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1962

SovietRxiv

Abstract

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CHEMISTRY

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DEGRADATION AND STRUCTURING OF POLYDIMETHYLSILOXANE (PDMS) UNDER THERMAL ACTIONS

(Presented by Academician V. N. Kondrat' ev on 24 VI 1961)

One of the most important problems in polymer chemistry is the creation of methods that make it possible to raise the temperature limit for the service of polymeric materials. Until recently, the main direction in solving this problem was the use of stabilizers that hinder the development of the chain process of thermal, photo-, and thermo-oxidative destruction of polymers. Nevertheless, the use of stabilizers has not made it possible to bring the thermal stability of polymeric materials substantially closer to the theoretically possible limit, determined mainly by the strength of the covalent bonds of carbo- and heterochain macromolecules ($t = 500$—800°). The reason for this situation, in our opinion, is that although the use of stabilizers hinders the development of the chain process of polymer decomposition, it has practically no effect on the rate of formation of active centers, i.e., macroradicals arising during cracking of polymer chains.

The primary cracking of macromolecules proceeds along the weakest bonds. These bonds may arise: at the sites of attachment of initiator, oxygen, impurity molecules and regulators, etc.

In this connection the question arises of the possibility of increasing the thermal stability of polymers after the destruction of weak bonds under conditions that exclude or hinder the development of the chain process of thermal destruction of macromolecules.

In this case one may expect that the polymer radicals formed during cracking will be capable of chain transfer, and the resulting "secondary macroradicals" of recombination leading to the formation of macromolecules with a smaller content of weak bonds. Such restructuring of the structure under thermal, photo-, or radiation actions, by itself in combination with effective stabilizers, could significantly bring the service temperature of known polymeric materials closer to the theoretical limit.

The first experimental data obtained by us confirm the correctness of the above.

Polydimethylsiloxane rubber was chosen as the object of investigation; its vulcanizates undergo considerable destruction when heated without access of air at

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

$t = 200°$. A paste-like mixture of polydimethylsiloxane rubber (average molecular weight $40—50 \cdot 10^4$) with an inorganic filler and benzoyl peroxide was placed in metal molds. The molds were hermetically closed, with part of the product being squeezed out; the thickness of the polydimethylsiloxane mass remaining in the mold was ~ 2 mm. The molds with the polydimethylsiloxane mass were then subjected to heat treatment in the range from 150 to 350°. At certain intervals of time some of the molds were removed and the hardness and mechanical strength of the specimens were determined. Observations showed that in the course of heat treatment without access of air the polydimethylsiloxane mixtures undergo changes passing through definite stages.

The first stage is the process of vulcanization of polydimethylsiloxane rubber under the action of benzoyl peroxide, occurring in the first minutes of heating and characterized by the transformation of a paste-like mass into a rubber-like material whose strength and hardness depend on the heat-treatment temperature.

As can be seen from Figs. 1 and 2, when the polydimethylsiloxane elastomer is heated without access of air at $t = 150°$, already after 20-30 h noticeable destruction is observed, manifested in a decrease in the hardness and tensile strength of the material.

Fig. 1. Change in tensile strength of the vulcanizate (PDMS) during heat treatment:
1—150°, 2—200°

Fig. 2. Change in hardness of the PDMS vulcanizate during heat treatment: 1 —150°, 2—200°

With more prolonged heating, after approximately 60-70 h, the destruction process is overlapped by structuring, which causes an increase in the hardness and strength of the material.

Fig. 3. Change in PDMS hardness during heat treatment at $t = 250°$

Fig. 4. Change in PDMS hardness during heat treatment: 1—300°, 2—350°

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

However, complete recovery of strength does not occur, since the material contains pores formed during its heat treatment. Similar studies carried out at $t = 200, 250, 300$, and 350° showed that, with increasing temperature, the rate and depth of destruction, as well as the rate of the reverse process—structuring—increase sharply (see Figs. 1-4). At the same time it was found that, beginning with $t = 200^\circ$, in the absence of air PDMS is destroyed to a viscous-liquid mass, which, with a longer duration of heat treatment, again turns into a rubber-like material with an elastic elongation of 80-100%, containing the more gas inclusions that weaken it, the higher the heat-treatment temperature. In view of this, data on Shore hardness give a more correct representation of the process of destruction and structuring.

It is very significant that PDMS subjected to heat treatment for the time required for repeated structuring and "return" of elastic-

of elastic properties, practically does not change its strength characteristics upon heat treatment for tens and hundreds of hours at the same temperature or at a temperature 50° higher. Thus, after 600 hours of holding in a closed mold at 180°, a polydimethylsiloxane elastomer does not worsen the elastic properties acquired after 100 hours of heat treatment at 150°.

Heat treatment of PDMS in hermetic molds at 350° for one hour is sufficient for the process of degradation and structuring to take place (see Fig. 4). The material treated in this way retains its elastic properties for 24 hours at 350°. Heat treatment of PDMS at 150° does not lead to such an increase in thermostability. Raising the temperature of heat treatment makes the material less sensitive to subsequent thermal effects. It must be emphasized that the above-described phenomenon of recovery of elastic properties is observed only when heat treatment is carried out in the absence of air. When samples of organosilicon elastomers are heated at 250-350° in an air atmosphere, a decrease in the elasticity of the material is observed. Thus, five-hour heating of PDMS at 350° leads to the formation of a hard, brittle product. It is highly significant that introducing into the mixture from 0.1% to 2% radical acceptors (for example, iodine) substantially delays the recovery of elastic properties during prolonged heat treatment ($t = 200\text{-}350^\circ$).

The experimental data presented above show that, when energy is imparted to the polymer in the absence of initiators of chain degradation, it is possible to achieve a rearrangement of its structure with the formation of macromolecules containing a smaller number of "weak bonds," and therefore more thermostable.

This process apparently proceeds by a radical mechanism and consists mainly of the following reactions: 1) degradation of macromolecules at the weakest bonds with the formation of macroradicals; 2) chain transfer by the macroradicals that have formed; 3) structuring of the system through recombination of macroradicals with the formation of bonds sufficiently stable under the conditions of heat treatment.

The two sharply distinct stages of PDMS transformations during heat treatment revealed in the present work reflect those periods when processes 1) and 2), or structuring, proceed predominantly. As can be seen from the curves presented above, structuring is preceded by a more or less prolonged induction period, possibly due to the comparatively high viscosity of the system, which hinders interaction of the macroradicals.

In this connection, it may be assumed that the phenomenon of recovery of strength during heat treatment can be observed for polymers with comparatively flexible chains and a sparse network of transverse bridging bonds.

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Received
19 VI 1961

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.