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Abstract

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On the Destruction of Molecular Chains and the Breakdown of Cross-Links in the Aging of Vulcanizates

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In sulfur vulcanizates, the bond energy between sulfur atoms in cross-bridges may differ substantially from the energy of the bonds in the molecular chains of polymers; therefore, as is known (1), the thermal decomposition of polysulfide bonds can be induced at considerably lower temperatures than the decomposition of molecular chains in vulcanizates. It was established by one of us (2) that the thermal decomposition of sulfur bonds in vulcanizates causes inhibition of the oxidation developing in the polymer chains. Consequently, the destruction of chains and the breakdown of cross-links cannot be regarded as independent processes. However, the difference in the rates of destruction and breakdown is sometimes so great that these processes can be separated.

There are different views in the literature as to which elements in the structure of vulcanizates are affected by aging processes. Tobolsky (3) asserts that the chemical relaxation of stress is caused by oxidative destruction of the polymer chain of the vulcanizate, independently of its structure. In contrast, Watson et al. (4) believe that the breakdown of the vulcanizate network is a consequence of rupture of transverse chemical bonds.

In the present investigation it was established that, depending on the composition of the vulcanizate and the experimental conditions, both the polymer chains and the cross-links forming the three-dimensional network of vulcanizates may be involved in the aging process.

It is known that small chemical transformations of polymers cause substantial changes in mechanical properties; therefore, in the early stages of aging, when it is still impossible to detect the reaction that has begun by chemical methods, mechanical methods are sufficiently sensitive.

We investigated the chemical relaxation of stress in vulcanizates differing both in the nature of the cross-links and in the reactivity of the polymer chain toward oxygen.*

The investigation of chemical stress relaxation was carried out on a specially constructed instrument—a uniaxial-compression relaxometer (5). The degree of

Figure 1

Figure 1: Figure 1

deformation of the specimens was kept constant throughout the entire experiment and was equal to 30% compression. Before the beginning of the experiment the specimens, in the deformed state, were held for two days at room temperature in order to eliminate physical relaxation.

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* As the principal objects of investigation, vulcanizates based on natural and sodium-butadiene rubbers were selected, prepared according to the following formulations: I rubber—100.0; stearic acid—2.0; zinc oxide—5.0; phenyl-β-naphthylamine—2.0; tetramethylthiuram disulfide—3.0; II rubber—100.0 parts by weight; stearic acid—2.0; zinc oxide—5.0; phenyl-β-naphthylamine—2.0; diphenylguanidine—1.0; sulfur—6.0.

Figure 1 presents data on the kinetics of chemical stress relaxation of vulcanizates based on natural and sodium-butadiene rubbers with a predominant content of monosulfide bonds. The kinetic curves of these vulcanizates, with the exception of a small initial segment, are described by the equation of a monomolecular reaction ($\sigma_t = \sigma_0 e^{-kt}$), which indicates the decomposition of one type of bond. The rate constants of the process, calculated from the equation given above, are $1.54 \cdot 10^{-3}$ h^{-1} for vulcanizates from NR, and $2.1 \cdot 10^{-4}$ h^{-1} for the vulcanizate from SKB. Thus, the process of chemical relaxation in vulcanizates from natural rubber proceeds approximately 8 times faster than in the corresponding vulcanizate from sodium-butadiene rubber. It is known ([2]) that, at the same temperature, these rubbers differ in oxidation rate by approximately a factor of 7. The rate of chemical relaxation of these vulcanizates decreases sharply when experiments are carried out in vacuum (Fig. 2). A decrease in the oxygen concentration from atmospheric to 10^{-2} mm Hg leads to a fivefold decrease in the rate of the process. These facts indicate that chemical relaxation in this case is determined by the oxidative decomposition of polymer chains in the vulcanizates.

Fig. 1. Effect of the nature of the polymer on the kinetics of chemical relaxation of vulcanizates containing predominantly monosulfide (A) and polysulfide (B) bonds. Aging temperature 100°, compression 30%. 1 —vulcanizate based on NR, 2 —vulcanizate based on SKB.

An entirely different picture is observed in the study of chemical stress relaxation of vulcanizates with a predominant content of polysulfide bonds.

Obedience to an exponential dependence in this case is observed only after the stress in the vulcanizate has fallen by approximately 50% of the initial value.

At the initial stage of the process (up to a 50% drop in stress), the rates of stress relaxation for both types of rubber are identical; at the final stage they

Figure 2. Influence of oxygen concentration on the kinetics of chemical relaxation of an NR-based vulcanizate containing predominantly monosulfide bonds (A) and polysulfide bonds (B). Compression temperature (B) 90°. Aging temperature 100°, degree of compression 30%; 1 –air, 2 –vacuum (10^-2 mm Hg).

Figure 2: Figure 2. Influence of oxygen concentration on the kinetics of chemical relaxation of an NR-based vulcanizate containing predominantly monosulfide bonds (A) and polysulfide bonds (B). Compression temperature (B) 90°. Aging temperature 100°, degree of compression 30%; 1 –air, 2 –vacuum (10^-2 mm Hg).

are, for vulcanizates from NR, $4.2 \cdot 10^{-2}$ h^{-1}, and from SKB, $3.1 \cdot 10^{-2}$ h^{-1}, i.e., the difference in rates does not exceed 20%. For vulcanizates of this type, carrying out experiments in the absence of oxygen does not lead to a noticeable decrease in the rate of stress relaxation of the vulcanizates compared with the corresponding experiments carried out in an air atmosphere.

It should be noted that the decomposition of polysulfide bonds depends little on the oxygen concentration and proceeds immeasurably faster than the oxidative decomposition of the polymer molecular chains. The rate of chemical relaxation in an air atmosphere for an NR-based vulcanizate with polysulfide bonds is 20 times greater than the corresponding rate for vulcanizates with monosulfide bonds. Oxidative destruction of the polymer chain in these vulcanizates does not have time to develop and produce a noticeable drop in stress compared with the thermal decomposition of polysulfide bonds; therefore, the reactivity of the polymers and the oxygen concentration do not exert a substantial influence on the rate of chemical relaxation.

Analyzing the data presented, one can draw the following main conclusions. In the process of aging of vulcanizates, two competing tendencies are observed: oxidative destruction of the polymer molecular chains and thermal decomposition of transverse sulfur bonds.

In the presence in vulcanizates of strong transverse bonds (monosulfide), chemical stress relaxation is determined by oxidative destruction of the polymer molecular chains, and it is therefore natural that the relaxation rate depends on the reactivity of the polymers and on the oxygen concentration.

In those cases where the network of the vulcanizates is formed by polysulfide bonds, the rate of thermal decomposition of the latter exceeds the rate of oxidative destruction of the polymer chains by an order of magnitude and is the determining factor in the rate of the process of chemical stress relaxation.

Fig. 2. Influence of oxygen concentration on the kinetics of chemical relaxation of an NR-based vulcanizate containing predominantly monosulfide bonds (**A**) and polysulfide bonds (**B**). Compression temperature (**B**) 90°. Aging temperature 100°, degree of compression 30%; **1** –air, **2** –vacuum (10^{-2} mm Hg).

Comparison of the data on the change in the equilibrium modulus (the magnitude of which is proportional to the density of transverse bonds) and on stress relaxation during aging of the vulcanizates studied showed that, when the stress falls to zero, the equilibrium modulus changes by only 15–20%. This indicates that, during aging of vulcanizates in the stressed state, not only decomposition of bonds occurs, but also their further rearrangement. Naturally, destruction of bonds occurs in stressed regions, while formation of new bonds occurs in unstressed regions of the network. As a result of such rearrangement, a gradual decrease in the number of stressed bonds is observed, up to their complete exhaustion, while the total number of bonds remains close to the initial value.

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