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THERMOPHYSICAL PROPERTIES OF EPOXY COMPOUNDS AT LOW TEMPERATURES

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Thermophysical properties of epoxy resin and its compounds are studied experimentally in the temperature range of 4.2–400 K.

Epoxy resins possess a considerable drawback, namely, high brittleness at low temperatures. Therefore, they are subjected to modification or on their basis the compounds with higher cryogenic stability are synthesized. The composition of such compounds often includes different rubbers. The compounds can represent heterogeneous phases or a single phase when a homogeneous material such as, e.g., a silicone epoxy is formed as a result of chemical interaction of the components. Owing to the complicated structure of such polymers, the latter are characterized by a definite number of relaxation transitions. Their manifestation depends, to a great extent, on the method adopted for investigations. The methods of mechanical and dielectric relaxation are most often used for recording. It has been believed that heat capacity is intensitive to mobility in polymers at low temperatures. However, if dynamic heat capacity is measured (continuous heating), then due to the nonequilibrium character of dynamic measurements in the regions of thawing-out of the mobility of elements of the molecular structure, thawing-out can manifest its dynamics.

The majority of works devoted to investigation of relaxation processes in polymers by calorimetric methods are restricted to temperatures higher than 77 K [1-3]. Moreover, as a rule, individual thermophysical characteristics, i.e., thermal conductivity, heat capacity, or thermal expansion, are studied.

The present work is aimed at simultaneous experimental determination of thermal conductivity, thermal diffusivity, and specific heat of epoxy compounds at temperatures of from 4.2 to 400 K as well as of the coeffciient of linear thermal expansion in the temperature range of 77–373 K. Based on independent calorimetric and dilatometric methods, an effort was made to employ relaxation spectrometry.

We investigated the properties of dianon epoxy resin ÉD-22, silicone epoxy resin DFMKR12, and epoxy compound K-80A. The compound composition included dianon epoxy resin ÉD-22 (33 weight parts), synthetic diene rubber SKD KTRA (35 weight parts), and oleic acid (10 weight parts) as a plasticizer. In all cases, isomethyltetrahydrophthalic anhydride (IMTHPA) in a ratio of 100:80 served as a hardener. The densities of the materials were 1.18 g/cm^3, 1.20 g/cm^3, and 1.04 g/cm^3, respectively.

Measurements were made by a quasistationary method that allowed simultaneous determination of thermal conductivity, thermal diffusivity, and specific heat using the same sample in a single experiment within the temperature range of 4.2–400 K. The sample was precooled to 4.2 K and then heated under adiabatic conditions at a rate of 2 K/min. The temperature and a temperature drop with respect to the sample thickness were measured by CuFe-chromel thermocouples. The limiting relative error amounted to 7%. The installation and the experimental procedure were described in detail in [4]. The coefficient of linear thermal expansion was determined in the temperature range of 77-373 K with the aid of an automatic quartz dilatometer, model DL-1500 "Ulvac-Rico" (Japan). An automatic differentiation unit recorded a characteristic proportional to the coefficient of linear thermal expansion. This allowed an increase in resolving power to $2 \cdot 10^{-7} \cdot K^{-1}$ [5]. The heating rate of the sample was 2 K/min.

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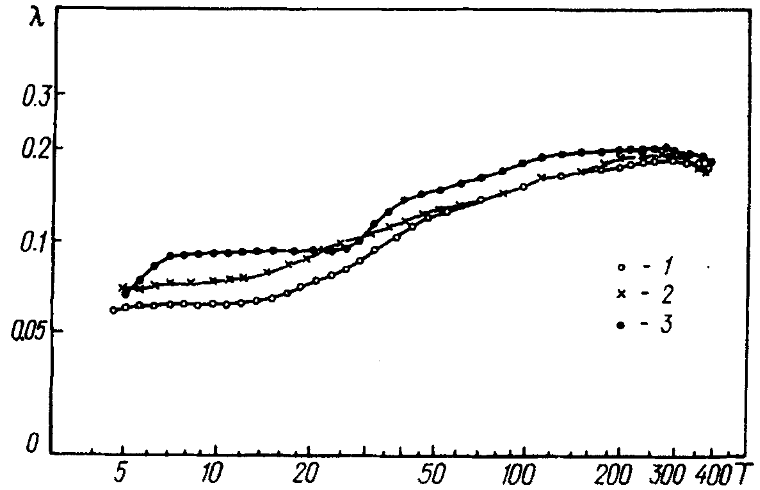

Fig. 1. Thermal conductivity (λ, W·m^{-1}·K^{-1}) of: 1) epoxy resin ÉD-22; 2) silicone epoxy resin DFMKR; 3) epoxy rubber compound K-80A.

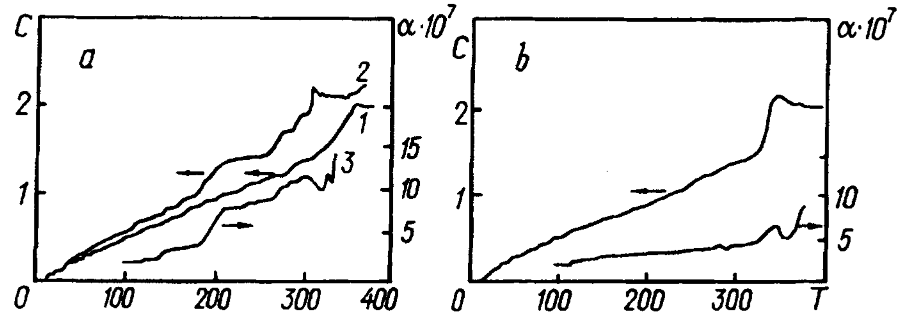

Fig. 2. Specific heat capacity (C, kJ·kg^{-1}·K^{-1}) (1) epoxy resin ÉD-22, 2) epoxy rubber compound K-80A) and coefficient of linear thermal expansion ($\alpha \cdot 10^7$, K^{-1}) of epoxy rubber compound K-80A (a) and of silicone epoxy resin DFMKR (b).

Figure 1 represents the results of experimental determination of the thermal conductivity of all the investigated materials. The temperature dependence of thermal conductivity shows the typical plateau of glass-like materials in the range of 4–15 K. It is noteworthy that the thermal conductivity of the silicone epoxy resin has the shortest plateau (up to T = 12 K), while the plateau of the epoxy compound with raw rubber spreads up to T = 25 K. Thus, structural scattering of waves in the silicone epoxy resin is faster than in the epoxy resin and especially in the epoxy compound. Such an extended plateau of the compound K-80A is apprently due to the presence of rubber and plasticizer in its composition. The absolute values of thermal conductivity of the compound are higher by 30% than those of the epoxy resin. As is shown in [6, 7], the lower the density of cross-linking in an epoxy resin, the higher the thermal conductivity. Thus, modification of epoxy resins by rubber and the introduction of plasticizers decrease the cross-linking density of the polymer and result in an increase in thermal conductivity. With a temperature rise, the thermal conductivity of all the materials increases. But this increase is not monotonic; it proceeds step by step. For the silicone epoxy resin, thermal conductivity is constant in the interval of from 200 to 330 K and is equal to 0.195 W·m^{-1}·K^{-1}, but then with a temperature rise it decreases. All the temperature dependences of thermal conductivity have a maximum, after which the thermal conductivity begins to decrease owing to the transition to a hyperelastic state and an increase in the free volume. The increase in molecular mobility upon incorporation of plasticizers and rubber in the epoxy resin results in a decrease in the glass transition temperature.

Figure 2a depicts temperature dependences of specific heat as well as a temperature dependence of the coefficient of linear thermal expansion of the epoxy resin and the epoxy compound, and Fig. 2b, those of the silicone

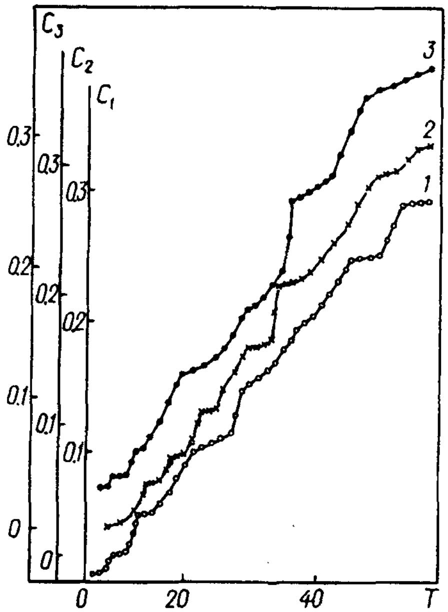

Fig. 3. Specific heat capacity in the temperaturte interval of 5–60 K: 1-3) see Fig. 1.

epoxy sresin. As is seen, the thermal conductivity of the compound is higher than that of the epoxy resin, since the oleic acid and rubber exert a plasticizing effect on the compound structure and loosen it (the density decreases from 1.18 to 1.04 g/cm^3). As a consequence, the mobility of macromolecules increases, thus causing a rise in heat capacity.

The dependences $C(T)$ and $\alpha(T)$ of the compound are of a nonmonotonic character. In the temperature range of 185–250 K, they display anomalous changes in specific heat and thermal expansion associated with transition of the rubber from the glass-like to the hyperelastic state, while the entire material undergoes a complete glass transition at a sufficiently low temperature, i.e., $T = 312$ K, which is also a consequence of the more friable and mobile structure of the plasticized compound. The temperature transitions observed on $\alpha(T)$ and $C(T)$ coincide with an accuracy of ±2 K. In the glass-transition region, an abrupt increase in α occurs followed by a "dip" caused by additional hardening of the resin and additional cross-linking. Experiments with an incompletely hardened resin have shown that the "dip" on the $\alpha(T)$ curve decreases after additional heat treatment and eventually disappears entirely. Studies of the structure of epoxy resins with a large content of rubber have revealed that the material consists of two phases [8]. Therefore, this compound has two regions with a glass transition.

In addition to these two α-transitions, the temperature dependences of heat capacity and thermal expansion exhibit many small-scale temperature transitions (β- and γ-transitions), which correspond to thawing-out of the mobility of some kinetic units of polymer macromolecules. The magnitudes and temperatures of these transitions in the epoxy resin above 77 K approximately correspond to the results obtained in [3] for the epoxy resin ED-6 cured by isomethyltetrahydrophthalic anhydride. In the authors' opinion [2, 3], the mobility of the smallest kinetic unit (structural element) of the epoxy polymer, $-CH_3$, is thawed out at 117 K. The lower-temperature transitions in the polymers containing methyl groups are explained in [9, 10] by quantum-mechanical reorientation tunneling of the methyl groups through the potential barrier, which confines their rotation about the symmetry axis C_3. At sufficiently high temperatures, the processes of tunneling and classical rotation can overlap.

Figure 3 shows the variation of the heat capacity of the discussed materials at cryogenic temperatures. Since the absolute values of the specific heat capacities are close, they are shifted, for clarity, relative to each other. At definite temperatures, the dependences $C(T)$ show "steps," which characterize relaxation transitions. Unlike the epoxy resin, in the epoxy compound these transitions are shifted toward lower temperatures, which is a consequence of the introduction of plasticizers into the epoxy resin. A plasticizer draws apart and disorients polymer macromolecules and screens reactive groups. Coherent interaction of the chains weakens, which can entail a change in the relaxation spectrum due to weakening of the potential barriers for the emergence of some kinds of motion.

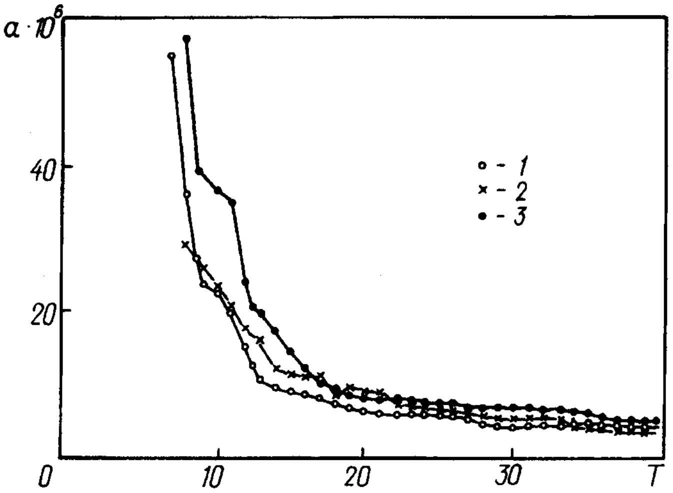

Fig. 4. Thermal diffusivity ($a \cdot 10^6$, $m^2 \cdot sec^{-1}$): 1-3), see Fig. 1.

Since in the temperature interval of up to 50 K intermolecular interaction exerts a crucial influence on heat capacity, the transition temperatures for the modified epoxy compound can be shifted toward the lower-temperature region. The distinct transition at 28 K and the weak transition at 38 K in the compound look as if they have interchanged their positions. The two transitions observed in the epoxy resin at 45 K and 52 K are overlapped in the compound, thus forming a large region of passage to a temperature range in which intermolecular interaction no longer exerts an influence on heat capacity, and now the governing mechanism is intramolecular interaction. In this case, the slope of $C(T)$ drastically changes.

The same figure shows the heat capacity of the silicone epoxy resin. Its absolute value is close to that of the heat capacity of the epoxy resin, but the temperatures of their relaxation transitions differ. Since in the silicone epoxy resin the number of methyl groups and the value of the potential barrier are considerably higher (due to a closer position of the methyl groups), the transition temperatures are shifted toward higher temperatures by almost 6 K.

Temperature dependences of thermal diffusivity of the investigated materials in the range of 5–40 K are represented in Fig. 4. With an increase in temperature, its value abruptly falls to approximately 20 K, which is due to a sharp decrease in the phonon free path. Unlike other thermophysical characteristics, thermal diffusivity is directly related to the phonon free path $a \sim l$. Upon thawing-out of certain types of molecular motion or certain types of oscillations, phonon scattering undergoes a resonance increase, which entails a sharp decrease in the free path length and, consequently, in thermal diffusivity. The variation of $a(T)$ is also stepwise rather than monotonic. The transition temperatures coincide with those obtained from heat capacity measurements.

Thus, the investigations have demonstrated that relaxation transitions occur in epoxy polymers not only at temperatures higher than 77 K but also at cryogenic temperatures. The transition temperatures determined by two independent methods, calorimetric and dilatometric, coincide with an accuracy of ±2 K. The quasistationary method of continuous heating of a sample under adiabatic conditions turned out to be very sensitive to various processes in the material with an increase in temperature. Unfortunately, it is rather difficult to identify these transitions only on the basis of the behavior of thermophysical characteristics. For this, it is necessary to employ other methods of investigation.

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