Network Degradation Accompanying the Vulcanization of Natural Rubber with a Sulfur–Diphenylguanidine System*

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Synopsis

Sol fraction and swelling values have been determined for a series of natural rubber–sulfur–diphenylguanidine vulcanizates. These data have been analyzed in terms of the Charlesby and Pinner gel network formation theory with a view to estimating the amount of permanent molecular chain scission accompanying the vulcanization. It is concluded that negligible chain scission occurs before the point of modulus reversion of these curves. In the region of cure reversion, permanent molecular chain scission does occur to a small extent. The principal factor responsible for cure reversion in this vulcanizate is crosslink scission. Chain scission is responsible for only about 3–8% of the observed cure reversion.

INTRODUCTION

Recently it was demonstrated that permanent molecular chain scission accompanying the vulcanization of natural rubber with dicumyl peroxide is insignificant for many experiments which require a knowledge of quantitative crosslinking.[1] The purpose of this paper is to estimate the extent of permanent molecular chain scission that might accompany a more traditional sulfur plus accelerator vulcanization of natural rubber. A semiquantitative description of cure reversion for these vulcanizates is also attempted.

EXPERIMENTAL

A. Materials

Samples were prepared by mill mixing the ingredients listed in the compounding recipes of Table I and press curing 0.76 mm. thick sheets for 15, 30, 60, 90, and 120 min. at 149°C. All concentrations are given in weight parts per hundred parts of rubber.

The intrinsic viscosities in toluene at 25°C. of the rubber in compound recipes A and D were determined after milling, i.e., just prior to the press

TABLE I
Compounding Recipes

	Density, g./ml.	Recipe			
		A	B	C	D
Natural rubber (smoked sheet)	0.912	100	100	100	100
Zinc oxide	5.57	5	5	5	5
Stearic acid	0.847	3	3	3	3
Sulfur	2.00	3	4	5	6
Diphenylguanidine	1.07	1.2	1.6	2.0	2.4
Total compound weight (W_c)		112.2	113.6	115.0	116.4

curing, and found to have the identical value of 2.01 dl./g., which corresponds to a viscosity-average molecular weight[2] of 250,000. If these samples have the same molecular weight distribution as the milled natural rubber samples used before,[1] then the number-average molecular weight of the samples would be 126,000. The lower intrinsic viscosity of these samples suggests that they have been broken down by milling a little more than had been those used previously.[1] This should lead to a somewhat narrower distribution than observed earlier, and if we assume that the distribution is now a most probable one, this leads to the estimate of 135,100 for the number-average molecular weight. For this paper we shall use the value of 135,100 as the number-average molecular weight of the milled rubber and assume that the distribution of molecular weights is sufficiently close to a most probable one for our purposes.

B. Sol and Swelling Measurements

Weighed pieces of the vulcanized rubber samples (W_0 about 2 g.) were extracted three times with acetone containing 100 mg./l. of N-phenyl-2-naphthylamine (PBNA) for 48 hr. each time in the dark at room temperature. A fourth extraction was similarly made with pure acetone. The samples were vacuum dried 2–4 hr. at 80°C. at 12 Torr and then weighed (W_A). The samples were then extracted twice with benzene containing 50 mg./l. of PBNA for 24 hr. each time in the dark at room temperature. A third extraction was similarly made with pure benzene. (Earlier experiments showed that the amount of sol increased slightly with the duration of the benzene extraction in the absence of an antioxidant. The addition of PBNA retarded this apparent oxidative degradation.) The swollen samples were rapidly blotted between filter paper and transferred to tared weighing bottles for weighing (W_S). The samples were vacuum dried 6–8 hr. at 60°C. at 12 Torr and then weighed (W_B). The benzene-soluble rubber sol fraction S is given by $S = W_C (W_A - W_B)/100 W_0$, where W_C represents the total compound weight (see Table I). This assumes that there are no other ingredients present which are insoluble in acetone but soluble in benzene. Q, the swelling value in grams of solvent per gram of rubber gel network, is given by

$$Q = (W_S - W_B)/[W_0(100/W_C) - (W_A - W_B)]$$

A corrected swelling value, Q_c, was calculated by using the following empirical formula which describes the experimental results of Pierson, et al.[3]

$$Q_c = v_0 (Q + 1) - 1$$

By definition, v_0 is the ratio of the volume of the rubber gel network to the total volume of rubber plus the volume of all soluble materials. The volume of all insoluble materials that exist as a separate phase during vulcanization is not involved in the calculation of v_0. The calculation of v_0 was based on the following assumptions. Stearic acid reacts stoichiometrically with zinc oxide,[4] so that during vulcanization we may consider these rubber compounds to contain 4.57 phr of zinc oxide, 3.335 phr of zinc stearate and 0.095 phr of water. Volumes of the various materials were calculated from room temperature density values, and it was further assumed that no volume change occurs on mixing these materials. The 4.57 phr of zinc oxide was considered to be the only insoluble, separate phase and hence is excluded from these calculations of v_0. The volume of the rubber gel network is given by $(1 - S)$ times the total volume of rubber used in the compound. Diphenylguanidine and sulfur are soluble in rubber at vulcanization temperatures.[5] Zinc stearate and water were assumed to be soluble at vulcanization temperatures. (0.0343 g. zinc stearate readily dissolved in 0.774 g. of the rubber model compound 2,6-dimethylocta-2-trans-6-diene at 100°C.; zinc stearate is also soluble in boiling toluene.[6]) No correction was made for the amounts of zinc sulfide which form, or the amounts of diphenylguanidine and sulfur which combine with the rubber throughout the vulcanization process.

An acetone-extracted natural rubber sample was crosslinked by 0.5 phr of dicumyl peroxide under conditions identical to those previously described.[7]

RESULTS AND DISCUSSION

The network formation theory of Charlesby and Pinner[8] which had been applied to estimate the molecular chain scission accompanying the vulcanization of natural rubber by dicumyl peroxide[1] is used to interpret the results of this work. For this purpose one needs to know how the polymeric sol fraction depends on the extent of chemical crosslinking. The polymeric sol fraction is taken as the fraction of the rubber soluble in benzene following a prior acetone extraction which is intended to remove the nonrubber reaction products of the crosslinking which might be soluble in benzene. An important reason for selecting diphenylguanidine as the accelerator in this study is that it is extractable by acetone.

The extent of chemical crosslinking may be estimated from the experimental dependence of the swelling value Q on C, the amount of the quantitative crosslinker dicumyl peroxide[9] used to vulcanize natural rubber.[7] But rather than using Q, an empirically corrected swelling value Q_c was calculated, since the swelling will depend on the amount of soluble diluents

present during vulcanization. Theoretically, the value of Q will be larger for a gel network crosslinked in the presence of a soluble diluent than it will be for a gel network crosslinked to the same extent but in the absence of diluent.[10] The vulcanized samples in this work had up to 8% soluble material, consisting of rubber sol and various compounding ingredients and their reaction products which are soluble at vulcanization temperatures. Rather than using a theoretical correction for the presence of diluent during crosslinking, it is preferable to use an empirical observation based on experimental swell volume data. Such data have been reported for various polymers crosslinked quantitatively in the presence of varying amounts of soluble hydrocarbon diluents.[3] The empirical observation is that the volume fraction of rubber gel present during crosslinking, v_0, times $(Q + 1)$ is approximately a constant. One may define a corrected swelling value Q_c which approximates the swelling value which would be obtained for a sample crosslinked to the same extent in the absence of any soluble diluent, by

$$Q_c + 1 = v_0 (Q + 1) \tag{1}$$

This relation is a decided improvement over either a neglect of the soluble material present during crosslinking or any of the current theoretical treatments of the presence of diluents during crosslinking. This empirical relation is consistent with the concept that the number of elastically effective chain entanglements present is approximately proportional to v_0. This concept has not been considered in the usual theoretical treatments which, to be useful here, would require the assumption of constancy of elastically effective crosslinks.

The influence of the insoluble zinc oxide phase on the value of Q was also examined. If the rubber merely wets the zinc oxide surface and pulls free from it during swelling in benzene, a high value of Q will result.[11] If, on the other hand, the rubber remains firmly attached to the zinc oxide surface, this will necessarily restrict the swelling and lead to low values of Q, as is characteristic of certain rubber–filler systems. The latter situation was observed.

Observation with an optical microscope by both ordinary and phase contrast illumination of zinc oxide particles in rubber vulcanizates during swelling in benzene indicated that the rubber adheres to the zinc oxide surface. This was observed both for the diphenylguanidine–sulfur vulcanizate A and also for a natural rubber containing 5 phr of zinc oxide crosslinked with 2 phr of dicumyl peroxide. If glass beads are substituted for zinc oxide in this latter vulcanizate, the rubber will not adhere to the surface of the glass beads during swelling in benzene.

A direct experimental check of the influence of zinc oxide on swelling was made by measuring Q for six natural rubber samples crosslinked with 1–4 phr of dicumyl peroxide in the absence and in the presence of 5 phr of zinc oxide. The presence of the zinc oxide leads to Q values which are lower by 0.9% on the average than the Q values of samples crosslinked in

TABLE II
Swelling Values for Natural Rubber Crosslinked with Dicumyl Peroxide

Dicumyl peroxide, phr	Swelling value Q, g. benzene/ g. rubber gel network	Sol fraction s	Volume fraction rubber gel network v_0	$Q_c = v_0(Q + 1) - 1$	$1/Q_c$	$\nu_e \times 10^4$, moles/g.[a]
0.5	5.83	0.02868	0.968	5.61	0.178	0.597
1.0	4.30	0.00995	0.982	4.20	0.238	1.113
1.5	3.56	0.00379	0.984	3.49	0.287	1.532
2.0	3.10	0.00209	0.982	3.03	0.331	1.926
2.5	2.70	(0.00160)	0.977	2.62	0.382	2.311
3.0	2.42	0.00123	0.973	2.33	0.429	2.691
4.0	2.01	0.00074	0.965	1.90	0.526	3.442

[a] From eq. (6).

the absence of zinc oxide. A statistical treatment of these data indicated that there is only slightly better than a 50–50 chance that the presence of zinc oxide leads to truly lower Q values. No correction was made on our experimental results for this minor effect.

The swelling values for natural rubber (number-average molecular weight of 144,000) crosslinked with dicumyl peroxide are given in Table II and are based on the data of Lorenz and Parks.[7] Q_c was calculated with the assumption that dicumyl peroxide is soluble at vulcanizing temperatures and on the basis of sol values previously reported.[1] In Figure 1, $1/Q_c$ is plotted versus the amount of dicumyl peroxide consumed C, whereby a linear relationship is formed over a fairly wide range. A least square fit of the data for $C = 1$–4 in Figure 1 is given by the expression

$$C = -1.469 + 10.403/Q_c \qquad (2)$$

where C is the dicumyl peroxide concentration in phr. The standard
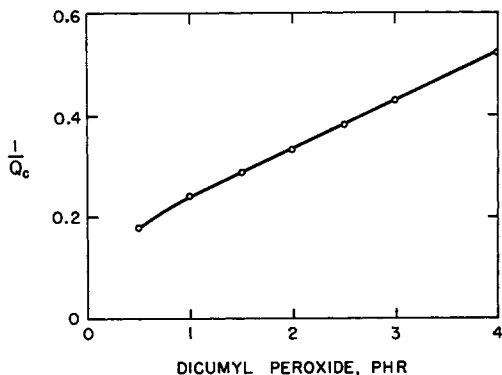

Fig. 1. Corrected swelling value of natural rubber cured with varying amounts of dicumyl peroxide.

deviation in C is only 0.017 over the range, $C = 1$–4, for which this expression applies.

From the above quantitative expression (2) and $1/Q_c$ of any natural rubber vulcanizate, one can determine C, the concentration of dicumyl peroxide which would lead to an equal swelling value and hence an equivalent number of chemical crosslinks as long as the number-average molecular weight is approximately 144,000.

However, since we might anticipate some chain scission to accompany the network destruction processes taking place during reversion of cure, we devised an alternative scheme which allows determining the extent of chemical crosslinking from swelling measurements even in the presence of substantial amounts of chain scission during vulcanization. This scheme also takes into account any difference in molecular weight between the samples investigated here and the samples used in the quantitative crosslinking of natural rubber by dicumyl peroxide.[7]

Mullins[12] has developed the following empirical expression (using Mullins' standard symbols) to describe the elastic behavior of natural rubber as a function of its molecular weight and degree of chemical crosslinking,

$$M_c^{-1} \text{(phys)} = [M_c^{-1} \text{(chem)} + 0.68 \times 10^{-4}] [1 - 2.3 \, M_c \text{(chem)} M^{-1}] \quad (3)$$

which may be rewritten as

$$\nu_e = (\nu_c + 0.68 \times 10^{-4}) [1 - 2.3 \nu_c \, M] \quad (4)$$

where ν_e is the number of moles of elastically effective network chains per gram of rubber, ν_c is the number of moles of network chains per gram of rubber arising from chemical crosslinking only, and M is the number-average molecular weight of the rubber. ν_c is also equal to the moles of chemically crosslinked structural units per gram of rubber. Equation (4) was developed on the assumption that no chain scission occurred during vulcanization with di-tert-butyl peroxide. This assumption would seem well founded on the basis of the vulcanization of natural rubber with dicumyl peroxide which has been shown to involve negligible amounts of chain scission, if any.[1] If chain scission occurs during vulcanization, then M in eq. (4) must be suitably modified to reflect that each mole of chain scission per gram of rubber increases by one the number of moles of molecules per gram rubber, M^{-1}. The moles of chain scission per gram of rubber is equal to $(p/q) \, \nu_c$, where p is the fraction of polymeric structural units that have undergone scission and q is the fraction of polymeric structural units that have been crosslinked. If chain scission during vulcanization is directly proportional to the number of chemical crosslinks, then (p/q) will be constant; otherwise, (p/q) will vary during the course of vulcanization. Modifying M in eq. (4) to take into account chain scission during crosslinking yields

$$\nu_e = (\nu_c + 0.68 \times 10^{-4}) [1 - 2.3 \, \nu_c \, M_0 - 2.3(p/q)] \quad (5)$$

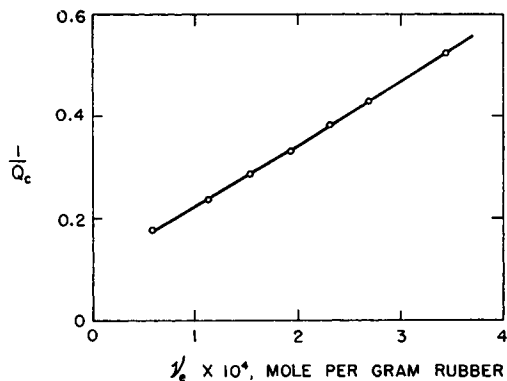Fig. 2. Dependence of the corrected swelling value, Q_c, of natural rubber in benzene on the concentration of elastically effective network chains ν_e from eq. (6).
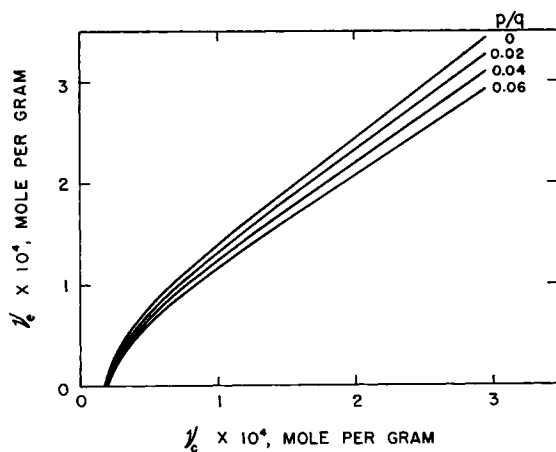

Fig. 3. Dependence of the concentration of elastically effective network chains on the concentration of chemically crosslinked units for natural rubber with $M_0 = 135,100$ from eq. (5).

where M_0 is the original number-average molecular weight before cross-linking. For the specific case of crosslinking polyisoprene with the quantitative crosslinking agent, dicumyl peroxide, $\nu_c = C/13,520$, where C is the dicumyl peroxide concentration (phr) decomposed, and hence

$$\nu_e = [(C/13,520) + 0.68 \times 10^{-4}] [1 - (31,090/CM_0) - 2.3 \, (p/q)] \quad (6)$$

Table II lists the corrected swelling values of natural rubber crosslinked by dicumyl peroxide and also the concentration of elastically effective network chains as given by eq. (6) with $M_0 = 144,000$ and $p/q = 0.$[1] Figure 2 illustrates the dependence of the reciprocal of the corrected swelling value Q_c on the concentration of elastically effective network chains. Figure 2 may now be used to determine ν_e for any natural rubber vulcanizate from its corrected swelling value in benzene, regardless of its molec-

TABLE III
Dependence of Sol Fraction and Swelling Values on Concentration of Crosslinked Units for a Natural Rubber–Sulfur–Diphenylguanidine Vulcanizate

Recipe	Cure time at 149°C, min.	Sol fraction S	Swelling value Q, g. benzene/g. rubber gel network	Volume fraction rubber gel network v_0	$Q_e = v_0(Q+1) - 1$	$v_e \times 10^4$, mole/g.[a]	$v_c \times 10^4$, mole/g.[b] $p/q = 0$	$p/q = 0.02$	$p/q = 0.06$
A	15	0.00687	4.582	0.9425	4.261	1.08	0.73		
	30	0.00279	3.783	0.9463	3.526	1.51	1.10		
	60	0.00286	3.608	0.9463	3.361	1.63	1.21		
	90	0.00525	3.876	0.9440	3.603	1.46	1.07	1.14	
	120	0.01180	4.376	0.9379	4.042	1.20	0.84		1.04
B	15	0.00388	4.005	0.9382	3.695	1.40	1.01		
	30	0.00187	3.265	0.9400	3.009	1.92	1.49		
	60	0.00120	3.074	0.9407	2.833	2.08	1.64		
	90	0.00273	3.304	0.9393	3.043	1.90	1.47	1.57	
	120	0.00909	3.659	0.9333	3.348	1.64	1.23		1.51
C	15	0.00279	3.798	0.9322	3.473	1.54	1.14		
	30	0.00158	2.999	0.9334	2.733	2.18	1.74		
	60	—	2.777	(0.934)[c]	(2.525)[c]	(2.42)[c]	(1.97)[c]		
	90	—	3.041	(0.932)[c]	(2.77)[c]	(2.15)[c]	(1.71)[c]	(1.82)[c]	
	120	0.00846	3.390	0.9269	3.069	1.87	1.44		1.76
D	15	0.00211	3.428	0.9260	3.101	1.84	1.41		
	30	0.00082	2.645	0.9272	2.380	2.61	2.16		
	60	—	2.566	(0.927)[c]	(2.305)[c]	(2.72)[c]	(2.26)[c]		
	90	0.00356	2.995	0.9247	2.694	2.22	1.78	1.89	
	120	0.01060	3.463	0.9182	3.098	1.84	1.41		1.73

[a] From Fig. 2.
[b] From Fig. 3.
[c] Values in parentheses are obtained by using an estimated sol fraction value. The error here is negligible.
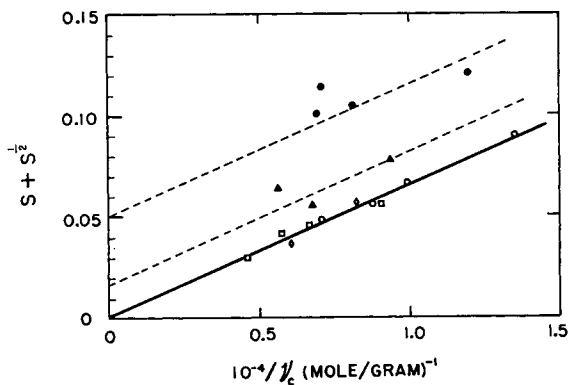
Fig. 4. Sol fraction dependence on the concentration of crosslinked units for natural rubber–sulfur–diphenylguanidine vulcanizates with $M_0 = 135,100$ and neglecting the effect of chain scission on the swelling value at various cure times at 149°C.: ($\bigcirc$) 15 min., ($\square$) 30 min., ($\Diamond$) 60 min., ($\blacktriangle$) 90 min., ($\bullet$) 120 min.

ular weight. This procedure is almost equivalent to determining ν_e from the modified Flory–Rehner swelling relation;[10] however, we prefer to use this empirical procedure because of the convenience and accuracy of interpolation afforded by the almost linear dependence shown in Figure 2. Having determined ν_e with the aid of Figure 2, one can now determine the degree of chemical crosslinking ν_c by substituting ν_e, M_0, and p/q in eq. (5). Figure 3 shows the relation between ν_e and ν_c as given by eq. (5) for natural rubber with $M_0 = 135,100$ and various values of p/q.

The amount of permanent molecular chain scission accompanying vulcanization may be estimated by making use of eq. (7), which results from the Charlesby and Pinner[8] theory of gel network formation for the case of random tetrafunctional crosslinking and random molecular chain scission of a polymer whose initial molecular weight distribution is the random or most probable one,

$$S + S^{1/2} = (p/q) + (q^- \bar{y}_n)^{-1} \qquad (7)$$

where $\bar{y}_n$ is the number-average degree of polymerization of the polymer. For polyisoprene,

$$q = 68.1\ \nu_2 \qquad (8)$$

Table III lists the experimentally determined sol fraction and corrected swelling values for the natural rubber–sulfur–diphenylguanidine vulcanizates studied here. ν_e is determined from the value of Q_c by the use of Figure 2. The value of ν_c is determined from the value of ν_e by the use of Figure 3 for various assumed values of p/q. Figure 4 is a plot of $S + S^{1/2}$ against ν_c^{-1} as suggested by eqs. (7) and (8) and where ν_c has been determined from the $p/q = 0$ curve of Figure 3, i.e., the effect of chain scission during vulcanization on the swelling value has been neglected. According to eq. (7), the intercepts of Figure 4 yield the value of p/q, the ratio of the
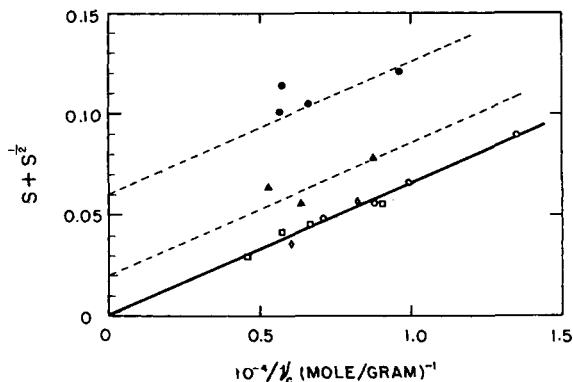
Fig. 5. Sol fraction dependence on the concentration of crosslinked units for natural rubber–sulfur–diphenylguanidine vulcanizates with $M_0 = 135,100$ and including the effect of chain scission on the swelling value at various cure times and assumed p/q values: (○) 15 min., $p/q = 0$; (□) 30 min., $p/q = 0$; (◇) 60 min., $p/q = 0$; (▲) 90 min., $p/q = 0.02$; (●) 120 min., $p/q = 0.06$.

structural units that have undergone scission to those that have been crosslinked.

Figure 4 indicates that scission is negligible for the 15, 30, and 60 min. cures at 149°C., while some network chain scission occurs for the vulcanizates cured for 90 and 120 min.   Table III (ν_e or ν_c data) indicates that the samples cured 90 and 120 min. are past the point of cure reversion.

The effect of chain scission during vulcanization on the swelling value may be determined by assuming trial values of p/q, using the corresponding curve of Figure 3 to determine ν_c, and plotting in the form of Figure 4. The correct value of p/q will have been selected when this same value is obtained as the intercept in a plot of $S + S^{1/2}$ versus $1/\nu_c$.   The correct value of p/q will be slightly larger than the intercept obtained as in Figure 4 when p/q was assumed to be zero, i.e., when the effect of chain scission during vulcanization on swelling value was neglected.

Figure 5 is the result of such a treatment.   Here a value of $p/q = 0.06$ was assumed for the 120 min. cure, $p/q = 0.02$ for the 90 min. cure, and $p/q = 0$ for the 15, 30, and 60 min. cures, Figure 3 being used to determine ν_c.   The agreement of the intercepts of Figure 5 with these assumed values of p/q is good.   The solid line of Figure 5 is the linear least-square fit of the 15, 30, and 60 min. cure data and is given by

$$S + S^{1/2} = 0.0002 + (6.522 \times 10^{-6}/\nu_c) \tag{9}$$

This is close to the relation[1] found for the crosslinking of natural rubber by dicumyl peroxide:

$$S + S^{1/2} = -0.0022 + (7.833 \times 10^{-6}/\nu_c)$$

The standard deviation (0.0027) of these data indicates that the intercept, $p/q = 0.0002$, is not significantly different from zero.   Alternatively, we

may assert at the 95% confidence level that p/q, the ratio of the rubber structural repeat units that have undergone scission to those that cross-link, is less than 0.0056. The slope of the solid line of Figure 5 according to eqs. (7)–(9) corresponds to a number-average molecular weight of 153,-000, which compares favorably with the expected value of 135,100. On the basis of these results one concludes that molecular chain scission during these short vulcanization times, prior to the point of modulus or crosslink reversion, is negligible.

The scatter of the 90 and 120 min. cure data precludes any exhaustive analysis. The dashed lines of Figure 5 have been drawn with the theoretically expected slope, i.e., the same as the solid line. The intercepts indicate that small amounts of molecular chain scission do occur at these longer vulcanization times, which are past the point of modulus reversion for these cures. These data suggest that not only does p/q increase with cure time but that p itself increases while q decreases at long cure times. To a first approximation p/q depends only on cure time, and this suggests that the principal consecutive reactions involved in crosslinking and reversion have a first order dependence on the various species involved. There appears to be a slight tendency for p/q to increase with increasing amounts of the vulcanization agents, sulfur and diphenylguanidine.

Similar data have been obtained and analyzed for another series of vulcanizates prepared by press curing at the lower temperature of 135°C. The 40, 60, and 80 min. cure samples are characterized by the value of zero for p/q while samples cured for 120 min. indicated $p/q = 0.01$.

Swelling value and sol fraction measurements were also made on vulcanizates containing 50 phr of HAF carbon black. The swelling values were multiplied by 1.33 to approximate the swelling value which would have been obtained for an equivalently cured gum stock.[7] Handling this corrected swelling value and sol fraction data as described above again leads to a very low value of p/q. Hence very little chain scission is observed for this vulcanization in the presence of carbon black.

While the above procedure of correcting for the presence of diluent during crosslinking is the preferred one, it should be pointed out that the results are not significantly changed if the uncorrected Q values are used to determine ν_c.

The Reversion Process

In this section we shall attempt to estimate the contributions of molecular chain scission and crosslink scission to the process of modulus reversion of these cures. To make this estimate we shall need to known the concentration of chemically crosslinked units remaining in a vulcanizate and also what the concentration of chemically crosslinked units would have been if crosslink scission had not occurred. The former values are equal to ν_c, which has been determined using the appropriate p/q value, namely zero for the 60 min. cure, 0.02 for the 90 min. cure, and 0.06 for the 120 min. cure. The concentration of chemically crosslinked units
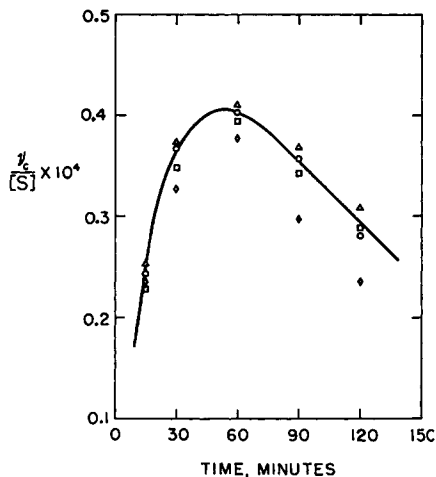
Fig. 6. Rate of crosslinking relative to the initial sulfur concentration for various recipes: (O) recipe A, [S] = 3; (Δ) recipe B, [S] = 4; (□) recipe C, [S] = 5; (◇) recipe D, [S] = 6.

that would have been obtained if crosslink scission had not occurred will be equal to ν_{c_0} which is an extrapolation of initial ν_c data in an attempt to estimate what ν_c would have been at longer times if crosslink scission did not occur. The concentration of network chains cut will then be equal to $\nu_c \, p/q$, while the concentration of network chains (twice the concentration of crosslinks) lost due to crosslink scission is equal to $\nu_{c_0} - \nu_c$. The fraction of the network destruction during reversion which is due to chain scission is defined by

$$ f = \frac{\nu_c \, p/q}{\nu_{c_0} - \nu_c + \nu_c \, p/q} \tag{10} $$

To make the estimation of ν_{c_0} less subjective, the following procedure was followed. It is assumed that the sulfur reacts with the rubber to form sulfur-bearing crosslinks all of which in turn may decompose to give other products (P). These reactions may be approximated as two consecutive first-order reactions with rate constants, k_1 and k_2,

$$ \text{Sulfur} \xrightarrow{k_1} \nu_c \xrightarrow{k_2} \text{P} \tag{11} $$

The integrated form of the rate expression for the concentration of crosslinked units has the familiar form for the build-up of the intermediate product in consecutive reactions,

$$ \nu_c = r \, [S] \, k_1 \, (e^{-k_2 t} - e^{-k_1 t})/(k_1 - k_2) \tag{12} $$

where ν_c is the concentration of chemically crosslinked units in moles/g. rubber, [S] is the initial sulfur concentration in phr, r is a conversion factor expressing how many moles of crosslinked units per gram of rubber are

potentially attainable from each phr of sulfur, and t is the time in minutes for k_1 and k_2 (given in min.$^{-1}$). According to eq. (12), $\nu_c/[S]$ depends only on time plus some constants. Figure 6 compares the experimental data in this form. Recipes A, B, and C yield data which are in good agreement with this expectation, while data for recipe D (highest [S]) are somewhat lower. The curve in Figure 6 is eq. (12) with the following numerical constants,

$$\nu_c = 7.4 \times 10^{-5} [S] (e^{-0.00747t} - e^{-0.0396t}) \qquad (13)$$

which corresponds to $k_1 = 0.0396$ min.$^{-1}$, $k_2 = 0.00747$ min.$^{-1}$, and $r = 6 \times 10^{-5}$ moles crosslinked units/g. rubber per phr of sulfur.

Since ν_{c_0} is the value of ν_c in the absence of crosslink scission, it may be calculated by considering that only the first reaction of eq. (11) occurs while the second reaction does not take place. For this simple first-order reaction we have the following integrated rate expression,

$$\nu_{c_0} = r [S] (1 - e^{-k_1 t}) \qquad (14)$$

which for the above values of the constants becomes

$$\nu_{c_0} = 6 \times 10^{-5} [S] (1 - e^{-0.0396t}) \qquad (15)$$

Table IV lists values for ν_{c_0} calculated on the basis of eq. (15) and also for f, the fraction of the network destruction during reversion which is due to chain scission. It is seen that chain scission is responsible for only 3% of the reversion after 90 min. cure and still only 8% after 120 min. cure. Hence, crosslink scission is the predominant process responsible for modulus reversion in natural rubber–sulfur–diphenylguanidine vul-

TABLE IV

Contribution of Molecular Chain Scission and Crosslink Scission to the Reversion Process

Recipe	Cure time at 149°C., min.	Network chains × 10⁴, moles/g. rubber				
		ν_c	$\nu_{c_0}{}^a$	$\nu_{c_0} - \nu_c$	$\nu_c \, p/q$	f^b
A	60	1.21	1.63	0.42	0	0
	90	1.14	1.75	0.61	0.023	0.036
	120	1.04	1.78	0.74	0.062	0.077
B	60	1.64	2.18	0.54	0	0
	90	1.57	2.33	0.76	0.031	0.039
	120	1.51	2.38	0.87	0.091	0.095
C	60	1.97	2.72	0.75	0	0
	90	1.82	2.92	1.10	0.036	0.035
	120	1.76	2.97	1.21	0.106	0.081
D	60	2.26	3.27	1.01	0	0
	90	1.89	3.50	1.61	0.038	0.023
	120	1.73	3.57	1.84	0.104	0.054

[a] From eq. (15).
[b] From eq. (10).

canizates. This is the same conclusion as that drawn from a Horikx[13] type treatment of sol fraction and ν_e data for a different natural rubber–sulfur–diphenylguanidine vulcanizate.[14]

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Résumé

On a déterminé la fraction "sol" et les valeurs de gonflement d'une série de vulcanisats de caoutchouc naturel–soufre–diphénylguanidine. Ces données sont analysées selon la théorie de formation de réseau "gel" de Charlesby et Pinner, dans le but d'estimer la quantité de ruptures permanentes de chaînes moléculaires pendant la vulcanisation. On conclut qu'il y a rupture de chaînes négligeable avant la réversion du module de ces matériaux. Dans la région de réversion il y a une faible rupture permanente des chaînes moléculaires. Le principal facteur responsable pour la réversion de cette vulcanisation est la rupture des chaînes latérales. La rupture de chaînes n'est responsable que pour environ 3–8% de la réversion observée.

Zusammenfassung

An einer Reihe von Naturkautschuk-Schwefel-Diphenylguanidin-Vulkanisaten wurden die Menge der Solfraktion und die Quellungswerte bestimmt. Zur Bestimmung des Betrages der die Vulkanisation begleitenden permanenten Molekülkettenspaltung wurden diese Daten anhand der Gelnetzwerksbildungstheorie von Charlesby und Pinner analysiert. Es ergibt sich der Schluss, dass vor dem Punkt der Modulumkehr dieser Vulkanisate nur eine vernachlässigbare Kettenspaltung eintritt. Im Gebiet der Vulkanisationsumkehr tritt in geringem Umfang permanente Molekülkettenspaltung auf. Der für die Vulkanisationsumkehr hier hauptsächlich verantwortliche Faktor ist die Spaltung von Vernetzungen. Kettenspaltung ist nur für etwa 3–8% der beobachteten Vulkanisationsumkehr verantwortlich.