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Thermophysical Properties of Polymer Composite Based on Multiwalled Carbon Nanotubes, Obtained by Electrospinning

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Abstract—The heat capacity and thermal diffusivity of a polymer composite based on multiwalled carbon nanotubes (95%), produced by electrospinning in the temperature range of $300 \leq T < 450$ K, are investigated during heating and cooling. Temperature hystereses are detected characteristic of first-order phase transitions.

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INTRODUCTION

Polymer materials are applied in many engineering systems and processes because of their ductility, chemical resistance, and low costs. The addition of carbon nanotubes (CNTs) into polymer matrix gives the material new and unique electrical, thermal, and mechanical properties. The main difficulty in improving the physical properties of composite materials is related to the need to ensure good mechanical coupling between the nanotube surface and matrix material. In the absence of such a coupling, nanotubes behave like a particle in the composite, moving freely within the matrix under load application. In this case, the introduction of nanotubes decreases rather than increases the mechanical strength of the composite. To overcome this problem, it is necessary to provide a chemical bond between the carbon nanotube surface and the matrix material, which requires surface functionalization of the nanotubes. The problem in preparing such composites consists in the fact that it is necessary to ensure a uniform distribution of CNTs of the same diameter and number of layers in the composite. The physical properties of these nanomaterials cannot be explained based on the conventional theory of composite materials. Inhomogeneous distribution of nanotubes in the polymer results in a considerable spread in the values of conductivity of the composite and the position of the conduction percolation threshold.

There is no single theory to date that enables the calculation of the optimal parameters of the electrospinning process. As a rule, the conditions for synthesizing nanowires are selected empirically [1]. The efforts of dozens of laboratories around the world are aimed at overcoming these challenges. Interest in the study of conductivity of composite materials based on a polymer with CNTs was stimulated by works [2, 3], where the percolation nature of charge transfer in the composite was demonstrated for the first time. Adding nanotubes to the polymer matrix in an amount of 0.1% causes a change in some physical properties, for example, an increase in the electrical conductivity of the synthesized composite by 8–10 orders of magnitude, thus switching it from dielectrics into conductors. Increasing the amount of CNTs in a polymer is accompanied by an increase in conductivity of the composite. Currently, more than 250 composites of different polymers with a low concentration of CNTs have been investigated. Their physical properties depend essentially on the polymer grade, type and geometry of nanotubes (single-layer or multilayer), and manufacturing method [4]. The temperature dependence of electrical and thermal properties are characterized by a considerable spread, even if the CNTs were obtained at the same installation. CNTs have a high concentration of structural defects [5].

Heat capacity, C_p, of single-walled and multiwalled CNTs is studied in detail both theoretically and experimentally from room temperature to liquid helium temperature. It is shown that at $T > 100$ K, C_p is satisfactorily described by the phonon contribution, and, in the region below 100 K, the dependence of $C_p(T)$ is nonlinear and is characterized by bends and overshoots for nanotubes of different structures [6–9]. It is believed that the conventional electron contribution to C_p at low temperatures is several orders of magnitude lower than the experimentally observed values of heat capacity. At the same time, it is found that a low-temperature behavior of C_p in disordered nanotubes strongly depends on the structure of these materials, and observed bends and overshoots in $C_p(T)$ cannot be explained by the phonon contribution. Egorushkin et al., calculating the electronic heat capacity, showed that the anomalous low-temperature behavior of C_p of disordered CNTs is electronic in nature and related to electrons involved in restructuring [10]. It was found by scanning electron microscopy that small crystallites are formed in the polymer structure under the effect of CNTs at the interface; they enhance packing density, thus deforming the nanotubes. At temperatures above room temperature, the heat capacity of polymer composites based on CNTs is much less studied. Interest in the study of the temperature dependence of C_p above room temperature arose after the discovery of the anomalous behavior of electrical resistance, ρ, in the range of $300 \leq T < 450$ K with peculiarities of behavior of ρ during heating and cooling of the composite [11–13].

The goal of this study is to investigate and determine the characteristics of heat capacity of films of the polymer composite produced by electrospinning, based on a large number of multiwalled carbon nanotubes (MWCNTs) (95 wt %) during cyclic heating and cooling in the range of $300 < T < 450$ K.

PREPARATION OF COMPOSITE FILMS, RESEARCH PROCEDURE

To obtain a polymer composite in a matrix of polytetrafluoroethylene lacquer, we used MWCNTs. Nanotubes (Fig. 1) were obtained by the plasma arc method under specially modified process conditions [14]. The main difference of this method from conventional classical arc plasma techniques for growing MWCNTs in gas phase is the use of a liquid hydrocarbon phase (in this case, benzene was used, although there may be other liquids, for example, toluene, etc.) at a constant dynamic feeding of argon into the plasma arc zone and the possibility of using inexpensive technical graphite with a low concentration of catalyst, that is, natural iron impurities (0.03–0.2 wt %), as an anode. MWCNTS obtained had the following morphological characteristics: the average most common length was 100–200 nm, the outer diameter was 10–20 nm, and the inner diameter was 1.2–3.5 nm [15]. The advantage of this method is an increasing yield of nanotubes, namely, approximately 100 g/h per anode with graphite conversion into MWCNTs up to 100%.

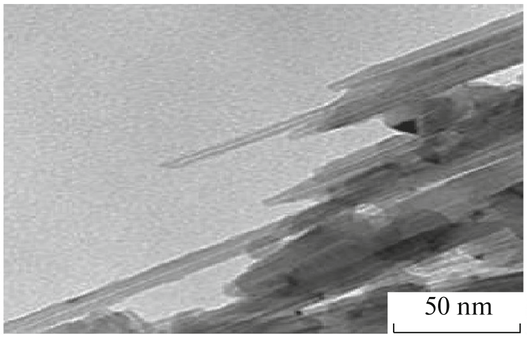

Fig. 1. Carbon multiwall nanotubes (antireflection electron microscopy).

MWCNTs were previously purified from trace nickel and iron by a chemical procedure using nitric acid, dried and ground in a disintegrator. To modify MWCNTs, they were treated in a high-frequency plasma discharge: the frequency of electrical discharge was 40 MHz, the plasma electric discharge power was 0.01–0.1 W/cm^3, and the argon pressure ranged from 0.2–1.13 Torr for 300–500 s.

After modification, MWCNTs were added into a liquid polymer matrix in a ratio of MWCNTs : polymer of 95 : 5 wt %, and stirred for 10 min. The resulting stable suspension (a suspension of MWCNTs in a polymer solution in acetone) was used to form a nanocomposite on a substrate by means of electrospinning from a liquid phase under natural evaporation of the solvent for 24 h under normal conditions. Nanowires are formed in the electric field in the flow of the polymer solution. Lacquer is prepared at different rates of swelling of crystalline sites and a varying degree of defectiveness, resulting in wrinkling [16]. The temperature of polymer decomposition is 630 K [17]. The modulation method was used to measure the heat capacity [18].

The modified modulation method (Fig. 2) is based on that upon heating the sample, and periodic temperature variations arise inversely proportional to its heat capacity, C_p, and frequency, ω. A sample with the area of 3 × 3 mm^2 was heated by light pulses with modulation frequency $\omega = 3$ Hz. The modulation of light was performed by optical chopper *3* (SR540). The reference signal is supplied to amplifier *1* from the same chopper. Modulated light falling on the sample causes temperature fluctuations of the sample (with an amplitude of up to 0.05 K) and periodic changes in the emf of a chromel–constantan thermocouple glued to

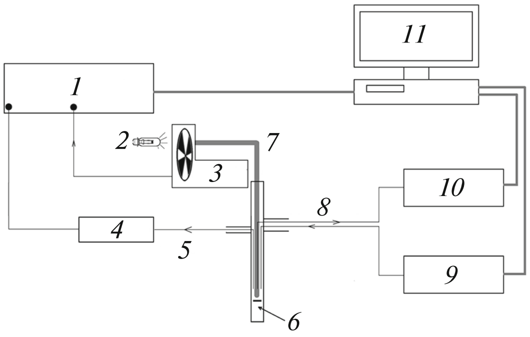

Fig. 2. Block diagram of the set-up for measuring heat capacity by the modulation method: (*1*) SR830 synchronous amplifier, (*2*) excitation source (lamp), (*3*) optical chopper, (*4*) SR554 transformer amplifier, (*5*) AC signal from the chromel–constantan thermocouple, (*6*) sample, (*7*) optical fiber, (*8*) signal from the copper–constantan thermocouple, (*9*) power supply, (*10*) Keihley-2000 multimeter, and (*11*) computer.

the opposite side of the sample. The diameter of the thermocouple wires was 0.025 mm. To improve the thermal contact with the sample, the thermocouple junction was flattened to 3–5 μm. The signal from the differential thermocouple passed through amplifier *4* and was measured by synchronous detector *1*. The general cell temperature was measured by a copper–constantan thermocouple, and it was controlled with the help of an oven that was a wound bifilar constantan wire and power supply *9*. Heating and cooling rates were 2 K/min. Thermal diffusivity was determined from the phase difference between the reference signal and the signal passed through the sample. The phase difference was measured by an SR830 synchronous detector simultaneously with the measurement of the sample temperature oscillation amplitude. The relative measurement error was less than 1%. The entire measurement process was automated.

RESULTS AND DISCUSSION

The temperature dependence of heat capacity of the polymer composite in the range of $300 \le T < 450$ K in two cycles of heating and cooling is given in arbitrary units in Fig. 3.

We found two anomalies of the heat capacity at $T \approx 340$ and 420 K. One anomaly in the C_p/T coordinates is rather weak, but it becomes noticeable in the C_p/T–T coordinates. In earlier works, the maxima of resistance, ρ, were found at $T \approx 340$ and 420 K in the range of $300 \le T < 450$ K in a composite with a specific behavior during heating and cooling [11–13]. In the process of cooling, the heat capacity maxima shift to $T \approx 330$ and 390 K, respectively. The presence of thermal hysteresis of $C_p(T)$ is characteristic of the first-order phase transitions. Note that the temperature dependence of the heat capacity of the polymer at $300 < T < 520$ K is slightly nonlinear, and any abnormalities were not observed in this temperature range. The experimentally observed behavior of the composite heat capacity can only be explained by phenomena occurring in the subsystem of carbon nanotubes. Note that the sample size is several millimeters, while MWCNTs obtained have an average length of 100–200 nm, and defects are formed between the tubes in preparation of the composite. CNTs have a high concentration of structural defects; they are heavily contaminated with various impurities such as nanocarbon particles and nanoparticles of metal catalyst surrounded by a graphite coating. Removal of these impurities represents a technological problem. The concentration of various structural defects is high; therefore, local short-range fields can be formed in the composite, changing the electronic structure of the tubes. The presence of the maxima of the heat capacity can be explained by assuming that, in heating and cooling, the amorphous mass of the polymer near the interface with MWCNTs becomes more ordered.

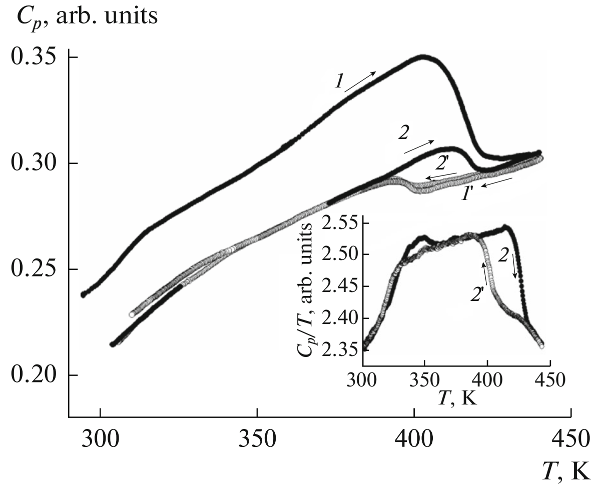

Fig. 3. Temperature dependence of C_p of the composite during (*1* and *2*) heating and (*1*' and *2*') cooling; inset: dependence of C_p/T on T.

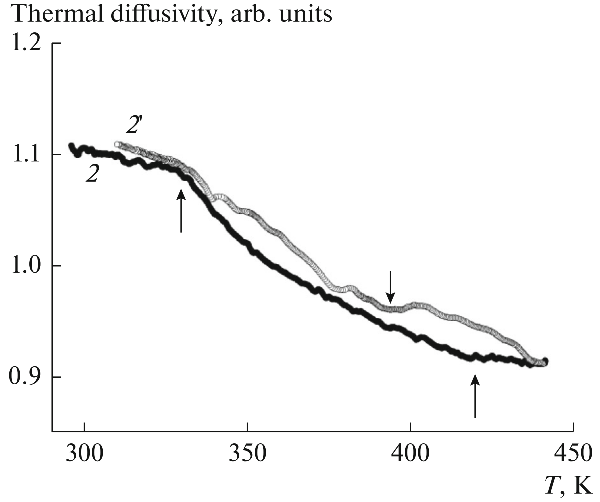

Fig. 4. Temperature dependences of thermal diffusivity upon (*2*) heating and (*2*') reheating of the composite.

The results of the study of thermal diffusivity of the composite during heating and cooling are presented in Fig. 4. It is shown that, during heating, the magnitude of thermal diffusivity decreases with increasing temperature. There are two anomalies in the temperature dependence of thermal diffusivity, as in the curves of heat capacity, with strong temperature hystereses. It should be noted that the nature of heat dissipation media changes, particularly in the field of $T = 340$ K: the maximum of C_p corresponds to the minimum of heat capacity. The presence of the maxima of $C_p(T)$ and thermal diffusivity indicates the possible existence of two different types of defects. The anomaly of heat capacity at $T = 340$ K is weakly pronounced, while the anomaly of thermal diffusivity is rather strong and, at $T = 420$ K, vice versa.

These studies have shown that, under the effect of uniform pressure, MWCNTs in the composite are structurally transformed into an ellipsoidal shape [19, 20], and the authors of [21, 22] explain these changes in the framework of a long-term elastic deformation theory. To identify intramolecular and intermolecular interactions and relaxation processes in the temperature range, where the abnormal behavior of $C_p(T)$ and thermal diffusivity is observed, it is necessary to study the composite through Raman spectroscopy.

CONCLUSIONS

The results of the study of heat capacity, $C_p(T)$, and thermal diffusivity of the polymer composite based on a large amount (95%) of MWCNTs in the range of $300 \leq T < 450$ K were obtained for the first time. The observed anomalies of heat capacity and thermal diffusivity are similar to the resistance maxima detected previously in this temperature range. A hysteretic behavior of the heat capacity and thermal diffusivity during heating and cooling of the composite was noted. An explanation of the anomalous behavior of heat capacity and thermal hysteresis was proposed, which can be confirmed by Raman spectroscopy.

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