

Estimation of Chain Scission during Vulcanization. Part III. Temperature Effects in the Peroxide Vulcanization of Natural Rubber

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Synopsis

The vulcanization of unextracted natural rubber by dicumyl peroxide is less efficient at 100–110°C. than at 140–160°C. Sol-gel data are presented which suggest that this is not the result of the presence of a temperature-dependent scission process. It is more likely that there is competition between the rubber hydrocarbon component of the natural rubber and the various nonrubbers also present for the cumyloxy and methyl radicals derived from the dicumyl peroxide and that the balance of this competition is temperature-dependent.

In Part I¹ of this series, sol-gel data were presented from which it was concluded that the vulcanization of natural rubber by dicumyl peroxide (DCP) at 130°C. is accompanied by very little main-chain scission. Scott² has analyzed very similar results by a somewhat different procedure and deduced that within experimental error scission is absent. The nature of the crosslinking and proposed³ scission processes suggests that scission might be facilitated at elevated temperatures, and Scheele et al.⁴ have published data consistent with this contention. These workers found that for a purified crepe rubber vulcanized with dicumyl peroxide for a period sufficient to effect virtually complete decomposition of the peroxide the equilibrium swelling in benzene of the vulcanizates increased as the cure temperature was raised from 125 to 160°C.; i.e., vulcanization was less efficient at the higher temperatures. This may be interpreted as the result of increasing chain scission as the temperature is raised.

Results are reported here for the vulcanization of several types of natural rubber and of a synthetic *cis*-1,4-polyisoprene with dicumyl peroxide over the temperature range 100–160°C.

Experimental

Two grades of natural rubber, pale crepe and ribbed smoked sheet, were used, both as received and after 24 hr. extraction with hot acetone and drying *in vacuo*. Natsyn, a high *cis*-1,4-polyisoprene manufactured by the Goodyear Tire and Rubber Co. was similarly treated. Dicumyl peroxide (DCP) from Hercules Powder Co., was recrystallized from aqueous metha-

nol. Antioxidants were commercial materials used without further purification. Techniques for the preparation of vulcanizates, for the determination of sol rubber content, and for the estimation of crosslink density by swelling in *n*-decane and application of the published calibration^{5,6} have been described previously.¹

Results and Discussion

The several rubbers were vulcanized with dicumyl peroxide at temperatures in the range 100–160°C. for times sufficient to effect >99.9% decomposition of the peroxide. These times were estimated from published data⁷ for the rate of dicumyl peroxide decomposition in various hydrocarbon media including natural rubber. At the lower temperatures, where the various published data are less consistent, the maximum time estimated as necessary for >99.9% decomposition of the peroxide was allowed. The general pattern of the results as recorded in Table I differs from that reported by Scheele.⁴ Whereas there is some tendency for the degree of crosslinking to decrease as the vulcanization temperature is increased from 140 to 160°C. in agreement with the trend noted by Scheele,⁴ the change in degree of crosslinking with temperature at temperatures below 140°C. is dependent on the purity of the rubber. For the acetone-extracted rubbers there is little dependence of ν_r on vulcanization temperature below 140°C., thus confirming the adequacy of the time allowed for complete peroxide decomposition under these conditions, but for the unextracted natural rubber the degree of crosslinking attained at 100°C. is appreciably less than that reached at 140°C.

The small decreases in vulcanization efficiency (i.e., the degree of crosslinking attained for a given amount of peroxide decomposed) observed in some cases on increasing the cure temperature from 140 to 160°C. could be the result of slightly enhanced scission at the higher temperature, although loss of peroxide through vaporization cannot be discounted. However, it seems very unlikely that scission effects could explain the reduced efficiency of vulcanization at low temperatures, especially since the extent of this reduction is very dependent on the purity of the rubber.

These conclusions are confirmed by the results of the sol-gel analysis of vulcanizates of extracted crepe and unextracted smoked sheet reported in Tables II and III, respectively. As in Parts I¹ and II⁸ of this series, these data have been analyzed in terms of the expression developed by Charlesby and Pinner⁹ for the simultaneous crosslinking and scission of a polymer having initially a random molecular weight distribution.

This expression is,

$$S + S^{1/2} = pq^{-1} + q^{-1}y_n^{-1}$$

where S is the weight fraction of rubber remaining unvulcanized, y_n is the number-average chain length of the rubber prior to vulcanization, and p and q the fraction of sites at which scission and crosslinking has occurred, respectively. If, as is observed for peroxide vulcanization, $p \ll q$, then a plot of

TABLE I
 Vulcanization of Natural Rubber and Synthetic *cis*-1,4-Polyisoprene with DCP at 100–160°C.

Rubber	DCP, %	[η], dl./g.	η , in <i>n</i> -decane after vulcanization at various times and temperatures									
			120 min., 160°C.	45 min., 160°C.	120 min., 150°C.	240 min., 140°C.	21 hr., 130°C.	58 hr., 120°C.	7 days, 110°C.	7 days, 110°C. + 60 min., 160°C.	18 days, 100°C.	
Unextracted crepe	1	3.31	0.239	0.235	0.236	0.248	0.243	0.242	0.230	0.196	0.204	
Unextracted crepe	5	2.85	0.428	0.416	0.425	0.413	0.418	0.408	0.381	0.384	0.356	
Extracted crepe	1	2.85	0.248	0.253	0.256	0.258	0.255	0.248	0.252	0.245	0.246	
Unextracted RSS	1	3.45	0.239	0.237	0.234	0.238	0.244	0.242	0.209	0.188	0.193	
Unextracted RSS	3	2.78	0.348	0.342	0.336	0.347	0.337	0.327	0.307	0.305	0.292	
Extracted RSS	1	2.93	0.255	0.252	0.256	0.258	0.259	0.256	0.257	0.249	0.243	
Extracted RSS	3	2.68	0.365	0.365	0.365	0.363	0.374?	0.363	0.359	0.354	0.323	
Unextracted Natsyn	1	3.10	0.239	0.244	0.250	0.252	0.247	0.243	0.251	0.236	0.245	
Unextracted Natsyn	3	2.93	0.341	0.350	0.350	0.346	0.351	0.333	0.353	0.325	0.332	
Extracted Natsyn	1	3.04	0.252	0.254	0.256	0.268	0.263	0.258	0.273?	0.256	0.262	
Extracted Natsyn	3	2.92	0.358	0.364	0.369	0.368	0.375	0.368	0.387?	0.363	0.360	

TABLE II
Sol Contents and Crosslink Densities for Extracted Crepe Vulcanizates Prepared at 110–160°C.

Initial mix		Vulcanization			Sol content			v_r	$q^{-1} \times 10^{-2}$		
$[\eta]$, dl./g.	$\bar{M}_n \times 10^{-5}$	DCP, %	Time, min.	Temp., °C.	Wt.-%	$S + S^{1/2}$	$(S + S^{1/2})_{cor}^*$				
2.19	1.75	10	60	110	10.73	0.4348	—	0.0972	11.21		
					11.54	0.4551	—				
					4.42	0.2544	—			0.1619	6.30
					5.11	0.2773	—			0.1572	6.83
					3.95	0.2382	—			0.1755	5.90
					2.19	0.1699	—			0.2186	3.80
					1.18	0.1202	—			0.2564	2.32
2.19	1.75	10	20	120	0.56	0.0798	—	0.3084	1.27		
					7.61	0.3519	—			0.1328	8.25
					6.20	0.3110	—			0.1556	6.90
					3.89	0.2360	—			0.1830	5.52
					2.28	0.1738	—			0.2125	4.10
					1.60	0.1423	—			0.2333	3.14
					1.29	0.1265	—			0.2475	2.60
2.74	2.10	2	20	130	0.89	0.1034	—	0.2756	1.85		
					5.35	0.2848	0.3456			0.1387	9.18
					2.67	0.1901	0.2331			0.1811	6.52
					1.78	0.1513	0.1860			0.2022	5.26
					1.14	0.1179	0.1471			0.2160	4.42
					1.20	0.1216	0.1484			0.2221	4.06
					0.62	0.0849	0.0995			0.2651	2.21
2.16	1.74	1	4	150	0.56	0.0804	0.0975	0.2530	2.59		
					14.96	0.5364	—			0.0850	12.77
					6.31	0.3144	—			0.1347	8.16
					4.35	0.2522	—			0.1489	7.27
					2.92	0.1999	—			0.1870	5.36
					2.25	0.1727	—			0.2042	4.52
					1.02	0.1113	0.1334			0.2352	3.35
2.40	1.89	0.20	40	160	0.85	0.1009	0.1186	0.2514	2.66		
					13.48	0.5020	0.5360			0.0901	12.13
2.26	1.81	0.35	40		7.37	0.3452	0.3552	0.1331	8.30		
2.19	1.75	0.50	40		4.31	0.2507	—	0.1678	6.37		
2.26	1.81	0.70	40		2.34	0.1763	0.1817	0.2063	4.50		
2.22	1.78	0.80	40		2.31	0.1750	0.1775	0.2114	4.22		
2.26	1.81	1.05	40		1.18	0.1202	0.1234	0.2458	2.70		
2.16	1.74	1.25	40		1.00	0.1097	—	0.2526	2.43		

* $S + S^{1/2}$ for $M_n = 1.75 \times 10^6$. Approximate correction derived from the Charlesby-Pinner equation, $S + S^{1/2} = A + BM_n^{-1}$, where A and B are constants.

$S + S^{1/2}$ versus q^{-1} should be linear of slope y_n^{-1} and intercept pq^{-1} , this intercept characterizing the relative frequency of scission and crosslinking. The data of Tables II and III are plotted in this manner in Figures 1 and 2. The results for extracted crepe (Fig. 1) vulcanized at 110–160°C. fit a single $S + S^{1/2}$ versus q^{-1} plot, there being no obvious dependence of the relative importance of crosslinking and scission on temperature. Similarly from

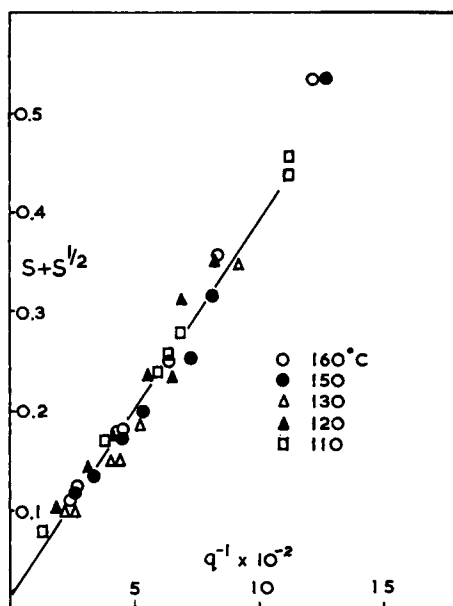


Fig. 1. $S + S^{1/2}$ vs. q^{-1} for DCP vulcanizates of extracted crepe.

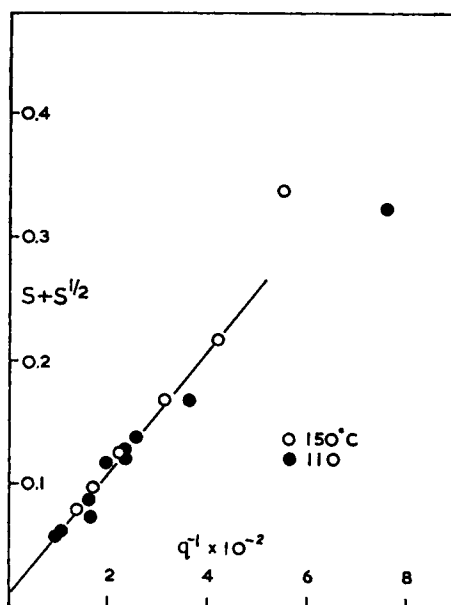


Fig. 2. $S + S^{1/2}$ vs. q^{-1} for DCP vulcanizates of unextracted RSS.

Figure 2, for unextracted smoked sheet, the same conclusion may be drawn, despite the fact that the vulcanization efficiency for this rubber is markedly less at 110°C. than at 150°C. It may be concluded therefore that the

TABLE III
Sol Contents and Crosslink Densities for Unextracted RSS Vulcanizates
Prepared at 110 and 150°C.

Initial mix		Vulcanization			Sol content			V_r	q^{-1}
$[\eta]$, dl./g.	$\bar{M}_n \times 10^{-5}$	DCP, %	Time, min.	Temp., °C.	Wt.-%	$S + S^{1/2}$	$(S + S^{1/2})_{cor}^a$	(<i>n</i> -dec- ane)	$\times 10^{-2}$
1.78	1.51	2.00	120	150	0.55	0.0800	—	0.2904	1.37
1.79	1.52	1.67			0.81	0.0982	—	0.2714	1.68 _s
1.93	1.61	1.33			1.15	0.1190	0.1258	0.2507	2.21
1.75	1.50	1.00			2.17	0.1690	—	0.2191	3.12
1.78	1.51	0.75			3.37	0.2171	—	0.1929	4.19
1.57	1.37	0.50			7.12	0.3379	0.3148	0.1452	5.50
1.78	1.51	2.00	10,000	110	0.47	0.0733	—	0.2735	1.65
1.79	1.52	1.67			1.19	0.1211	—	0.2421	2.36
1.93	1.61	1.33			1.90	0.1568	0.1680	0.2097	3.62
1.75	1.50	1.00			4.56	0.2591	—	0.1247	6.50
1.78	1.51	0.75			6.60	0.3230	—	0.0995	7.58
1.57	1.37	0.50			25.95	0.7689	—	0.0447	—
1.74	1.49	3.00	10,000	110	0.30	0.0573	—	0.3299	0.93
1.96	1.63	2.50			0.34	0.0621	0.0660	0.3154	1.07
2.08	1.70	1.83			0.64	0.0866	0.0952	0.2776	1.62
1.66	1.44	1.50			1.14	0.1179	0.1143	0.2585	1.93
1.69	1.46	1.22			1.33	0.1285	0.1257	0.2434	2.33
1.73	1.48	1.11			1.51	0.1381	—	0.2361	2.54

* $S + S^{1/2}$ for $\bar{M}_n = 1.50 \times 10^6$. Approximate correction derived from the Charlesby-Pinner equation, $S + S^{1/2} = A + B\bar{M}_n^{-1}$ where A and B are constants.

changes in vulcanization efficiency indicated by the results of Table I can not be interpreted as the consequence of a temperature dependent scission process.

Recently, evidence has been adduced¹⁰ that in the peroxide vulcanization of natural rubber, nonrubber materials which are inevitably present, play a significant part; some, but not all, of these nonrubber materials are readily extracted by hot acetone. It seems likely that some of the *tert*-alkoxy, *tert*-

TABLE IV
Effect of Antioxidants in the Vulcanization of Natural Rubber by DCP at 110, 150, and 160°C.

Antioxidant ^a	DCP, %	$[\eta]$, dl./g.	v_r in <i>n</i> -decane after vulcanization		
			7 days, 110°C.	120 min., 150°C.	60 min., 160°C.
Nil	1	2.53	0.249	0.248	0.243
0.3% PBN	1	2.31	0.218	0.234	0.234
0.3% AO 2246	1	2.30	0.235	0.238	0.234
0.3% Flectol H	1	2.42	0.237	0.244	0.241
Nil	3	2.49	0.345	0.361	0.355
1% PBN	3	2.20	0.289	0.312	0.311
1% AO 2246	3	2.23	0.318	0.323	0.323
1% Flectol H	3	2.46	0.341	0.344	0.340

* PBN, phenyl- β -naphthylamine; AO 2246, 2,2'-methylenebis(4-methyl-6-*butyl*-butyl phenol); Flectol H, polymerized 1,2-dihydro-2,2,4-trimethylquinoline.

aryloxy, and methyl radicals generated by the thermal decomposition of the peroxide instead of reacting with the rubber hydrocarbon to produce cross-links, react with the nonrubbers leading to a reduction in vulcanization efficiency. If these competing reactions have different temperature coefficients the vulcanization efficiency will be temperature-dependent, and the results of Table I can be interpreted in this manner. Confirmatory evidence for this explanation has been obtained by the vulcanization at 110, 150, and 160°C. of extracted crepe rubber containing small amounts of antioxidants—materials which are known to react readily with free radicals. The results, recorded in Table IV, conform to the predicted pattern. In the absence of added antioxidant there are only small changes of vulcanization efficiency with temperature. However, in the presence of antioxidant not only is there a marked decrease in vulcanization efficiency in each case but this decrease is appreciably greater when vulcanization is effected at 110°C. than at 150 or 160°C.

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Résumé

La vulcanisation, par le peroxyde de dicumyle, du caoutchouc naturel, non extrait, est moins efficace à 100–110°C qu'à 140–160°C. Les résultats "sol-gel" présentés ici, montrent que cet effet n'est pas dû à un processus de scission dépendant de la température. Il est plus probable que la partie hydrocarbonée du caoutchouc naturel et les divers produits non caoutchouteux, qui sont également présents, réagissent de manière compétitive avec les radicaux oxycumyles et méthyles provenant du peroxyde de dicumyle et que l'équilibre de cette compétition dépend de la température.

Zusammenfassung

Die Vulkanisation von nicht extrahiertem Naturkautschuk durch Dicumylperoxyd ist bei 100–110°C weniger wirksam als bei 140–160°C. Sol-Geldaten zeigen, dass dieses Verhalten nicht durch das Vorhandensein eines temperaturabhängigen Spaltungsprozesses bedingt ist. Es ist wahrscheinlicher, dass die Kautschukkohlenwasserstoffkomponente des Naturkautschuks und die verschiedenen vorhandenen nicht-Kautschuksubstanzen um die aus dem Dicumylperoxyd gebildeten Cumyloxy- und Methylradikale konkurrieren und das Verhältnis dieser Konkurrenzreaktionen temperaturabhängig ist.

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