Conductivity of a carbon nanotubes-epoxy resin nanocomposite

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Abstract. Multi-walled carbon nanotubes (CNTs) were used to reduce the electrical resistivity (i.e., increase the conductivity) of industrial epoxy. Samples loaded with 6 wt.% CNTs showed a 9-fold increase in the conductivity. The starting epoxy resin is dielectric. The electrical resistivity data showed a percolation threshold between 0.5 and 2 wt.% CNTs loading. The temperature coefficient of electrical resistivity of the samples containing 2 wt.% in the temperature range from 20 to 60°C was $11.5 \times 10^{-3} \text{ K}^{-1}$. These results suggested that the conductivity of the CNTs-epoxy composites is improved, without any need for chemical functionalization of the nanotubes.

1. Introduction

The interest in developing novel hybrid composite materials based on carbon nanotubes (CNTs) is caused by the unique properties of the latter [1-4], which leads to a wide range of applications, from electronic elements to antistatic coatings. These materials include conductive composites [5-8], high-strength lightweight construction materials [9-12], and composites used as sensors [10,13-15] and even as sorbents [12,16-18]. When developing new materials, one should focus on components manufactured on an industrial scale. CNTs are mainly produced in laboratory amounts, but in the present work, we address the manufacturer of CNTs in large amounts.

The methods used for a long time to impart electrical conductivity to polymeric materials are based on introducing large quantities (60-80 %) of electrically conductive materials (graphite, metals, and various titanium compounds), which results in a softening of the matrix and a decrease in strength and performance characteristics. Considering this fact, the guideline of this work is the development of a physico-mechanical method for introducing and dispersing CNTs (trademark Taunit and Taunit-M) in an epoxy matrix (trademark ED-20) in order to achieve electrical conductivity of about 2-3 Ohm·m, with small amounts of the nanocarbon additive (6-9 %). The proposed method should combine the filling of CNTs with conventional fillers to positively affect its industrial application due to the conductivity indicators comparable with that of competitors’ and reduced cost.

In the present paper, we measured electrical resistivity, but we also talk about electrical conductivity, implying that the former is the inverse of the latter.

Therefore, the aim of the work is to determine the effect of CNTs (their type and concentration) on the conductive properties of a polymer matrix.
2. Materials and methods

Taunit and Taunit-M multi-walled CNTs (hereinafter referred to as CNTs-t and CNTs-m, respectively) commercially produced by NanoTechCenter Ltd. (Tambov, Russia) were used as conductive additives. Their characteristics are presented in Table 1, whereas their structure is shown in figures 1 and 2.

| Parameters                              | CNTs-t | CNTs-m |
|-----------------------------------------|--------|--------|
| Outer diameter, nm                      | 20-50  | 10-30  |
| Internal diameter, nm                   | 10-20  | 5-15   |
| Length, μm                              | ≥ 2    | ≥ 2    |
| Bulk density, g/cm³                     | 0.3-0.6| 0.025-0.06|
| Specific surface area (nitrogen sorption), m²/g | 160 | 270 |

The difference in the CNTs diameters means various quantities of layers, and as a result, larger CNTs amounts contained in 1 g of substance and, respectively. Consequently, when introducing the same weight percent amounts of the CNTs, the CNTs effect on the composite conductivity will be different.

The percent of the CNTs introduction into the epoxy matrix was 0.5-6 wt.%. Since the CNTs represent agglomerates, which can be seen in the scanning electron microscopy (SEM) images of the pristine CNTs (figures 1 and 2), their introduction was accompanied by dispersion in a viscous matrix that impeded their agglomeration. The dispersion and distribution in the monomer bulk occurred in a gap of 5 μm, with a shear flow at a speed of 120 rpm for 30 min, and with subsequent sonication at a power of 2 kW for 30 min. The effect of the method proposed on the particle dispersion was assessed through dynamic light dispersion (i.e., dispersion of light over particles in the course of Brownian motion) on a “Nicomp 380 ZLS” analyzer (Particle Sizing Systems inc., USA). The dynamic light dispersion technique makes it possible to estimate the effective size of disperse phase which would be the true size if these particles were spherical. Since the CNTs and the agglomerates formed by them are not spherical, the results obtained allow assessing only changes in the disperse composition of the analyzed suspensions of the CNTs in the epoxy monomer. The analysis time was 5 min. The initial dispersion of the CNTs-t and CNTs-m was within the region of 5-35 μm, and after their introduction in the proposed way, it was 500 nm.

To determine specific electrical resistivity, a "Teraommetr E6-13A" measuring instrument (Punane RET, Estonia) was used. Samples represented cylinders with a diameter of 4 mm and a length of 40 mm.
The contacts were connected by applying the same downforce from the sample ends. Knowing the sample resistivity and geometry, the specific volume resistivity was calculated using the standard formula. The temperature coefficient of resistivity was evaluated according to the standard approach. The specific resistivity of the sample was determined at 20 °C and 60 °C and the temperature coefficient of resistance was estimated according to equation (1):

$$\alpha = \frac{1 \cdot \Delta \rho}{\rho \cdot \Delta T}$$

where, $\rho$ – the electrical resistivity; $\Delta \rho$ – the difference in electric resistivities at $\Delta T$; and $\Delta T$ – the temperature difference, at which the resistance was measured.

The error of all the studies carried out was < 10 % (six replicates per one experimental point).

3. Results and discussion

The SEM images of the CNTs-t and CNTs-m incorporated into the epoxy matrix structure are represented in figures 3 and 4, respectively. From these images, it can be concluded that the CNTs distribution in the epoxy matrix is fairly uniform and has no air cavities.

![Figure 3. An SEM image of the CNTs-t (5 wt.%) microstructure in the epoxy resin (sample fracture, scale bar is 200 nm).](image1)

![Figure 4. SEM image of the CNTs-m (5 wt.%) microstructure of in the epoxy resin (sample fracture, scale bar is 200 nm).](image2)

The research conducted showed that the CNTs-m possess the best conductivity, in comparison with the CNTs-t (figure 5), presumably they had various chirality. Besides, it was confirmed that using the CNTs-m made it possible to develop novel conductive polymer nanocomposites with a resistivity of about 2.5 Ohmꞏm and filling degree of 6 wt.%. The introduction of more than 6 wt.% of the CNTs makes the monomer considerably thicker (i.e., they increase viscosity). It can be assumed that being an electrical conductor, the CNTs form a percolation circuit which lines up on the boundary of macromolecules during their polymerization, thereby imparting the conducting properties to the material (this occurs when 2 wt.% of CNTs are introduced).
Figure 5. Specific resistivity changes depending on the additive type and content.

Figure 6. The average volume of the epoxy resin corresponding to 1 CNTs-m one in the 2-wt.% nanomodified epoxy binder.

According to the estimates, in the nanocomposite reinforced with 2 wt.% of the CNTs, the epoxy polymer volume of $0.5 \times 10^{-20}$ corresponds to 1 CNTs-m (figure 6). In the same way, the temperature coefficient of resistivity of the samples containing 0.5 wt. % of the CNTs was measured. The coefficient values were found to be as follows: $\alpha_{0.5\%}=8.8 \times 10^{-3} \text{ K}^{-1}$, and $\alpha_{2\%} = -11.5 \times 10^{-3} \text{ K}^{-1}$.

The negative coefficient value refers to semiconductors and hybrid materials. In the nanocomposite developed, the CNTs were separated with contact barriers, and the temperature increase caused the electrical resistivity decrease, which lies in accordance with the fluctuation induced tunneling model described elsewhere. In case of the sample containing 0.5 wt.% of the CNTs, the increase in the resistivity with raising the temperature can be explained with a negative effect of the rather large coefficient of bulk thermal expansion found for the epoxy matrix on the unstable percolation circuit.

4. Conclusion
The effect of CNTs-t and CNTs-m effect on the electrical conductivity of the epoxy matrix as a function of concentration was determined. Only CNTs-m can be used effectively to provide conductivity for the epoxy-based composites. The electrical resistivity data showed a percolation threshold between 0.5- and 2-wt.% CNTs loading. The methods proposed for the introduction and dispersion of CNTs showed their effectiveness with the aim of obtaining an electrically conductive polymer nanocomposite that is not inferior in the properties to analogs, but significantly differs in price, due to the use of CNTs-m (price 1.6 USD per gram) [20].

Acknowledgement
The reported study was funded by RFBR (Russian Foundation for Basic Research) according to the research project No. 18-29-19121/18.

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