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INFLUENCE OF THERMOCYCLING ON THE THERMOPHYSICAL PROPERTIES OF EPOXY COMPOSITIONS HARDENED WITH PHOSPHORUS CARBON FIBERS

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The thermal-conductivity coefficient and the specific heat of polymer composites filled with phosphorus carbon fibers have been determined experimentally in the range of temperatures –100 to 150°C. The influence of thermocycling on thermophysical properties has been investigated.

Stable operation of products made of composite materials under low temperatures requires that these materials possess a high cryogenic resistance, i.e., sustain not only deep cooling but also multiple cyclic thermal loads (heating–cooling) without substantially changing their properties.

In the case of employment under low temperatures, for example, in devices of cryogenic and space technology, polymer composite materials can experience thermal fatigue and be subjected to cyclic thermal loads. Finally, we have large thermal stresses in the materials which result from the difference between the coefficients of thermal expansion of the binder and the filler, formation conditions, and other factors. When such composite materials are operated under conditions with a comparatively large temperature difference, defects (ruptures, microcracks) appear, which leads to the formation of pores and hence a change in the thermophysical characteristics.

The stresses in composites under thermal loads are analogous to those developing under mechanical loading. Therefore, many authors have investigated the failure of materials under multiple mechanical loads and, as a rule, these were anisotropic composites reinforced with unidirectional fibers or laminar composites with cross reinforcement.

However, thermocycling imposes higher requirements on the strength of composite materials and their cryogenic resistance, since not every material will sustain the same number of thermocycles as in tests for mechanical fatigue without substantially changing its properties. Hartwig et al. [1] have investigated the failure of unidirectional and laminar carbon fibers in thermo- and mechanical cycling depending on the type of matrix and have shown that epoxy-resin composites possess better fatigue characteristics than thermoplastic resins.

The amplitude of thermocycling (upper bound of heating and lower bound of cooling) exerts a significant influence on the structure and behavior of polymer composites at failure and on the possibility of fatigue itself. Henaff-Gardin et al. [2] have considered the influence of the thermocycling amplitude on the failure of unidirectional and laminar carbon fibers and have shown that the formation of new cracks is more intense in thermocycling with a high-temperature amplitude. For low amplitudes (–200°C/+20°C and –200°C/+50°C), we can have no failure even in multiple thermocycling. Furthermore, there is a saturation threshold: the density of the cracks is maximum for a small number of cycles (to 10) and remains constant with further increase in the number of cycles.

The thermal fatigue of laminar composites implies biaxial intraplane stresses in each layer of a sample. In the case of orthonormal laminar materials the stresses lead to a failure in the form of cracks in the matrix along the fibers in the direction of both 0° and 90°. This cracking reduces the thermal conductivity of the materials.

It is of interest to analyze the influence of thermocycling on polymer composite materials with a discrete element-carbon fibrous filler in which the latter simultaneously acts as the hardener, since investigations on this problem are absent, in practice. In the case of a certain modification of carbon fiber by different chemical elements, in particu-

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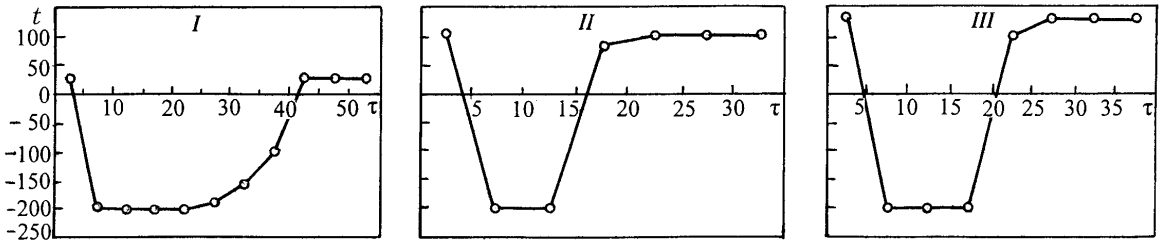

Fig. 1. Schemes of thermocycling.

lar, by phosphorus, the active centers formed on the fiber surface substantially affect the reactions of transformation of the oligomer in the boundary zone and lead to the formation of an interphase layer with a supermolecular structure differing from the structure of the polymer on the surface of untreated fibers and in the volume of the composite. The interphase layer contributes to a decrease in the internal thermal stresses. Furthermore, the employment of discrete fibers randomly arranged in the material instead of long unidirectional fibers also contributes to the improvement of the stability to the action of cryogenic temperatures.

The present work sought to investigate the influence of low temperatures and thermocycling on the thermophysical characteristics of epoxy compositions discretely reinforced with element-carbon fibers. The experiments were carried out with two compositions of a carbon-fiber composite. The first (KM-1) contained phosphorus carbon fibers as the discrete filler, while the second (KM-2) included additionally a highly heat-conducting powdered filler. The samples were manufactured in the form of cylindrical pellets 15 mm in diameter and 4 mm high. We carried out several experiments on thermocycling with different amplitudes of the temperature bounds of the cycle.

The thermocycling involved alternate stay of a sample at the boiling temperature of liquid nitrogen and storage in the drying cabinet in an air medium. The lower bound of the thermocycle remained fixed and equal to -196^{o}C, while the upper temperature of the thermocycle varied. We carried out thermocycles with the following amplitudes: -196^{o}C/$+25^{o}$C, -196^{o}C/$+100^{o}$C, and -196^{o}C/$+130^{o}$C (I–III, respectively, in Fig. 1).

To determine the thermophysical characteristics in a wide temperature range we used the monotonic-mode method [3], which is based on the regularities of an approximate analysis of the nonlinear heat-conduction equation in monotonic heating of a thin plate when the temperature field remains close to the stationary one. This method was implemented in IT-λ-400 devices, making it possible to determine the thermal-conductivity coefficient in a wide temperature range. The specific heat was determined with an IT-C-400 device whose operation is based on the comparative method of a dynamic *C* calorimeter with a heat flow meter and an adiabatic shell. The measurement error amounted to 3 to 4%.

First we carried out experiments on determination of the thermal-conductivity coefficients at temperatures of -100 to 25^{o}C.

Figure 2 gives the temperature dependences of the thermal-conductivity coefficient of the materials under study, which show that the absolute values of the thermal conductivity of the KM-2 material are thrice as high as those in the KM-1 material. This is due to the differences in the composition of the fillers of the materials under study and primarily to the presence of the highly heat-conducting filler in KM-2.

In the course of repeated experiments with the KM-2 sample, we detected changes in the absolute values of the thermal-conductivity coefficient, namely, the values of λ decreased by about 30% throughout the temperature range (Fig. 3). Then we carried out five more cycles of cooling and heating in mode I (see Fig. 1). The difference in the values of λ was insignificant (the discrepancies are within the experimental error). The measurements were carried out after each cycle.

Subsequently, the same sample staying at room temperature for a month was subjected to a series of thermocycling experiments according to scheme II (Fig. 1) with an increased amplitude of the thermocycle and a higher rate of heating and cooling. The result turned out to be quite unexpected, since the absolute values of the thermal-conductivity coefficient increased as compared to the previous five cycles and became lower than the initial value by 6%. Then we carried out 5, 10, and 20 thermocycles with an amplitude of -196^{o}C/$+100^{o}$C; the thermal conductivity did not change. Thereafter we carried out 15 thermocycles with an amplitude of -196^{o}C/$+130^{o}$C (a total of 40 cycles) according to the scheme III presented in Fig. 1; the absolute values of λ increased somewhat, having approached the in-

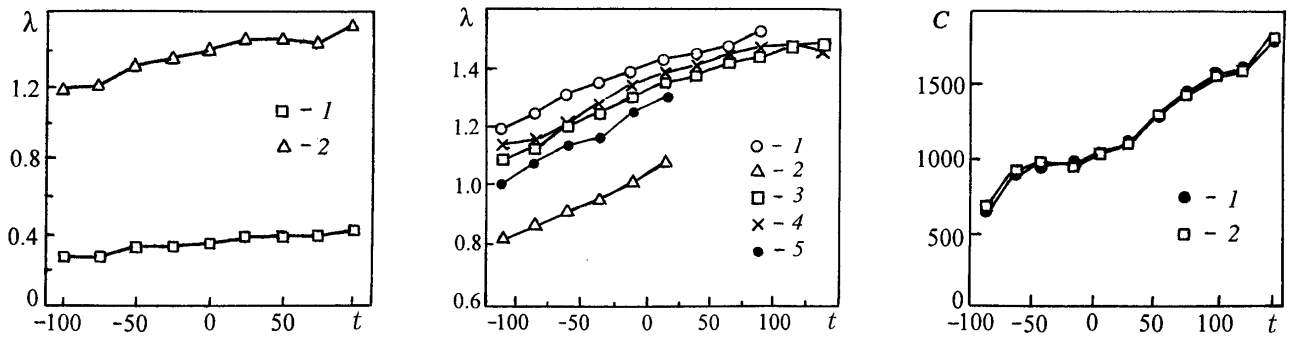

Fig. 2. Temperature dependence of the thermal-conductivity coefficients: 1) KM-1; 2) KM-2. λ, W/(m·K); *t*, ^{o}C.

Fig. 3. Temperature dependences of the thermal-conductivity coefficients of KM-2 upon thermocycling: 1) first test; 2) 5 cycles; 3) 10–25 cycles; 4) 40 cycles; 5) 45 cycles.

Fig. 4. Temperature dependence of the specific heat [1, 2) notation is the same as in Fig. 2]. *C*, J/(kg·K).

itial value even closer. However, after the 40th cycle each subsequent cycle led to a decrease in the thermal-conductivity coefficient. Up to 45 cycles were carried out in the experiments.

The results obtained demonstrate that substantial structural changes in the KM-2 material under the action of low temperatures begin even in the first cooling cycles. Unlike unidirectional carbon fibers [4] in which a significant decrease in the thermal-conductivity coefficient occurred as a result of cracking at the first thermal shocks and a constant decrease in the thermal conductivity was observed in subsequent thermocycling, while the material turned to a bound system with communicating pores, in this material we have changes due to the structural organization of the composite itself, which is specified in its formation, rather than the formation of microcracks. The phosphorus carbon fiber employed as part of the composite performs two functions simultaneously — those of the filler and the hardener of the epoxy binder. Due to the effective interaction at the filler–epoxy matrix phase boundary, a rigidly bound space-network structure is formed which prevents the failure of the composites under thermocycling conditions. The introduction of a powdered carbon filler (which is inert in relation to the matrix) into the composite material leads to the formation of a more labile structure of the polymer in the interphase layer, which is confirmed by the results of a thermomechanical analysis (the glass-transition temperature of KM-2 is 12^{o}C lower than the glass-transition temperature of KM-1).

Apparently, after the first series of thermocycling experiments, the sample, having stayed for a rather long time at room temperature, relaxed and restored its initial structure. Furthermore, the increased thermocycle temperature, namely, the fact that the upper temperature bound was higher than the glass-transition temperature of the polymer binder, contributed to the "healing" of defects formed earlier in cooling down to low temperatures. However, in further thermocycling, the process of formation of cracks does begin to prevail and the thermal conductivity decreases step by step.

No sharp decrease in the thermal conductivity was revealed for the KM-1 material after the first cycles of cooling, which speaks of its higher stability to the action of cryogenic temperatures as compared to KM-2.

The values of the specific heat do not change in thermocycling, at least, the differences are within the experimental error (Fig. 4).

Thus, we can speak of the fact that the materials under study possess a rather high cryogenic resistance and they can be used in different structures and products operating at low temperatures. In particular, KM-1 carbon-fiber composite was employed in manufacture of a thermal absorbing shield for a vacuum cryogenic pump. Materials discretely reinforced with phosphorus carbon fibers possess a higher cryogenic resistance than unidirectionally reinforced carbon fibers.

NOTATION

t, temperature, ^{o}C; τ, time, min; λ, thermal-conductivity coefficient, W/(m·K); C, specific heat, J/(kg·K).

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