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## Abstract

## Full Text

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## THE INFLUENCE OF FILLER ON THE AGING OF POLYDIMETHYLSILOXANE RUBBER

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Polysiloxane rubbers are among the most heat-resistant elastomers and at the same time retain highly elastic properties at very low temperatures. However, the siloxane bonds of these polymers can be destroyed under the action of nucleophilic and electrophilic reagents ([1–3]). By the present time a number of studies have been carried out devoted to the investigation of the oxidation and thermal decomposition of polydimethylsiloxane rubber, which forms the basis of almost all industrial types of polysiloxane rubbers ([4–9]), but the effect of filler on these processes has not been studied. At the same time, investigation of the latter question is a very important problem, since in practice only filled vulcanizates are used.

The present work is devoted to studying the influence of a silica filler, which is the principal filler of polysiloxane rubbers, on the processes occurring during aging. Two cases are considered mainly, in one of which, as will be shown below, the filler exerts a positive effect on the stability of the rubber, and in the other a negative one—namely, aging upon heating in an oxygen atmosphere with removal of volatile products and in vacuum without their removal. It was previously established ([4–8]) that, when polydimethylsiloxane is heated in a stream of oxygen at 200–250° and above (the first of the aging cases considered), a chain free-radical process of oxidation of methyl groups takes place, leading to their cleavage and to the formation in their place of siloxane bonds and silanol groups. The formation of siloxane bonds between the polymer macromolecules leads to its structuring. Along with this, destruction of the main polymer chains occurs (accompanied by the evolution of low-molecular cyclic organosilicon compounds), mainly under the action of groups formed in the polymer as a result of oxidation of the organic substituents of the chains. In the present work the action of the filler on the oxidation process was studied from its influence on the kinetics of cleavage of methyl groups, of low-molecular organosilicon compounds, and on the rate of structuring. Changes in the polymer upon heating in vacuum were judged from its solubility and from the molecular weight of the soluble fraction, determined viscometrically. The methods used in the work have been described previously ([6]).

As objects of investigation we used purified polydimethylsiloxane rubber SKT ([6]) and a domestic silica filler—white carbon black of grade U-333. In addition, in a number of experiments another filler for polysiloxane rubbers was used—titanium dioxide (titanium white of grade TS). The filler was introduced into

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

the rubber on rolls, after which plates were molded from the mixture in a press at 100°. In experiments carried out in a stream of oxygen at 250-330°, it was established that the introduction into polydimethylsiloxane rubber of white carbon black in an amount of 50 parts by weight per 100 parts by weight of rubber (the dosage used in actual rubbers) pri-

leads to a strong decrease in the rate of oxidation of the methyl groups of the polymer. During 3 hours of oxidation at 300-320°, 20-30 times more methyl groups are split off from the unfilled rubber than from the filled rubber (Fig. 1). The decrease in the rate of splitting off of methyl groups upon introduction of white carbon black is greater than upon lowering the temperature by 60°.

Structuring of polydimethylsiloxane rubber upon heating in an oxygen atmosphere is a consequence of oxidation of the side groups. Therefore, the decrease in the rate of oxidation of the latter upon introduction of white carbon black leads to a decrease in the rate of structuring,* although to a

**Fig. 1.** Effect of white carbon black U-333 on the kinetics of splitting off of methyl groups during oxidation of polydimethylsiloxane rubber.
1 –unfilled rubber at 311°; 2 –filled rubber at 311°; 3 –unfilled rubber at 256°.

**Fig. 2.** Effect of white carbon black U-333 on the kinetics of evolution of low-molecular-weight organosilicon compounds during oxidation of polydimethylsiloxane rubber at 316°.
1 –unfilled rubber, 2 –filled rubber.

somewhat lesser extent than might have been expected on the basis of the dependence, established for unfilled rubber, between the number of crosslinks formed and the number of methyl groups split off. After 2.5 hours of heating in oxygen at 315°, only about one crosslink per 1000 monomer units of the chain is formed in the filled rubber, whereas the unfilled rubber, in even less time, is converted into a glass-forming crumb. The decrease, during oxidation, in the rate of structuring due to white carbon black also occurs in peroxide and radiation vulcanizates.

The rate of evolution of low-molecular-weight organosilicon compounds formed as a result of destruction of the main rubber chains during a prolonged initial period of oxidation is also lower in rubber filled with white carbon black than in unfilled rubber (Fig. 2). At least one of the main reasons for this is the lower rate of oxidation of the side groups of the filled rubber, since as a result of the latter process, as indicated above, groups arise in the polymer that promote destruction of the main chains. With a long duration of oxidation, when the degree of oxidation of the unfilled rubber is already significant, the rate of evolution of low-molecular-weight siliinorganic compounds becomes greater for the filled rubber. This should be explained by the formation by this time, in the unfilled rubber, of a large number of crosslinks and, in all probability, cyclic segments, which hinders the development of the process of destruction of the main chains (8).

It is important to note that another filler for polysiloxane rubbers—titanium dioxide—has approximately the same inhibiting action as white carbon black (at a dosage of 50 parts by weight per 100 parts by weight of rubber).

It may be assumed that the inhibiting action of the filler is explained by the fact that recombination of the free radicals formed during oxidation of the side groups of the rubber is facilitated on its surface.

Table 1

**Structural changes in polydimethylsiloxane rubber upon heating in vacuum at 300° for 8.5 hours***

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* The rate of structuring upon heating mixtures of rubber with more active silica fillers than white carbon black U-333 (for example, with aerosil) is higher, mainly owing to the greater rate of "bonding" of the polymer to the surface of such a filler. This "bonding" can be suppressed to a considerable extent by the use of appropriate reagents, which are essential components of rubbers with fillers of the aerosil type.

| No. | Sample | Initial sample: solubility, % | Initial sample: mol. wt. of soluble fraction, thous. | Heating without removal of volatile products: solubility, % | Heating without removal of volatile products: mol. wt. of soluble fraction, thous. | Heating with freezing-out of volatile products**: solubility, % | Heating with freezing-out of volatile products**: mol. wt. of soluble fraction, thous. |
|---|---|---|---|---|---|---|---|
| 1. | Rubber filled with white carbon black U-333 | 54 | 920 | 95 | 100 | 32 | 900 |
| 2. | Unfilled rubber | 100 | 980 | 100 | 3000 | 5 | – |
| 3. | Unfilled rubber, kept during the experiment in the same ampoule with sample 1 | 100 | 980 | 100 | 100 | 25 | – |

* Ratio of the volume of the ampoule to the volume of the sample ~200. During evacuation of the ampoule before the experiment, part of the water sorbed on the filler surface was removed (approximately half).

** The density of the spatial network of the insoluble fraction after the experiments in this series is less than 1 crosslink per 1000 monomer units of the chain.

When rubber is heated without removal of volatile products (or with their slow removal) and with poor access of oxygen, white carbon black has a negative effect on the thermal stability of the rubber, promoting its destruction. Thus, when rubber filled with white carbon black is heated in vacuum at 250-300° without removal of volatile products, a considerable decrease is observed in the fraction of rubber bound to the filler, as well as in the molecular weight of the soluble fraction, whereas unfilled rubber under these conditions does not undergo destruction (Table 1). This is explained by the fact that the sorbed water released upon heating from the surface of the white carbon black (10)*, as well as water formed as a result of condensation of silanol groups on its surface (11), promotes heterolytic destruction of the siloxane bonds of the polymer chains. The correctness of this explanation is confirmed by the following data, obtained in studying the structural changes of unfilled and filled rubber in vacuum $5 \cdot 10^{-4}$—$10^{-5}$ mm Hg at 300°.

1) Unfilled rubber, upon heating without removal of volatile products in the same ampoule with filled rubber or with such an amount of water vapor as is released from the filled rubber, is strongly destruc—

* In the present work, white carbon black containing ~6% water was used.

is destroyed (and after the experiment has a molecular weight close to the molecular weight of the rubber in the filled specimen after the experiment), whereas on heating in the absence of a filled specimen and water vapor it is not destroyed (Table 1).

2) Filled rubber, when heated with freezing out of volatile products, is not destroyed (there is even some structuring, also observed in the case of unfilled rubber).

During storage of the heated specimen in air at room temperature, water is again bound by the filler.

Thus, the filler plays an extremely large role in the aging of rubbers based on polysiloxane rubbers, affecting both free-radical and heterolytic processes occurring in the rubber. Moreover, depending on the aging conditions, it may exert either a positive or a negative effect.

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