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TEMPERATURE DEPENDENCE OF THE VELOCITY OF ULTRASOUND AND ELECTRICAL CONDUCTIVITY OF AN EPOXY COMPOSITE WITH A CARBON FILLER

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Experimental data are given on the behavior of the velocity of ultrasound and electrical conductivity as a function of the temperature in an epoxy composite material filled with carbon fiber.

Objective prerequisites have now been established for adaptation to the general industrial application of composite materials [1]. This fact necessitates comprehensive investigation of the properties of new materials to test their compliance with the set of requirements imposed on structural materials in various branches of engineering, the variations of the properties in service, aging, etc. The complexity of these systems makes it rather difficult to employ conventional research techniques such as, for example, chemical and spectroscopic procedures. In recent years, therefore, acoustical and electrophysical methods have begun to enjoy widespread application [2, 3], and multiparameter methods are being developed for the comprehensive investigation of composites with simultaneous measurement of their various properties.

We have studied the temperature dependence of the electrical conductivity and velocity of propagation of ultrasound in an epoxy composite material without filler and with a filler of powdered quartz and metal-infused carbon fiber (the lengths of the fiber segments were up to 1 mm). In the conventional classification scheme the investigated composites are statistical mixtures.

The electrical conductivity was measured by means of stainless-steel electrodes. The structure of the measurement cell ensured parallelism between the working surfaces of the electrodes and an invariant spacing between them during the experiment. The working surfaces of the electrodes were polished to a high degree of purity, minimizing adhesion of the material to the electrode.

The velocity of ultrasound in the hardened epoxy composite was measured by the buffer-rod method [4] with the application of continuous ultrasonic waves.

The measurement cells for determining the conductivity and velocity of ultrasound were placed in an air thermostat. A Chromel–Copel thermocouple and a PP-63 potentiometer were used to monitor the temperature of the material during the experiment. The resistance of the material was recorded with a Straton Teralin III instrument with a measurement range of 10^3-10^{16} Ω.

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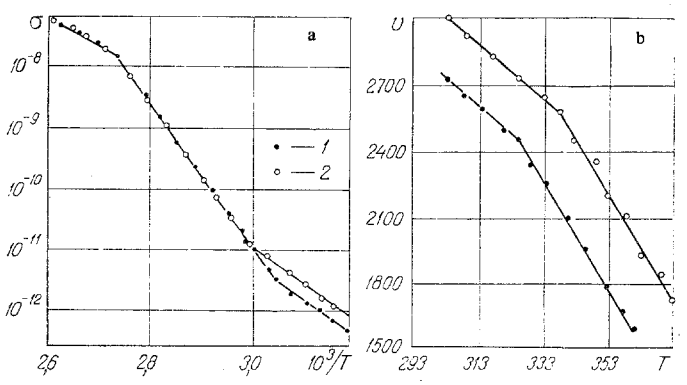

Fig. 1. Experimental graphs of the logarithm of the electrical conductivity versus the reciprocal temperature (a) and of the velocity of ultrasound versus the temperature (b) for an epoxy composite. 1) Without filler; 2) filled with powdered quartz and metal-infused carbon fiber.

The experimental procedure may be summarized as follows. The hardened epoxy composite was placed in the measurement cell and heated to a prescribed temperature. Then the heater was shut off, and the sample was cooled at an average rate of 0.3°C/min. During cooling of the sample, the conductivity of the epoxy composite was measured every minute, after the application of a voltage to the sample. In this case only the steady-state current was recorded. The measurement error was ±5%.

Figure 1a shows a typical graph of the logarithm of the conductivity as a function of the reciprocal of the absolute temperature for two samples in an electric field with a strength of $5 \cdot 10^3$ V/m. It is evident from the figure that the slope of the curves $\ln \sigma = f(1/T)$ changes in the interval of temperatures 54-61°C. Outside this interval the curve is linear (except at very high temperatures). The following relation is valid for the linear intervals [5]:

$$\sigma = \sigma_0 \exp(-E/kT). \tag{1}$$

Relation (1) and the data of Fig. 1a in the temperature interval 40-50°C are used to obtain the value of the conductivity activation energy E_1 = 120.6 kJ/mole, and in the temperature interval 51-93°C the value E_2 = 239.1 kJ/mole, where the values of E_1 and E_2 are the same for both samples. In regard to the quantity σ_0 in Eq. (1), in the temperature interval 61-93°C it is identical for both samples and equal to 10^{25} $(\Omega \cdot m)^{-1}$, while in the interval 40-54°C it is many orders of magnitude smaller, being equal to $1.63 \cdot 10^7$ $(\Omega \cdot m)^{-1}$ for the filled composite and $0.87 \cdot 10^7$ $(\Omega \cdot m)^{-1}$ for the unfilled material.

The type of carrier was determined from the direction of the thermo-emf current flowing between the hot and cold electrodes; it was established that the conductivity is associated with cation-acceptor groups in the temperature interval 40-90°C.

It follows from the experimental data that $E_1 < E_2$, where $E_1/E_2 = 0.504$. This ratio agrees satisfactorily with the theoretical value $E_1/E_2 = 0.5$ [5].

Cation-acceptor vacancies induced by structural imperfection or the presence of an impurity exist at low temperatures, and for them to participate in the charge-transport process it is necessary to expend sufficient energy to ensure mobility of the vacancy in the external electric field. The activation energy E_1 is smaller than E_2 because it does not include the energy required for the formation of a defect (vacancy). A more rigorous theoretical relation for the temperature dependence of the intrinsic conductivity has the form [5]

$$\sigma = \sigma_0 \exp\left(-\frac{0.5E_d + E_a}{kT}\right). \tag{2}$$

If the type of vacancies induced by structural imperfection and by thermal action is identical, it may be assumed that the relations $E_1 = E_a$, $E_2 = 0.5\,E_d + E_a$ are valid, whence we obtain E_a = 120.6 kJ/mole and E_d = 237 kJ/mole.

It is customarily assumed [3] that the temperature of the bend in the curve $\ln \sigma = f(1/T)$ corresponds to the glass-transition temperature T_g of the composite. In our situation this temperature is equal to 61 and 54°C for the filled and unfilled composite, respectively.

The temperature dependence of the velocity of ultrasound was investigated on a specially designed automated system [6], which operates in the continuous-tracking mode and can be used to measure increments of the ultrasonic velocity in the investigated materials within error limits of 0.05 m/sec. The results of the experiments for the same two samples are shown in Fig. 1b. It is evident from the figure that two intervals are observed, in which the temperature dependence of the ultrasonic velocity v is linear. This kind of behavior for composites has been confirmed by other authors [7-9]. It turns out that the nature of the temperature dependence of the velocity for all polymers is not in good agreement with the theoretical model [7-9], according to which this dependence must be nonlinear over the entire temperature range. In reality, the velocity of ultrasound always depends linearly on the temperature, and only with a change in the nature of the molecular mobility does the temperature coefficient make an abrupt change [7-9]. The slope of the straight lines is smaller at low temperatures than at high temperatures. The bend in the lines for the filled and unfilled samples corresponds to respective temperatures of 65 and 52°C, which practically coincide with the temperatures corresponding to the bend in the lines of Fig. 1a. Thermomechanical studies have shown that this happens in the vicinity of the glass transition for the investigated composites. It is well known [10] that the glass-transition temperature T_g is one characteristic of the degree of hardening of a composite and, in turn, is directly related to the physicomechanical and other properties [11]. Considering the abrupt bend in the curves of Fig. 1b, the acoustical method affords a more accurate means for determining the glass-transition temperature T_g.

We call attention to the parallelism of the lines for both samples, despite the difference in their composition, although the velocity of ultrasound does differ in the samples. This difference is clearly attributable to the fact that the elastic modulus of a composite filled with carbon fiber is higher than for the polymer binder, since the density of the two samples scarcely differs. The temperature coefficient of the ultrasonic velocity dv/dT, on the other hand, is clearly determined by the properties of the binder and so is identical for both materials. In the temperature interval below the bend in the straight lines it is equal to $b_1 = -12.28$ m/sec·°C, and in the interval above the bend $b_2 = -24.3$ m/sec·°C. It is interesting to note that the ratio $b_1/b_2 = 0.50$ practically coincides with the experimentally determined ratio E_1/E_2.

We have thus established a definite relationship between the temperature behavior of the conductivity and the velocity of ultrasound for the investigated composites. The temperature dependence of the velocity for such composites is at least as informative as the analogous dependence for the conductivity. As for the glass-transition temperature, in our opinion the acoustical method should be a more accurate method than the electrophysical method for determining it in the case of multicomponent systems. The acoustical, like the electrophysical, method is sensitive to structural changes in the material. In the case of complex composites it could even be preferable insofar as it is directly related to the elastic properties and is entirely independent of the presence and distribution of impurities affecting the conductivity. Also, the acoustical method is the most acceptable for the investigation of composites containing a current-carrying filler, as in our specific situation with the use of metal-infused carbon fiber, because with a high content of conducting fibrous filler the electrical conductivity can be nonuniform throughout the volume owing to the formation of current-carrying chains (electrical closure of the fibers).

In these cases the electrophysical method imparts a large scatter to the data from one sample to the next and can be totally inapplicable. These random circumstances will not affect the velocity of ultrasound, whose value is determined primarily by the constituency of the composite and the temperature.

It is known [12] that the main drawback of carbon and graphite fibers is their structural inhomogeneity, as a result of which composites synthesized with them have a large coefficient of variation of the strength properties. In the development of composite structural materials and in the design of their production technology, therefore, the acoustic method is more informative insofar as it allows the direct acquisition of data on the physicomechanical properties of the material. The advantages of acoustic methods are even more conspicuous in the investigation and development of a technology for the production of so-called hybrid composites, which consolidate several types of reinforcing fibers with different properties into a single polymer matrix.

It must be stated in conclusion that in the production of a composite each of the investigated methods provides a separate means for determining the behavior of one of the properties of the material. The combination of these methods as mutually complementary and independent entitles will make it possible, on the one hand, to significantly enhance the reliability of the results and, on the other, to obtain more extensive information on both the structure and the properties of materials.

NOTATION

T, absolute temperature; σ, electrical conductivity; σ_0, a constant coefficient; k, Boltzmann constant; E, conductivity activation energy; E_d, energy of dissociation for the production of ions; E_a, activation energy for the mobility of ions; b = dv/dT, temperature coefficient of the velocity of ultrasound.

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HEAT FLOW THROUGH FIBER-REINFORCED COMPOSITE LAYER

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The problem of heat flow through a layer with a finite number of rows of periodically positioned fibers all oriented along the same direction is solved.

1. Let a layer of thickness h contain s infinite rows of cylindrical fibers, whose longitudinal axes are parallel to one another and to the flat boundary of the layer. The radius of a fiber in the p-th row equals R_p and we shall denote the distance between two neighboring fibers in a row by a. Let us introduce a Cartesian system of coordinates so that the z axis coincides with the longitudinal axis of one of the fibers in the first row, while the y axis is perpendicular to the boundaries of the layer. The coordinates of the center of the k-th fiber in the p-th row in the system Oxy are $(-x_p^0 + ka, \quad -y_p^0)$, where $k = 0, \pm 1, \pm 2, \ldots, p = \overline{1, s}$; $(-x_p^0, -y_p^0)$ are the coordinates of the center of a fiber in the p-th row closest to the origin of coordinates. We shall also introduce the notation $z_p^0 = x_p^0 + iy_p^0$, $h_p = y_p^0 - y_{p-1}^0$, $p = \overline{1, s}$; h_1 is the distance from the center of the fiber in the first row to the upper boundary of the layer; h_{s+1} is the distance from the center of the fiber in the s-th row to the lower boundary (Fig. 1).

Let us examine the following boundary value heat-conduction problem:

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) t = 0;$$

$$\left.\frac{\partial T}{\partial y}\right|_{y=h_1-h} = -q; \quad \left.\left[\frac{\partial T}{\partial y} + \beta(T - T_0)\right]\right|_{y=h_1} = 0; \tag{1}$$

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