EPOXY COMPOSITES HARDENED BY PHOSPHORUS CARBON FIBERS. INFLUENCE OF THERMAL CYCLING ON THERMAL PROPERTIES.

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ABSTRACT

Measurements of thermal conductivity and specific heat for epoxy composites using short phosphorus carbon fibers as filler under and without thermal cyclic loading in the temperature range -100^{0}C ÷ +130^{0}C are presented. It was shown an essential thermal conductivity changes just after the first thermal cycle. The elevated amplitude of the thermal cycle (403 K) promotes to "healing" of defects formed under deep cooling, and the thermal conductivity increases to the initial level.

1. INTRODUCTION

Epoxy carbon fiber reinforced plastics are an important class of structural materials for aerospace and cryogenic application. In the space environment, advanced composite materials may experience thermal cyclic loading. One of the most important problems is to provide the cryogenic stability of the material under numerous deep cooling and heating (thermal cycles). Large thermal strains and stresses may be developed in composite structures due to the mismatch in the coefficients of thermal expansion of fibers and polymer matrix. Thermophysical properties such as the thermal conductivity, the thermal diffusivity and the specific heat are very informative characteristics about structure changes in composite materials under different external effects. Thermal exposure is likely to enhance damage similar to that observed under mechanical loading.

In the present study we focus our attention on the thermal cycling with different temperature amplitude for epoxy composites using short phosphorus carbon fibers as filler. Simultaneously this filler is a hardener.

The aim of the present work was the investigation of the influence of low temperatures and thermal cyclic loading on the thermophysical properties (thermal conductivity and specific heat) of epoxy composites reinforced by short phosphorus carbon fibers in the temperature range 150 – 403 K (-100^{0}C ÷ +130^{0}C).

2. EXPERIMENTAL DETAILS

Investigations have been performed on the epoxy composite, which was reinforced by discrete short carbon fibers, which specially treated by phosphorus. These fibers operate as a hardener on the epoxy matrix. Fiber surface-active centers effect essentially on reactions of the epoxy oligomer transformation in the boundary layer and lead to the creation of the boundary layer with a permolecular structure, which differs from a bulk polymer or from the surface of untreated fibers. This interface boundary layer promotes to a decrease of internal thermal stresses. Moreover, a use of discrete fibers chaotically located in composite instead of long unidirectional fibers, promotes composite's cryogenic stability.

The thermal conductivity and the specific heat have been studied. Measurements were carried out using a monotonous regime method [1], in the temperature range from 77,3 K to 423 K. This method is realized in the IT-λ-400 and IT-C-400 installations. The relative error was 5-6%.

First, the sample was cooled to a liquid nitrogen temperature and then heated under adiabatic conditions at a rate of 6 K/min. After the first cooling thermal cyclic loading was performed. The specimens were alternatively cooled in a liquid nitrogen cold chamber and heated in a circulating air hot chamber. This entails immersing the sample manually in liquid nitrogen for 15 minutes and then placing it in air-oven for 30 minutes.

Henaff-Gardin *et al.* [2] and Fang *et al.* [3] showed that both rates and amplitudes of the thermal excursions affect the extent and form of damage of polymer composites.

The effect of the maximum temperature is investigated (up to 403 K), with a minimum temperature remaining constant (equal to 77,3 K). Three different tests at different amplitudes have been conducted (*Fig.1*):

77,3 K to 293 K (room temperature)
77,3 K to 373 K
77,3 K to 403 K.

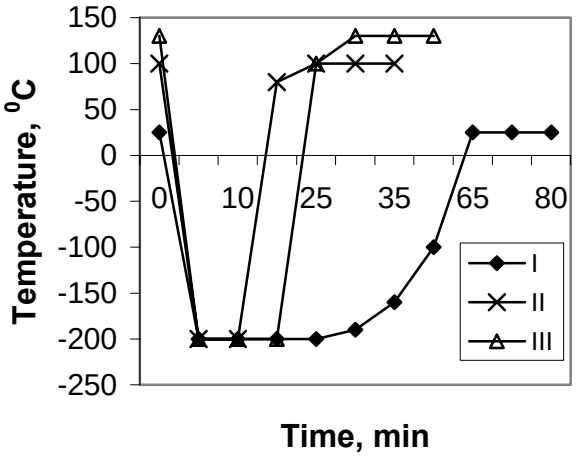

Figure 1. Schemes of thermal cycling

3. RESULTS & DISCUSSION.

The stability to thermal cyclic loading depends on the temperature compression, the thermal conductivity and the elasticity of the material. Powder and particle fillers of polymers always improve the resistance of polymer composites to the thermal cyclic loading [4]. In a previous papers [5,6] the thermophysical properties of glass fiber and carbon fiber reinforced composites were investigated. It was showed that the thermal cycling leads to the essential, sometimes anomalous, changing of thermal properties, due to the destruction of the material under the thermal cyclic loading. The material's behavior at the thermal cycling is likely to their behavior at the long exposition at low temperatures, but it induces the accelerated aging and the destruction of materials.

It is interesting to analyze the effect of thermal cycling on the polymer composite with discrete carbon fibers.

Figure 2 presents thermal conductivity temperature dependences for samples tested under the first cooling and heating at rate 6 K/min (curve 1). After one thermal cycle (regime I *Fig.1*) absolute λ-values was less by 30% than initial values in the whole

temperature range (curve 2). Then five thermal cycles were carried out (regime I *Fig.1*). There was not an essential difference from thermal conductivity after one thermal cycle. Measurements were performed after every cycle.

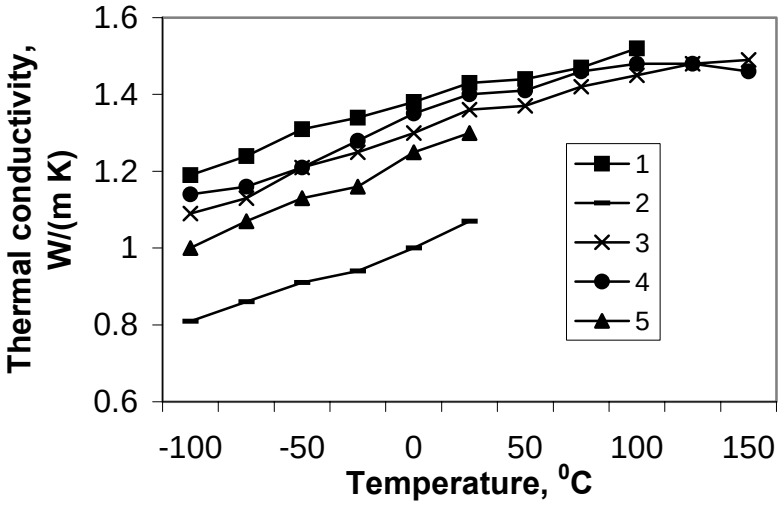

Figure 2. Thermal conductivity *versus* temperature for composites tested under thermal cycling:1 - the first test, 2 - 5 thermal cycles, 3 – 10-25 thermal cycles, 4 – 40 thermal cycles, 5 – 45 thermal cycles.

Then this sample was undergone to elevated temperature amplitude of the thermal cycle and cooling and heating rates (regime II *Fig.1*). The result was very unexpected because the absolute λ-values was increased compared to last five cycles. They are only by 6% less than after initial test. After 5, 10 and 20 thermal cycles with the amplitude 77,3K – 373K, thermal conductivity doesn't change (curve 3). After additional 15 thermal cycles (total number 40 cycles) with amplitude 77,3 K – 403 K (regime III *Fig.1*) thermal conductivity is slightly increased and become almost equal to the initial value (curve 4). However, after 40th cycle each next cycle result in a decrease of the thermal conductivity. Experiments were performed up to 45 thermal cycles (curve 5).

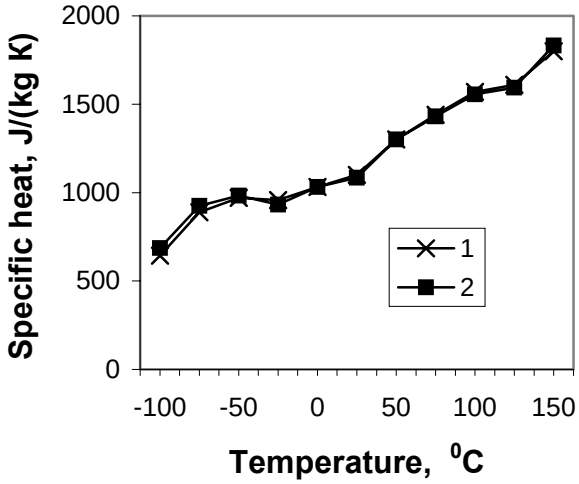

Figure 3. Specific heat *versus* temperature for composites tested under thermal cycling:1 - the first test, 2 – 45 thermal cycles

Our results show that essential structure changes which take place in the composite material just after a first thermal cycle. This leads to a decrease in the thermal conductivity under first 5 cycles (Fig1). After following thermal cyclic loading with cooling to 77,3 K and heating to 373 K, the thermal conductivity increases to the initial level. The elevated amplitude of the thermal cycle (403 K) promotes to "healing" of defects formed at the cooling. However, at further thermal cyclic loading the damage of composite begins to take preference and the thermal conductivity starts to reduce again. Specific heat doesn't change under the thermal cyclic loading (*Fig.3*).

The thermal cycling affects on the structure and properties of polymer composites. Sometimes it leads to the whole destruction of the material. So it is very important to choose right fillers for composites with a good cryogenic stability.

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