

Structural Characterization of Vulcanizates. Part IX. Comparison of the Vulcanization of Natural Rubber and *cis-trans*-Isomerized Natural Rubber with Sulfenamide-Accelerated Sulfur and Dicumyl Peroxide Vulcanization Systems

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Synopsis

Large variations in the microstructure of 1,4-polyisoprenes, from ca. 100% *cis*-trialkylethylene groups, as in natural rubber (NR), to ca. 40% *cis*- and 60% *trans*-trialkylethylene groups, as in an equilibrium-isomerized NR, have little influence on the overall chemistry of vulcanization of the polyisoprenes by a *N*-cyclohexylbenzothiazole-2-sulfenamide-accelerated sulfur system or by a dicumyl peroxide system. The peroxide crosslinks the equilibrium-isomerized NR more efficiently than it crosslinks NR; this is attributed to the sulfur dioxide, which is used to isomerize the NR, scavenging some of the nonrubber constituents in the NR, which are known to compete with the rubber hydrocarbon for reaction with free radicals from the peroxide. By comparison with NR vulcanizates, the corresponding equilibrium-isomerized NR vulcanizates have higher values of the C_2 term of the Mooney-Rivlin stress-strain equation and higher χ (polymer-swelling liquid interaction parameter) values of the Flory-Huggins equation.

INTRODUCTION

This paper describes a preliminary investigation of the influence of the stereo structure of 1,4-polyisoprenes, in terms of the amount of *cis*- and *trans*-trialkylethylene groups present, on the vulcanization characteristics of two chemically dissimilar vulcanization systems and on the stress-strain and swelling characteristics and chemical structural features of the derived gum vulcanizate networks. Two 1,4-polyisoprenes were examined: natural rubber (NR), which contains about 100% *cis*-1,4 groups, and an isomerized NR, which contains the equilibrium proportion of about 60% *trans*-1,4 and ca. 40% *cis*-1,4 groups. The vulcanization systems used were, first, a sulfur system, accelerated by *N*-cyclohexylbenzothiazole-2-sulfenamide (CBS), containing CBS and sulfur levels commonly used in NR tire-tread compounds and, second, dicumyl peroxide (DCP).

MATERIALS AND EXPERIMENTAL METHODS

Materials

The NR was RSS1 (Yellow Circle). A sample of *cis-trans*-isomerized NR was prepared by heating NR in an atmosphere of sulfur dioxide for 3 days at 100°C.¹ To ensure that a homogeneously isomerized sample was produced, the NR was exposed to sulfur dioxide in thin sheets, and after each day's exposure it was mixed and resheeted on a two-roll mill. The isomerized NR then contained the equilibrium proportions of *cis*- and *trans*-trialkylethylene groups (ca. 60% *trans* and ca. 40% *cis*).

CBS was a recrystallized grade, and DCP was purified by recrystallization (twice) from methanol. Sulfur, zinc oxide, and lauric acid were normal technical grades.

Preparation of Vulcanizates

With CBS-Accelerated Sulfur Systems. Mix formulations and properties of the mixes are given in Table I. The relationship between $[\eta]_{\text{benzene}}$ and the number-average molecular weight \bar{M}_n (Table I), originally derived for NR, was shown to be approximately valid for the equilibrium-isomerized NR. Mixes were prepared on a two-roll mill 12 × 6 in. The temperature of the rolls was maintained at 70–80°C. for the NR mix (to avoid excessive breakdown) and at 20–30°C. for the equilibrium-isomerized NR. The latter rubber, because of its low green strength, can be satis-

TABLE I
Mix Formulations and Properties of the
Mixes for CBS-Accelerated Sulfur Systems

	Mix no.	
	A	B
Parts, wt.		
NR (RSS1)	100	—
Equilibrium-isomerized NR	—	100
Sulfur	2.5	2.5
CBS	0.6	0.6
Zinc oxide	5	5
Lauric acid	1	1
Wallace plasticity (100°C., 1 cm. platen)	22	23
Mooney viscosity ML-4 (100°C.)	41	42
$[\eta]_{\text{toluene}}$ of rubber component of mix at 25°C. (dl./g.)	3.3	2.4
$\bar{M}_n \times 10^{-5}$ of rubber component of mix ^a	2.3	2.0

^a Calculated from the relationships² $[\eta]_{\text{toluene}} = 1.076[\eta]_{\text{benzene}} - 0.15$ (for $[\eta]$ in dl./g.) and $[\eta]_{\text{benzene}} = 2.29 \times 10^{-7} \bar{M}_n^{1.33}$ ($[\eta]$ in dl./g.), which apply for masticated natural rubber.

factorily processed only at the lower temperature. A range of vulcanizates was prepared by heating the mixes in a mold 1 mm. thick for various times at 140°C. in a steam-heated press.

Dicumyl Peroxide Vulcanizates. The rubbers were sheeted on a mill and then heated to 50°C., and the requisite amount of DCP was then melted on to the rubber surface and allowed to dissolve slowly into the rubber. Homogeneous mixes were obtained by milling according to the procedure described in the previous section. This procedure was found to be the best safeguard against loss of peroxide. Vulcanizates (1 mm. thick) were prepared by heating the mixes for 1 hr. at 140°C. in the press. On the basis of published data³ the peroxide is 67% decomposed in 1 hr. at 140°C. Vulcanizates were prepared from the following types of rubber: unextracted NR, unextracted equilibrium-isomerized NR, extracted NR, extracted equilibrium-isomerized NR, and extracted NR which was subsequently isomerized prior to vulcanization. The extraction conditions used were continuous hot-acetone extraction for 24 hr. The vulcanizates were continuously extracted for 2 days with a boiling azeotropic mixture of acetone, methanol, and chloroform under nitrogen prior to physical characterization of the networks.⁴

Physical Characterization of Vulcanizate Networks

Equilibrium stress-strain measurements and equilibrium swelling measurements in *n*-decane were determined as described fully in Part VI⁴ of this series and in references therein. These measurements were made on unextracted CBS-accelerated sulfur vulcanizates and on extracted peroxide vulcanizates.

At low and moderate extensions the elastic behavior of a vulcanizate is described by the Mooney-Rivlin equation:

$$f[2A_0(\lambda - \lambda^{-2})]^{-1} = C_1 + C_2\lambda^{-1} \quad (1)$$

where f is the force required to maintain the sample at an extension ratio λ , A_0 is the unstrained cross-sectional area of the sample, C_1 is a term pertaining to ideal elastic behavior, and C_2 is a term which expresses departures from ideal elastic behavior. Values of C_1 and C_2 for the unswollen unextracted or extracted vulcanizates were obtained from plots of $f[2A_0(\lambda - \lambda^{-2})]^{-1}$ versus λ^{-1} . Confidence is placed in the validity of the C_1 values obtained as described above on unswollen (dry) vulcanizates of both NR and equilibrium-isomerized NR, because, as shown in Table II, closely similar C_1 values are obtained for DCP vulcanizates which were either unswollen or swollen to different extents in liquid paraffin.

Values of C_1 were then corrected to values of $C_{1,RH}$ (the elastic parameter C_1 pertaining to the *rubber hydrocarbon component* of the network) by making allowance for the stiffening effect of nonreinforcing fillers and for the diluent effect of soluble extra-network material and of sulfur combined in the network.⁵ Values of $C_{1,RH}$ were then used to derive values of the degree of chemical crosslinking of the rubber hydrocarbon network, $(2M_{c,chem}^{RH})^{-1}$

TABLE II

Relationship Between the Elastic Parameters C_1 and C_2 and the Degree of Swelling in Liquid Paraffin of Extracted DCP Vulcanizates of Natural Rubber and Equilibrium-Isomerized Natural Rubber (Cure 1 hr. at 140°C.)

Rubber type	DCP, pphr	v_r (liquid paraffin) at 21°C.	Measured values, dyne/cm. ² × 10 ⁻⁶	
			C_1	C_2
Natural rubber	1.75	1.0 (dry)	0.98	0.79
		0.528	1.02	0.35
		0.292	1.06	0.13
Natural rubber	2.5	1.0 (dry)	1.32	0.86
		0.575	1.37	0.42
		0.326	1.41	0.17
Equilibrium- isomerized NR	1.0	1.0 (dry)	1.11	1.44
		0.559	1.11,	0.62,
			1.17	0.56
		0.318	1.10	0.30

(gram-moles of chemical crosslinks per gram of rubber hydrocarbon network) by means of the expression⁶

$$C_{1,RH} = [\rho RT(2M_{c,chem}^{RH})^{-1} + 0.78 \times 10^6](1 - 2.3M_{c,chem}^{RH}\bar{M}_n^{-1}) \text{ dyne/cm.}^2 \quad (2)$$

where ρ is the density of the rubber hydrocarbon (0.915 g./ml. at 25°C.), $M_{c,chem}^{RH}$ is the number-average molecular weight of the polyisoprene chain segments between adjacent crosslinks in the network, \bar{M}_n is the number-average molecular weight of the rubber hydrocarbon prior to crosslinking, R is the gas constant, and T is the absolute temperature. Equation (2) was developed for peroxide vulcanizate networks of NR,^{6,7} and it is assumed to apply also to networks obtained from the equilibrium-isomerized NR. A. G. Thomas of these laboratories has suggested that this assumption may not be strictly warranted, since the NR and isomerized-NR networks may require different chain-entanglement corrections owing to differences in the chain flexibility of the parent rubbers.

Values of v_r (the volume fraction of rubber *network* in the swollen network at equilibrium swelling in *n*-decane) and values of $C_{1,ERM}$ (corrected values of C_1 which pertain to the extracted rubber matrix⁵) were used to obtain values of χ , the polymer-swelling liquid interaction parameter, by means of the expression:

$$-[\ln(1 - v_r) + v_r + \chi v_r^2] = 2V_0 C_{1,ERM} v_r^{1/2} (RT)^{-1} \quad (3)$$

where V_0 is the molar volume of the swelling liquid.

Chemical Analysis of CBS-Accelerated Sulfur Vulcanizates

Sulfur combined in the network, $[S_c]$, in gram-atoms of sulfur combined per gram of rubber hydrocarbon in the network, was determined on 100 mg. samples of extracted vulcanizates as described in Part VI⁴ of this series.

The quoted $[S_c]$ values include the small quantity of sulfur (ca. 0.03% or ca. 10^{-5} g.-atoms of sulfur per gram of rubber) present in the original NR and in the equilibrium-isomerized NR. Inorganic sulfide ion, $[S^{2-}]$, in gram-ions of sulfur as zinc sulfide per gram of rubber hydrocarbon in the network, was determined on unextracted vulcanizates as described in Part VI.⁴

Values of $(2M_{c, \text{chem}}^{\text{RH}})^{-1}$, $[S_c]$ and $[S^{2-}]$ then yielded values of E and F , defined respectively as (E), atoms of sulfur combined in the rubber hydrocarbon network per chemical crosslink present in the network and (F), sulfide ions as zinc sulfide formed in the vulcanizate per chemical crosslink present in the rubber hydrocarbon network:

$$E = [S_c]/(2M_{c, \text{chem}}^{\text{RH}})^{-1}$$

$$F = [S^{2-}]/(2M_{c, \text{chem}}^{\text{RH}})^{-1}$$

Determination of Crosslinking Efficiency of DCP in Vulcanization of NR and Equilibrium-Isomerized NR

The crosslinking efficiency of the peroxide is defined as

$$(2M_{c, \text{chem}}^{\text{RH}})^{-1}/[\text{DCP}]_{\text{decompd.}} \times 100$$

and is expressed as a percentage.

RESULTS AND DISCUSSION

Table III details the physical and chemical characteristics of the vulcanizate networks of NR and equilibrium-isomerized NR derived from the CBS-accelerated sulfur vulcanization system at various cure times at 140°C. At a given cure time changes in the microstructure of the polyisoprene (i.e., the relative amounts of *cis*- and *trans*-trialkylethylene groups present) have little effect on the degree of chemical crosslinking, $(2M_{c, \text{chem}}^{\text{RH}})^{-1}$ or on the E and F values of the vulcanizate networks. Further, these structural features show the same general changes with cure time for both types of polyisoprene. The data suggest that a close similarity exists in the overall chemistry of the vulcanization process for both polyisoprenes. By contrast, the values of $C_{2, \text{measured}}$ of the vulcanizates and the χ values of the vulcanizate networks are substantially greater for the equilibrium-isomerized NR system.

Results for the DCP vulcanizates are given in Table IV. The peroxide crosslinks the unextracted equilibrium-isomerized NR much more efficiently than the unextracted NR. This effect is not regarded as being due to an influence of the microstructure of the polyisoprenes on the stoichiometry of the crosslinking process. It is attributed to some reaction between sulfur dioxide and the nonrubber constituents during the *cis-trans* isomerization of the natural *cis*-1,4-polyisoprene which renders the nonrubbers less active towards cumyloxy and methyl radicals and hence less important as competitors of the polyisoprene crosslinking process. This conclusion is

TABLE III. Physical and Chemical Characterization of CBS-Accelerated Sulfur Vulcanizates of NR and Equilibrium-Isomerized NR

Rubber type	Cure time 140°C., min.	Stress-strain properties at 25°C., dyne/cm. $^2 \times 10^{-6}$			Deg. crosslink. ^a in <i>n</i> -decane ($\times 10^4$)	Equil. ν_r at 25°C.	$[S_2]$ ($\times 10^4$) ^b	$[S_2^-]$ ($\times 10^4$) ^c	E^d	F^e	χ
		$C_{1,ERM}$	$C_{1,RH}$	$C_{2,meas.}$							
Natural rubber (mix A, Table I)	20	1.71	1.77	1.24	0.53	0.2999 0.3000	6.0	1.1	11	2.1	0.43
	35	1.82	1.89	1.31	0.57	0.3176 0.3131	6.7	1.3	12	2.3	0.44
	50	1.74	1.80	1.28	0.54	0.3129 0.3122	6.6	1.5	12	2.8	0.44 ₅
	80	1.60	1.66	1.31	0.48	0.3022 0.3041	6.5	1.6 ₅	14	3.4	0.44 ₅
	120	1.45	1.50	1.31	0.42	0.2933 0.2988	6.4	1.8 ₅	15	4.5	0.45 ₅
Equilibrium- isomerized natural rubber (mix B, Table I)	20	1.65	1.71	2.00	0.51	0.3218 0.3216	6.6	0.8	13	1.6	0.47
	35	1.67	1.73	2.01	0.52	0.3264 0.3263	7.2 ₅	1.1	14	2.1	0.47 ₅
	50	1.59	1.65	1.98	0.49	0.3228 0.3247	6.7	1.2 ₅	14	2.6	0.48
	80	1.54	1.59	1.85	0.46	0.3176 0.3168	7.1	1.4	15.5	3.0	0.48
	120	1.44	1.49	1.89	0.42	0.3124 0.3126	6.9	1.5 ₅	16	3.7	0.48

^a Gram-mole chemical crosslinks per gram of rubber hydrocarbon in the network.

^b Gram-atoms of sulfur combined per gram of rubber hydrocarbon in the network.

^c Gram-ion of sulfide formed per gram of rubber hydrocarbon in the network.

^d Number of sulfur atoms combined in rubber hydrocarbon network per chemical crosslink present.

^e Number of sulfide ions as zinc sulfide formed per chemical crosslink formed.

TABLE IV
Physical and Chemical Characterization of Dicumyl Peroxide (DCP) Vulcanizates of NR and Equilibrium-Isomerized NR (Cure: 1 hr. at 140°C.)

Nat. rubber type	DCP, pphr	\bar{M}_n^a	Stress-strain properties at 25°C, dyne/cm. ² × 10 ⁻⁶		Deg. crosslink. (×10 ⁴) ^b	Cross-linking effc. of DCP, %	Equil. ν_r in <i>n</i> -decane at 25°C.	χ
			$C_{1,ERM}$	$C_{1,RH}$				
Unextracted (RSSI)	1.0	2.0	0.62	0.63	0.72	53	0.190	0.42
	1.75	2.0	0.99	1.01	0.80	54	0.238	0.42 ₆
	2.5	2.0	1.33	1.36	0.87	58	0.274	0.43 ₈
Unextracted equilibrium-isomerized	1.0	3.0	1.13	1.15	1.46	100	0.263	0.44 ₆
	1.75	3.0	1.53	1.56	1.45	94	0.298	0.44 ₅
	2.5	3.0	1.92	1.96	1.36	91	0.315	0.43
Extracted (RSSI)	1.75	2.0	1.26	1.27	0.83	74	0.258	0.42
Extracted equilibrium-isomerized	1.75	2.3	1.46	1.46	1.42	89	0.289	0.44
Equilibrium-isomerized (extracted before isomerization)	1.75	2.0	1.46	1.46	1.39	92	0.287	0.44

^a \bar{M}_n of rubber component of mix (×10⁻⁵), based on $[\eta]_{\text{toluene}}$ data.

^b Gram-mole chemical crosslinks per gram of rubber hydrocarbon in the network.

based on the observations that extraction of NR results in an increased crosslinking efficiency of the peroxide⁸ (Table IV) and that under comparable vulcanization conditions (1.75 parts DCP per 100 rubber, cure 1 hr. at 140°C.) the efficiency with which the peroxide crosslinks the equilibrium-isomerized NR is insensitive to whether or not the rubber has been extracted or to whether the rubber was extracted before or after isomerization (Table IV). As observed with the CBS-accelerated sulfur system, the peroxide vulcanizates of the equilibrium-isomerized NR have significantly higher $C_{2, \text{measured}}$ and χ values than the corresponding NR vulcanizates.

We cannot comment usefully on the variations of $C_{2, \text{measured}}$ with changes in the microstructure of the polyisoprene, since the fundamental significance of the elastic parameter C_2 and its relationship to network structure are still unknown.

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References

1. J. I. Cunneen, G. M. C. Higgins, and W. F. Watson, *J. Polymer Sci.*, **40**, 1 (1959).
2. G. M. Bristow and B. Westall, *J. Appl. Polymer Sci.*, **9**, 495 (1965).
3. Hercules Product Data Sheet No. NS-232 (1959).
4. C. G. Moore and M. Porter, *J. Appl. Polymer Sci.*, **5**, 293, 299 (1961); **8**, 581, 1957 (1964); **11**, 2215, 2227, 2255, 2271 (1967): Parts I-VIII of the series.
5. G. M. Bristow and M. Porter, *J. Appl. Polymer Sci.*, **11**, 2215 (1967).
6. L. Mullins, *J. Appl. Polymer Sci.*, **2**, 1 (1959).
7. C. G. Moore and W. F. Watson, *J. Polymer Sci.*, **19**, 237 (1956).
8. G. M. Bristow, C. G. Moore, and R. M. Russell, *J. Polymer Sci. A*, **3**, 3893 (1965).

Résumé

Des grandes variations dans la microstructure de polyisoprènes-1,4[d'environ 100% de groupes *cis*-trialkyléthylène comme dans la caoutchouc naturel (NR) à environ 40% de groupes *cis*-trialkyléthylène et 60% de groupes *trans*-trialkyléthylène tel que dans le NR isomérisé à l'équilibre] ont peu d'influence sur la chimie globale de vulcanisation des polyisoprènes par le système au soufre accéléré par la *N*-cyclohexylbenzothiazole-2-sulfénamide ou par le système au peroxyde de dicumyle. Le peroxyde permet le pontage du NR-isomérisé à l'équilibre de façon plus efficace que le pont du NR; ceci est attribué au dioxyde de soufre qui est utilisé pour isomériser les NR, ignorant certains des constituants non-caoutchouteux dans le NR qui sont connus comme agents compétitifs avec l'hydrocarbure caoutchouteux pour la réaction avec des radicaux libres issus du peroxyde. Par comparaison avec les vulcanisats NR, les vulcanisats NR isomérisés à l'équilibre correspondant ont des valeurs plus élevées du terme C_2 de l'équation de tension-relaxation de Mooney-Rivlin et des valeurs plus élevées (le paramètre d'interaction polymère-liquide gonflant) de l'équation de Flory-Huggins.

Zusammenfassung

Grosse Änderungen der Mikrostruktur von 1,4-Polyisoprenen [von ca. 100% *cis*-Trialkyläthylengruppen wie in Naturkautschuk (NR) bis ca. 40% *cis*- und 60% *trans*-Trialkyläthylengruppen wie in einem gleichgewichts-isomerisierten NR] besitzen nur geringen Einfluss auf den Gesamtchemismus der Polyisoprenvulkanisation mit einem *N*-Cyclohexylbenzothiazol-2-sulfenamid-beschleunigten Schwefelsystem oder mit einem

Dicumylperoxydsystem. Das Peroxyd vernetzt gleichgewichts-isomerisierten NR wirksamer als NR; das wird auf die Abfangung einiger nicht-kautschukartiger Bestandteile von NR, deren Konkurrenz mit dem Kautschukkohlenwasserstoff in der Reaktion mit den freien Radikalen aus dem Peroxyd bekannt ist, durch das bei der Isomerisation von NR verwendete Schwefeldioxyd zurückgeführt. Im Vergleich zu NR-Vulkanisaten besitzen die entsprechenden gleichgewichts-isomerisierten NR-Vulkanisate höhere Werte für den C_2 -Term in der Spannungs-Dehnungsgleichung von Mooney-Rivlin und höhere χ -Werte (Polymer-Quellungsflüssigkeit-Wechselwirkungsparameter) in der Flory-Huggins-Gleichung.

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