Influence of the magnetic field on the formation and properties of polyvinyl alcohol - multi-walled carbon nanotube nanocomposites

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Abstract. The effect of a magnetic field on the polymerization process and the electrophysical characteristics of polyvinyl alcohol (PVA) films with the inclusion of multiwalled carbon nanotubes (MWCNTs) was studied. Using SEM micrographs, it was shown that the films obtained under the action of a magnetic field have a more homogeneous structure, while a significant number of MCNT agglomerations are present in the control samples. In the study of the conductivity at direct and alternating current, it was found that the films obtained in a magnetic field have a conductivity that significantly exceeds the conductivity of the control samples. It has been shown that the use of a magnetic field during polymerization has a noticeable effect on the properties and characteristics of nanocomposite films based on PVA and MWCNTs.

1. Introduction
The excellent mechanical and electrical properties of carbon nanotubes (CNTs) have made them one of the best filler materials for nanocomposites [1]. Even a small amount of CNTs added to a polymer matrix greatly alters 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 convey the desired unique properties of CNTs to the composite, because these properties, as a rule, are localized along CNTs axis. It has been shown that alignment of CNTs is an effective way of transferring these properties to the surrounding matrix [4-5]. Moreover, the alignment of CNTs in nanocomposites can lead to the use of a significant decrease in their proportion for the desired results [6].

To control the orientation of CNTs in a polymer matrix, a number of methods are used: self-assembly [7], the Langmuir-Blodgett method [8], exposure to an electric [9] or/and magnetic field [3,5,6,10], etc. Since CNTs have a low magnetic susceptibility, alignment of CNTs using a magnetic field requires a significant field strength (on the order of 15–25 T) [3,5]. To solve this problem, CNTs coated with magnetic nanoparticles are usually used, which exhibit a much higher magnetic susceptibility and can align in ordinary magnetic fields [10]. In addition, 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 catalyst metals. Most of these impurities are in an encapsulated state between CNT molecules, and some are inside them, and can only be removed using complex, multistage purification.
methods. This allows one to expect that commercially produced CNTs can have an increased magnetic susceptibility and can be aligned in a polymer matrix using magnetic fields below 1 T.

In this work, we studied the effect of the magnetic field generated by conventional neodymium magnets on the polymerization process and the electrophysical characteristics of PVA films with the inclusion of MWCNTs. PVA is a widely used polymer and one of the best materials as a polymer matrix for creating film nanocomposite structures [11].

2. Materials and methods
To produce the nanocomposite, we used a commercially available PVA of the 17-99 label and MWCNTs under the «Taunit» trademark manufactured by NanoTechCenter LTD (Tambov). According to the manufacturer's data, MWCNTs had a diameter of 20-50 nm, a length of ≥2 μm, and the total amount of impurities was ≤10%. 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 desired ratio by a sonicator. To improve the compatibility of MWCNTs with the polymer matrix, the so-called non-covalent functionalization was used. Before dispersing MWCNTs, 0.1% sodium dodecyl sulfate (SDS) was added to the water. Then both solutions were mixed in a magnetic stirrer for 30 minutes and cooled. After that, the required amount of the 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 neodymium magnets, the second sample (hereinafter referred to as "c-film") was dried without the influence of a magnetic field. The magnetic field strength of a neodymium magnet was measured with an ATE-8702 (Aktakom) magnetic meter and was 0.3 T.

After evaporation of the solvent, nanocomposite films with a thickness of 30 μm were obtained. To measure the thickness of the films, an optical micrometer MOV-1-16 was used in combination with a 10-x lens, with an absolute error of 0.5 microns.

Electrical measurements were carried out on these films using flat metal contacts. To measure the current-voltage (I–V) characteristics, we used an installation based on the APS-7313 (Aktakom) programmable power supply, DM4040 (Tektronix) precision multimeter and A2-4 (MNIPI) picoammeter. Immittance measurements were carried out in the frequency range 50 kHz - 15 MHz on an E7-29 (MNIPI) meter. The surface morphology of the films was investigated using an optical and scanning electron microscope (SEM, Phenom).

Figure 1. Water dispersion of MWCNTs after 3 hours of being near a neodymium magnet.
3. Results and discussion
First of all, we needed to make sure that the MWCNTs we used exhibit sensitivity to the magnetic field. For this, a small amount of MWCNTs was dispersed in water and placed near a magnet. After 3 hours, it can be observed (figure 1) that the bulk of the MWCNTs are grouped near the magnet. This suggests that the used MWCNTs contain a significant amount of metallic impurities and one can expect the production of nanocomposites with ordered MWCNTs when exposed to a magnetic field.

Figure 2 shows SEM images of PVA films containing 10% MWCNTs. It can be seen that the control films contain a large number of agglomerations of MWCNTs with a size of a few microns. At the same time, the film in which the polymerization took place under the influence of a magnetic field have a sufficiently homogeneous structure. It should be noted that in our experiment the magnetic field was directed perpendicular to the film surface, therefore, the ordered structures of MWCNTs should also be expected in the same direction. Unfortunately, the resolution of the SEM used by us is not enough to directly confirm or deny the fact of MWCNTs alignment. Indirect methods confirming the alignment of MWCNTs in the direction of the magnetic field can be measurements of the conductivity of the films in the same direction.

![Figure 2. SEM images of control nanocomposite films (c-film) and films obtained under the influence of a magnetic field (m-film).](image)

Figure 4 shows the current–voltage characteristics of the samples under study, measured at DC current. It can be seen that the current in films polymerized in a magnetic field exceeds the current in the control samples by almost two orders of magnitude for films with a 10% MCNT concentration. This ratio is retained up to a concentration of MWCNTs of the order of 1%, when the resistivity becomes close to the resistivity of pure PVA, and it is no longer possible to detect a significant difference between control samples and samples exposed to a magnetic field. Measurement of the conductivity on an alternating signal showed that the frequency dependence of the conductivity has a form characteristic of polarized dielectrics, namely, with increasing frequency, there is a noticeable increase in conductivity (figure 5). 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 is more than an order of magnitude, further, with increasing frequency, the difference decreases. Thus, a significant increase in the conductivity of films polymerized 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.
In summary, we investigated the effect of a magnetic field during polymerization on the properties of nanocomposite PVA films with MWCNTs as a filler. Using SEM micrographs, it was shown that the films obtained under the action of a magnetic field have a more homogeneous structure, while a significant number of MCNT agglomerations are present in the control samples. In the study of the electrical conductivity in the same direction with a magnetic field it was found that the films obtained in a magnetic field have a conductivity that significantly exceeds the conductivity of the control samples. Thus, the use of a magnetic field during polymerization has a noticeable effect on the properties and characteristics of nanocomposite films based on PVA and MWCNTs.

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