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Abstract

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ON THE INTERACTION OF DI-2-BENZTHIAZYL DISULFIDE WITH RUBBERS OF DIFFERENT STRUCTURE

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It had previously been established that vulcanization accelerators (sulfenamide and disulfide derivatives of 2-mercaptobenzothiazole) chemically interact with rubber (^{1}-^{3}), accompanied by a structuring effect. The latter was regarded as a consequence of the formation of accelerator radicals and their interaction with the molecular chains of the rubber.

In the present communication we present data characterizing the reactivity of rubbers of different structure with respect to thiobenzthiazyl radicals $RS^{\cdot}$, where R = benzothiazyl group. The objects of investigation were natural rubber, butadiene-styrene rubber (SKS-30A), sodium-butadiene rubber (food-grade SKB), and butadiene rubber (SKD). Thiobenzthiazyl radicals, reacting with rubber, are capable of accepting hydrogen from its molecular chains, which leads to the appearance of polymer radicals and to the formation of 2-mercaptobenzothiazole (^{1},^{2}). Thus, from the amount of 2-mercaptobenzothiazole formed one may judge the interaction of thiobenzthiazyl radicals with rubber.

As the source of thiobenzthiazyl radicals we used a mixture consisting of di-2-benzthiazyl disulfide and N-cyclohexyl-2-benzthiazolesulfenamide, since when this mixture is used a larger amount of $RS^{\cdot}$ radicals is formed than under the separate action of the indicated accelerators (^{4},^{5}). It was established that at 140° thiobenzthiazyl radicals $RS^{\cdot}$ do not abstract hydrogen either from solvent molecules—xylene—or from cyclohexylamide groups, but are capable of readily dehydrogenating rubber. The kinetics of formation of 2-mercaptobenzothiazole (2-MBT) in systems containing rubbers differing in their structure is presented in Fig. 1. As is evident from the data given, sodium-butadiene rubber SKB is dehydrogenated most strongly (curve 1). In the case of natural and butadiene (SKD) rubber, containing a 1-4 cis-structure (curves 3 and 4), only the formation of traces of 2-mercaptobenzothiazole is observed. Dehydrogenation of natural rubber in appreciable amounts was also not observed when the experiments were carried out in vacuum. Butadiene-styrene rubber, in its ability to undergo dehydrogenation, occupied an intermediate position (Fig. 1, curve 2) between sodium-butadiene and natural rubbers.

The data obtained indicate that the difference in the rate of dehydrogenation of rubbers during their interaction with thiobenzthiazyl radicals is associated with the presence in these rubbers of different carbon-hydrogen bonds. As in the case of hydrocarbon oxidation, tertiary C—H bonds, which are more readily dehydrogenated, are the most active. Sodium-butadiene rubber (SKB), owing to the presence of a large number of butadiene units in the 2-1 position, contains the greatest number of tertiary C—H bonds in comparison with other rubbers. In this case the amount of 2-mercaptobenzothiazole formed at a reaction duration of 60 min. is 24% of the initial disulfide.

(Table 1). In butadiene-styrene rubber the tertiary C—H bonds are present in butadiene units linked in the 2—1 position, and also in styrene groupings; moreover, the number of these bonds is smaller than in the case of SKB rubber. Natural rubber and SKD rubber, on the other hand, contain almost no tertiary

Table 1

Rubber grade	Structural formula	Number of double bonds in position 4 —1, %	Amount of 2-MBT formed (after 60 min heating at 140°); % of the initial disulfide
SKB	$-CH_2-CH{=}CH-CH_2-CH_2-CH-CH_2-CH-CH_2-CH{=}CH-CH_2-\vert\vert CHCH\ \ CH_2CH_2$	30	24
SKS-30A	$-CH_2-CH{=}CH-CH_2-CH_2-CH-CH_2-CH{=}CH-CH_2-CH_2-CH-\vert\ CH\ CH_2$	78	11.5
NR	$-CH_2-CH{=}C(CH_3)-CH_2-CH_2-CH{=}C(CH_3)-CH_2-$	94—97	Traces
SKD	$-CH_2-CH{=}CH-CH_2-CH_2-CH{=}CH-CH_2-$	94—97	Traces

Figure 1: Kinetics of formation of 2-mercaptobenzothiazole

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Figure 2: Change in the maximum swelling of mixtures

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C—H bonds, and in the presence of these rubbers under the experimental conditions only small amounts of 2-mercaptobenzothiazole are observed to form. An analogous fact—the differing reactivity of rubbers differing in the content of structural units 1—4 and 1—2 toward tetramethylthiuram disulfide radicals—was established in the work of B. A. Dogadkin and V. A. Shershnev (6).

Fig. 1. Kinetics of formation of 2-mercaptobenzothiazole during the interaction of rubbers with accelerators (di-2-benzthiazyl disulfide + N-cyclohexyl-2-benzothiazolesulfenamide) in xylene at 140°: 1 —SKB; 2 —SKS-30A; 3 —NR; 4 —SKD.

Fig. 2. Change in the maximum swelling of rubber + di-2-benzthiazyl disulfide mixtures (5.0 parts by weight) as a function of the duration of their heating at 143°: 1 —SKB; 2 —SKS-30; 3 —NR.

It was of interest to determine whether the different reactivity of rubbers toward thiobenzothiazolyl radicals (manifested in dehydrogenation of the rubber and, consequently, in the formation of polymer radicals) affects their structuring, i.e., the formation of crosslinks characteristic of a vulcanizate. The source of the thiobenzothiazolyl radicals dehydrogenating the rubber is di-2-benzthiazyl disulfide. The interaction of the accelerator with the rubber was carried out under press-vulcanization conditions in the bulk rubber at 143°. Natural, butadiene-styrene (SKS-30), and sodium-butadiene (SKB) rubbers were used with 5.0 parts by weight of di-2-benzthiazyl disulfide. The formation

crosslinks between rubber molecular chains was estimated from data on swelling in xylene of rubber compounds heated for different times. As can be seen from the data presented in Fig. 2, rubbers, in their ability to become structured under the influence of thiobenzthiazolyl radicals, are arranged in the same order as in their ability to undergo dehydrogenation. The greatest structuring is observed for sodium-butadiene rubber, and the least for natural rubber.* For the case of sodium-butadiene rubber, the number of crosslinks corresponding to one act of abstraction of a hydrogen atom from the rubber by thiobenzthiazolyl radicals was calculated. The number of crosslinks was determined from data on the maximum swelling of the rubber in xylene, using the corresponding nomograms ([7]). The number of hydrogen atoms accepted from the rubber was calculated from the amount of 2-mercaptobenzthiazole released from the rubber compound upon treatment with hot acetone.

Table 2

Number of crosslinks arising in SKB rubber upon heating with di-2-benzthiazyl disulfide (5.0 parts by weight)

Heating time, min	Number of crosslinks $N_c \cdot 10^{-19}$ ml^{-1}	Number of crosslinks per 1 H atom accepted from the rubber	Number of H atoms accepted from the rubber per 1 crosslink
60	1.59	0.17	5.8
120	2.38	0.26	3.8
180	3.62	0.4	2.5

Calculation of the number of H atoms accepted from the rubber per one crosslink (Table 2) shows that several acts of abstraction of a hydrogen atom from the polymer chain correspond to the formation of one crosslink.

The experimental data described in this communication make it possible to regard the structuring of rubbers under the influence of thiobenzthiazolyl radicals mainly as the result of dehydrogenation of the rubber and subsequent recombination of polymer radicals.

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* In the experiments of B. A. Dogadkin and V. A. Shershnev ([6]) with tetramethylthiuram disulfide, the opposite dependence was observed. This difference may be connected with a difference in the activity of the TMTD and DBTD radicals, as well as with the conditions under which the experiments were carried out, in particular with the possible influence of sulfur and oxygen.

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