

The Use of Sol-Gel Analysis to Estimate Chain Scission during Vulcanization. Part I. Peroxide Vulcanization of Natural Rubber

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The statistical theory of rubber elasticity¹ indicates that in a crosslinked network certain types of chain segment are elastically ineffective, i.e., do not contribute to the support of an applied stress. In particular, segments consisting of pendent chain ends, such as must remain after the crosslinking of a polymer of *finite* chain length, are ineffective. Chain scission occurring as a concomitant of the crosslinking process will enhance the number of these chain ends and an elastically inferior network will thereby result. It is, therefore, of practical as well as theoretical interest to investigate the extent to which such scission reactions are occurring.

While it is well established from model compound studies² that the vulcanization of diene polymers, such as natural rubber, with dialkyl peroxides is the result of the formation of carbon-carbon crosslinks, there is little published evidence on the incursion of chain scission as a side reaction. In this respect evidence from model compounds is suspect in view of the large difference in environment of a reactive radical in a low molecular weight olefin and a highly viscous rubber. Moore and Scanlan³ have suggested, from stress relaxation data obtained during the further reaction of a strained natural rubber vulcanizate with dicumyl peroxide, that degradation of the primary network occurs equivalent to about 10% of the number of physically effective crosslinks formed, but they comment that this result is only obtained by the application of the admittedly deficient two-network theory of stress relaxation.

A further investigation of this system with the use of the so-called sol-gel method is reported here. This method involves the measurement of the fraction of rubber remaining unconnected to the network (i.e., soluble rubber) as a function of the degree of cure. Sol fractions have been estimated by benzene extraction of carefully purified vulcanizates; crosslink density, by measurement of swelling in *n*-decane and application of the Moore-Watson calibration^{4,5} with the understanding that this calibration assumes no scission.

EXPERIMENTAL

Materials

Pale crêpe rubber was homogenized by light milling, extracted with hot acetone for 24 hrs., and dried *in vacuo* at 40°C. Dicumyl peroxide (Hercules Powder Co.) was recrystallized from aqueous methanol. Reagent-grade *n*-decane (British Drug Houses) was redistilled *in vacuo*. Benzene and acetone were of reagent grade except where indicated otherwise.

Preparation of Vulcanizates

Dicumyl peroxide was incorporated in the rubber either by cold milling or by imbibition of a benzene solution (twice the volume of the rubber) followed by removal of the benzene *in vacuo*. All mixes were stored *in vacuo* for at least 48 hrs. before curing. Samples for viscosity and osmotic-pressure measurements were taken at this stage; these measurements were effected by previously reported techniques.⁶ Press cures at 130°C. were made in a 10 × 10 × 0.1 cm. mold, the platens being cooled before the mold was opened. The peripheral 1 cm. of the sheet was rejected. The vulcanizates were extracted in the dark with cold acetone for 12–14 days, four to six 200 ml. portions of acetone being used, and dried *in vacuo* at 40–50°C. for 48 hrs.

Determination of Sol Content

Sol contents were determined as the loss in weight of 3 g. samples after cold benzene extraction in the dark for 7–10 days, three or four 200 ml. portions of benzene being used, followed by drying *in vacuo* at 60–70°C. for 48 hrs. Duplicate determinations were made in all cases and, for sol contents over the range 0.5–10%, these were generally consistent to 0.02–0.2%. In a few cases deviations much greater than this were attributed to lack of homogeneity across the sheet.

Determination of Swelling

1 g. samples were swollen in *n*-decane for 48 hrs. at 20°C., the surface was quickly dried, and then they were reweighed. The difference in weight on removing the decane *in vacuo* indicated that this treatment had removed only ca. 50% of the sol rubber as determined above, a deviation which is doubtless due to the high viscosity and relatively poor solvent power of *n*-decane compared with those of benzene, as well as the relatively short time of immersion. The weight of rubber was therefore corrected for sol content by means of the sol values determined in benzene. Values of v_r , the equilibrium volume fraction of rubber in the swollen vulcanizate, were then calculated with the use of the values 0.915 and 0.725 for the densities of rubber and *n*-decane, respectively, and by assuming no volume change on mixing. Duplicate determinations of v_r (made in all cases) were consistent to ± 0.001 .

TABLE I
Sol Contents and Crosslink Densities of Natural Rubber Vulcanizates

Initial rubber		Cure (at 130°C.)			Wt. fract. of sol	v_r (<i>n</i> -decane)	q , $\times 10^8$
$[\eta]$, dl.-g. ⁻¹	$\bar{M}_n \times$ 10^{-5}	DCP, % ^a	Time, min.				
2.21	2.12	1.0	20	0.2765	0.041	(b)	
			40	0.1022	0.096	(b)	
			60	0.0800	0.112	(b)	
			80	0.0485	0.154	1.20 ₅	
			100	0.0442	0.161	1.28	
			150	0.0321	0.182	1.54 ₅	
			200	0.0256	0.198	1.82	
2.11	1.96	2.0	20	0.1129	0.087	(b)	
			40	0.0413	0.159	1.35	
			60	0.0299	0.176	1.55	
			80	0.0175	0.215	2.34	
			100	0.0149	0.224	2.63	
			150	0.0098	0.249	3.73	
2.19	1.95	3.0	20	0.0604	0.132	(b)	
			40	0.0229	0.201	1.98	
			60	0.0141	0.219	2.48	
			80	0.0087	0.253	3.93 ₅	
			100	0.0072	0.258	4.23	
			150	0.0047	0.290	6.27	
			200	0.0042	0.300	6.99	
2.03	2.09	5.0	20	0.0277	0.174	1.44 ₅	
			40	0.0119	0.239	3.15	
			60	0.0073	0.251	3.77	
			80	0.0052	0.273	4.98	
			100	0.0037	0.297	6.68	
			150	0.0026	0.327	9.30	
			200	0.0017	0.364	(b)	
1.25	0.835	3.0	20	0.2940	0.061	(b)	
			40	0.0890	0.140	2.52	
			60	0.0653	0.152	2.68	
			80	0.0566	0.167	2.91 ₅	
			100	0.0347	0.205	2.74	
			150	0.0188	0.256	5.79	
3.91	2.67	3.0	20	0.0132	0.276	6.96	
			40	0.0312	0.183	1.29 ₅	
			60	0.0213	0.230	2.45	
			80	0.0142	0.224	2.22	
			100	0.0065	0.261	4.00	
			150	0.0073	0.261	3.98	
			200	0.0037	0.294	6.19	
			200	0.0029	0.310	7.58	

^a Dicumyl peroxide.

^b Values unobtainable since the calibration^{4,5} only covers the range $0.15 < v_r < 0.35$.

To minimize any effect of variation in crosslinking across the vulcanizate sheets and to avoid any correction for sol content, attempts were made to measure the *n*-decane swellings on the benzene-extracted vulcanizates. The values so obtained were not very consistent and it seems likely that during the removal of the benzene *in vacuo* at 60–70°C. some small degree of chain scission was induced. The procedure described previously was therefore deemed to be more reliable.

RESULTS AND DISCUSSION

In Table I values for the sol fractions S and crosslink densities q are recorded for a wide range of vulcanizates. Crosslink density is expressed as the fraction of monomer units involved in crosslink formation and scission density p similarly defined. The relation between S , p , and q has been most conveniently expressed by Charlesby and Pinner.⁷ For the random crosslinking and scission of a polymer of number-average chain length \bar{y}_n and having a random chain length distribution, they show that:

$$S + S^{1/2} = pq^{-1} + (q\bar{y}_n)^{-1} \quad (1)$$

The crosslinking and scission processes will doubtless be random in the present system, so that this requirement is not very stringent; on the other hand, the necessity that the unvulcanized polymer have a random distribution is more important, since other distributions do not lead to an algebraically simple form such as eq. (1). Though the degradation of rubber by mastication is believed to be a nonrandom process,⁸ recent investigations⁹ have shown that the deviations from a random distribution are not large for rubbers masticated to a limiting viscosity number in the range $1.5 < [\eta] < 4.0$ dl.-g⁻¹. Equation (1) should therefore reasonably apply to the present data. The application of eq. (1) to experimental data is much simplified by the assumption that scission and crosslink formation are alternative fates for the same radical and hence p/q is constant (since $p \ll q$, any deviations from this constancy as the cure proceeds are unlikely to be significant). With this assumption, plots of $S + S^{1/2}$ vs. q^{-1} should be linear, of slope \bar{y}_n^{-1} , and intercept p/q . The data plotted in this manner (Fig. 1) give excellent linear plots. The lines in Figure 1 were obtained by the method of least squares and are of the form:

- A. $S + S^{1/2} = 0.0081 + 8.31 \times 10^{-4}q^{-1}$
- B. $S + S^{1/2} = 0.0243 + 2.92 \times 10^{-4}q^{-1}$
- C. $S + S^{1/2} = 0.0289 + 2.33 \times 10^{-4}q^{-1}$

The values of \bar{M}_n of 0.82, 2.32, and 2.92×10^5 , deduced from the slopes of these lines, are in fair agreement with the respective osmotic values of 0.835, 1.95–2.12, and 2.67×10^5 . The rather small values of p/q obtained from the intercepts indicate that scission is only a minor reaction,

there being 1-3% as many sites of scission as crosslinked centers. This compares with the value of 5% given by Moore and Scanlan.³

Clearly, several experimental errors may beset the sol-gel method. In the present work the most serious of these is doubtless the possibility that the loss in weight of the vulcanizates on extraction with benzene, which is attributed entirely to sol rubber, may, despite all precautions, be due in part to nonrubbers or residual solvents. Recovery of the extracted sol rubber by freeze-drying the benzene extract (using in this case Analar benzene) showed, however, that this was not so. There was satisfactory

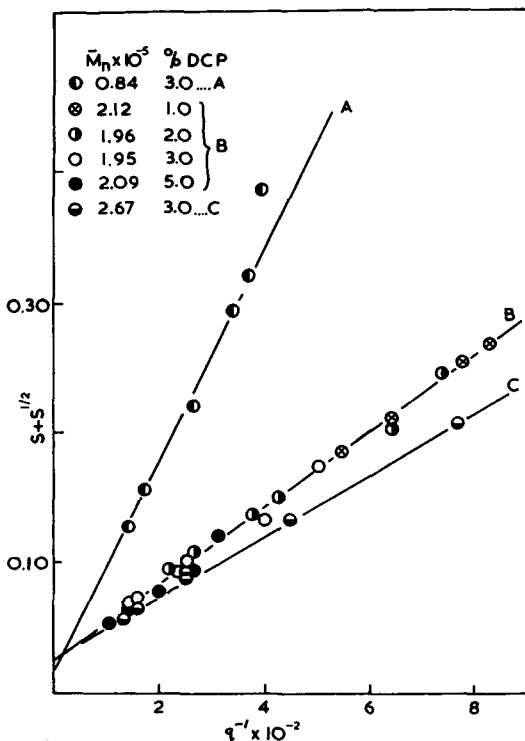


Fig. 1. Plot of $S + S^{1/2}$ (where S is the sol fraction) versus $(\text{crosslink density})^{-1}$ for natural rubber vulcanized with dicumyl peroxide at 130°C.

agreement between the weight loss of the vulcanizate and the amount of sol recovered, and both the elemental analysis and the infrared spectrum of the sol corresponded to rubber hydrocarbon. As a more stringent test, a careful comparison was made between the infrared spectrum of the 3.3% sol extracted from a lightly cured sample (0.5% dicumyl peroxide, 200 min. at 130°C.; $v_r = 0.185$) and that of the 0.19% sol from an extensive cure (5% dicumyl peroxide, 200 min. at 130°C.; $v_r = 0.366$). Only a very slight relative accumulation of nonrubber materials was indicated in the sol from the highly cured material.

A further source of error is the possible incursion of oxidative degradation, more especially during benzene extraction, when the vulcanizates are highly swollen. Previous work¹⁰ suggests that such degradation is negligible provided great care is taken to exclude light. However, since oxidation is expected to have a more pronounced effect upon swelling than upon the amount of sol, swelling measurements were made on the vulcanizates after the acetone extraction rather than after the benzene extraction. As previously indicated, this procedure was found to be more reliable experimentally.

A source of error of a rather different type lies in any contribution to the crosslink density made by gel or branched structures in the unvulcanized rubber, leading to relatively enhanced values of q . The crosslink density of the gel fraction of an unmilled crêpe rubber is very low, typically the swelling in *n*-decane is $v_r = 0.01-0.02$, so that any contribution to q from this source will certainly be negligible. The effect of branched structures is more complicated and depends on whether these structures are sufficiently stable to survive the vulcanization at 130°C. Thermally stable structures, such as might be due to branching through C—C bonds, will lead to erroneously high values of q . In the absence of any definite knowledge as to the presence of C—C branching in well-masticated natural rubber, it is impossible to make a quantitative estimate of the contribution of branching to q . For tetrafunctional crosslinking the critical value of q for gel formation is $q_c = \bar{y}_w^{-1} = 1/2\bar{y}_n^{-1}$ for a random initial molecular-weight distribution, where y_w and y_n are the weight- and number-average degrees of polymerization. Hence, $q_c = 3.4 \times 10^{-4}$ for a rubber of $\bar{M}_n = 2 \times 10^5$; this figure represents the maximum density of tetrafunctional branching for a soluble polymer. Branches which are trifunctional contribute less to the network density. The values of q for the vulcanizates are considerably greater than 3×10^{-4} , especially for the more extensive cures, which data are especially important in defining the intercept p/q . It seems likely, therefore, that for the rubbers studied here the presence of any C—C branching will not seriously affect the estimated values of p/q .

The presence of thermally labile structures such as branching through peroxide groups (or peroxide groups incorporated in linear chains) will have two effects. First, by their thermal decomposition during cure at 130°C. these peroxides will react so as slightly to enhance the degree of cure and proportionately, therefore, the extent of chain scission. There will be no change in the overall p/q ratio. Second, since some rubber chains will be ruptured by this thermal decomposition, the initial molecular weight used in calculating q will be in error and, hence, a slightly low value indicated for q . However, the number of scissions produced by the "rubber peroxide" decomposition is constant, and this effect will therefore be minimal at high degrees of crosslinking. It may readily be shown that in the presence of such additional scissions the linear plots of Figure 1 would become curved but the value of p/q indicated by the extrapolation would be unaltered. Clearly, therefore, even in the presence of thermally labile branched struc-

tures extrapolation of $S + S^{1/2}$ vs. $1/q$ enables p/q to be estimated. The linear nature of the plots of Figure 1 suggests that branching through thermally labile groups is not significant in the rubbers used here.

It has been suggested previously that the scission of the polyisoprenyl radical leads to a shorter polyisoprenyl radical and a shorter rubber molecule terminated by a conjugated diene unit.³ Some evidence for this was found in a comparison of the ultraviolet spectrum of a sol rubber extracted from a peroxide vulcanizate with that of a crêpe rubber purified by the same extraction process. The sol rubber was estimated to contain a maximum of $1-2 \times 10^{-5}$ moles/g. of diene. This sample had $[\eta] = 0.78$ dl.-g.⁻¹ in toluene, probably corresponding to $\bar{M}_n < 5 \times 10^4$ which represents $> 4 \times 10^{-5}$ moles of chain ends per gram. Since not all the sol will be produced by chain scission and only one diene group is produced per scission, the observed amount of diene is of the expected order of magnitude.

In conclusion, it is important to consider the consequences of the small amount of scission upon the properties of the vulcanizate and, in particular, on the validity of the n -decane swelling calibration.^{4,9} Clearly, since some of the peroxide (ca. 2%) is wasted in producing scission rather than crosslinks, the calibration is in error to this negligible extent. A more subtle source of error is in the chain end correction necessary to allow for the finite initial molecular weight of the rubber prior to crosslinking. The calibration is based on the assumption that the molecular weight of the polymer produced by cutting all crosslinks is equal to that of the unvulcanized material. In the presence of chain scission this cannot be so, and we have:

$$(\bar{M}_n)_{\text{corr}}^{-1} = (\bar{M}_n)_{\text{init}}^{-1} + p/M_0 \text{ (where } M_0 = 68.1\text{)}$$

The reduction in molecular weight due to this cause is greatest for high values of p (and hence high values of q) and high values of $(M)_{\text{init}}$. However, it is under just these conditions that the calibration is least sensitive to variations in initial molecular weight, and a study of the numerical magnitudes involved indicates that 2% scission is not very significant in its effect upon the swelling calibration, although in the most precise work it could be important. In particular, it was established that the error in the calculated values of q occasioned by not applying a correction for this amount of scission was insufficient to alter materially the value of p/q indicated by the extrapolation of Figure 1.

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Synopsis

Sol-gel analysis, that is, the measurement of the fraction of rubber remaining unconnected to the network as a function of the degree of cure, has been used to estimate the extent of chain scission in the vulcanization of natural rubber with dicumyl peroxide at 130°C. For peroxide concentrations in the range 1-5% and masticated rubbers of $\bar{M}_n = 0.84-2.67 \times 10^5$ there are only 1-3 sites of scission per 100 crosslinked isoprene units.

Résumé

On utilise l'analyse sol-gel comme mesure de la fraction de caoutchouc non-attachée au réseau, en fonction du degré de vulcanisation pour déterminer le degré d'avancement de la scission de la chaîne dans la vulcanisation, du caoutchouc naturel par le peroxyde de dicumyle à 130°C. Pour des concentrations en peroxyde de 1 à 5% et pour des caoutchoucs mastiqués de $\bar{M}_n = 0.84-2.67 \times 10^5$, il n'existe que 1 à 3 sites de scission par 100 unités d'isoprène pontées.

Zusammenfassung

Sol-Gelanalyse, d.h. Bestimmung des Bruchteils des nicht an das Netzwerk gebundenen Kautschuks als Funktion des Vulkanisationsgrades, wurde zur Ermittlung des Ausmasses an Kettenspaltung bei der Vulkanisation von Naturkautschuk mit Di-cumylperoxyd bei 130°C verwendet. Bei Peroxydkonzentrationen im Bereich von 1-5% und mastiziertem Kautschuk mit $\bar{M}_n = 0,84-2,67 \times 10^5$ treten nur 1-3 Kettenspaltungen auf 100 vernetzte Isopreneinheiten auf.

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