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## Structure and electrical conductivity of polyvinyl alcohol films with multi-walled carbon nanotubes cured in a magnetic field

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**Abstract:** The results of the study of the effect of the permanent magnetic field of a neodymium magnet on the polymerization process and the electrophysical characteristics of polyvinyl alcohol (PVA) films with the inclusion of multi-walled carbon nanotubes (MWCNTs) are presented. When studying the morphology of films using a scanning electron microscope, it was found that nanocomposite films with a thickness of 30 microns, cured in the presence of a magnetic field with the direction of the magnetic induction vector perpendicular to the surface of the films, have a homogeneous structure, while a significant number of MWCNTs agglomerations are observed in control samples of films. Measurements of the conductivity of films in the direction of the MWCNTs orientation at direct and alternating current showed that the conductivity of films obtained in a magnetic field significantly (by almost two orders of magnitude) exceeds the conductivity of control samples. The obtained results are analyzed on the basis of known models of electrical conductivity of nanocomposites with oriented MWCNTs. The degree of orientation of the MWCNTs during the curing of films in a magnetic field is estimated, taking into account the increase in the viscosity of the nanocomposite during the curing process.

**Keywords:** polymer nanocomposites, orientation of carbon nanotubes, magnetic field, nanocomposite films, electrical conductivity

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## 1. INTRODUCTION

The excellent mechanical and electrical properties of carbon nanotubes (CNTs) have made them one of the best fillers for nanocomposites [1]. Even a small amount of CNTs added to the polymer matrix is significantly changes the functional properties of nanocomposite polymer structures [2]. However, the observed improvements in the mechanical and electrical properties of nanocomposites are lower than expected [3]. The random orientation of CNTs in the matrix cannot properly transfer the desired unique properties of CNTs to the composite, since these properties are, as a rule, localized along the axis of the CNTs. It has been shown that CNTs alignment is an effective way to transfer these properties to the surrounding matrix [4-5]. Moreover, the alignment of CNTs in nanocomposites can lead to a significant decrease in their proportion to achieve the desired results [6].

A number of methods are used to align CNTs in a polymer matrix: self-assembly [7], the Langmuir-Blodgett method [8], exposure to electric [9] or/and magnetic field [3,5,6,10], etc. Since ordinary CNTs have a low magnetic susceptibility, fields of about 10-25 T are required to align CNTs in a magnetic field. [3,5,11]. In [11], for example, for the orientation of CNTs in a polypropylene-based nanocomposite, repeated exposure to a magnetic field pulse with magnetic induction at a maximum of 10 T and a duration of about 1 ms was used.

To solve this problem, CNTs containing magnetic impurities are usually used. Such CNTs exhibit high magnetic susceptibility and can be aligned in magnetic fields not

exceeding 1 T and easily achievable in conventional laboratories [10]. It should be noted that CNTs obtained by standard methods (such as, for example, CVD) and not subjected to additional purification can contain a sufficiently large amount of impurities, including ferromagnetic catalysts (for example, iron compounds), which increase the magnetic susceptibility of CNTs. Most of these impurities are encapsulated between CNT molecules, and some are inside them, and they can only be removed using complex multi-stage purification methods. This allows us to expect that commercially produced CNTs can have increased magnetic susceptibility and can be aligned in a polymer matrix with using magnetic fields below 1 T.

This paper presents the results of a study of the influence of the magnetic field of a conventional neodymium magnet on the polymerization process and the electrophysical characteristics of polyvinyl alcohol (PVA) films with the inclusion of multi-wall carbon nanotubes (MWCNTs).

## 2. MATERIALS AND METHODS

For the production of the nanocomposite, we used commercially available PVS 17-99 and MWCNTs of the «Taunit» brand produced by NanoTechCenter LLC (Tambov, Russia). According to the manufacturer, the MWCNTs had a diameter of 20-50 nm, a length of the order of 2  $\mu\text{m}$ , and the total amount of impurities did not exceed 10%. PVA is a widely used polymer and one of the best and widely used materials as a polymer matrix for creating film nanocomposite structures [12].

An aqueous solution of PVA was prepared in deionized water by continuous

stirring in a magnetic stirrer for an hour at a temperature of 90°C. The MWCNTs were dispersed in deionized water in the required ratio using an ultrasonic disperser. To improve the compatibility of the MWCNTs with the polymer matrix, the so-called non-covalent functionalization was used: 0.1% sodium dodecyl sulfate (SDS) was added to the water before dispersing MWCNTs. Then both solutions were mixed in the proportion necessary to obtain a given concentration of MWCNTs in relation to the weight of PVA, mixed in a magnetic stirrer for 30 minutes and cooled. The required amount of solution was poured into Petri dishes and dried at room temperature for 48 hours. During drying, one of the samples (hereinafter referred to as "m-film") was dried on the surface of a neodymium magnet, the second sample ("c-film") was dried without exposure to a magnetic field. The magnetic field strength near the surface of the neodymium magnet we used was measured by the ATE-8702 magnetometer (Aktacom) and was 0.3 T.

After evaporation of the solvent, nanocomposite films with a thickness of 30 microns were obtained. Square-shaped samples with dimensions of 1×1 cm were cut from the obtained films, which were clamped between flat brass contacts for electrical measurements. Measurements of current-voltage (I-V) characteristics were carried out on a setup including a programmable power supply APS-7313 (Aktakom), a DM4040 multimeter (Tektronix), and an A2-4 picoammeter (MNIPI). Frequency dependences of conductivity in the frequency range 50 kHz - 15 MHz were measured on an E7-29 meter (MNIPI). The surface morphology of the films was investigated using an

optical and scanning electron microscope (SEM, Phenom).

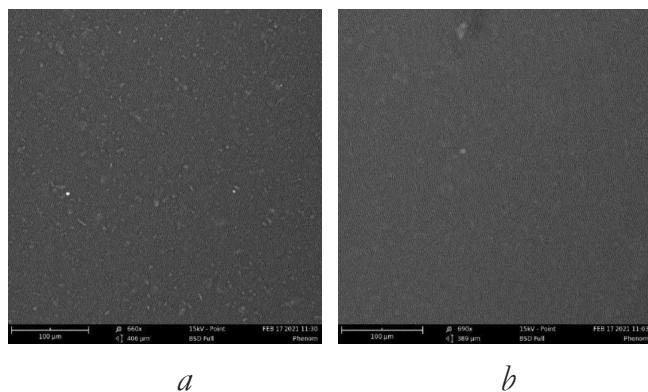
### 3. RESULTS AND DISCUSSION

To confirm the sensitivity of the MWCNTs used by us to the magnetic field, a glass with an aqueous suspension of a small amount of MWCNTs was placed in close proximity to a neodymium magnet. After 3 hours, the bulk of the MWCNTs in the suspension was grouped near the magnet (**Fig. 1**), which indicates that the used MWCNTs contain a significant amount of ferromagnetic impurities, which noticeably increase the magnetic susceptibility of MWCNTs.

**Fig. 2** shows the SEM images of the obtained samples of PVA films containing 1% of the mass fraction of MWCNTs. The photographs clearly show that the



**Fig. 1.** Aqueous dispersion of MWCNTs after 3 hours of exposure to a neodymium magnet.

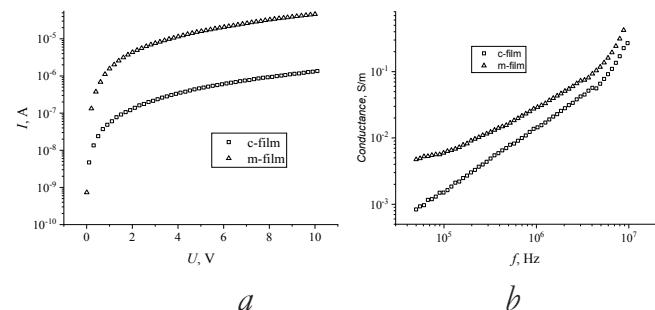


**Fig. 2.** SEM images of control nanocomposite films (c-film) (a) and films produced under the influence of a magnetic field (m-film) (b).

control films contain a large number of agglomerations several microns in size. At the same time, the films in which polymerization took place under the influence of a magnetic field have a fairly homogeneous structure.

Since in our experiment the m-film during the curing process was located coplanar to the surface of the magnet, then under the influence of the magnetic field the MWCNTs should be oriented along the field, that is, perpendicular to the surface of the film. With this orientation of the MWCNTs, the resolution of the SEM used by us, unfortunately, was not enough to directly reveal the fact of alignment of the MWCNTs.

An indirect confirmation of the alignment of the MWCNTs in the direction of the magnetic field can be a change in the conductivity of the films. **Fig. 3a** shows the I-V characteristics of the studied samples of films with a concentration of 1% MWCNTs measured at constant current. It can be seen that the current in films cured in a magnetic field is almost two orders of magnitude higher than the current in control samples. This ratio is maintained up to an MWCNTs



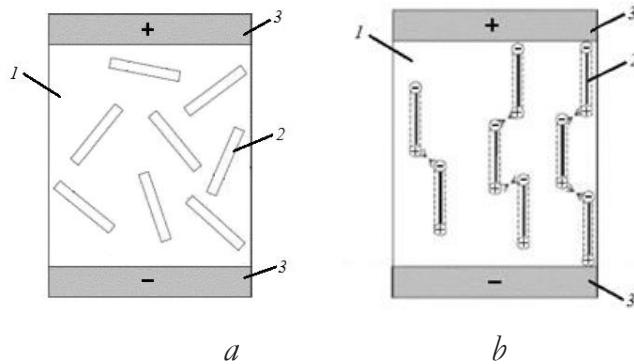
**Fig. 3.** Current-voltage characteristics (a) and frequency dependences of conductivity (b) of a control nanocomposite film (c-film) and a film cured under the influence of a magnetic field (m-film).

concentration of about 0.1%, when the resistivity becomes close to that of pure PVA, and it is no longer possible to detect a significant difference between the control samples and the samples exposed to the magnetic field.

Measurements of the conductivity of the films at alternating current (Fig. 3b) showed that the frequency dependence of the conductivity has a form characteristic of polarized dielectrics, namely, with an increase in frequency, a noticeable increase in conductivity is observed. In the entire frequency range, the conductivity of the films obtained in a magnetic field is noticeably higher than the conductivity of the control samples. At a frequency of 50 kHz, this difference was more than an order of magnitude, and with an increase in frequency, the difference decreases.

A similar frequency dependence of the conductivity was observed in epoxy nanocomposite films with oriented CNTs [13].

In the known models of electrical conductivity of nanocomposites [9,13], it is shown that the conductivity of a nanocomposite strongly depends on



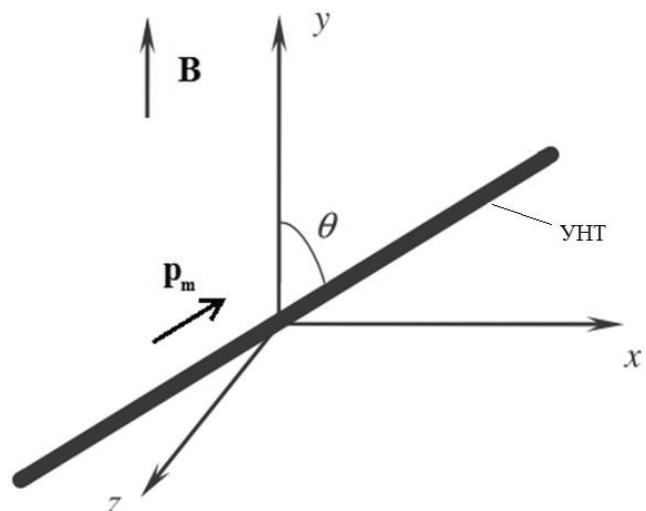
**Fig. 4.** Model of a film with unoriented (a) and ideally oriented (b) CNTs: 1 – polymer matrix; 2 – carbon nanotube; 3 – brass contacts.

the orientation angle of the CNTs with respect to the direction of the applied electric field. The schematic models of PVA films with randomly and oriented CNTs and metal contacts are shown in **Fig. 4**. At a low concentration of CNTs, an increase in electrical conductivity in films with oriented CNTs is explained by the appearance of an additional number of percolation chains of CNTs along the axis of their orientation.

In turn, the angle of CNTs orientation is determined by the intensity and time of application of the external magnetic field. To estimate, we will use a simplified model of the orientation of CNTs in a magnetic field, given in [14]. According to this model, CNT with a magnetic moment vector  $p_m$  and located in a magnetic field with a magnetic induction vector  $B$  (**Fig. 5**) are subjected to a torque  $M = [p_m \cdot B]$ , and the angle  $\theta$  between the vectors of magnetic induction and magnetic moment of the CNT is determined from the equation

$$8\pi r^3 \eta \frac{d\theta}{dt} = p_m B \sin \theta, \quad (1)$$

where  $t$  is the time of exposure to the magnetic field;  $\eta$  is the viscosity of the polymer nanocomposite;  $r$  is the radius of a



**Fig. 5.** Geometry of the CNT orientation problem in a magnetic field.

sphere with a volume equal to the volume of a carbon nanotube.

The numerical example given in [14], shows the possibilities of application for the alignment of the CNT field with the magnetic induction 0.28 T. For estimates in [14] the polymer viscosity was 30 Pa·s, however, the initial viscosity of real solutions of monomers before curing is significantly less and increases during the curing process. Let us estimate the change in the orientation angle taking into account the change in the viscosity of the polymer during the curing process. The simplest and, in our opinion, adequate law of viscosity change during polymer curing is the exponential law [15]:

$$\eta(t) = \eta_0 \exp(kt) = \eta_0 \exp\left(\frac{t}{\tau_0}\right), \quad (2)$$

where  $k^{-1} = \tau_0$  is the characteristic time that determines the curing rate, during which the viscosity increases by a factor of  $e$ .

Equation (1) with such a law of change in viscosity is reduced to the form

$$\frac{d\theta}{\sin \theta} = \frac{p_m B}{8\pi r^3 \eta_0} \exp\left(-\frac{t}{\tau_0}\right) dt. \quad (3)$$

Integrating both parts of (3) over the curing time, we obtain the following transcendental equation for the orientation angle:

$$\begin{aligned} \log \left[ \operatorname{tg} \left( \frac{\theta_{\text{cure}}}{2} \right) \right] - \log \left[ \operatorname{tg} \left( \frac{\theta_0}{2} \right) \right] = \\ = \frac{p_m B \tau_0}{8\pi r^3 \eta_0} \left( 1 - \exp \left( -\frac{t_{\text{cure}}}{\tau_0} \right) \right), \end{aligned} \quad (4)$$

where  $t_{\text{cure}}$  – is the curing time of the polymer,  $\theta_0$  – is the initial angle between the magnetic moment of the CNT and the vector  $B$ ,  $\theta_{\text{cure}}$  – orientation angle of the CNT in a cured nanocomposite.

To estimate, we take the initial orientation of CNT  $\theta_0 = 90^\circ$ , and the curing time is much greater than  $\tau_0$ , then we obtain a general expression for finding  $\theta_{\text{cure}}$

$$\log \left[ \operatorname{tg} \left( \frac{\theta_{\text{cure}}}{2} \right) \right] = \frac{p_m B \tau_0}{8\pi r^3 \eta_0}. \quad (5)$$

After substituting in (5) the approximate numerical values of the sizes of the used MWCNTs:  $r = 20 \text{ nm}$ ,  $l = 10 \mu\text{m}$ ; magnetic induction  $B = 0.3 \text{ T}$ , and, taking according to [14] the value of  $p_m = 1.0 \text{ meV/T}$ , we obtain the following expression for estimating the angle  $\theta_{\text{cure}}$  of the CNT orientation in the field of a neodymium magnet:

$$\log \left[ \operatorname{tg} \left( \frac{\theta_{\text{cure}}}{2} \right) \right] \approx -4 \cdot 10^{-4} \frac{\tau_0}{\eta_0}. \quad (6)$$

As can be seen from (6), with the accepted model law of the change in the viscosity of the mixture and prolonged curing, the orientation angle of the CNT does not depend on the curing time, but is determined, other things being equal, by the initial viscosity of the solution and the curing time constant. The values of these parameters were not determined by us, but

taking for example  $\tau_0 \approx 2400 \text{ s}$  (i.e. 40 min) and the initial viscosity of the solution  $\eta_0 = 1 \text{ Pa}\cdot\text{s}$  for the orientation angle  $\theta_{\text{cure}}$ , from (6) we obtain the value  $10^\circ$ . With an increase in the initial viscosity the orientation angle will increase. Expression (6) is convenient to use for a qualitative assessment of the expected angle of orientation of MWCNTs in PVA solutions cured in the field of a neodymium magnet, depending on the initial viscosity of the solution.

#### 4. CONCLUSION

As a result of the studies carried out on the effect of a constant magnetic field on the properties of nanocomposite PVA films with MWCNTs during their curing, it was shown that films, obtained under the influence of a magnetic field have a more homogeneous structure, while in the control samples there is a significant amount of agglomerations of MWCNTs. In the study of the electrical conductivity of the obtained samples, it was found that the films obtained in a magnetic field have a conductivity in the direction of the MWCNT orientation, which significantly exceeds the conductivity of the control samples.

A significant increase in the conductivity of nanocomposite films, cured under the influence of a magnetic field, can serve as an indirect fact confirming the alignment of MWCNTs along the direction of the magnetic field, which is well explained on the basis of existing models of electrical conductivity of polymer nanocomposites with oriented CNTs and qualitatively corresponds to the results obtained by other authors on other polymer nanocomposites.

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