Zusammenfassung

Latices mit 55 Teilen Styrol, $(45 - X)$ Teilen 2-Athylhexylacrylat und X Teilen Methylacrylsäure, wo $X \geq 15$, liefern beim Trocknen diskontinuierlich, rissbildende Filme. Die klaren, transparenten Polymerkörnchen werden beim Einbringen in eine wässrige Base peptisiert und bilden wieder einen Latex mit kugelförmigen Teilchen derselben Grösse wie die ursprünglichen Latexteilchen. Zusatz kleiner Mengen eines Filmbildungsmittels zum ursprünglichen oder rückgebildeten Latex erlaubt die Gewinnung eines kontinuierlichen Polymerfilms, der durch Erwärmen wasserbeständig gemacht werden kann. Die Fähigkeit transparenter Polymerflocken zur Redispergierung in Wasser wird auf eine begrenzte Teilchenkoaleszenz im Polymeren zurückgeführt. Für die Redispergierung des Polymeren in verdünnten Basenlösungen ist der Einbau eines verhältnismässig grossen Anteils von Karboxylgruppen in das Polymere notwendig. Ionisation der Karboxylgruppen an der Teilchenoberfläche beim Zusatz von Basen führt zur plötzlichen Entwicklung Coulombscher Abstossungskräfte und Teilchentrennung; nun genügen die Oberflächenkräfte, um die ursprüngliche Kugelgestalt der halbplastischen Teilchen wider hersuztellen. Die Unfähigkeit den Film ein zweites Mal zu redispergieren kann auf eine Weichmachung des Polymeren oder auf die Wanderung von Karboxylgruppen ins Teilcheninnere unter dem Einfluss der Koaleszenzkräfte zurückzuführen sein.

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Crosslinking Efficiencies of Dicumyl Peroxide in Unsaturated Synthetic Rubbers

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INTRODUCTION

Following previous work in these laboratories on the efficiency of dicumyl peroxide in crosslinking natural rubber[1] it was thought that similar work with unsaturated synthetic rubbers would be of interest. In the present paper the crosslinking efficiencies in butadiene–styrene rubber, *cis*-polybutadiene, butadiene–acrylonitrile rubber, and polychloroprene have been measured.

The number of crosslinks formed was obtained from equilibrium swelling measurements, necessitating, in the case of *cis*-1,4-polybutadiene, the prior determination of the solvent–polymer interaction constant, χ.

EXPERIMENTAL

Materials

Dicumyl peroxide was obtained from Hercules Powder Co., and was recrystallized from methanol and water before use. Benzene and carbon tetrachloride were of Analar grade and *n*-decane was distilled under vacuum.

The SBR used was Polymer Corporation Polysar Krylene NS, a cold-polymerized type containing 28 wt.-% styrene. The *cis*-polybutadiene was Shell Cariflex BR and was 97% *cis*-1,4. The nitrile rubber was Polymer Corporation Polysar Krynac 805, a cold-polymerized type containing 61% butadiene. The polychloroprene was Du Pont Neoprene W. All of these polymers were purified by acetone extraction for 48 hr. before use, to remove antioxidants.

The peroxide was milled into the rubber on a 6 in. × 2 in. two-roll mill at room temperature and was normally cured for 70 min. at 153°C. to give virtually complete decomposition of the peroxide. Where the vulcanizates were to be used for the determination of the solvent interaction parameter a shorter cure was sometimes employed.

Swelling Procedure

Equilibrium swelling values for the vulcanized rubbers were obtained by immersing samples, about 0.2 g. and 0.7 mm. thick, in solvent until (normally, 2 days at 25°C.) a constant-weight swollen specimen was obtained. The volume of fraction of rubber, v_2, was calculated from solvent and rubber densities assuming no volume change on mixing.

Stress–Strain Measurements

Vulcanized sheets approximately 0.3 mm. thick were used, and the equilibrium strain under given stress was measured at room temperature. The results were plotted according to the following equation,[2] to give C_1:

$$f/2A_0(\lambda - \lambda^{-2}) = C_1 + C_2/\lambda$$

Product Analysis

Dicumyl peroxide has been shown to decompose by a first-order reaction to give cumyloxy radicals in neutral or alkaline environments. The radicals so formed may abstract hydrogen atoms if suitable donors are present, or they may undergo a first-order decomposition and give acetophenone and methyl radicals.[3] The ratio of acetophenone to cumyl alcohol in the reaction products may therefore be used as a measure of the ease of the hydrogen abstraction reaction. An analysis for these low molecular weight products is conveniently made by infrared or ultraviolet spectroscopy. At low initial peroxide concentrations such determinations are difficult, practically, and the higher concentrations used with SBR were introduced to give more reliable analyses. The cured samples were rapidly weighed and immersed in pure carbon tetrachloride for at least 24 hr. and the absorptions of the resulting solutions at 3520 and 1730 cm.$^{-1}$ were used to determine cumyl alcohol and acetophenone, respectively.

Initial Molecular Weight

These weights were determined from intrinsic viscosities according to the published equations.

			MW
SBR:	$[\eta] = 5.25 \times 10^{-4} M^{0.67}$	in benzene at 25°C.[4]	$2.17 \times 10_5$
cis-Polybutadiene:	$[\eta] = 3.37 \times 10^{-4} M^{0.715}$	in benzene at 30°C.[5]	1.91×10^5
Nitrile:	$[\eta] = 1.3 \times 10^{-4} M^{0.55}$	in benzene at 25°C.[4]	3.70×10^5
Polychloroprene:	$[\eta] = 1.55 \times 10^{-4} M^{0.71}$	in benzene at 25°C.[6]	2.52×10^5

RESULTS AND DISCUSSION

Determination of χ (or "μ value") for *cis*-polybutadiene in *n*-Decane

A range of peroxide vulcanizates was prepared, and stress–strain measurements were used to determine C_1; samples of the same cures were swollen in *n*-decane and by comparison using the equation below, where V_1 is the molal volume of the swelling liquid,

$$-\ln(1 - v_2) - v_2 - \chi v_2^2 = 2C_1V_1(v_2^{1/3} - {}^1/_2v_2)/RT$$

the value of χ was obtained. The detailed results are shown in Table I. The mean value was 0.546 with no significant upward trend with increasing v_2. The published values[5] for SBR's containing 28.5, 12.5, and 4% styrene are 0.671, 0.631, and 0.568, respectively, and the present figure falls into this sequence.

TABLE I
Values of the Solvent–Polymer Interaction Constant for *cis*-Polybutadiene and *n*-Decane

Cure no.	v_2	$C_1/RT \times 10^5$	χ
2	0.315	4.75	0.540
2A	0.253	2.10	0.539
3	0.225	1.35	0.539
6	0.317	4.43	0.549
7	0.413	12.35	0.550

Determination of Crosslinking Efficiency

Compounds of various dicumyl peroxide contents were vulcanized and C_1/RT was determined for each by swelling by using the published,[7] or presently determined, χ values. SBR vulcanizates were swollen in *n*-decane and benzene, nitrile and polychloroprene in chloroform, and *cis*-polybutadiene in *n*-decane.

The C_1/RT determined in this way is identified[2] with the number of effective crosslinks per unit volume of the Flory theory;[8] to obtain the number of actual chemical crosslinks a correction is required and this correction has been the subject of several investigations.[9–12] In most cases the correction produced has been mainly in the form of an additive term resulting from the effect of free chain ends in the network and physical entanglements, and thus, in the present work, the increase in effective crosslinks produced by a given change in peroxide concentration has been assumed equal to the increase in actual chemical crosslinks.

SBR and cis-Polybutadiene

The results for these polymers are shown in Figures 1–3. The Flory-Rehner equation shows the form of the dependence of v_2 upon C_1 expected theoretically, and independent determinations of v_2 and C_1 over a range of crosslink densities have shown good agreement with the theory.[13] In the present SBR results, however, the value of χ used was the result of a single determination at $v_r = 0.4593$ (decane) and 0.1814 (benzene), and use of these values for results from the grossly overcured rubbers included in Figures 1 and 2 provides a very severe test of theory. Close examination of these graphs shows that the linear parts of the C_1/RT curves are placed

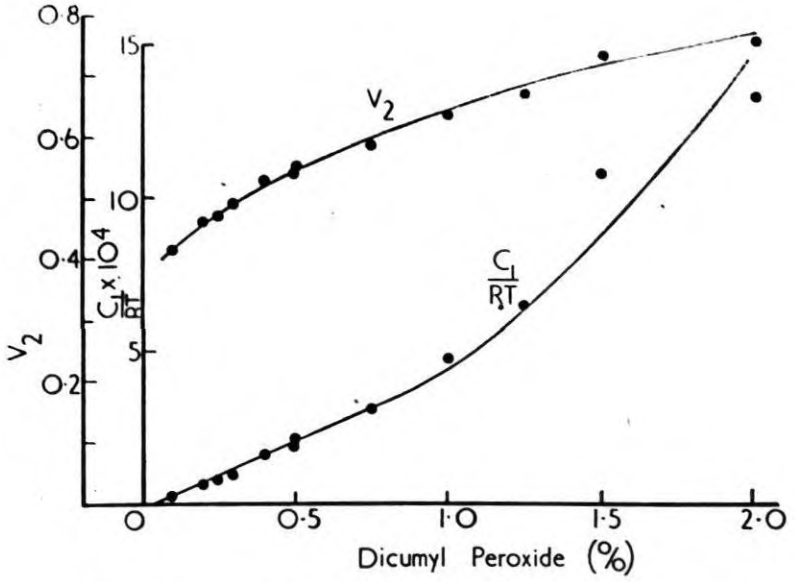


Fig. 1. Variation of v_2 for SBR in *n*-decane with initial peroxide concentration, together with the resulting values of C_1/RT.

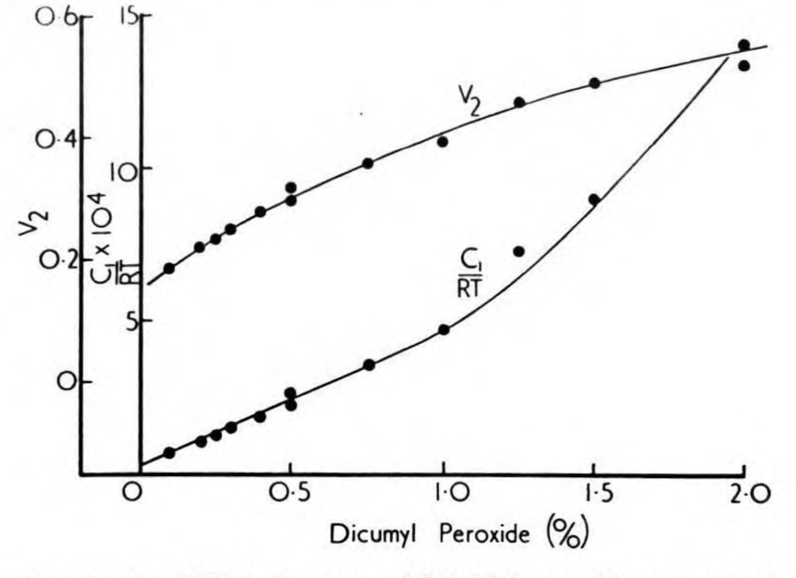


Fig. 2. Variation of v_2 for SBR in benzene with initial peroxide concentration, together with the resulting values of C_1/RT.

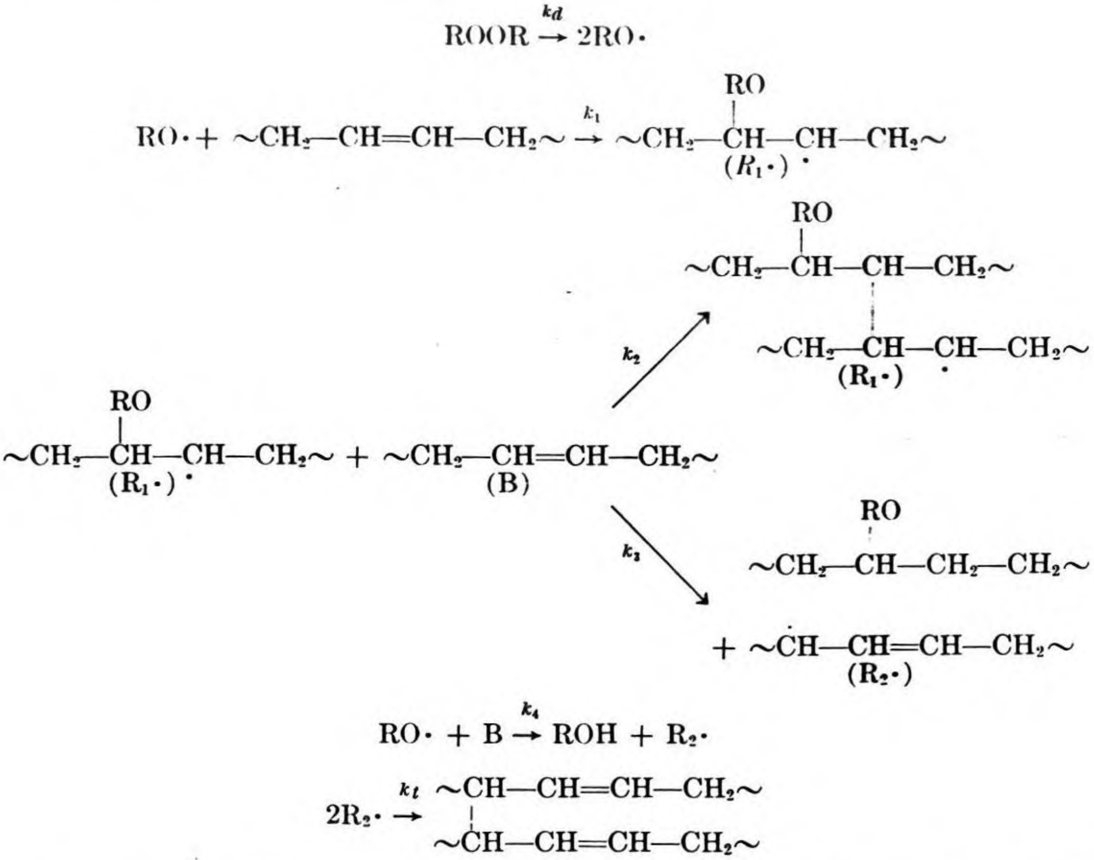
in slightly different positions while the slopes in each case are very nearly equal, this displacement is presumably due to a slight inconsistency in the solvent interaction parameters used for swelling in the two solvents.

The initial slopes of the C_1/RT versus peroxide curves give a measure of the efficiency of peroxide crosslinking; for SBR this leads to a value of 12.5 crosslinks per molecule of peroxide, while for *cis*-polybutadiene each peroxide molecule forms 10.5 crosslinks.

The results of the analyses of the low molecular weight products of the SBR crosslinking are shown in Figure 4; both cumyl-alcohol and acetophenone concentrations depend linearly upon the initial peroxide concentration, and throughout the range covered these two compounds account for only 78% of the peroxide added. The conditions of cure are such that virtually all the peroxide is decomposed and thus the remaining 22% presumably decomposes to peroxy radicals which do not then hydrogen-abstract or decompose to acetophenone and methyl radicals.

In summary, dicumyl peroxide initiates a high efficiency crosslinking reaction in both SBR and *cis*-polybutadiene, the crosslinking reaction being first order with respect to peroxide. The cumyloxy radicals react largely by hydrogen abstraction, while about 20% react in some other way. Both reactions are relatively fast, the molar ratio of ketone/alcohol, 0.07, indicating a slightly higher rate of reaction than that observed in natural rubber.[1]

The high efficiency of crosslinking could most easily result from a cross-polymerization reaction but, for such a reaction to give a first-order dependence of crosslinking on peroxide concentration, chain termination must be by degradative chain transfer or rearrangement. The following reaction scheme appears to give an adequate explanation of the results obtained:



$$\mathrm{ROOR} \xrightarrow{k_d} 2\mathrm{RO}\cdot$$

$$\mathrm{RO}\cdot + \sim\mathrm{CH_2{-}CH{=}CH{-}CH_2}\sim \xrightarrow{k_1} \sim\mathrm{CH_2{-}\overset{RO}{CH}{-}\underset{\cdot}{CH}{-}CH_2}\sim \quad (R_1\cdot)$$

$$\underset{(\mathrm{R_1}\cdot)}{\sim\mathrm{CH_2{-}\overset{RO}{CH}{-}\underset{\cdot}{CH}{-}CH_2}\sim} + \underset{(\mathrm{B})}{\sim\mathrm{CH_2{-}CH{=}CH{-}CH_2}\sim} \xrightarrow{k_2} \begin{array}{c}\sim\mathrm{CH_2{-}\overset{RO}{CH}{-}CH{-}CH_2}\sim \\ | \\ \sim\mathrm{CH_2{-}CH{-}\underset{\cdot}{CH}{-}CH_2}\sim \\ (\mathrm{R_1}\cdot)\end{array}$$

$$\xrightarrow{k_3} \sim\mathrm{CH_2{-}\overset{RO}{CH}{-}CH_2{-}CH_2}\sim + \underset{(\mathrm{R_2}\cdot)}{\sim\mathrm{\dot{C}H{-}CH{=}CH{-}CH_2}\sim}$$

$$\mathrm{RO}\cdot + \mathrm{B} \xrightarrow{k_4} \mathrm{ROH} + \mathrm{R_2}\cdot$$

$$2\mathrm{R_2}\cdot \xrightarrow{k_t} \begin{array}{c}\sim\mathrm{CH{-}CH{=}CH{-}CH_2}\sim \\ | \\ \sim\mathrm{CH{-}CH{=}CH{-}CH_2}\sim\end{array}$$

It seems unlikely that crosslinking is occurring by polymerization of pendant unsaturated groups, since these must, at least in the case of the *cis*-polybutadiene, be present in very low concentration and their reactivity consequently would need to be unexpectedly high.

For convenience, the participation of methyl radicals is omitted; the possibility of such radicals replacing cumyloxy radicals in some or all of the above reactions will be discussed below.

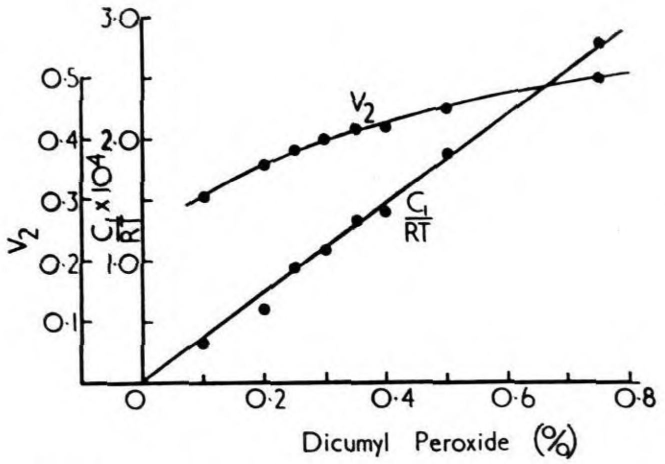


Fig. 3. Variation of v_2 for *cis*-polybutadiene in *n*-decane with initial peroxide concentration together with the resulting values of C_1/RT.

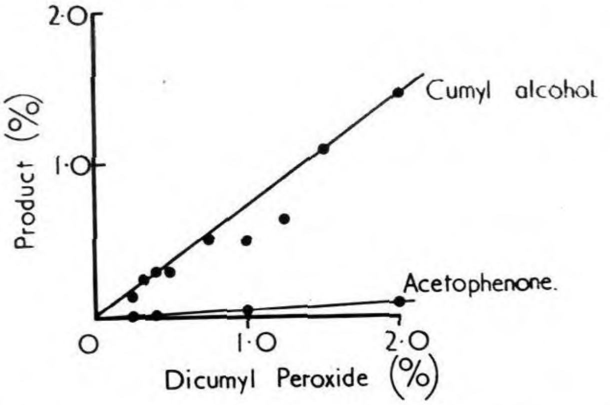


Fig. 4. Variation of low molecular weight products with initial peroxide concentration in the crosslinking of SBR.

The presence of a small amount of ketone in the products shows that some peroxy radicals decompose to produce methyl radicals by the reaction:

$$C_6H_5C(CH_3)_2O\cdot \rightarrow C_6H_5COCH_3 + CH_3\cdot$$

and thus the peroxy radical will be replaced by methyl in some of the above reactions. From the above scheme, making the usual stationary-state assumption for radical concentrations, the equation for rate of crosslinking becomes:

$$k_2[R_1\cdot][B] = k_1k_2k_d\,[P]\,/k_3(k_1 + k_4)$$

which shows the required first-order dependence upon peroxide.

It is impossible at present to decide whether cumyloxy radicals alone are able to initiate chains or whether methyl radicals also do this. It is also conceivable that the cumyloxy radicals which do not abstract hydrogen take part in some reaction not listed above, and the estimate of polymerization chain length made must depend on which assumption is made. If either cumyloxy or methyl can initiate, the chain length must be about 40, and if only methyl radicals initiate, the chain length must be about 50,

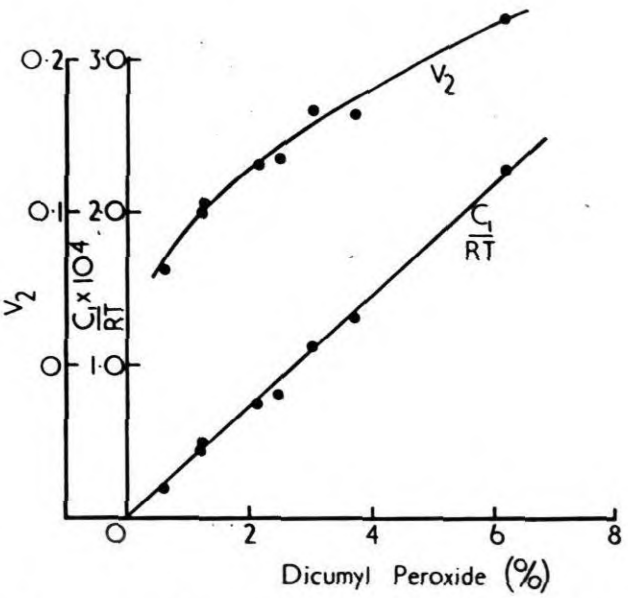


Fig. 5. Variation of v_2 for acrylonitrile–butadiene rubber in chloroform with initial peroxide concentration, together with the resulting values of C_1/RT.

but the failure to account for all the peroxide would be unexplained. Further experiments are planned to find which radical is responsible for initiating polymer chains.

Butadiene–Acrylonitrile Rubber

The results given in Figure 5 show that the dependence of crosslinking upon peroxide is again first-order but the efficiency here is much reduced, the value obtained being 0.96 crosslinks per molecule of peroxide.

The most probable agent causing this reduction is the nitrile group, and to check that such interference is possible the crosslinking efficiency of peroxide in the SBR previously used was measured in the presence of an added nitrile. Succinodinitrile was used in concentrations of up to 10%, and at this level a 68% drop in crosslinking efficiency occurs. Since the nitrile group content of the rubber is about four times that in this mixture, it appears that the observed drop in efficiency in passing from SBR to nitrile rubber could be accounted for by the interference of this group.

The product analyses were complicated somewhat by some interference at 3520 cm.$^{-1}$, the frequency used for cumyl alcohol determination but, by making a zero adjustment for this, satisfactory results were obtained. A value of the ketone/alcohol ratio of 0.3 was obtained. This is rather higher than those obtained with natural rubber, SBR, and *cis*-polybutadiene, and suggests a more difficult hydrogen abstraction step, presumably due to the electron withdrawing effect of the nitrile group.

Polychloroprene

The results obtained with this rubber are shown in Figure 6. The efficiency of crosslinking was here found to be even lower, the calculated value being 0.48 crosslinks per molecule of peroxide.

In this case the plot of C_1/RT against peroxide does not pass through the origin because a certain amount of crosslinking occurs in the absence of peroxide. Such crosslinking is quite common in polychloroprene compounds, and its small extent in the present results may be considered purely additive, since the mechanism by which it occurs is probably quite different from that being studied.

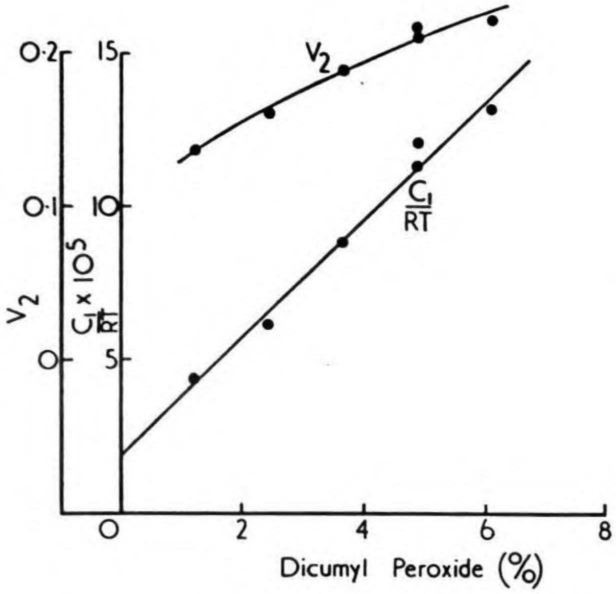


Fig. 6. Variation of v_2 for polychloroprene in chloroform with initial peroxide concentration, together with the resulting values of C_1/RT.

Unfortunately, the product analyses were unsatisfactory; only cumyl alcohol could be measured because of interference at the ketone wavelength. However, only 18.3% of the initial peroxide was recovered as alcohol, suggesting a yet more difficult hydrogen abstraction step than in the case of nitrile rubber and this is, of course, consistent with a lower crosslinking efficiency.

Product Analysis

The results obtained in the present study are combined in Table II with previous results from work with natural rubber.[1,14] As the ease of the hydrogen abstraction reaction (as measured by the ketone/alcohol ratio) increases, the crosslinking efficiency increases. This may be coincidental in the case of SBR and *cis*-polybutadiene, since here a new crosslinking reaction appears; in the case of the remaining rubbers it indicates that the hydrogen abstraction is the primary and, to some extent at least, determining step for crosslinking. The figure of 4.4 for the ketone/alcohol ratio for polychloroprene is quite probably too high by, perhaps, a factor of 2, since in this case a 50% wastage of peroxide molecules occurs. The reaction by which these radicals are lost is at present unknown, but presumably, radical reactions between low molecular weight materials occur.

TABLE II
Results of Product Analyses

Rubber	Crosslinking efficiency, links/molecule	Ketone/alcohol
SBR	12.5	0.07
cis-Polybutadiene	10.5	—
Natural rubber	1.0	0.13 (extrapolated from values at 110–140°C.)
Acrylonitrile–butadiene	1.0	0.3
Polychloroprene	0.5	4.4? (only alcohol measured)

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Synopsis

The crosslinking efficiencies of dicumyl peroxide in SBR, *cis*-polybutadiene, acrylonitrile–butadiene rubber, and polychloroprene have been measured. For the first two rubbers approximately ten crosslinks are formed per molecule of peroxide decomposed, while for the acrylonitrile–butadiene rubber an efficiency close to unity is found. With polychloroprene approximately two molecules of peroxide are used for each crosslink formed. Analysis of the low molecular weight products of the reaction shows that ease of hydrogen abstraction by cumyloxy radicals decreases in the order given above.

Résumé

Nous avons mesuré l'efficacité de pontage du peroxyde de dicumyle dans le SBR, le *cis*-polybutadiène, le caoutchouc acrylonitrile–butadiène et dans le polychloroprène. Dans les deux premiers caoutchoucs il se formait à peu près 10 pontages par molécule de peroxyde décomposé tandis que pour le caoutchouc acrylonitrile–butadiène on trouve une efficacité proche de l'unité. Dans le cas du polychloroprène, il faut approximativement deux molécules de peroxyde pour chaque pontage. L'analyse des produits de réaction de bas poids moléculaire montre que la facilité d'enlever un hydrogène d'un radical cumyloxy- diminue dans l'ordre indiqué plus haut.

Zusammenfassung

Die Vernetzungswirkung von Dicumylperoxyd in SBR, *cis*-Polybutadien, Acrylnitril-Butadienkautschuk und Polychloropren wurde gemessen. Bei den beiden erstgenannten Kautschuksubstanzen werden auf ein Molekül zersetztes Peroxyd etwa 10 Vernetzungen gebildet, während beim Acrylnitril–Butadienkautschuk eine nahe bei eins liegende Vernetzungsausbeute gefunden wird. Bei Polychloropren werden für jede gebildete Vernetzung etwa zwei Peroxydmoleküle verbraucht. Analyse der niedrigmolekularen Reaktionsprodukte zeigt, dass die Leichtigkeit der Wasserstoffabspaltung durch Cumyloxyradikale in der oben angegebenen Reihenfolge abnimmt.

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