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Fig. 1

Figure 1: Fig. 1

Abstract

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ON THE EFFECT OF MOLECULAR OXYGEN ON THE DESTRUCTION OF THE MAIN CHAIN OF POLYDIMETHYLSILOXANE RUBBER

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When polydimethylsiloxane is heated above 200-250° in the presence of oxygen, oxidation of the side methyl groups occurs, accompanied by their cleavage, as well as destruction of the main chain, leading to the formation of low-molecular-weight cyclic polydimethylsiloxanes (1-3). The latter process occurs when the polymer is heated not only in oxygen but also in an inert medium (4, 5). For an understanding of the processes occurring during the oxidation of polydimethylsiloxane, an important question is the effect of oxygen on the destruction of the main chain of the polymer.

Fig. 1. Stress relaxation in samples of oxidized polymer at 278° in a stream of nitrogen purified from oxygen in an ammoniacal solution of NH_4Cl with copper turnings *(1, 2)* and in a stream of oxygen *(3, 4)*. Number of moles of chains of the spatial network (in cm^3) of polymer before the experiment ($×10^{5}$): *1, 3—3.5; 2, 4—2.7*

In the present work, to clarify this question, the "chemical" relaxation of stress in stretched samples of structured rubber was investigated. As is known (6), the rate of "chemical" stress relaxation characterizes the rate of rupture of the bonds forming the three-dimensional structure. Owing to the fact that, upon oxidation, a three-dimensional network is formed in polydimethylsiloxane, it proved possible to apply the stress-relaxation method to study the behavior of the polymer during oxidation and during its heating in nitrogen (or argon), without creating cross-links in it by special methods. Stress relaxation was studied with the aid of a spring dynamometer with a microscale at constant deformation of the sample.

In studying stress relaxation in previously oxidized samples during their further oxidation in a stream of oxygen or during heating in a stream of nitrogen ($<0.01\%$ O_2), it was established that the rate of stress relaxation* decreases with increasing density of the spatial network in the sample before the experi-

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

ment (Fig. 1). Theoretical consideration (6) shows that such a character of the dependence of the relaxation rate on the density of the spatial network should be observed in cases where rupture of the spatial network occurs predominantly along the main chain, and not along cross-links.

* In the present work, by the rate of stress relaxation is meant

$$-\frac{d \lg f/f_0}{dt},$$

where f/f_0 is the decrease in stress over time t.

As is seen from Fig. 2, the rate of stress relaxation in the oxidized polymer when heated in a stream of argon (0.05% O_2) is considerably higher than in the radiation vulcanizate of the same polymer and than in the oxidized polymer after preliminary heating in vacuum for 1 day at 300°. When heated in a stream of oxygen, the initial rate of stress relaxation in the oxidized polymer, preliminarily heated in vacuum, is also considerably lower than in the oxidized polymer; however, with time it increases (Fig. 3). The data presented indicate that, upon oxidation, active groups accumulate in the polymer (not free radicals) that promote destruction of the main chain and, at least in part, are deactivated upon heating in vacuum. It may be assumed that such groups are $\equiv \mathrm{Si-OH}$ groups, since, upon oxidation of the polymer, as we have established, accumulation of these groups occurs (3), while upon heating in vacuum their amount decreases (judging from the infrared absorption spectra of the polymer)*.

Fig. 2. Effect of the method of preparation of specimens on stress relaxation in them at 282° in a stream of argon (0.05% O_2). Equilibrium modulus ~ 1 kg/cm^2. 1 —oxidized polymer; 2 —oxidized polymer after heating in vacuum for 1 day at 300°; 3 —radiation vulcanizate (vulcanized in vacuum)

Fig. 3. Stress relaxation in specimens of oxidized polymer at 268° in argon (1) and in oxygen (2, 3). Equilibrium modulus ~ 1 kg/cm^2. 1, 2 —oxidized polymer after heating in vacuum for 1 day at 300°; 3 —oxidized polymer

When polydimethylsiloxane rubber is heated in oxygen, the rate of cleavage of methyl groups (as a result of their oxidation) is many orders of magnitude higher than in thermal decomposition of the polymer. Nevertheless, the initial rates of stress relaxation in the oxidized polymer (after preliminary heating in vacuum and without such heating) in oxygen are not much greater than in nitrogen or

Fig. 4. Effect of oxygen on the kinetics of evolution of low-molecular-weight organosilicon compounds at 302°: 1—in an oxygen stream; 2—in a nitrogen stream (0.5% O_2)

Figure 4: Fig. 4. Effect of oxygen on the kinetics of evolution of low-molecular-weight organosilicon compounds at 302°: 1—in an oxygen stream; 2—in a nitrogen stream (0.5% O_2)

argon (for example, see Figs. 1 and 3). At 278°, the ratio of the initial rates of stress relaxation— ···in the oxidized polymer in oxygen and nitrogen is approximately 1.3. The number of destruction events (calculated from the initial rate of stress relaxation) upon heating the oxidized polymer in oxygen at 278° is an order of magnitude smaller than the number of methyl groups split off as a result of oxidation. In the case of an oxidized polymer previously heated in vacuum, the ratio between the number of destruction events and the number of methyl groups split off is still smaller. These data show that the direct action on the main chain of the polymer by oxygen and free radicals formed as a result of oxidation of the side groups does not play a significant role in the process of destruction of the main chain.

Fig. 4. Effect of oxygen on the kinetics of evolution of low-molecular-weight organosilicon compounds at 302°: 1—in an oxygen stream; 2—in a nitrogen stream (0.5% O_2).

Thus, the accelerating action of oxygen on the destruction of the main chain of polydimethylsiloxane rubber is reduced, chiefly, to the accumulation of the above-mentioned active groups, which arise as a result of oxidation of the side groups of the polymer and promote destruction of the main chain, apparently by a heterolytic mechanism. This is one of the principal differences between the oxidation processes of polydimethylsiloxane rubber and hydrocarbon rubbers, in which the breakdown of the main chain is associated mainly with isomerization of the peroxide radical ([7]).

The accumulation in the polymer, under the action of oxygen, of active groups that promote destruction of the main chain is also indicated by the presence of an autocatalysis period on the kinetic curve for the evolution of low-molecular-weight organosilicon compounds ([3]), and by a more rapid increase in the rate of splitting-off of these compounds in the initial period when the polymer is heated in oxygen than in nitrogen ([8]).

It should be noted that, during heating in oxygen, the decrease in the rate of

* When the oxidized polymer is heated in vacuum, water evolution and structuring of the polymer are also observed. This indicates that the reaction
$2(\equiv \mathrm{Si}-\mathrm{OH}) \rightarrow \equiv \mathrm{Si}-\mathrm{O}-\mathrm{Si}\equiv + H_2O$
takes place.

splitting-off of organosilicon compounds with time begins after a smaller amount of organosilicon compounds has been split off and proceeds more rapidly than in nitrogen. This leads, for example, to an intersection of the kinetic curves for the evolution of organosilicon compounds in oxygen and nitrogen at 302° (Fig. 4). The indicated regularity does not contradict what was said above and is explained by more rapid structuring of the polymer upon heating in oxygen, which naturally should hinder the process of splitting off organosilicon compounds.

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