden bei diesen stereoregulären Kautschuken festgestellt. Bei niedrigem Vulkanisationsgrad besteht ein ausgeprägtes kristallines Verhalten. Nach Zerstörung der Kristallinität durch zunehmende Vernetzung verhalten sich die beiden Polymeren wie typische amorphe vernetzte Stoffe. Es werden Hinweise dafür erhalten, dass sowohl die Polymerstruktur als auch die chemische Reaktionsfähigkeit eine wichtige Rolle beim Chemismus der Vulkanisation spielen können.

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