SPECIAL FEATURES OF HEAT TRANSFER IN CARBO- AND GLASS-FIBER MATERIALS AT LOW TEMPERATURES

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The article presents the results of the experimental investigation of the thermophysical properties of composite polymer materials in the low-temperature region.

At present new polymer materials are being worked out which are successfully used instead of metals in various low-temperature devices. Experimental investigation of the thermophysical properties of these materials in a broad temperature range makes it possible to use them most efficiently as heat insulation and in structural elements. The most widely used materials are composite polymers: glass-fiber, carbo-fiber, and glass-carbo-fiber materials. Their properties depend largely on the nature of the filler, the technology, and conditions of operation.

For many years the present authors have accumulated much experimental material on the properties of structural and heat-insulation materials in a broad temperature range. The investigations were carried out with a device for determining the thermophysical characteristics in the range of temperatures 4.2-400°K by the quasistatic method which makes it possible to determine the thermophysical properties (λ, a, c) in one complex as a result of a single experiment [1]. The specimen of the investigated material is made in the form of an unbounded plate with an internal heat source of constant power. The specimen is heated under adiabatic conditions. The maximum relative error of measuring λ, a, c does not exceed 7-8%.

It was demonstrated in [2, 3] that after repeated cooling, glass-fiber materials change their properties substantially. The change in the thermophysical properties is due to structural changes in the polymer film of the bond and to the appearance of anisotropy in the properties of the polymer. Very important in the rearrangement of the polymer is the interaction of the filler and bond at molecular level, and also the high internal stress of the material due to great differences in the coefficient of linear expansion of the components. An analysis of the experimental data of [2] makes it possible in some cases tentatively to predict the direction of anisotropy of the polymer film. Many times (60, 100) repeated cooling gradually leads to a decrease in heat conductivity of glass-fiber materials which is associated with cracking and lamination of the polymer film and rupture of the material.

Carbo-fiber materials differ substantially from glass-fiber materials. The reasons are in the first place a number of unique properties of carbon fibers such as high anisotropy of the mechanical and thermal properties, a combination of very high rigidity (modulus of elasticity), strength, and heat resistance with low specific weight. Domorod et al. [4] examined the results of the experimental investigation of the thermophysical characteristics of carbo-fiber material in dependence on the temperature and the number of repeated coolings.

The temperature dependences of heat conductivity along and across the fibers increase monotonically, whereas the curves of thermal diffusivity have a maximum typical of carbon because of the high content (up to 70%) of carbon fibers and the anisotropy of the film of epoxy-resin bond.

In fact, a carbon fiber consists of several thousand fibrils extending, as a rule, in the direction of the axis of the fiber. The cross section of the fibrils varies between hundreds and thousands of angstroms. Each fibril consists of band-shaped graphite-like layers of condensed carbon, the microfibrils, which are separated by narrow, long pores whose orientation coincides with the orientation of the microfibrils.

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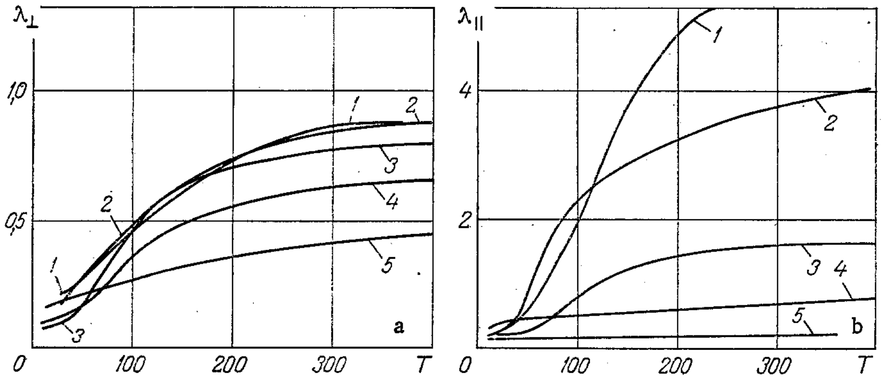

Fig. 1. Dependence of heat conductivity (W/m·deg) across (a) and along the fiber (b) on the temperature: a) 1) glass-carbo-fiber material (65/35 vol. %); 2) glass-carbo-fiber material (55/45 vol. %); 3) carbo-fiber material; 4) porous GCF; 5) glass-fiber material; b) 1) glass-carbo-fiber material (55/45 vol. %); 2) carbo-fiber material; 3) porous glass-carbo-fiber material; 4) glass-fiber material; 5) epoxy resin. T, °K.

The anisotropy of the properties of a carbon fiber is determined by the degree of orientation of the band-shaped layers of condensed carbon along the axis of the fiber. Hence there also exists a maximum of thermal diffusivity which is most pronounced in a specimen along the fiber in the region of hydrogen—nitrogen temperatures.

The temperatures at which the thermal diffusivity along and across the fiber has its maximum coincide with the points of inflection of the corresponding curves of heat conductivity [2].

The temperature dependence of the thermal diffusivity of carbo-fiber materials is due to the peculiar temperature dependence of the free path of the phonons of the composite, which is a result of the correlation of the free paths of the components of the composite. At low temperatures (below the Debye temperature), the free path is commensurable with the linear size of a crystal [5].

It is probable that in the microspaces around each monofiber two parallel processes occur under the effect of residual and thermal stresses caused by the anisotropy of the coefficient of linear expansion of the carbon fiber (negative along the fiber and positive transversely) and the substantial difference in the thermal coefficients of the fiber and the bond: the origin of supramolecular formations of higher order from the microfibrils of the carbon fibers, and the transition of the bonding film into the crystalline state entailing the formation of crystallites [6].

In addition to that, the carbon fiber plays the part of a certain screen for the polymer bond. The low-molecular components of the polymer penetrate into the micropores of the fiber, leaving on the surface the high-molecular components which, under the effect of the surface of the filler, order the structure and change their properties considerably.

These new supramolecular structures and crystallites have very anisotropic properties. Since the emerging anisotropy of the properties is a consequence of the temperature stresses whose magnitude and direction depend on the temperature range, this anisotropy is also of variable nature.

Many times repeated cooling of carbo-fiber materials [4] causes a reduction of heat conductivity along the fibers, i.e., destruction of carbo-fiber materials sets in more rapidly than of glass-fiber materials.

Experiments in vacuum and in a helium atmosphere showed that the thermophysical characteristics of carbo-fiber materials after repeated cooling depend on the presence of an exchange gas; this confirms the assumption of the cracking and rupture of the materials.

The fact that the kind of functional dependence of heat conductivity across the fibers (after 5 cycles) is maintained is an indication that crystalline structures in the bonding

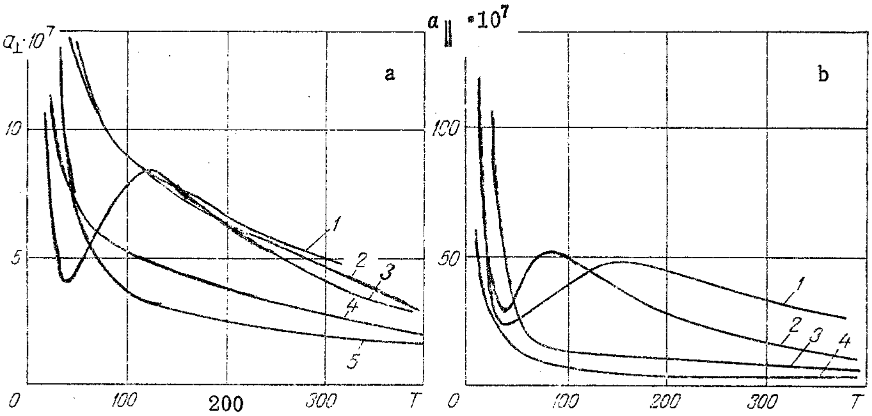

Fig. 2. Dependence of thermal diffusivity (m^2/sec) across (a) and along (b) the fibers on the temperature: a) 1) glass-carbo-fiber material (65/35 vol. %); 2) glass-carbo-fiber material (55/45 vol. %); 3) carbo-fiber material; 4) porous GCF; 5) glass-fiber material; b) 1) glass-carbo-fiber material (55/45 vol. %); 2) carbo-fiber material; 3) porous GCF; 4) glass-fiber material.

film across the fibers continue to form under the effect of thermal stresses in the material, and the anisotropy of its properties manifests itself longer than in a specimen where the heat flux is directed along the fibers.

This confirms the assumption, emphasized in the investigation of glass-fiber materials based on epoxy-resin bond, that anisotropy of the bonding film appears. However, in carbo-fiber material the anisotropy of properties of the carbon fibers is greater, and the effect of the anisotropy of the bonding film is therefore smaller than in glass-fiber materials.

It is interesting to examine the properties of glass-carbo-fiber material which combines the best properties of glass-fiber and of carbo-fiber materials.

When glass fibers are added to carbo-fiber material, this increases substantially the durability of the material, and also makes it considerably cheaper. However, the experimental values of heat conductivity of glass-carbo-fiber materials are not only not below the heat conductivity of carbo-fiber materials, they even exceed them considerably (Fig. 1). This fact is very important in evaluating the existing methods of calculating the effective heat conductivity of composite polymer systems [7]. The obtained experimental results demonstrate fairly convincingly that it is indispensable to take into account the interaction between the bond and the filler at the molecular level in the construction of a model of multicomponent polymer materials.

The thermophysical properties of glass-carbo-fiber materials were investigated by the present authors in the temperature range 10-400°K along and across the reinforcing fibers; the degree of anisotropy (ratio of the values $\lambda_{\parallel}$ to $\lambda_{\perp}$) increases from 2 to 7. It should be pointed out that the anisotropy of the properties of glass-carbo-fiber materials is much greater than that of carbo-fiber and of glass-fiber materials.

For the sake of comparison, Fig. 1a and b shows the temperature curves of heat conductivity across and along the fibers of glass-fiber (GF), carbo-fiber (CF), and glass-carbo-fiber materials (GCF).

In the region of the nitrogen-helium temperatures, the nature of the dependence of heat conductivity of glass-carbo-fiber materials along the fiber on the temperature is analogous to $\lambda_{\parallel\,CF}(T)$ of carbon-fiber material, whereas $\lambda_{\perp}\,GCF(T)$ is analogous to $\lambda_{\perp}\,GF(T)$ of glass-fiber material.

The forces of interaction between the polymer molecules and the molecules of glass and of the carbon fibers differ. In the longitudinal direction with glass and carbon fibers, the bond is covalent; transversely the bond between the phases is effected by the van der Waals forces, which are weaker than the covalent forces. Heat transfer along the fibers is therefore more intensive than across the fibers.

In [2, 8] it was noted that the anisotropy is the greater, the stricter the orientation of the polymer bond along the surface of the filler is.

Since the glass and carbo fibers in glass-carbo-fiber material are not uniformly distributed but are arranged in braids, it may be assumed that in the bonding layers between glass and carbon braids there originate new supramolecular formations of higher order than in carbo-fiber materials and that they extend in the direction of the reinforcement.

Figure 2a, b shows the temperature dependences of thermal diffusivity. It can be seen from the figure that the temperature curve $a_{\parallel GCF}(T)$ is anomalous in the region 50-200°K, the maximum lies at $T = 150°K$, the minimum at 35°K. Here, like for heat conductivity, the nature of the change in $a_{\parallel GCF}(T)$ is similar to that of $a_{\parallel CF}(T)$, whereas $a_{\perp GCF}(T)$ is analogous to $a_{\perp GF}(T)$. On the average, the absolute values of $a_{\parallel GCF}$ and of $a_{\perp GCF}$ are larger than the corresponding values for carbo-fiber and glass-fiber materials.

The experimental investigations show that the thermophysical properties and their dependence on the temperature are greatly affected by the nature of the structural formations at the molecular and supramolecular levels. This, in particular, is the reason that the heat conductivity of crystalline polymers may either increase or decrease with increasing temperature, and that it has a point of inflection in the region of transition [6].

It is imperative to carry out more wide-ranging experimental investigations of the thermophysical properties of modern polymer materials, to shed more light on the mechanism of heat transfer in polymers, and to investigate the influence of fillers on the structure of the bond in composites.

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