Investigation of the influence of polymerization temperature on the agglomeration process of the CNT in the composite matrix

A AGoshev¹, M K Eseev¹,²
¹Northern Arctic Federal University named after M.V. Lomonosov, Severnaya Dvina Emb. 17, 163002, Arkhangelsk, Russia
²Federal Center for Integrated Arctic Research, the Russian Academy of Science, Severnaya Dvina Emb. 23, 163000, Arkhangelsk, Russia

Abstract
The goal of this work is experimental study of electrophysical properties of polymer nanocomposites reinforced with multiwalled carbon nanotubes (MWCNTs) in alternating electric field in low frequency band of 0.01 Hz – 10 MHz. In this paper we present investigation concentration properties, different conduction mechanism, agglomeration effects and activation carrier process in composites based on epoxy resin with CNTs as addition of temperature region from 150÷300 K.

1. Introduction
At present, intensive research is being carried out in the field of nanocomposite materials, that is, one of the phases of which is nanoscale. It should be noted that the properties of such composites are not additive quantities of their phases and can differ very much from the properties of each component separately. Moreover, this concept allows to create a material with the required mechanical, electrophysical and other properties. A special place for such a filler is given carbon nanotubes (CNTs). The structure of CNT – tubular in the form of folded graphene sheets, it features a high aspect ratio (α ~ 100–1000) and a large surface area. Also, CNTs have good conductivity. This is related to the characteristic electronic band structure of graphene π-electrons and the type of its convolution (chirality) [1]. CNTs can have semimetallic or semiconductor conductivity, high individual specific strength, high adsorption capacity and other special properties. Recently, attention has been paid to composites with ultra-low concentration of CNTs. In this aspect, study the interphase layer in polymer composites with the addition of small concentrations of CNTs presented in [2] is of interest. The task of reducing the propensity of CNTs to agglomeration and the increase connection with the polymer matrix itself is also of interest [3], [4], [5].

2. Method
For the preparation of polymer composites we used epoxy ED–20 with solidifier of cold solidification PEPA as a composite matrix. MWCNTs Taunit–MD were used as a filler. For uniform distribution in the polymer matrix in the sample tubes were dispersed by ultrasonic disperser (MEF 91.1).
solidifier was added at fixed temperature after this. We have investigated the frequency dependence of our nanocomposite electrical characteristics by dielectric relaxation spectroscopy method [4, 6], according to which the sample is placed between the plates of the capacitor. The sample was exposed to an alternating electric field with a frequency varying in the band of 0.01 Hz – 10 MHz. The measured values were real and imaginary part of permittivity ($\varepsilon'$, $\varepsilon''$) and conductivity $\sigma$. To identify the activation properties of carriers in composites, we also used the dielectric relaxation spectroscopy method in the range of temperatures $T$ from 150 to 400 K.

3. Concentration dependence and agglomeration effect
To identify percolation processes, we prepared and investigated samples of different concentrations of CNTs. Below we show the dependence of the conductivity from the frequency of the electromagnetic field for the sample of different concentrations (Figure 1a) and dependence of the conductivity from the concentration at different frequency (Figure 1b).

![Figure 1](image)

**Figure 1.** a) Dependence of the conductivity from the frequency of the alternating field for polymer composites of different concentrations of CNTs ■ -0%, ■ - 0.025%, ■ - 0.05%, ■ - 0.1%, ■ -0.2%, ■ - 0.4%, ■ - 0.8%, ■ - 100%, for $T=22^\circ$C. b) Dependences of the conductivity of the polymer composite from the concentration for different frequency: ▲ -0.01 Hz, ▲ -0.013 Hz, ▲ -1.15 Hz, ▲ -9.98 Hz, ▲ -1.15 $10^3$ Hz, ▲ -1.15 $10^4$ Hz, ▲ - $10^7$ Hz.

Analysis of the data shows that the addition of CNT less than 0.1% practically does not contribute to the conductive properties of the composite (figure 1a). The transition to through conductivity occurs quite sharply, which is typical for such systems. The criterion in this case is the inflection point of the graph of the function $\sigma(n)$ (figure 1b). In the low–frequency region the percolation threshold is in the concentration range 0.12–0.14% and disappears at high frequencies (figure 1b). Conditionally, figure 1a can be divided into three intervals for CNT concentrations: the first from 0% to 0.1%, a slight increase in $\sigma$ due to the hopping conductivity, the second from 0.1% to 0.15% formation of the through conduction channel (percolation threshold), the third interval roughly from 0.15% to 0.8% is a smooth increase in $\sigma$, associated with the increase in the quantity channels of through conductivity. As mentioned earlier, CNTs tend to form agglomerates in a polymer matrix. To detect this phenomenon, a series of samples of equal concentration but different temperature input of the curing agent was prepared and measured. The more the temperature of the mixture where the hardener is injected, the faster the polymerization process takes place. Therefore, CNTs have less time to form agglomerates. As can be seen from figure 2, the conductivity of composites of equal concentration of CNT varies over a wide range of $10^3$, depending on the temperature input of the hardener entering the mixture (polymerization time). This in turn is a criterion for the degree of agglomeration of CNTs.
As can be seen from the above results (figure 1, 2), the $\sigma(F)$ dependences have a similar character. It is known that the frequency ($f$) dependence of conductivity for composite is well described following expression [6]:

$$\sigma(f) = \sigma_{dc} + Bf^t$$  \hspace{1cm} (1)

Where $\sigma_{dc}$ – is direct conductivity, $B$, $t$ – empirical parameters. The coefficients $B$, $t$ were chosen by fitting the experimental curves with a good degree of correlation. The results are shown in the tables below. The presented in tables results make it possible distinguish two groups of the samples: were conductivity is linear or non-linear dependents from $f$. As can be seen linearity with respect to $f$ is observed in a sample with good conductivity ($n = 0.8\%$), or on the contrary in dielectric sample ($n = 0\%$, $n = 0.1\%$).

**Table 1.** Fitting of Curves of concentration by the relation (1).

| n%, T=Const | $\sigma_{dc}$ S/cm | $B$ S/(cm·Hz$^t$) | $t$ |
|-------------|-------------------|-------------------|-----|
| 0.8         | $9.2\cdot10^{-5}$ | $2\cdot10^{-11}$  | 1   |
| 0.4         | $2.1\cdot10^{-6}$ | $6\cdot10^{-10}$  | 0.67|
| 0.2         | $1.5\cdot10^{-8}$ | $1\cdot10^{-10}$  | 0.67|
| 0.1         | $3\cdot10^{-13}$  | $4\cdot10^{-13}$  | 1   |
| 0           | $3\cdot10^{-13}$  | $4\cdot10^{-14}$  | 1   |

**Table 2.** Fitting of Curves of temperature by the relation (1).

| $^\circ\text{C}$, n=0.2% | $\sigma_{dc}$ S/cm | $B$ S/(cm·Hz$^t$) | $t$ |
|--------------------------|-------------------|-------------------|-----|
| 100                      | $1.8\cdot10^{-6}$ | $3\cdot10^{-11}$  | 1   |
| 80                       | $0.95\cdot10^{-5}$| $1.8\cdot10^{-11}$| 1   |
| 60                       | $0.8\cdot10^{-6}$ | $7\cdot10^{-10}$  | 0.67|
| 25                       | $2.5\cdot10^{-8}$ | $8\cdot10^{-11}$  | 0.67|
As suggested by the authors the reason for non–linearity with respect to \(w\) is associated with an equal contribution of two types of conductivity in the transition region: residual hopping and through conductivity, which is evident from figure 1a.

4. Activation processes in polymer composites

To study the activation processes in the samples with the same concentration but different time of polymerization, we researched temperature dependence these composit at the temperature range from 150 to 400 K. The following are the dependencies of conductivity \(\sigma\), real and imaginary part of permittivity \(E_1, E_2\) from the frequency of the external field \(F\), at different temperatures, show in figure 3 (a), (b), (c) respectively.

![Figure 3](image)

**Figure 3.** The dependence of conductivity (a), real part of permittivity (b), and the imaginary part of permittivity (c), from the frequency of the external field \(\log \|F\|\), at different temperatures. Green plot ■ – clean epoxy resin, yellow ■ – composite with CNT concentration \(n = 0.1\%\), polymerized at \(T_{\text{start}} = 40 ^\circ \text{C}\), red ■ – composite with CNT concentration \(n = 0.1\%\), polymerized at \(T_{\text{start}} = 100 ^\circ \text{C}\).

From the present results (figure 3), the agglomeration effect is also evident, which affects both quantitatively and qualitatively on the electrophysical properties of the composite. It is note that at a hardener input temperature \(T_{\text{input}} = 40 ^\circ \text{C}\), the composite in its electrophysical properties is almost similar to pure resin, in contrast to a composite of the same concentration but with \(T_{\text{input}} = 100 ^\circ \text{C}\). This is explained by the large dielectric layer between the conductive structure of the CNT in the matrix, and consequently the inhomogeneity of the distribution of individual CNTs in the composite (high degree of agglomeration). For example, in the low-frequency region at room temperatures, the conductivity of the sample with \(T_{\text{input}} = 100 ^\circ \text{C}\) exceeds the sample of the same concentration but with \(T_{\text{input}} = 40 ^\circ \text{C}\) at \(10^6\) times, and in the frequency range \(10^7 \text{ Hz}\) by almost 2 orders of magnitude (Figure 3a).

Calculation of the activation energy of carriers for certain regions can be carried out within the framework of the follow relation:

\[
\sigma_{dc} = A \cdot \exp \left( \frac{-E_a}{kT} \right)
\]  

(2)

To calculate the activation energy of carriers, it is convenient to represent the results in Arrhenius coordinates (see figure 4). As seen (from figure 4) the temperature dependence of the composite (\(n = 0.1\%\), \(T_{\text{input}} = 100 ^\circ \text{C}\)), is linear in the Arrhenius coordinates, in contrast to both the pure polymer and the composite (with \(n = 0.1\%\) and \(T_{\text{input}} = 40 ^\circ \text{C}\)). In the latter samples, two regions are clearly pronounced. The region of low temperatures (140–280 K), where the conductivity weakly depends on temperature. And the activation region (280–400 K) with activation energy \(E_a = 1.22 \text{ eV}\) (calculated from formula (2)). For a composite with \(n = 0.1\%, T_{\text{input}} = 100 ^\circ \text{C}\), the activation energy
of carriers $E_a = 0.041$ eV. This in turn also indicates a significant contribution to the conductivity of the tubes, and a reduction in the potential barrier between them. For pure resin, as well as for a composite ($n = 0.1\%$, $T_{\text{input}} = 100 \, \text{°C}$), there is a phase transition point $T_g$, in which character the temperature dependence of the conductivity varies. In the temperature region below the phase transition $T_g$, a conduction mechanism is realized that is associated with tunneling induced by thermal fluctuations. According to this mechanism, the electrical conductivity is due to the tunneling of electrons through a potential barrier of variable height, which is determined by local temperature fluctuations [6].

![Figure 4](image)

**Figure 4.** Dependences of the conductivity of polymer composites from temperature in Arrhenius coordinates: ● – clean epoxy resin, ■ – composite with CNT concentration $n = 0.1\%$, polymerized at $T_{\text{input}}=40 \, \text{°C}$, ♦ – composite with CNT concentration $n = 0.1\%$, polymerized at $T_{\text{input}}=100 \, \text{°C}$. $T_g$ – glass transition temperature.

5. Conclusions

We formulate main conclusions and results.

- A group of composites of various concentrations was studied by relaxation spectroscopy method. In the low-frequency region the percolation threshold is in the concentration range $0.12-0.14\%$ and disappears at high frequencies. Concentration dependence are presented, where find characteristic conductivity mechanisms in specific concentration regions. Such as area with hopping conductivity, area where through conduction channel is form (percolation threshold area) and area where directly increase in the quantity channels of through conductivity.

- A group of composites of equal concentration but different in the temperature hardener input was investigated. It is shown that the frequency dependences arising in this case are similar to the concentration dependences. In the framework of the well-known model (1) the fitting of the curves was carried out. A region deviating from linearity in $w$ is revealed. The reason for this behavior is associated with an equal contribution of two types of conductivity in the transition region: residual hopping and through conductivity.

- The processes of agglomeration of CNTs in a polymer composite are examined, it is shown that they strongly depend on the initial polymerization temperature of the sample. A method for minimizing the concentration of CNTs and their uniform distribution over a polymer matrix is proposed.

- Activation processes in a composite at various degrees of agglomeration are investigated. Qualitative and quantitative differences in activation processes of composites polymerized at different temperatures were revealed. Characteristic activation energies of carriers in the system are found.
References

[1] Meunier V, et al. 2016 Rev. Mod. Phys. 88 (2) 025005
[2] Mikitaev A K, Kozlov G V. 2016 Tech. Phys. 61 (10) 1541
[3] Dyachkova T P, et al. 2013 Nanosystems: Phys., Chem., Math. 4 (5) 605
[4] Goshev A A, Eseev M K, et al. 2016 J. Phys.: Conf. Series 741 012191
[5] Eseev M K, Vinnik L N, et al. 2016 AIP Conf. Proc. 1767 020026
[6] Eletskii A V, et al. 2015 Phys. Usp. 58 (3) 209