VULCANIZATION OF NATURAL RUBBER BY DICUMYL PEROXIDE IN THE PRESENCE OF SULPHUR

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The mode of combining of sulphur and the formation of polar groups during vulcanization of natural rubber with sulphur and dicumyl peroxide was studied. The samples contained from 5 to 30 mg of sulphur and from 0 to 100 mg of dicumyl peroxide per 1 g of rubber. Besides measuring the dependence of the network density and free sulphur content on the time of vulcanization and the mixture composition also the frequency course of the complex permittivity of the samples was followed. From the dielectric measurements the product of the number or polar groups per unit volume and the square of their dipole moment was calculated. The dipole moment referring to one atom of combined sulphur was compared with dipole moments of similar sulphide bonds in low molecular compounds.

Vulcanization of natural rubber proceeds *via* a radical mechanism[1,2]. Primary radicals I• formed by the decomposition of peroxide react with hydrogen of the polymer. The reaction, taking place on α-carbon atom with respect to double bond, produces a polymer radical R•:

$$RH + I^{\bullet} \rightarrow IH + R^{\bullet} \qquad (B)$$

$$R^{\bullet} + R^{\bullet} \rightarrow R-R. \qquad (C)$$
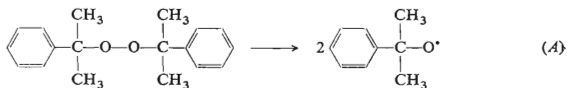
Recombination of radicals R• leads to the formation of links between rubber molecules; the network is formed, the rubber vulcanizes. The reactions described can be substantially influenced by the presence of such admixtures which change either the acidity of the composition or take part in radical reactions. In an acid medium the reaction (A) is suppressed because dicumyl peroxide decomposes *via* an ionic and not *via* a radical mechanism. Sulphur, added to the system — rubber–dicumyl peroxide — does not change the rate of dicumyl peroxide decomposition[3], but it takes part in radical reactions; its combination is faster but the crosslinking efficiency is simultaneously decreased (compare with ref.[4]).

In the present study our attention was focussed on the reactions proceeding in the system during vulcanisation at different molar ratios of dicumyl peroxide to sulphur.

Special interest was paid to the mode of sulphur combination. For studying this system we have used, besides usual physico-chemical methods, also dielectric measurements, which make possible to determine the number of polar groups formed during vulcanisation with sulphur.

The presence of polar groups manifests itself in the shape of the frequency dependence of the components of the complex permittivity $\varepsilon^* = \varepsilon_1 - j\varepsilon_2$. This frequency dependence can be expressed as[5,6]:

$$\varepsilon^*(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \int_0^\infty \frac{F(\tau)}{1 + j\omega\tau}\, d\tau, \qquad (1)$$

where ω is angular velocity, τ is relaxation time and $F(\tau)$ is the distribution function of relaxation times. Parameters ε_s and ε_∞ are limit values of the real part ε_1 of the permittivity at very low and very high frequencies, respectively, with regard to the frequency at which imaginary part of the permittivity reaches the maximum value. For the system natural rubber–sulphur it was shown[5] that the frequency course of the permittivity can be described by the Cole—Cole's distribution function of relaxation times. The course of the real and the imaginary part of the permittivity as a function of angular velocity ω can be then expressed as

$$\varepsilon_1(\omega) = \tfrac{1}{2}(\varepsilon_s - \varepsilon_\infty)\left[1 - \frac{\sinh\{(1-\alpha)\ln\omega\tau_0\}}{\cosh\{(1-\beta)\ln\omega\tau_0\} + \cos\beta\pi/2}\right] \qquad (2)$$

$$\varepsilon_2(\omega) = \tfrac{1}{2}(\varepsilon_s - \varepsilon_\infty)\frac{\cos\beta\pi/2}{\cosh\{(1-\beta\ln\omega\tau_0\} + \sin\beta\pi/2}. \qquad (3)$$

The parameter τ_0 determines the position of the disperse curves on the frequency scale and the parameter β gives the curve width. The difference $\varepsilon_s - \varepsilon_\infty = \Delta\varepsilon$ is so called dielectric increment, the value of which is, in the first approximation, directly related to the number of polar groups n per unit volume and the square of dipole moment μ of one group. Onsager's equation

$$\Delta\varepsilon\, \frac{2\varepsilon_s + \varepsilon_\infty}{\varepsilon_s(\varepsilon_s + 2)^2}\bigg| = \frac{4\pi}{9kT} n\mu^2, \qquad (4)$$

where k is Boltzman's constant and T is absolute temperature, describes the relationship among these parameters more accurately.

EXPERIMENTAL

The compositions of rubber with the additives were prepared on a laboratory roll-mill. Natural rubber "Partially Purified Crepe" (NRPRA) and dicumyl peroxide 95% pure (Perkadox SB) were used in our experiments. The concentration of sulphur varied from 5 to 30 mg and that of dicumyl peroxide from 0 to 100 mg per 1 g of rubber. Disc-shaped samples, having the diameter of 105 mm and the thickness of 1·8 mm, were vulcanized in forms placed in a thermostat heated to 146°C. The vulcanization temperature was controlled by a thermocouple placed directly in the form. The vulcanisation times at this temperature varied from 0·5 to 22 hours. For measuring the dielectric properties an aluminium foil was vulcanized on the sample surface and

served as an electrode. Molecular weight was measured viscometrically; using toluene solutions. Limit viscosity numbers obtained were in the range of $149-244$ cm^3/g. The differencies are due to an impaired reproducibility of milling on the roll-mill and the composition of the mixtures (dicumyl peroxide does not effect the molecular weight in a wide range of concentrations). The content of free sulphur was determined either by the sulphite method or by the polarography[7] of acetone extracts. The network density was determined by measuring equilibrium swelling in benzene and expressed as a number of mol of chains between network cross-links per 1 cm^3 of gel according to the Flory–Rehner's equation[8]

$$v_b = - \frac{\ln(1 - v_r) + v_r + \varkappa v_r^2}{V_s(v_r^{\frac{1}{3}} - v_r/2)} , \tag{5}$$

where V_s is the molar volume of the solvent (cm^3 mol^{-1}); v_r is the volume fraction of rubber in the swollen network, $\varkappa$ is the Huggins solvent-rubber interaction parameter, the value of which is 0·423 (ref.[9]). This value was checked with the aid of the following equation[10]

$$v_{el} = 2C\left(1 - \frac{d}{C\overline{M}_n}\right) + 2F\left(1 - \frac{d}{C\overline{M}_n}\right)^a , \tag{6}$$

in which C denotes the number of cross-links (it was calculated from dicumyl peroxide concentration, assuming that one molecule of peroxide forms one cross-link of the network[11,12]), d is the polymer density expressed in g cm^{-3}, M_n is the number-average molecular weight of the polymer before crosslinking, F is the concentration of physical cross-links in mol cm^{-3} (the value for natural rubber is $0.4 \cdot 10^{-4}$ mol cm^{-3}), a is the empirical constant, the value of which is $a = 3$.

The dielectric properties of the samples were measured in the frequency range of $4 \cdot 10^1$ to $3 \cdot 10^5$ Hz by means of a Schering bridge, type Ulrych 921. The frequency dependence of the real and the imaginary part of the permittivity was measured at $-30°C$ (at this temperature the imaginary part of the permittivity (absorption curve) reaches maximum approximately in the middle of the frequency range selected).

Dielectric increment $\Delta\varepsilon$ was determined from the value of the imaginary part of the permittivity ε_{2m} in the maximum of the absorption curve and from the values of parameter β of the Cole–Cole's distribution function. It holds that,

$$\Delta\varepsilon = \varepsilon_{2m} \frac{2(1 + \sin \beta\pi/2)}{\cos \beta\pi/2} , \tag{7}$$

Parameter β was determined from the width of the absorption curve at its half height. The value of the product $n\mu^2$ was calculated according to the equation (4); the values ε_s and ε_∞ were determined from circular diagrams. Probable error in determination of the product $n\mu^2$ is about 5%.

RESULTS AND DISCUSSION

From the comparison of the network densities v_b, determined by swelling according to equation (5), with the values calculated from equation (6), it follows, that the selected value of the parameter $\varkappa = 0.423$ is valid in the network density range up to $4 \cdot 10^{-4}$ mol cm^{-3}; for higher network densities this value of $\varkappa$ can not be used in equation (5). For natural rubber dicumyl peroxide is a quantitative crosslinking agent having the efficiency near to 1. Deviation of some importance

are observed at low dicumyl peroxide concentration when the crosslinking efficiency is lowered by the admixtures present in the rubber[13].

The addition of sulphur to the system natural rubber–dicumyl peroxide lowers, substantially, the crosslinking efficiency of dicumyl peroxide. The highest decrease of crosslinking efficiency is caused by the initial additions of sulphur and then the effect of sulphur gradually diminishes and finally, at a certain dicumyl peroxide–sulphur molar ratio, further addition of sulphur exhibits no effect on crosslinking density (Fig. 1). At low concentration of dicumyl peroxide in the composition, the crosslinking density, after an initial decrease, gradually increases with increasing amount of combined sulphur. This increase of crosslinking density corresponds to a nonaccelerated vulcanization of rubber with sulphur.

FIG. 1

Dependence of Network Density on the Amount of Sulphur and Dicumyl Peroxide (mg per 1 g of rubber)

Parameters at individual curves denote peroxide concentrations.
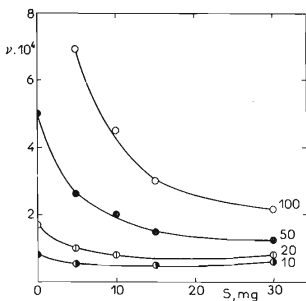
The addition of dicumyl peroxide to the composition–sulphur manifests itself mainly in an increased rate of sulphur combination. Dicumyl peroxide acts as an accelerator (Fig. 2a). The effect of dicumyl peroxide on the rate of sulphur combination is remarkable: at the sample which contained 100 mg of dicumyl peroxide 90% of sulphur was incorporated in the structure during 1·7 hours, while the time needed for attaining the same amount of combined sulphur without addition of dicumyl peroxide was 9·5 hours.

As the reaction products of dicumyl peroxide do not effect the rate of vulcanization[14,15], the rate of crosslinking depends only on the ratio of sulphur to peroxide (r). We have assumed that the crosslinking process obeys first order law and therefore it should hold that

$$v_t = v_m[1 - e^{-kt}], \tag{8}$$

where v_m is the maximum value of the crosslinking density for the given system being vulcanized (mol cm^{-3}); v_t is the crosslinking density at the time of vulcanization t, k is the rate constant (min^{-1}).

The values of crosslinking densities at gradual vulcanization were used for determining the rate constants of crosslinking:

r		0·633	1·58	2·0	2·5	3·17	4·75	9·50	19·0
$k \cdot 10^2$, min^{-1}:		2·3	2·8	3·7	3·4	3·2	2·2	2·1	2·1	2·2

With increasing addition of dicumyl peroxide to the rubber–sulphur composition, the rate constant increases and attains the maximum value at the molar ratio of peroxide to rubber $r = 2·2$. Further increase of peroxide concentration has an adverse effect; the rate constant decreases and finally attains the value characteristic for dicumyl peroxide only. The appearance of maximum can be explained by the fact that the formation of cross-links containing sulphur is easier than the formation of carbon — carbon cross-links. The rate constant can be increased up to a certain limit because if an excess of dicumyl peroxide is used the part of sulphide cross-links is so small that it does not effect the value of the crosslinking rate constant. The ratio of combined sulphur increases both with the time of vulcanization and with the increasing ratio r (Fig. 2b). The vulcanisation time five hours is important as a time interval during which, under our experimental conditions, all dicumyl peroxide is decomposed. To attain, simultaneously, complete combination of sulphur, the molar ratio of dicumyl peroxide to sulphur has to be at least 2·5. At lower molar ratios, the complete combination of sulphur can not be obtained before the time interval required for full decomposition of peroxide. With further increase of the vulcanisation time the part of combined sulphur increases, but the increase corresponds to a nonaccelerated
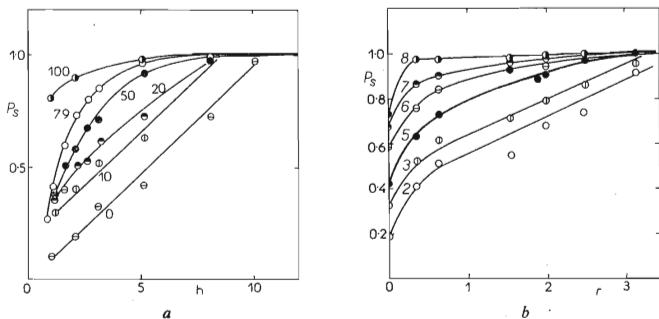

Fig. 2

Dependence of the Ratio of Combined Sulphur on Time of Vulcanization (a) and on Molar Ratio of Dicumyl Peroxide to Sulphur, r (b).

Parameters at individual curves denote: a peroxide concentration in mg per 1 g of natural rubber containing 30 mg of sulphur per 1 g of rubber, b time of vulcanization (h).

reaction of sulphur with the rubber. At higher concentrations of dicumyl peroxide, when the molar ratio $r > 2.5$, the complete bonding of sulphur is attained during a shorter time interval than that needed for full decomposition of dicumyl peroxide. From the results of crosslinking efficiency measurements follows, that even if all sulphur is combined, the crosslinking efficiency of the peroxide does not approximate the value of one. Hummel and Desilles[4] have found that it is needed to add per 1 mol of sulphur (S_8) $3.7 - 10$ mol of dicumyl peroxide, in order to obtain the same cross-linking density as before the addition of sulphur. This indicates that the radicals originated from the peroxide react also with already combined sulphur. When evaluating the amount of dicumyl peroxide needed for complete combination of sulphur, we have to consider also other effects which may take place at this process. Certain part of sulphur reacts with rubber without the participation of radicals originated from peroxide, and besides that, the radicals form the cross-links without sulphur, i.e. the carbon–carbon links. The measurements of crosslinking densities and the content of combined sulphur in the system studied were complemented by electric measurements, which enabled us to determine the multiple of the number of polar groups per unit volume and the square of their dipole moments μ.

For natural rubber, according to equation (4), we have determined the value of $n\mu^2 = 2.0 \pm 0.2 \cdot 10^{-16}$ sC^2 cm^{-1}. This relatively small polarity can be explained either by the polarity of the monomer unit or by the presence of oxygen-containing groups formed on the chain during the manufacturing process. If we consider only the polarity of isoprene itself, then to the determined value of $n\mu^2$ would correspond the value of monomer unit dipole moment of about 0.16 D, which is a plausible value.

For dicumyl peroxide vulcanisates without sulphur, the dependence of $n\mu^2$ on peroxide concentration is linear (Fig. 3). We assume, that polar groups are predominantly formed by oxygen-containing groups formed during vulcanization, and to a smaller extent by oxygen-containing compounds by side reactions of peroxide with rubber. The dependence of $n\mu^2$ on sulphur concentration is, in the concentration range studied, also linear; the slope of which is the same for samples containing no peroxide or samples with peroxide; in the last mentioned case the line is shifted to higher values because of the dicumyl peroxide contribution. By calculating the average dipole moment corresponding to one sulphur atom from this slope, we obtain at least some idea of the mode of sulphur incorporation. In our case we have obtained $\mu = 1.71$ D, which is a slightly higher value than the value of dipole moments of low-molecular weight monosulphides[16,17] (e.g. propyl sulphide 1.55 D butyl sulphide 1.57 D, amyl sulphide 1.58 D). On the other hand cyclic tetrahydrothiophene has the dipole moment of 1.87 D. We assume, that at the process of incorporation of sulphur to rubber, besides the network crosslinks are also formed similar five- or six-member rings. Double bonds, present in these rings, would slightly lower the dipole moment of sulphur with respect to saturated ring of tetrahydrothiophene and therefore the dipole moment of sulphur bound to rubber can be expected to be about 1.7 . D — as it was found. As we have found the same dipole moment corresponding to one sulphur atom for vulcanizates with dicumyl peroxide, we assume, that also in this case the sulphur is combined analogously.

The value of $n\mu^2$ increases with the time of vulcanization and after a certain time interval, depending on the composition of the system, attains the maximum value.

The dependence of these maximum values on the concentration of dicumyl peroxide and sulphur was discussed previously. These maximum values were mostly obtained when the time of vulcanization was longer then the time interval needed either for the complete combination of sulphur or for the complete dicumyl peroxide decomposition. If we denote the value of $n\mu^2$ at the vulcanization time t as $(n\mu^2)_t$ and its maximum value as $(n\mu^2)_{max}$ and if we then compare the course of the time dependence of their ratio $P_{el} = (n\mu^2)_t/(n\mu^2)_{max}$ with the time dependence of the combined sulphur ratio P_s, we find, that the combination of sulphur is faster than the increase of P_{el} (Fig. 4). This means, that with increasing time of vulcanization increases the dipole moment corresponding, in average, to one atom of combined sulphur. This effect can be observed for both samples crosslinked by sulphur only and crosslinked by sulphur and dicumyl peroxide. Some part of combined sulphur must have a lower polarity and therefore it has to be combined in the form of polysulphides; this is in agreement with the results of the studies of vulcanization. This difference is gradually disappearing as polysulphides are being transformed to di- and monosulphides. This phenomenon becomes particularly distinct when an excess of peroxide is used; sulphur combination is very fast, but the amount of relaxing groups increases less rapidly. In the composition containing, *e.g.* 30 mg of sulphur and 100 mg of dicumyl peroxide per 1 g of rubber, 92% of sulphur was combined after 2 hours of vulcanization under our experimental conditions, but the ratio P_{el} during this time interval
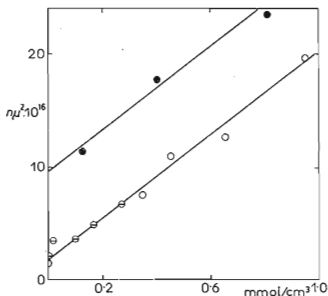

FIG. 3

Dependence of $n\mu^2$ on Dicumyl Peroxide Concentration ⊖ and Sulphur (○ without peroxide, ● with 100 mg of peroxide per 1 g of rubber)
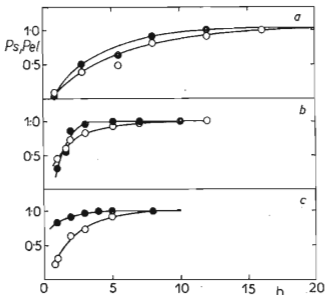
FIG. 4

Dependence of the Ratio of Combined Sulphur P_s ● and of the Ratio P_{el} ○ on the Time of Vulcanization

$P_{el} = (n\mu^2)_t/(n\mu^2)_{max}$. Concentration of sulphur (peroxide) in mg per 1 g of rubber: *a* 15 (0), *b* 15 (100), *c* 30 (100).

attained only 61% of its maximum value. The values of $n\mu^2$ are still increasing even if the vulcanization time is longer than that required for complete sulphur combination or dicumyl peroxide decomposition. This means, that the transformation of polysulphidic sulphur to monosulphidic one proceeds also after the time interval mentioned.

The mechanism of sulphur combination and the formation of network cross-links in the ternary system rubber–sulphur–dicumyl peroxide is inevitably quite complex, because different types of radicals of different reactivity can be formed and also the possibility of formation of mono-, di- and polysulphides would not make it simpler. From the results obtained, we can put forward the following reaction mechanism: Dicumyl peroxide decomposes according to reaction (A) to form primary radicals. We assume, that these primary radicals I˙ react only to a small extent with sulphur and that the main reaction takes place between radical I˙ and α hydrogen on methylene carbon of polyisoprene forming thus polyisoprenyl radical R˙ (reaction B), which forms with sulphur a polysulphidic radical and by recombination with another R˙ radical a polysulphide. The polysulphide formed can be either intra or intermolecular, whether the recombination took place with another or with the same molecule of rubber:
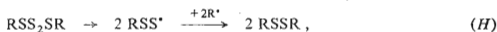
$$R^\bullet + S_8 \rightarrow RSS_6S^\bullet, \qquad (D)$$

$$R^\bullet + RSS_6S^\bullet \rightarrow RSS_6SR. \qquad (E)$$

Polysulphidic radical $RSS_6S^\bullet$ and also polysulphide are labile species which decompose to lower polysulphides and sulphur. Therefore the amount of dicumyl peroxide required for combining 1 mol of S_8 depends on the amount of sulphur released at this decomposition. We think, that tetrasulphides are formed most probably as follows:

$$RSS_6SR \rightarrow RSS_2SR + 4S, \qquad (F)$$

$$RSS_6S^\bullet \rightarrow RSS_2S^\bullet + 4S, \qquad (G)$$
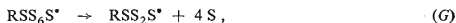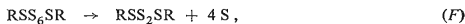
Reactions (D), (E), (F) and (G) indicate, that this reaction scheme requires 4 mol of R˙ radicals for combining 1 mol of S_8 and therefore the molar ratio of dicumyl-peroxide to sulphur is equal to 2, which is in good agreement with the value of r we have found. The decomposition of polysulphides to sulphides which would have less than 4 atoms of sulphur in the molecule can be almost ruled out or, in other words, these lower sulphides may be formed only to a very small extent because, for combining such an amount of sulphur released at this process would be needed at least 4 mol of dicumyl peroxide and therefore it would be in contradiction with our results. Sulphur is also combined without the participation of radicals formed from dicumyl peroxide. Polysulphides are again the primary products of these reactions.

Regardless the way by which they were formed — with or without the participation of radicals — they are gradually transformed to di- and monosulphides. Radicals $R^\bullet$ also participate in these reactions.

$$RSS_2SR \;\rightarrow\; 2\,RSS^\bullet \;\xrightarrow{+2R^\bullet}\; 2\,RSSR\,, \qquad\qquad (H)$$

$$RSSR \;\rightarrow\; 2\,RS^\bullet \;\xrightarrow{+2R^\bullet}\; 2\,RSR\,. \qquad\qquad (J)$$

Radical $R^\bullet$ and radicals $RS^\bullet$ are polymeric and therefore their mobility in rubber and particularly in the network being formed is very limited. To facilitate the contact and recombination according to reactions (H) and (J), it is necessary to assume the transfer of $R^\bullet$ radical from the place where it was originated. The vulcanisate structure can be visualised as:
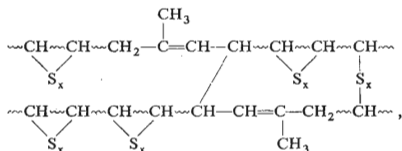
where x is predominantly equal to 1 and to a smaller extent to 2; at lower peroxide concentrations, or at shorter vulcanisation times, it may become equal up to 4. The network cross-links are partly formed by C—C bonds and partly by C—S_x—C bonds. Most of sulphur is incorporated in five- or six-member rings.

REFERENCES

1. Moore C. G., Watson W. F.: J. Polymer Sci. *19*, 237 (1956).
2. Rado R.: *Transfer Reactions of Polymers Initiated by Peroxides*. Alfa, Bratislava 1970.
3. Hummel K.: Kautschuk u. Gummi *15*, WT 1 (1962).
4. Hummel K., Desilles J.: Kautschuk u. Gummi—Kunststoffe—Asbest *15*, WT 492 (1962).
5. Bakule R.: *Lecture at the Conference Plastko*, Mariánské Lázně 1970.
6. Mullins L., Watson W. F.: J. Appl. Polymer Sci. *1*, 245 (1959).
7. Kubík J., Zytka A.: *Testing Methods in Rubber Industry*. Published by SNTL, Prague 1962.
8. Flory P. J., Rehner J. J.: J. Chem. Phys. *11*, 521 (1943).
9. Meissner B., Klier J., Kuchařík S.: J. Polymer Sci. *16*, 793 (1967).
10. Meissner B.: J. Polymer Sci. *16*, 781 (1967).
11. Parks C. R., Lorenz O.: J. Polymer Sci. *50*, 287 (1961).
12. Lorenz O., Parks C. R.: J. Polymer Sci. *50*, 299 (1961).
13. Bristow G. M., Moore C. G., Russel R. M.: J. Polymer Sci. *3*, 3893 (1965).
14. Kraus G.: Rubber World *135*, 65 (1956).
15. Ducháček V., Brajko V.: Chem. průmysl *22*, 178 (1972).
16. Brown W. F.: *Dielectrics, Handbuch d. Physik* XVII, Berlin 1956.
17. Weson L. C.: *Tables of Dielectric Dipole Moments*. Cambridge Univ. Press, 1948.