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HEAT CAPACITY OF THE POLYMER COMPOSITE BASED ON CARBON NANOTUBES

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The paper examines heat capacity of the polymer composite based on a large number of multiwall carbon nanotubes (95%/5%) in the temperature range of 300 K $\leq T < 450$ K in the course of heating and cooling. It identifies the anomalies of heat capacity and thermal diffusion that are responsible for structural phase transitions of the first order.

Keywords: thermal diffusion, heat capacity, multiwall carbon nanotubes, polymer composite.

Polymer materials find their application in many engineering systems and technological processes owing to their good mechanical characteristics, plasticity, chemical stability, and low cost. Adding carbon nanotubes (CNT) into the polymer matrix endows the material with new unique electrical, thermophysical and mechanical properties. When producing such composites, the problem consists in the need to ensure uniform distribution of CNT in the composite, as well as good mechanical linkage and chemical bond between the nanotube surface and the matrix material. The interest in studying conductivity of composite materials based on polymer with CNT was generated by publication [1, 2], where for the first time researchers showed the percolation nature of the charge transfer in a composite. Increase in the number of CNT in a polymer is accompanied by the increase in the composite conductivity. At present, there are studies on more than 250 composites containing different polymers with small concentrations of CNT. Physical properties of composites to a large extent depend on the sort of polymer, type and geometry of nanotubes (single-layer, multi-layer), production method, and non-uniform nanotube distribution [3]. Temperature dependences of electro- and thermophysical properties are characterized by considerable dispersion, even if CNT were produced on the same unit. CNT have high concentration of structural defects [4, 5]. Heat capacity (C_p) of single-wall and multiwall carbon nanotubes is studied in great detail both theoretically and experimentally in the range from room to helium temperature. It was demonstrated that at $T > 100$ K C_p is satisfactorily described by phonon contribution, while in the range of low T (below 100 K) the temperature dependence of heat capacity $C_p(T)$ is non-linear [6–9]. It is commonly believed that the usual electron contribution to C_p at low temperatures is by several orders of magnitude lower than the experimentally observed values of heat capacity. At the same time, it was found that low-temperature behavior of C_p in non-ordered nanotubes strongly depends on the structure of these materials, while observed leaps and bends in $C_p(T)$ are not explained by the phonon contribution. When calculating the electron heat capacity, the authors of [10] demonstrated that anomalous low-temperature behavior of C_p of non-ordered CNT has an electronic nature and is associated with electrons participating in the structural reordering. In the range of temperatures above room temperature, heat capacity of polymer composites based on CNT is significantly less studied. The interest in studying the temperature dependence of C_p above room temperature of the composite emerged after anomalous behavior of specific resistance (ρ) was

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revealed in the temperature range of 300 K $\leq T <$ 450 K [11–13]. The goal of the present paper is to study the temperature dependence of heat capacity of composite films based on a large number (95%) of multiwall carbon nanotubes (MWCNT), produced by the modified method of directed spinning, in the course of cyclical heating and cooling in the range of 300 K $< T <$ 450 K.

PRODUCTION OF COMPOSITE FILMS, RESEARCH METHODOLOGY

In order to produce a polymer composite in the fluoroplastic lacquer matrix (polytetrafluorethylene), MWCNT with average lengths of 100–200 nm, external diameters of 10–20 nm and internal diameters of 1.2–3.5 nm were used. They were produced by plasma arc method under special technological conditions. Unlike conventional plasma arc technologies of MWCNT growth in the gas phase, the liquid hydrocarbon phase was used with constant feed of argon to the plasma arc discharge zone. Cheap technical graphite with low catalyst content (natural iron admixture) was used as an anode. An advantage of this method is the increase in nanotube output. The output of deposit is around 100 g/h per anode with up to 100% conversion of graphite into MWCNT. MWCNT were first cleaned from micro-impurities of nickel and iron relying on the chemical technique using HNO_3; then they were dried and disintegrated. For the sake of modification MWCNT were treated in high-frequency plasma discharge for 300 s at the frequency of 40 MHz, power of 0.01–0.1 W/cm^3 and argon pressure in the range of 0.2–1.13 torr. After modification, MWCNT were injected into the liquid polymer matrix in the MWCNT/polymer mass proportion of 95/5 and were stirred for 10 minutes. The produced stable suspension (suspended MWCNT in the solution of polymer with acetone) was used to form a nanocomposite on the substrate by method of directed spinning from the liquid phase. The lacquer was produced at a varying crystallization rate, which leads to its shriveling and emergence of the varying degree of defectiveness [14]. The temperature of polymer decomposition corresponds to 630 K [15]. The study of the composite heat capacity was performed by method of AC calorimetry [16]. Average micro-calorimeter temperature was measured by copper-constantan thermocouple, the temperature oscillations on the sample – by chromel-constantan thermocouple, the junction of which was produced by spot welding of wires of 25 micron in diameter flattened to the width of around 3 μm. The thermocouple junction was glued to the sample with butvar-phenolic adhesive 2. One could notice that the glue was partially absorbed by the sample, but this should not influence the observed features of heat capacity of the composite, as far as heat capacity of the glue does not have any anomalies in this temperature range. The rate of heating and cooling was 2 K/min. Sample temperature oscillations were generated using the light flux from the incandescent lamp, modulated by mechanical interrupter. Samples with 3×3 mm dimensions were used for measurements. Relative measurement error is no more than 1%. The entire measurement process is automated.

RESEARCH RESULTS AND DISCUSSION

Figure 1 presents the results of research on the temperature dependence C_p of the polymer composite in the temperature range of 300 K $\leq T <$ 450 K.

Two heat capacity anomalies were identified on the presented curves – at $T \approx$ 340 and 420 K. In the coordinates of $C_p(T)$ anomaly near $T \approx$ 340 K is weakly manifested, but anomaly becomes more noticeable in the coordinates of C_p/T on T (see insert on Fig. 1). In the course of cooling, heat capacity maximums shift towards low temperatures (to $T \approx$ 330 and 390 K respectively), which indicates that these transitions are phase transitions of the first order. Let us note that temperature dependence of the polymer heat capacity in the range of 300 K $< T <$ 520 K is weakly non-linear and there are no anomalies in this temperature area [17]. Only certain processes occurring in the CNT subsystem can explain the experimentally observed behavior of the composite heat capacity. Let us note that the identified maximums on the temperature dependence of heat capacity $C_p(T)$ correspond to the maximums of specific resistance dependence on temperature $\rho(T)$ listed in publication [11]. Anomalies of physical properties of the composite are caused by the complexity of its structure. CNTs have high concentration of structural defects and are strongly contaminated by various admixtures, such as nanocarbon particles, metallic catalyst nanoparticles surrounded by graphite shell. Decreasing the concentration of structural defects is a serious technological challenge. Presence of heat capacity

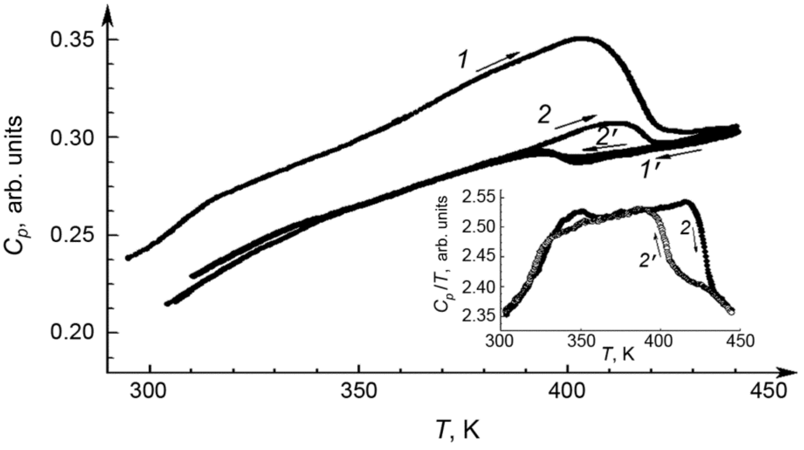

Fig. 1. Temperature dependence C_p of the composite in the course of heating and cooling: curve *1*, *1′* – first heating and cooling, curve *2*, *2′* – second heating and cooling, respectively. Insert – dependence of heat capacity on temperature in coordinates C_p/T on T.

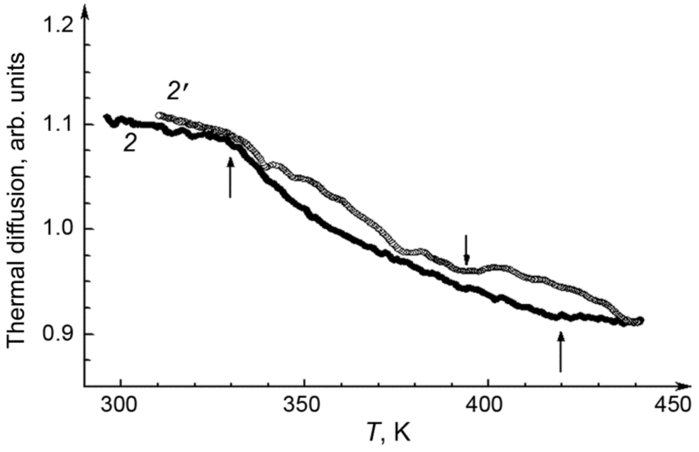

Fig. 2. Temperature dependences of the thermal diffusion coefficient in the course of composite heating and cooling: curve *2* – second heating, curve *2′* – cooling.

maximums can be explained, if one supposes that the ordering of amorphous polymer mass occurs near the interface with MWCNT in the course of heating and cooling of the composite. Scholars invest a lot of effort into studying the mechanisms of heat and charge transfer and corresponding transport characteristics of nanotubes depending on temperature. This is due to stochastic nature of CNT growth, the result of which is a wide variety of structural features of nanotubes.

Figure 2 presents the results of research on the composite thermal diffusion in the course of composite heating and cooling. It was demonstrated that its value decreases with the rise in temperature. Two anomalies are observed on the temperature dependence of the thermal diffusion coefficient, as well as on the heat capacity curves, with pronounced temperature hysteresis. The nature of dispersion of heat carriers in the composite changes, especially in the area of $T = 340$ K. Maximum C_p corresponds to the minimum of thermal diffusion. The presence of two maximums $C_p(T)$ and $\rho(T)$ indicates possible existence of two different defect types. Heat capacity anomaly in the area of $T = 340$ K is weakly expressed, while thermal diffusion is strongly expressed, and in the area of K it is the other way around. Our observations showed that the shape changes from round to ellipsoidal in MWCNT under the impact of omnidirectional pressure of the examined composite [18], and the authors of [19, 20] provided a theoretical explanation for the structural changes within the concept of long-term elastic deformation. In order to resolve these issues and identify intramolecular and intermolecular interactions and relaxation processes in the temperature range, where $C_p(T)$ and $\rho(T)$ are observed, one needs to carry out research by means of Raman spectroscopy.

CONCLUSIONS

For the first time, the scholars have obtained the results of research on temperature dependence C_p and thermal diffusion of the polymer composite based on a large number of MWCNT (95%) in the range of $300\text{ K} \leq T < 450\text{ K}$. Observed anomalies of C_p and thermal diffusion are analogous to the anomalies ρ in this temperature range identified earlier. Hysteresis behavior of heat capacity and thermal diffusion in the course of composite heating and cooling is identified. A possible mechanism of anomalous behavior of heat capacity and hysteresis is suggested that can be confirmed by the method of Raman spectroscopy.

REFERENCES

1. A. V. Eletskii, Advances in Physical Sciences, **50**, Issue 3, 225–261 (2007).
2. A. V. Eletskii, Phys. Usp., **50**, Issue 3, 225 (2007).
3. A. V. Eletskii, A. A. Knizhnik, B. V. Potapkin, J. M. Kenny, Advances in Physical Sciences, **58**, Issue 4, 209–251 (2015).
4. C. Se, H. Cuniberti, and T. Cagin, Nanolitt., **11**, 4971–4977 (2011).
5. J. Hone, Topics Appl. Phys., **80**, 273 (2001).
6. M. I. Bagatskii, M. S. Barabashko, and V. V. Sumarokov, Low Temp. Phys., **39**, 568 (2013).
7. M. I. Bagatskii, M. S. Barabashko, A. V. Dolbin, *et al.*, **38**, Issue 6, 667 (2012).
8. G. A. Jorge, V. Bekeris, and M. M. Escobar, Carbon, **48**, 525 (2010).
9. C. Masarapu, L. L. Henry, and B. Wei, Nanotechnology, **16**, 1490 (2005).
10. V. E. Egorushkin, N. V. Melnikova, A. N. Ponomarev, in: Proceedings of the International Scientific-Technical Conference "Nanotechnologies of Functional Materials" (NFM 2014) [in Russian], St. Petersburg (2014), 16–18.
11. A. A. Babaev, P. P. Khokhlachev, E. I. Terukov, *et al.*, Phys. Solid State, **57**, Issue 2, 424– 427 (2015).
12. A. A. Babaev, P. P. Khokhlachev, Yu. A. Nikolaev, *et al.*, Perspektivnye Materialy [in Russian], Issue 13, 846 (2011).
13. A. A. Babaev, P. P. Khokhlachev, Yu. A. Nikolaev, in: Proceedings of the International Scientific Conference "Pressing Problems of Solid State Physics" (FTT 2013) [in Russian], Minsk (2013), 143–145.
14. N. A. Bugorkova, D. D. Chegodaev, L. V. Chereshkevich, Plastic Masses [in Russian], Issue 5, 65 (1970).
15. Reference Book of CJSC Ftoroplastovye Tekhnologii [in Russian]; http://www.plastpolymer.org/f.42.htm.
16. P. Sullivan and G. Seidel, Phys. Rev., **173**, 679–685 (1968).
17. V. E. Egorushkin, N. V. Melnikova, A. N. Ponomarev, N. G. Bobenko, in: Proceedings of the International Scientific-Technical Conference "Nanotechnologies of Functional Materials" (NFM 2014) [in Russian], St. Petersburg (2014), pp. 16–18.
18. T. E. Arslanov, A. A. Babaev, R. K. Arslanov, *et al.*, Appl. Phys. Lett., **105**, Issue 20, 103 (2014).
19. H. Shima and M. Sato, Phys. Status Solidi, **A206**, Issue 10, 2228–2233. DOI: 10.1002/pssa.200881706 (2009).
20. H. Shima, S. Ghosh, M. Arroyo, *et al.*, Computat. Mater. Sci., **52**, 90–94 (2012).