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Electrically Conductive Composite based on Functionalized Carbon Nanotubes/Epoxy Resin

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Abstract*: *This work is devoted to the study of the effect of carbon nanotubes functionalization on the electrical conductivity of composite materials based on them. Carbon nanotubes were functionalized by treatment in nitric acid and isopropyl alcohol. Changes in the morphology of multi-walled carbon nanotubes during liquid-phase functionalization were investigated using Auger-electron* microscopy. *Samples of composite material on the basis of initial and functionalized carbon nanotubes and epoxy resin were prepared and the concentration dependence of electrical conductivity using the four-probe method was studied. The study reveals the effect of functionalization in various solutions on the electrophysical properties of the obtained carbon nanotubes/epoxy composites.

Keywords*: *Carbon nanotubes, composite material, electrical conductivity, functionalization

I. INTRODUCTION

Due to their unique physicochemical properties and high aspect (length to diameter) ratio, carbon nanotubes (CNTs) are considered as promising fillers for various materials for the directed change in their mechanical and electrophysical properties [1]. It is known [2] that carbon nanotubes in its original form have a large surface energy and therefore form agglomerates. Agglomeration of CNTs leads to their irregular distribution in the material being modified. In addition, the surface of the nanotube forms only weak van der Waals bonds with the material [3]. Thus, the interaction between the nanotube and the material is weak. The most effective way to solve this problem is the functionalization of CNTs, which involves the attachment of various active functional groups to the surface of nanotubes. On the one hand, this allows to solve the problem of agglomeration of carbon nanotubes, and, on the other hand, to ensure the creation of covalent bonds between the nanotube and the material.

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Depending on the type of nanotubes, different processing methods are used [4-9]. However, in the process of thermochemical treatment, destructive processes may occur, leading to high defects of the tubes. High defects of nanotubes can lead to a decrease in the efficiency of material modification due to the deterioration of the physical properties of the tubes. There is also the possibility of complete destruction of nanotubes to amorphous carbon.

This work is devoted to the study of the influence of the treatment of multi-walled carbon nanotubes (MWCNTs) on their morphology and the electrical conductivity of composites based on them.

II. MATERIALS AND METHODS

The multi-walled carbon nanotubes (BAYTUBES C 150P) were purchased from Bayer Material Science and were used as received. These MWCNTs were produced in a high-yield catalytic process based on chemical vapor deposition with an outer mean diameter of 13-16 nm and inner mean diameter of 4 nm and approximately 1μm length. The purity of as-received MWCNTs was more than 95%.

Two types of MWNTs treatment was performed: functionalization of multi-walled carbon nanotubes in isopropyl alcohol and functionalization in HNO_3 in a ratio of 0.1 g of carbon nanotubes per 100 ml of solution. The treatment was carried out at 70°C for 1.5 hours in ultrasonic bath. After that, functionalized carbon nanotubes were washed with distilled water to a neutral pH and dried under vacuum at 90°C for 8 hours. At the output, samples of functionalized carbon nanotubes were used in the form of a dry powder.

The structure studies of the initial and functionalized carbon nanotubes were carried out using Auger-electron spectrometer JAMP 9510F ("JEOL", Japan) at ultrahigh vacuum (< 10^{-9} mmHg).

To prepare samples of composite material, MWCNTs were introduced into epoxy resin (ED-20) in the form of a dry powder. Carbon nanotubes were mixed with epoxy resin using a magnetic stirrer. Curing of the obtained composition were carried out by mixing with the hardener Triethylenetetramine.

The study of the conductive properties of the composite material was carried out by four-probe method. To do this, electrodes were attached to the surface of the samples using silver paste.

III. RESULTS AND DISCUSSION

3.1. Auger microscopy

Auger microscopy was used to establish the morphological changes and fragmentation of carbon nanotubes after functionalization (see Fig.1-3).

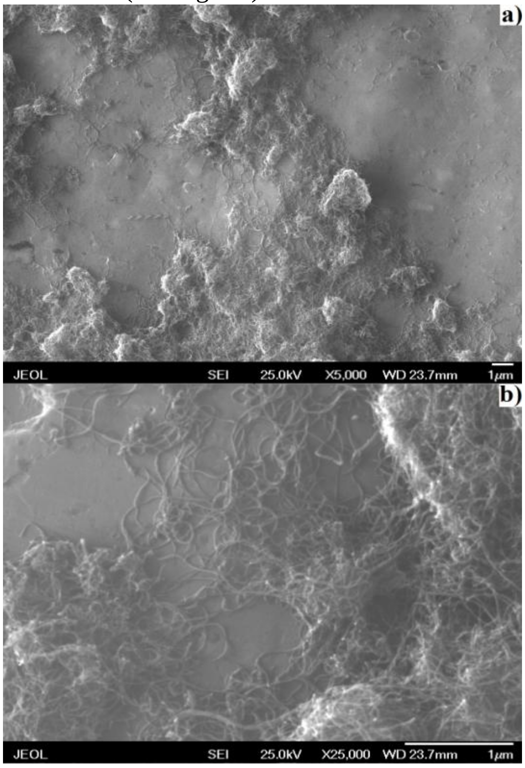

Fig. 1. Electronic micrographs at different magnifications of initial multi-walled carbon nanotubes.

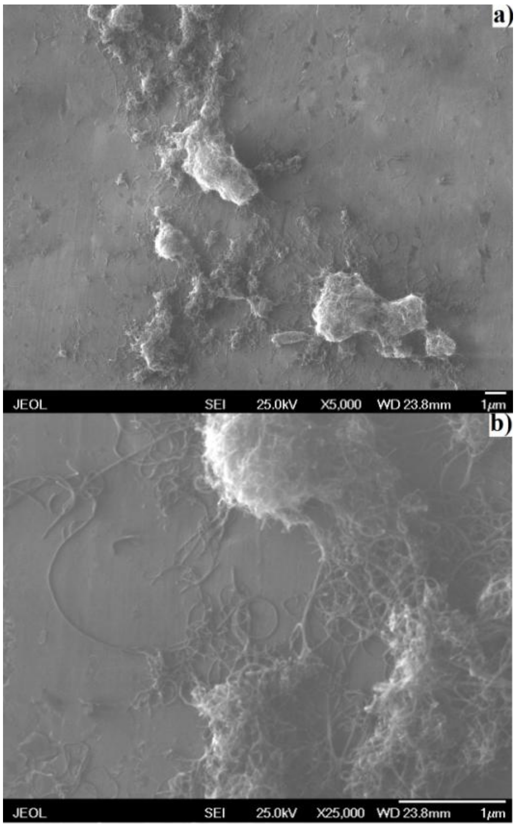

Fig. 2. Electronic micrographs at different magnifications of multi-walled carbon nanotubes treated in isopropyl alcohol.

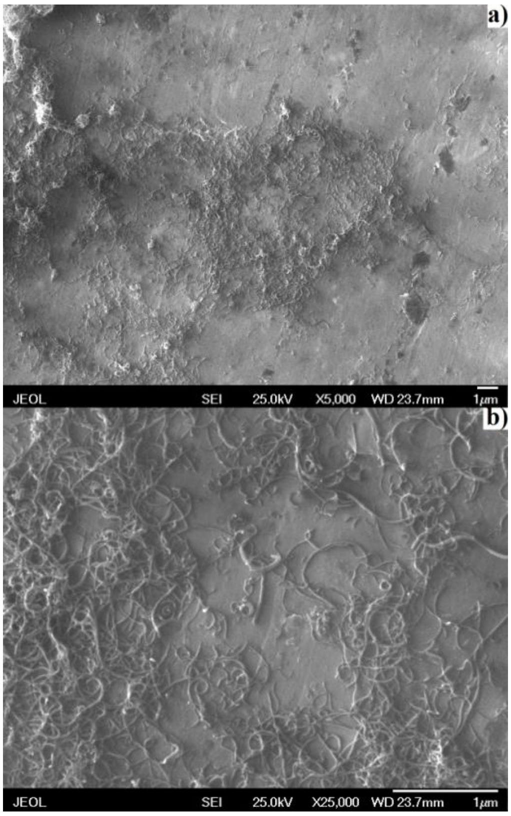

Fig. 3. Electronic micrographs at different magnifications of multi-walled carbon nanotubes treated in nitric acid.

Micrographs show that the treatment in isopropyl alcohol led to partial disintegration of agglomerates (Fig.2), whereas the treatment in concentrated HNO_3 (Fig.3) led to the agglomerates disintegration into individual nanotubes and MWNTs shortening.

3.2. Investigation of the conductive properties of the composite material using the four-probe method

In order to define the effect of the functionalization in different solutions on the electroconducting properties of the composite material, samples of the composite material based on epoxy with different concentrations of MWNTs were prepared. Figure 4 shows the concentration dependence of the electrical conductivity of the composite material. As one can see, the concentration dependence of the conductivity is nonlinear. Besides, the electrical conductivity of the composite based on MWNTs treated in a HNO_3 (sample №3) is 60% lower than that for sample based on initial MWNTs (sample №1). In the case of samples based on MWNTs treated in isopropyl alcohol (sample №2), the electrical conductivity is 27% higher than that for initial sample. The decrease in electrical conductivity for sample №3 may be due to the shortening of carbon nanotubes and their high functionalization, which makes the interaction of separate MWNTs more complicated and, therefore, hampers the formation of percolation channels.

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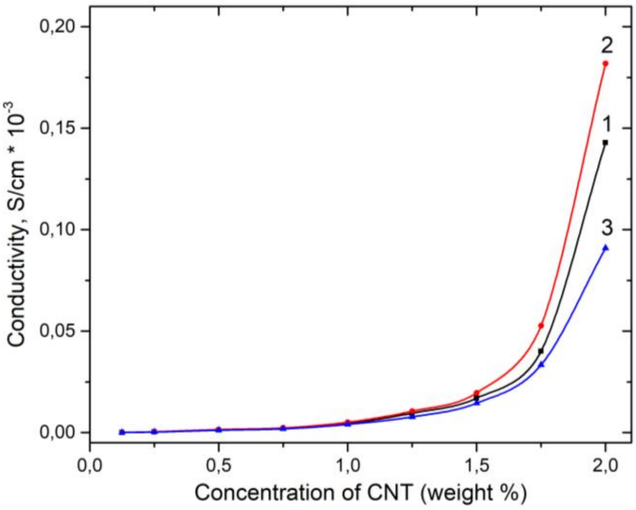

Fig. 4. Concentration dependence of the electrical conductivity of composite material (1-initial MWNTs; 2-MWNTs treated in isopropyl alcohol; 3- MWNTs treated in nitric acid).

Table 1 shows the experimental values of electrical conductivity of composite material samples.

Table - I: Electrical conductivity of composite material samples

Concentration of MWNTs, weight %	Electrical conductivity of samples of composite material based on carbon nanotubes, * 10^{-6} S/cm		
	Initial	Treated in isopropyl alcohol	Treated in nitric acid
2	143	182	91
1,75	40	52,6	33,3
1,5	16,95	19,61	14,49
1,25	9,52	10,5	7,69
1	4,5	5,03	4
0,75	2,01	2,22	1,84
0,5	1,25	1,43	1,14
0,25	0,33	0,36	0,22
0,125	0,04	0,042	0,031

In the case of sample №2, the increase in electrical conductivity could be due to the fact that the treatment in isopropyl alcohol led to partial disintegration of agglomerates but at the same time, MWNTs were not shortened during treatment, that allowed forming percolation channels in the polymer matrix more effectively. Differences in the electrical conductivity for composites could also be associated with diversed distribution of MWNTs processed in different solutions.

IV. CONCLUSIONS

Changes in the morphology of multi-wall carbon nanotubes during functionalization in different were studied. Using the Auger microscopy method, it was shown that the treatment of MWNTs in isopropyl alcohol allowed splitting agglomerates with minimal effect on the MWNTs length. In the case of carbon nanotubes treatment in nitric acid, their significant shortening was observed. The concentration dependence of the electrical conductivity of a composite material based on epoxy resin and CNT of different concentrations was studied using a four-probe method. It was shown that the concentration dependence of the electrical conductivity of a composite material was nonlinear, and a significant shortening of carbon nanotubes could lead to a decrease in the electrical conductivity of composites based on them.

In the literature, methods of MWNTs liquid-phase oxidation using nitric acid are applied and the functionalization degree of carbon nanotubes is usually being evaluated as an indicator of the effectiveness of the approaches used. However, much less attention is paid to changes in the structure and morphology of carbon nanotubes as a result of functionalization and the effect of these changes on the electrophysical properties of materials doped with them. Thus, the results obtained can be used in the development of epoxy composites doped with carbon nanotubes and having high electrical conductivity.

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