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Effect of Carbon Nanotubes on the Electrical Properties of the Polymeric Composites

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***Abstract* – Experimental study of single-wall carbon nabotubes (CNT) effect on the electrical properties of polymeric composite materials based on epoxy matrix has been carried out. Direct-current (DC) as well as alternating-current (AC) electrical conductivity of nanocomposites with different CNT concentrations have been investigated in the temperature interval from 293 K to 373 K. Measurements of Seebeck coefficient confirm n-type conductivity of composite with CNTs.**

Percolation threshold of the composite material under study has been estimated. It has been found that addition of single-wall CNT at low concentration causes hysteresis of current-voltage characteristics and the temperature dependences of electrical conductivity as well as its anisotropy in the samples under study. No noticeable frequency dependence of the AC electrical conductivity has been found in the frequency range from 100 Hz to 300 kHz.

Keywords* – *polymeric composites, carbon nanotubes, electrical conductivity.

I. NTRODUCTION

Carbon nanotubes (CNT) have a great influence not only on mechanical but also on electrical properties of polymeric composites [1 – 5]. Due to the large aspect ratio of CNT, even a small amount of doping (at a level of 0.01 – 0.1%) is enough to increase the electric conductivity of the material by many orders of magnitude when CNT concentration exceeds the percolation threshold [5].

Electrical properties of CNT / polymer composites depend upon many factors including aspect ratio, type and geometry of CNTs, their concentration, spatial distribution and orientation, state of the contact between adjacent nanotubes as well as between CNT guest substance and polymer host matrix [4, 5].

Nonhomogeneous distribution of CNTs inside the volume of composite material leads to the large scatter of measured electrical characteristics of the sample under study. Thus, there exists a strong dependence of electrical properties of CNT / polymer composites on their preparation experimental procedure.

In this work, electrical properties of polymeric composite materials CNT / epoxy based on host epoxy matrix with glass fibers and single-wall CNT guest substance has been studied.

II. Materials and Methods

Methods of the samples' preparation and their structure were described in detail in [6].

The temperature dependences of the electrical characteristics of the samples with graphite electrodes in the temperature interval from 293 K to 373 K were obtained upon continuous heating or cooling with a rate of 1 to 2 degrees per minute. Alternating-current (AC) conductivity was measured by an E7-13 impedance meter at the frequency of 1 kHz. Direct current (DC) measurements were carried out by micro ammeters F195 and M95 or multimeter APPA 605. Frequency dependence of the AC electrical conductivity has been analyzed by admittance bridge MPP 300 in the frequency range 100 Hz – 300 kHz.

Thermal electromotive force of the samples under study was measured by pulse method proposed in [7].

III. Results and Discussion

Fig. 1 shows SEM image of the glass fibers arrangement in epoxy-based composite under study containing carbon nanotubes [6]. One can assume that CNTs inside the composite material are partly oriented in parallel to these glass fibers.

Fig. 2 confirms this assumption, demonstrating noticeable anisotropy of direct-current (DC) specific electrical conductivity σ of *CNT / epoxy* composite: $\sigma_{\parallel} : \sigma_{\perp} \approx 2$, i.e., electrical conductivity along glass fibers is about two times larger than that across them.

Such anisotropy of conductivity (or electrical resistance) was observed earlier in other experimental works (especially at low content of CNT additive) and received a theoretical explanation [5]. The reason for this is that at a low concentration of the additive, the percolation network containing a small number of

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conduction channels changes significantly as a result of giving the nanotubes even a small ordering, since this significantly affects the structure of the percolation network (at a low content of the additive, even weak anisotropy increases the number of percolation paths).

It should be noted that one can approximate the current-voltage characteristics of *CNT / epoxy* composite by a power law $I = U^{m}$, where $m \geq 1$ (Fig. 3). When direct current flows across the glass fibers, m = 1 in all the investigated voltage diapason (Fig. 2, curve 1). Direct current flowing along glass fibers obeys Ohm's law only for small values of applied voltage (Fig. 2, curve 2).

Besides the pronounced nonlinearity, attention is also drawn to hysteresis of the current-voltage characteristics measured in the longitudinal direction, and the magnitude of the current on the descending branch of the hysteresis loop exceeds the corresponding value on the ascending branch at the same voltage (Fig. 2, curve 2). This result can be presumably associated with the formation of new conducting channels near the ends of nanotubes, where the electric field strength reaches values sufficient for the local breakdown of the thin layers of the dielectric surrounding the nanotubes. It is noted in the literature [8] that internal discharges are a common phenomenon for polymers; in the systems containing nanotubes, the probability of such processes obviously should increase.

Formation of new conducting paths may also occur as a result of sample heating. Therefore, the weak temperature dependence of the electrical conductivity of the nanocomposites under study often also demonstrates hysteresis (Fig. 4).

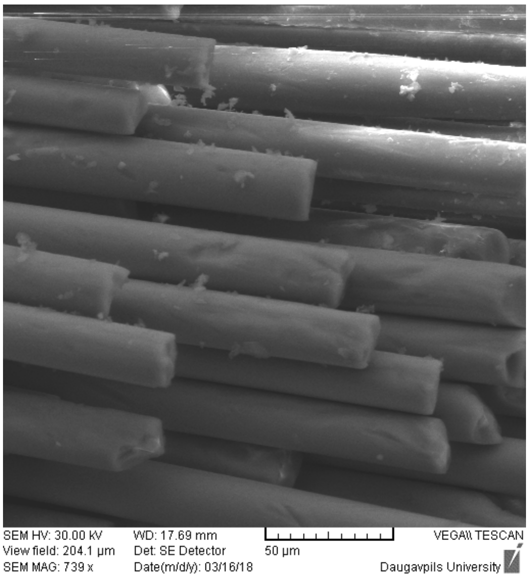

Fig. 1. SEM image of the glass fibers arrangement in epoxy-based nanocomposite containing carbon nanotubes [6].

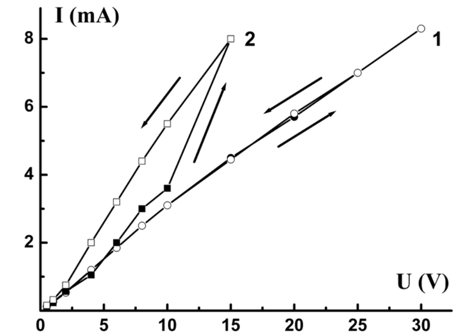

Fig. 2. Current-voltage characteristics of *CNT / epoxy* composite. Direct current flows across (curve 1) and along (curve 2) glass fibers. Arrows indicate forward and reverse directions of voltage changes.

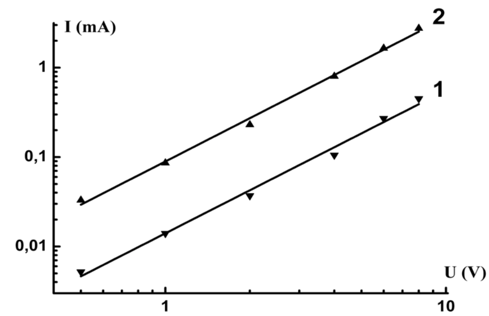

Fig. 3. Direct current-voltage characteristics of the nanocomposite samples under study with different CNT concentration values in polymer matrix: 0.02 wt. % (curve 1) and 0.08 wt. % (curve 2), respectively.

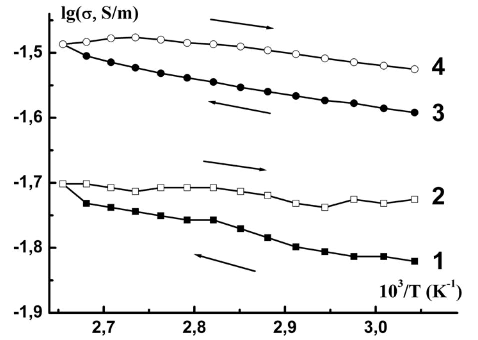

Fig. 4. Arrhenius temperature dependences of the specific electrical conductivity of nanocomposite sample under study with CNT concentration value in polymer matrix W = 0.08 wt. %. Direct current (curves 1, 2) and alternating current (curves 3, 4) flow across glass fibers. Arrows indicate heating (curves 1, 3) and cooling (curves 2, 4) of the sample.

We did not observe any significant frequency dependence of the AC conductivity of *CNT / epoxy* composites under study in the frequency range from 100 Hz to 300 kHz. Frequency independence of the electrical conductivity of such systems is associated [5] with the presence of a large number of percolation junctions in the samples, which provides a sufficiently high conductivity at concentrations of nanotubes above the percolation threshold W_0.

The value of this percolation threshold $W_0 \approx (0.001 - 0.01)$ wt.% can be estimated from the concentration dependence of the DC electrical conductivity (Fig. 5), which obeys the power law [5]:

$$\sigma = A(W_{CNT} - W_0)^{t},$$

where t is the critical index (for the *CNT / epoxy* composites under study $t \approx 1$).

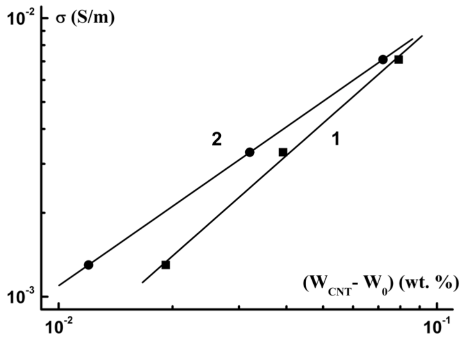

Fig. 5. Dependences of the DC specific electrical conductivity σ of CNT / epoxy composite under study on the CNT concentration W_{CNT} near the percolation thresholds $W_{01} \approx 0.001$wt.% (curve 1) and $W_{02} \approx 0.001$wt.% (curve 2) in double logarithmic scale.

Our investigations of the thermoelectric properties of the *CNT / epoxy* composite samples under study confirm *n*-type conductivity of composite with CNTs. Thus, the addition of CNTs leads to the formation of 3D conductive network within the dielectric matrix, hence the typical conductivity mechanism is observed (tunnelling of electrons from one filler to another [4]).

IV. Conclusions

Addition of carbon nanotubes (CNT) has a great effect on electrical properties of polymer-based composites due to the percolation processes even at a very low doping level.

Anisotropy and hysteresis of electrical conductivity of the *CNT / epoxy* composite samples under study have been experimentally observed. These results have been attributed to the peculiarities of conducting paths formation in the percolation network.

Electronic mechanism of the *CNT / epoxy* nanocomposites conductivity has been confirmed by the measurements of Seebeck coefficient sign of the samples under study.

Acknowledgements

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