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LINEAR THERMAL EXPANSION COEFFICIENT OF EPOXY-RUBBER COMPOUNDS AT LOW TEMPERATURES. INFLUENCE OF THE HEAT-TREATMENT PROCESS

L. E. Evseeva and S. A. Tanaeva

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The influence of the thermal-hardening conditions on the linear thermal expansion coefficient of epoxy-rubber compounds is studied experimentally in the temperature range 95–333 K.

Materials based on mixtures of epoxy resins with low-molecular-weight rubbers are widely used as adhesives in various impregnating compounds and electric-insulation materials working at low temperatures since the presence of rubber imparts higher elasticity to the entire material and increases its resistance to heat shocks. In our previous investigations we used rubber in small amounts (5–10%). However, the need for compositions with high elastic properties and, therefore, with a large content of rubber requires knowledge of their properties, including the linear thermal expansion coefficient, in a wide temperature range.

We investigated temperature dependences of the linear thermal expansion coefficient (α) of epoxy-rubber compound K-80A in the temperature range 95–333 K. Epoxy resin ED-22 (33 parts by weight), diene rubber SKD KTRA (35 parts by weight), and oleic acid as a plasticizer (10 parts by weight) constituted the K-80A composition. Isomethyltetrahydrophthalic anhydride in the proportion 100:80 relative to the epoxy resin served as the hardening agent. Samples were prepared by mechanical mixing of the components, followed by hardening at room temperature.

The linear thermal expansion coefficient was determined using an automatic vertical quartz indicator dilatometer, model DL-1500 of "Ulvac-Rico" (Japan). Its atomatic-discrimination block allowed recording of a characteristic that is proportional to the value of the thermal expansion. This made it possible to increase the resolving power to $2 \cdot 10^{-7}$ K^{-1}. The sample was first cooled by liquid nitrogen to the temperature $T = 77.3$ K and then heated at a rate of 2 K/min.

Figure 1 shows temperature dependences of the linear thermal expansion coefficient $\alpha(T)$ of epoxy compound K-80A in the temperature range 95–333 K before and after heat treatment. The behavior of $\alpha(T)$ is steplike but not monotonic. It is known [1, 2] that using the temperature dependence of the linear thermal expansion coefficient one can determine the temperatures of the relaxation transitions of three-dimensional polymers, in particular, those based on epoxy resins, which, in turn, can undergo considerable changes since the properties depend on both the chemical composition of the polymer and the temperature-time conditions of structure formation. Each step on the $\alpha(T)$ plot characterizes a relaxation transition.

A study of the structure of mixtures prepared by simple mechanical mixing with a rubber content from 9 to 50% [3] has shown that all such systems possess two phases, with their best stability (nonstratification) manifested at a 50% content of rubber. Therefore the relaxation spectrum of $\alpha(T)$ displays two α-transitions especially distinctly. One (in the range 182–212 K) is associated with the transition of rubber from the vitreous to the high-elasticity state, while the other (305–335 K) is associated with the transition to the high-elasticity state of the entire material. Complete structural vitrification occurs at a rather low temperature, i.e., namely, $T = 312$ K, which is also a consequence of a looser and more mobile structure for the plasticized compound. These findings agree with data of [3] on the thermal resistance of epoxy-rubber compounds. In the case of vitrification, α decreases sharply, which is related with additional hardening occurring in the material at this temperature.

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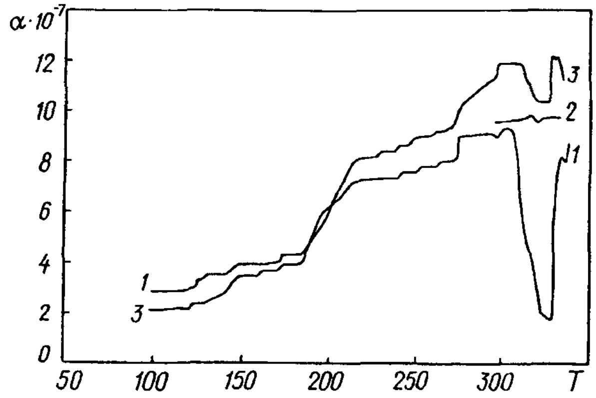

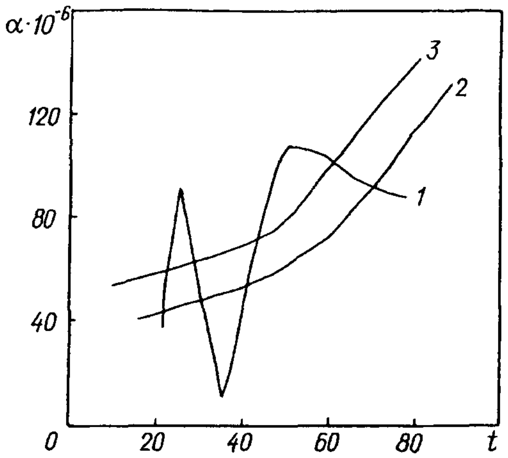

Fig. 1. Linear thermal expansion coefficient of epoxy-rubber compound K-80A: 1) hardening at 20°C; 2, 3) hardening at 50°C for 3 h. α, 1/K; T, K.

Fig. 2. Plot of α versus the hardening temperature [5]: 1) hardening at 20°C for 10 days; 2, 3) hardening at 60°C for 3 and 6 h, respectively. t, °C.

Besides these two α transitions one can observe a large number of small-scale temperature transitions (β and γ transitions) on the temperature dependences of the linear thermal expansion coefficient that correspond to freezing-out of some kinetic units of polymer macromolecules. The number and temperature of these transitions agree well with results of investigations of thermophysical properties of epoxy-rubber compounds, in particular, the specific heat capacity [4], whose temperature dependence also reveals a spectrum of relaxation transitions whose temperatures coincide, with an accuracy of ±2 K, with the temperatures of relaxation transitions obtained from dilatometric measurements.

We also investigated the influence of the heat treatment on the linear thermal expansion coefficient. Hardening of the epoxy compositions is not completed after holding them for a long time at room temperature, the materials remain incompletely hardened. In [5], an investigation was made of the dependence $\alpha(T)$ of epoxy resin ED-20 hardened by polyaminoamide in the range 293–373 K under different hardening conditions. In [5], it was shown (Fig. 2) that in the temperature range of vitrification the linear thermal expansion coefficient decreased abruptly and then it increased rapidly. Preliminarily heated compositions were characterized by a smooth increase in α with temperature.

The experiments with epoxy-rubber compounds showed that samples subjected to prolonged hardening at room temperature also possess a "dip" on the temperature plot of $\alpha(T)$ in the vitrification zone. Additional hold of samples at $T = 323$ for 3 h leads to disappearance of the dip (curve 2), and the curve becomes smooth. Under thermal-hardening conditions the cross-linking density increases, and the network of chemical bonds becomes more stable. However, after cooling to $T = 77.3$ K followed by heating the temperature dependence $\alpha(T)$ again displays a dip in the vitrification temperature range (curve 2). All relaxation transitions become more pronounced, especially the α transition of rubber in the temperature range 182–210 K. At low temperatures the linear thermal expansion coefficient of a sample subjected to additional heat treatment turns out to be lower than that of the initial sample since under the heat-treatment conditions the cross-linking density increases and the free volume decreases. However, after vitrification of rubber $\alpha(T)$ increases considerably as compared to $\alpha(T)$ of the untreated material. This indicates insufficient stability of the chemical bonds after heat treatment and it is devitrification of rubber that destroys them. As a result, relaxation of the free volume occurs, and therefore a "dip" appears again on the curve $\alpha(T)$.

Consequently, low temperatures and thermal cycling lead to breaking of chemical bonds. The character of the temperature dependence $\alpha(T)$ and the absolute value of α can differ considerably for the same epoxy composition upon changing the thermal-hardening conditions.

The kinetics of the temperature dependence $\alpha(T)$ of high-density cross-linked polymers must be taken into consideration in designing structural and composite materials working at low temperatures.

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