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ON THE MECHANISM OF VULCANIZATION IN THE PRESENCE OF 2-MERCAPTOBENZOTHIAZOLE

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The mechanism of action of one of the most widespread accelerators of vulcanization, 2-mercaptobenzothiazole (captax, MBT), has not been sufficiently elucidated. L. Vistinghausen ([1]) and B. A. Dogadkin and D. M. Pevzner (published in 1951) showed that MBT is consumed during vulcanization; however, no quantitative regularities were obtained because of the imperfection of the methods for determining the consumption of MBT.

In the present work a preparation of MBT labeled with the radioisotope S^{35} in the thiazole ring was used. The synthesis of this preparation was carried out as follows. First, MBT labeled in both sulfur atoms was synthesized from phenyl mustard oil and elemental S^{35} ([2]). Then the MBT obtained was heated in a sealed ampoule with an excess of elemental inactive sulfur at 140° for 6 hours. Under these conditions the exchange reaction between elemental sulfur and the sulfur of the sulfhydryl group of MBT reaches equilibrium ([3]). The activity of the MBT obtained decreased by half. Thus the benzothiazolyl radical was labeled; moreover, the radioisotope S^{35} introduced into the MBT molecule does not exchange, under the conditions of vulcanization, with elemental sulfur, which made it possible to measure in parallel the rate of sulfur addition and the rate of accelerator addition to the rubber.

Table 1

Composition of mixture	Vulcanization temperature (°C)	Vulcanization time (min.)	Bound S, elemental (g-atom/g · 10^4)	Bound MBT (mol/g · 10^5)	Number of cross-links (mol/g · 10^5)	Number of attached MBT mol., per 1 cross-link
NR–100S–4MBT–2Neozone D–1ZnO–5Stearic acid–2	121	0	–	1.00	–	–
NR–100S–4MBT–2Neozone D–1ZnO–5Stearic acid–2	121	20	3.52	2.84	6.27	0.29
NR–100S–4MBT–2Neozone D–1ZnO–5Stearic acid–2	121	40	5.10	3.16	8.97	0.24

Composition of mixture	Vulcanization temperature (°C)	Vulcanization time (min.)	Bound S, elemental (g-atom/g · 10^4)	Bound MBT (mol/g · 10^5)	Number of cross-links (mol/g · 10^5)	Number of attached MBT mol., per 1 cross-link
NR—100S—4MBT—2Neozone D—1ZnO—5Stearic acid—2	121	60	5.65	3.72	10.80	0.25
NR—100S—4MBT—2Neozone D—1ZnO—5Stearic acid—2	121	80	6.22	4.11	10.26	0.30
NR—100S—4MBT—2Neozone D—1ZnO—5Stearic acid—2	121	1.0	7.16	4.12	10.88	0.28

Composition of mixture	Vulcanization temperature (°C)	Vulcanization time (min.)	Bound S, elemental (g-atom/g · 10^4)	Bound MBT (mol/g · 10^5)	Number of cross-links (mol/g · 10^5)	Number of attached MBT mol., per 1 cross-link
NR—100S—4MBT—2Neozone D—1ZnO—5Stearic acid—2	121	120	8.38	4.22	14.0	0.23
SKB—100S—2MBT—1Neozone D—1	140	0	—	0.37	—	—
SKB—100S—2MBT—1Neozone D—1	140	5	3.88	0.47	0.45	0.20
SKB—100S—2MBT—1Neozone D—1	140	10	5.04	0.56	0.91	0.20
SKB—100S—2MBT—1Neozone D—1	140	20	5.97	0.92	1.20	0.45

Composition of mixture	Vulcanization temperature (°C)	Vulcanization time (min.)	Bound S, elemental (g-atom/g · 10^4)	Bound MBT (mol/g · 10^5)	Number of cross-links (mol/g · 10^5)	Number of attached MBT mol., per 1 cross-link
SKB–100S–2MBT –1Neozone D –1	140	30	5.95	1.38	1.60	0.63
SKB–100S–2MBT –1Neozone D –1	140	40	5.95	1.36	1.66	0.59
SKB–100S–2MBT –1Neozone D –1	140	60	6.11	1.66	2.19	0.58

Vulcanization was studied on mixtures of natural rubber (NR), extracted and precipitated from a benzene solution, and sodium-butadiene rubber (SKB). The composition of the mixtures is given in Table 1. In the vulcanizates, after extraction with acetone, bound sulfur (elemental and that included in the accelerator) was determined by oxidizing the vulcanizate with a mixture of HNO_3 and Br_2 in the presence of MgO ([4]). The MBT that had attached to the rubber was determined by a radiometric method ([5]). From the maximum swelling of the vulcaniza-

···in xylene the number of crosslinks was calculated from the Flory–Rehner equation ([6]).

Fig. 1 presents data on the kinetics of the addition of sulfur and MBT during vulcanization of NR at 121°. The reactions of addition of sulfur and of the accelerator to rubber proceed in parallel. In the presence of the activator ZnO, a more intense addition of the accelerator is observed, whereas the activator has no effect on the rate of sulfur addition.

Fig. 1. Kinetics of the addition of sulfur (1) and MBT during vulcanization of natural rubber in a mixture with ZnO (2) and without ZnO (3)

A small amount of MBT is added to the rubber already on the rolls during preparation of the compound. To elucidate the mechanism of MBT addition to rubber during milling, purified natural rubber* was milled for 20 min under conditions excluding the action of atmospheric oxygen, with the addition of 1 part by weight of MBT. The plasticate was then separated into fractions by lowering the temperature of the solution in a binary solvent (benzene–methyl alcohol). The intrinsic viscosity of each fraction in benzene solution and the amount of MBT added were determined by a radiometric method. From the data of Table 2 it is seen that the amount of added MBT increases (up to a certain limit) with increasing serial number of the fraction, i.e., with decreasing molecular weight. Such a phenomenon can be explained by the fact that MBT adds to polymer radicals formed during mechanical rupture. Rupture of the molecular chains of rubber most probably occurs at the bond connecting the allylic groupings, since this bond is weakened by the effect of conjugation by approximately 45 kcal/mole. The radicals formed interact with MBT molecules, apparently according to the scheme:

Table 2

Fraction No.	$[\eta]/[\eta]_0$	Amount of bound MBT (mol/l · 10^3)	$[\eta]$
Unfractionated	–	–	12.0
1	0.053	3.21	27.0
2	0.091	5.45	24.5
3	0.110	6.22	9.2
4	0.071	4.28	8.0
5	0.090	5.39	5.5

$$\sim CH_2{-}C(CH_3){=}CH{-}CH_2{-}CH_2{-}C(CH_3){=}CH{-}CH_2 \sim \xrightarrow{\text{rupture}} 2 \sim CH_2{-}C(CH_3){=}CH{-}CH_2^{\bullet}$$

$$+\ C_6H_4\begin{smallmatrix}N\\ \\ S\end{smallmatrix}CSH \longrightarrow \sim CH_2{-}C(CH_3){=}CH{-}CH_2{-}SC\begin{smallmatrix}N\\ \\ S\end{smallmatrix}C_6H_4 + \sim CH_2{-}C(CH_3){=}CH{-}CH_3.$$

As a result, the MBT content in the low-molecular-weight fractions is substantially greater than in the high-molecular-weight fractions. If MBT reacted at the sites of double bonds, then in this case no dependence of its distribution over the fractions of the plasticized rubber should have been observed.**

* The rubber was purified by extraction with cold acetone in an atmosphere of pure nitrogen for 20 h.

** In the scheme given, MBT reacts in the thiol form; interaction in the thione form leads to the same result with respect to distribution among the fractions.

Fig. 2

Figure 1: Fig. 2

Fig. 3

Figure 2: Fig. 3

The MBT that has combined with the rubber during milling, although it accelerates the vulcanization process, does so to a substantially lesser degree.

Figure 2 presents the kinetics of the addition of sulfur and MBT during the vulcanization of SKB. In this case as well, a correspondence is observed between the kinetic curves for the addition of sulfur and MBT. By the moment of complete addition of sulfur (30 min), the rate of MBT addition sharply decreases, although the concentration of the latter in the mixture is still sufficiently high. This fact indicates that the reaction of MBT with rubber proceeds at a substantial rate only in the presence of sulfur, which agrees with the data ([7]) on the catalytic action of sulfur on the addition of mercaptans to olefins. Indeed, our experiments showed that the additional introduction of sulfur into the vulcanizate during its swelling (at the stage when free sulfur has been exhausted) leads to a new acceleration of the reaction of MBT addition to rubber (Figs. 2, 3).

Fig. 2. Kinetics of the addition of MBT (1) and sulfur (2) during vulcanization; 3—after introduction of 2% sulfur by diffusion from solution

The kinetics of the addition of sulfur to rubber in the presence of MBT is satisfactorily described by the equation for a first-order reaction with respect to sulfur. The kinetic constants calculated from this equation depend linearly on the concentration of MBT (Fig. 3). The activation energy for the vulcanization of SKB, for the commonly used ratios of sulfur and accelerator, is 20.6 kcal/mol.

Fig. 3. Dependence of the kinetic constants of sulfur addition on the concentration of MBT

The ratio of consumed MBT to the number of cross-links (see Table 1) is substantially less than unity and remains constant during the main period of vulcanization. Calculation shows that for one act of accelerator addition there are about two acts of cross-linking.

The experimental data presented indicate the coupled character of the interaction of sulfur, MBT, and rubber. This interaction apparently follows the scheme proposed earlier ([8]):

$$C_6H_4 \quad \overset{N}{\underset{S}{C{=}}}{-}SH + S_8 \rightleftarrows C_6H_4 \quad \overset{N}{\underset{S}{C{=}}}{-}S^* + HS_8^* \rightleftarrows C_6H_4 \quad \overset{N}{\underset{S}{C{=}}}{-}S_{xH} + S_{8-x}^{**}$$

I II III

Under vulcanization conditions the radical

$$C_6H_4 \quad \overset{N}{\underset{S}{C{=}}}{-}S^*$$

either interacts with the α-methylene groups of the molecular chains of the rubber (being restored to MBT), or adds at the site of double bonds. In both cases polymer radicals are formed, capable of

interact with one another or with low-molecular-weight active groups. The radical $HS_n^\bullet$ adds to rubber molecules with the formation of polymeric permercaptans; oxidation of the latter, or their interaction with double bonds, leads to the formation of polysulfide bonds between rubber chains. Recombination of radicals I and II causes the formation of 2-benzothiazolyl hydropolysulfide (III), which liberates a variable number of sulfur atoms in the form of biradicals that directly bring about the joining of rubber molecular chains at the sites of double bonds.

In the complex sequence of the indicated vulcanization reaction, the initial act is the interaction of MBT with sulfur. For this reason, the rate of sulfur addition to rubber, as already indicated, is linearly dependent on the concentration of MBT.

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Note: Figure translations are in progress. See original paper for figures.