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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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SOME REGULARITIES IN THE OXIDATION PROCESS OF POLYDIMETHYLSILOXANE RUBBER

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Polyorganosiloxanes, to the class of which polydimethylsiloxane belongs, in comparison with hydrocarbon polymers, have a number of features in their structure that may cause substantial differences in the mechanism of their thermal oxidation. Among these features the most important are the following: in polyorganosiloxanes carbon and hydrogen are found only in the side

groups, while the main chain consists of strongly polar units –Si–O–;

hydrocarbon groups are separated from one another by these units; the silicon atom, electropositive relative to the carbon atom, has a strong influence on the electron density in the side groups (1, 2). These factors are especially significant in polymers with the shortest side groups—methyl groups.

There are very few data in the literature on the regularities of the thermooxidative transformations of polydimethylsiloxane. It is known that when this polymer is heated at temperatures above 200-250° in the presence of oxygen, oxidation of the methyl groups occurs, leading to their cleavage and to structuring of the polymer, as well as to destruction of the main chain, accompanied by the liberation of low-molecular cyclic polydimethylsiloxanes (3-5). It is assumed that oxidation of the methyl groups proceeds by a free-radical mechanism through the formation of hydroperoxides (4, 5); however, this point of view has been substantiated neither experimentally nor theoretically. The formation of cyclic polydimethylsiloxanes takes place not only in oxygen but also in an inert atmosphere, and is strongly accelerated in the presence of acidic and alkaline additives (6-9). The opinion has been expressed that the process of chain destruction in vacuum proceeds by an ionic mechanism (8). The question of how oxygen affects this process has not been clarified.

Fig. 1. Dependence of the kinetics of cleavage of methyl groups at 280° on film thickness. Film thickness in mm: 1—0.1; 2—0.25; 3—0.45; 4—0.6; 5—0.95; 6—1.6. Dashed line—film 0.6 mm after grinding.

Fig. 2. Changes in the IR absorption spectrum of a film about 1 μ thick, covered with a 0.5 mm film, after oxidation at 300° in air (NaCl prism). 1 –initial; 2 –after 6 h; 3 –after 14 h.

Figure 2: Fig. 2. Changes in the IR absorption spectrum of a film about 1 μ thick, covered with a 0.5 mm film, after oxidation at 300° in air (NaCl prism). 1 –initial; 2 –after 6 h; 3 –after 14 h.

In the present work, some important features of the thermal oxidation of a polydimethylsiloxane elastomer are reported. As the object of study, a purified high-molecular fraction of polydimethylsiloxane rubber was taken (molecular weight, determined by viscosity, ~900 thousand). To study the processes of cleavage of methyl groups and of organosilicon compounds, a procedure and apparatus were developed and used for determining the total amounts of carbon, hydrogen, and silicon in the compounds released from the rubber during oxidation. The principal

the scheme of this method is as follows: carefully purified O_2, passing at a constant rate (40 ± 1.5 ml/min) through the reaction vessel containing the oxidizing polymer, carries the products evolved from it into the combustion zone, where they are completely oxidized to H_2O, CO_2, and SiO_2. H_2O and CO_2 are determined from the gain in weight of Pregl absorption apparatuses filled with anhydrone and ascarite (10), and SiO_2 from the gain in weight of a specially constructed quartz tube in which the combustion takes place. From the weight of the trapped SiO_2, the amount of organosilicon compounds evolved was calculated, based on polydimethylsiloxane. From the difference between the amount of carbon in all volatile compounds and in volatile organosilicon compounds, the number of methyl groups split off was calculated. When the experiment was carried out in a stream of nitrogen in a quartz tube ($t \simeq 950°$), partial pyrolysis of the organosilicon compounds evolved from the polymer occurred; after completion of the experiment, these pyrolysis products were oxidized in a stream of oxygen to SiO_2.

Fig. 2. Changes in the IR absorption spectrum of a film about 1 μ thick, covered with a 0.5 mm film, after oxidation at 300° in air (NaCl prism). 1 –initial; 2 –after 6 h; 3 –after 14 h.

In studying the influence of sample thickness on the process of methyl-group splitting in an O_2 stream at 250–300°, an anomalous phenomenon was found: with increasing film thickness the rate of the process of methyl-group splitting increases, and consequently also the rate of the oxidation process underlying it. This increase in rate occurs up to a certain sample thickness (we shall call it "optimal"), after which the rate begins to decrease. Fig. 1 shows kinetic curves for methyl-group splitting at 280° ("optimal"thickness 0.6 mm). In the oxidation of the polymer in air, the "optimal" thickness corresponds approximately to 0.3 mm at 300°; 0.75 mm at 270°; 2.5 mm at 250°; and > 4 mm at 230°*.

Fig. 3. Effect of oxygen on the release of low-molecular-weight organosilicon compounds at 278° (gas flow rate 40 ml/min): 1 $-O_2$, 2 −technical nitrogen (0.5% O_2), 3 −nitrogen purified in an ammoniacal NH_4Cl solution (with copper shavings)

Figure 3: Fig. 3. Effect of oxygen on the release of low-molecular-weight organosilicon compounds at 278° (gas flow rate 40 ml/min): 1 $-O_2$, 2 −technical nitrogen (0.5% O_2), 3 −nitrogen purified in an ammoniacal NH_4Cl solution (with copper shavings)

The observed dependence of the rate of oxidation of methyl groups on film thickness is a consequence of the action of two competing factors. The first factor consists in the formation, during oxidation of the polymer, of volatile compounds that promote acceleration of the process (possibly formaldehyde). As the film thickness increases, that fraction of these compounds which leaves the film without having reacted in it decreases, and thus the rate of oxidation increases. The correctness of this proposition is confirmed by the following facts. It has been established that a film 0.25–0.5 mm thick lying on another film of polydimethylsiloxane rubber becomes structured at a higher rate than a film of the same thickness lying directly on a quartz substrate. Increasing the charge of oxidizing rubber (with an O_2 flow of 40 ml/min) also leads to an increase in the rate of oxidation of methyl groups. Finally, it was found that a film about 1 μ thick on a KBr substrate, even after 36 h of heating in air at 300°, is not appreciably oxidized, as shown by the IR absorption spectrum of the polymer. At the same time, if the glass with such a film is covered with another film of polydimethylsiloxane rubber 0.5 mm thick, then the 1 μ film is oxidized significantly already after 6 h of heating at 300° (Fig. 2): the intensity of the bands at 1260 and 800 cm^{-1} decreases, correspondingly—···groups = $Si(CH_3)_2$, and the absorption intensity increases in the region 1100–1025 cm^{-1}, which is attributed to bonds $\equiv SiO-$(during oxidation at the site of the cleaved methyl groups, mainly siloxane bonds are formed) (11).

The second factor determining the dependence of the oxidation rate of methyl groups on thickness is oxygen-diffusion retardation in the film. In sufficiently thick films (for example, 0.8 mm at 280°) their lower half, adjacent to the substrate, becomes structured more slowly than the upper half, and this difference increases with increasing film thickness. Above the "optimum" thickness the effect of oxygen-diffusion retardation outweighs the action of the first factor, and therefore a decrease in the oxidation rate is observed with increasing specimen thickness.

* These data were obtained by comparing the rate of structuring of oxidized samples of different thicknesses (from the degree of swelling in toluene). As we have established, there is a definite relationship between the number of crosslinks formed and the number of methyl groups split off.

Fig. 3. Effect of oxygen on the release of low-molecular-weight organosilicon compounds at 278° (gas flow rate 40 ml/min): 1 —O_2, 2 —technical nitrogen (0.5% O_2), 3 —nitrogen purified in an ammoniacal NH_4Cl solution (with copper shavings).

The very fact of the strong acceleration of oxidation of methyl groups under the influence of volatile products formed during the process requires that one assume a chain character for the oxidation of polydimethylsiloxane. Additional evidence of this phenomenon is the sharp slowing of methyl-group cleavage (by one and a half orders of magnitude) upon introduction of 0.5–1% di-β,β'-naphthyl-*n*-phenylenediamine (it is an antioxidant for hydrocarbons), as well as of a filler—white carbon black U-333 (50 parts by weight).

A question of fundamental importance is whether the oxidation of side groups and the process occurring in the main chain are interconnected and, in general, whether oxygen affects the latter. As is evident from Fig. 3, oxygen clearly accelerates the process of cleavage of low-molecular-weight organosilicon compounds in its initial period. It is possible that the accelerating action of oxygen on this process is a consequence of oxidation of methyl groups. Thus, di-β,β'-naphthyl-*n*-phenylenediamine and white carbon black, while slowing the cleavage of side groups, also reduce the release of organosilicon compounds. However, when oxidation was studied under various conditions, it turned out that there is no connection between the amount of cleaved methyl groups and organosilicon compounds.

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