Investigation of dielectric properties of polymer composites reinforced with carbon nanotubes in the frequency band of 0.01 Hz - 10 MHz

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Abstract. The goal of this work is experimental study of dielectric properties of polymer nanocomposites reinforced with multiwalled carbon nanotubes (MWCNTs) in alternating electric field in low frequency band of 0.01 Hz – 10 MHz. We investigated the influence, functionalization degree, aspect ratio, concentration of carbon nanotubes (CNTs) on dielectric properties of polymer sample. We also studied the dependence of dielectric properties on the polymerization temperature. The dependence of CNTs agglomeration on sample polymerization temperature and temperature's influence on conductivity has been shown. We conducted model calculation of percolation threshold and figured out its dependence on CNTs aspect ratio.

1. Introduction

Intensive research of composite materials which include nanostructures such as CNTs as filler are being conducted recently. Due to large surface area of CNT and significant differences in the physical properties between nanocomposite and macrostate material, properties of nanocomposites are not additive characteristics of each phase and can radically differ from those of each of its components [1]. The data on the study of electrical and other properties of nanocomposites with CNTs is provided in the review [2]. As is known, the functionalization of CNTs - is an effective way to reduce their tendency to agglomerate, increasing the affinity of the components to the matrix of polymer compositions. Methods of functionalization are presented in the review [3]. Early we conducted experimental study of dielectric properties of composites with a matrix of silica filled with multi-walled CNTs at different concentrations in the scattering and absorption of electromagnetic radiation [4,5]. The aim of this work is an experimental study of dielectric properties of polymer nanocomposites with a matrix of epoxy reinforced with multi-walled CNTs at different concentrations and influence of functionalization degree and the concentration of CNTs on the dielectric properties.

2. The influence of polymerization temperature on composite conductivity

As we assume, a significant dispersion of dielectric characteristics values noted in [2] is connected with the parameter unconsidered earlier (polymerization temperature). In this work we additionally studied the influence of this temperature on composites electric properties. We used epoxy ED-20 with solidifier of cold solidification PEPA as a composite matrix. MWCNTs Taunit-MD (0.1% by weight) were used as a filler. For uniform distribution in the polymer matrix in the sample tubes were dispersed by ultrasonic disperser (MEF 91.1). The solidifier was added at fixed temperature after this. We have investigated the frequency dependence of our nanocomposite electrical characteristics by dielectric relaxation spectroscopy method [2,4], 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 (ε', ε'') and conductivity σ. Study of electrical properties of composites was accomplished using broadband dielectric spectrometer *Novocontrol concept 80*. We studied experimentally the dependence of polymer composite conductivity on temperature, at which the addition of solidifier had been made (figure 1).

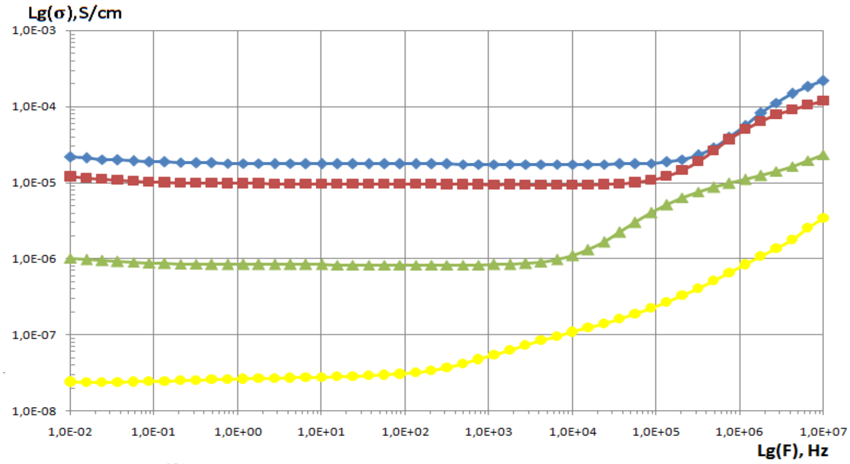

Figure 1. The dependence of conductivity of the composite with 0.1% of CNTs on the frequency of alternating electric field. Data for composites obtained by varying the polymerization temperature: curve ● – belong to the temperature T=20°C, curve ▲ – T=60°C, curve ■ –T=80°C, curve ♦ – T=100°C.

The result obtained agrees with the agglomeration mechanism studied by us earlier [4]. CNTs are prone to agglomeration because they have poor wettability by polymeric matrix in liquid state. That's why the bigger the solidification time, which directly depends on the temperature in the moment of addition of solidifier into dispersed medium, the bigger amount of CNTs transfer from the state of homogeneous distribution into agglomeration state (figure 2). Figure 2 also shows the model demonstrating behavior of the sample in measuring cell between plates of the capacitor.

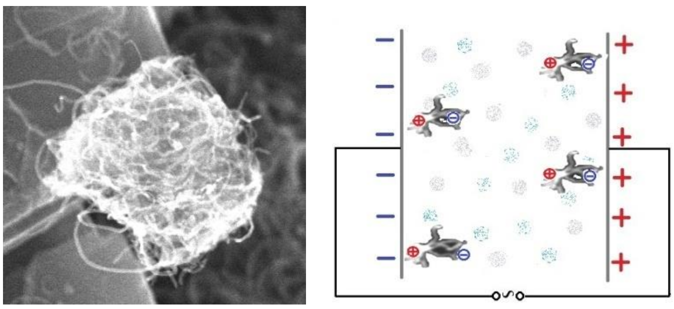

Figure 2. Image of the CNTs agglomerates (*Tescan 3SEM*). Model representation of the agglomerates in the measuring cell.

The effect of agglomeration is well observed on figure 1. In particular, we can see the displacement of percolation threshold into high frequency band from 10^2 Hz at T=20°C to $1.1\cdot10^5$ Hz at T=100°C. Table 1 shows the difference in conductivity of samples of same concentration at different frequencies.

Table 1.Increase of the conductivity at different frequencies depending on the sample temperature.

F(Hz)	$\frac{\sigma_{T=100℃}}{\sigma_{T=80℃}}$	$\frac{\sigma_{T=100℃}}{\sigma_{T=60℃}}$	$\frac{\sigma_{T=100℃}}{\sigma_{T=20℃}}$
10^6	1,13	5,08	67,6
10^3	1,86	20,8	319
1	1,84	21,1	675

3. Dielectric properties of composite with CNTs depending on functionalization degree

As known graphene sheet of CNTs can form only weak the van der Waals forces. For an uniform distribution in the polymer matrix and the formation of covalent bonds on the nanotubes surface they are functionalized.

Functionalization of MWCNTs is an effective way to decrease their tendency for agglomeration, to provide directed derivatization of the surface (figure 3), to increase affinity to a binder and other components of polymeric composition (figure 4). However, the oxidation process is accompanied with the destruction of MWCNTs external wall and with the decrease of aspect ratio, which is the consequence of shortening (burning of the ends) (figure 4).

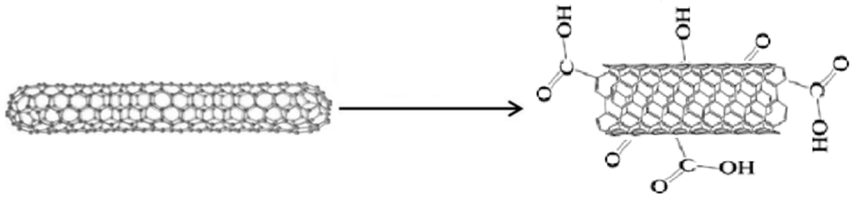

Figure 3. The process of CNTs functionalization in quasi liquid layer of hydrogen peroxide

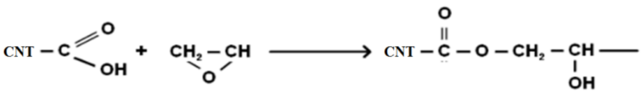

Figure 4. The connection scheme of CNTs functionalization to the polymer matrix through carboxyl groups.

In this experiment dielectric properties of samples of equal concentration of MWCNTs obtained by CVD method [3] were compared with ones of MWCNTs undergone the process of functionalization in quasi liquid layer of hydrogen peroxide during four hours at temperature of T=150℃ and the velocity of addition of v=10(ml/h). According to the data obtained in section 1, the temperature of solidifier addition was fixed to be constant T=60°C. The results of real part of permittivity dependence on frequency are shown below.

Journal of Physics: Conference Series **741** (2016) 012191 doi:10.1088/1742-6596/741/1/012191

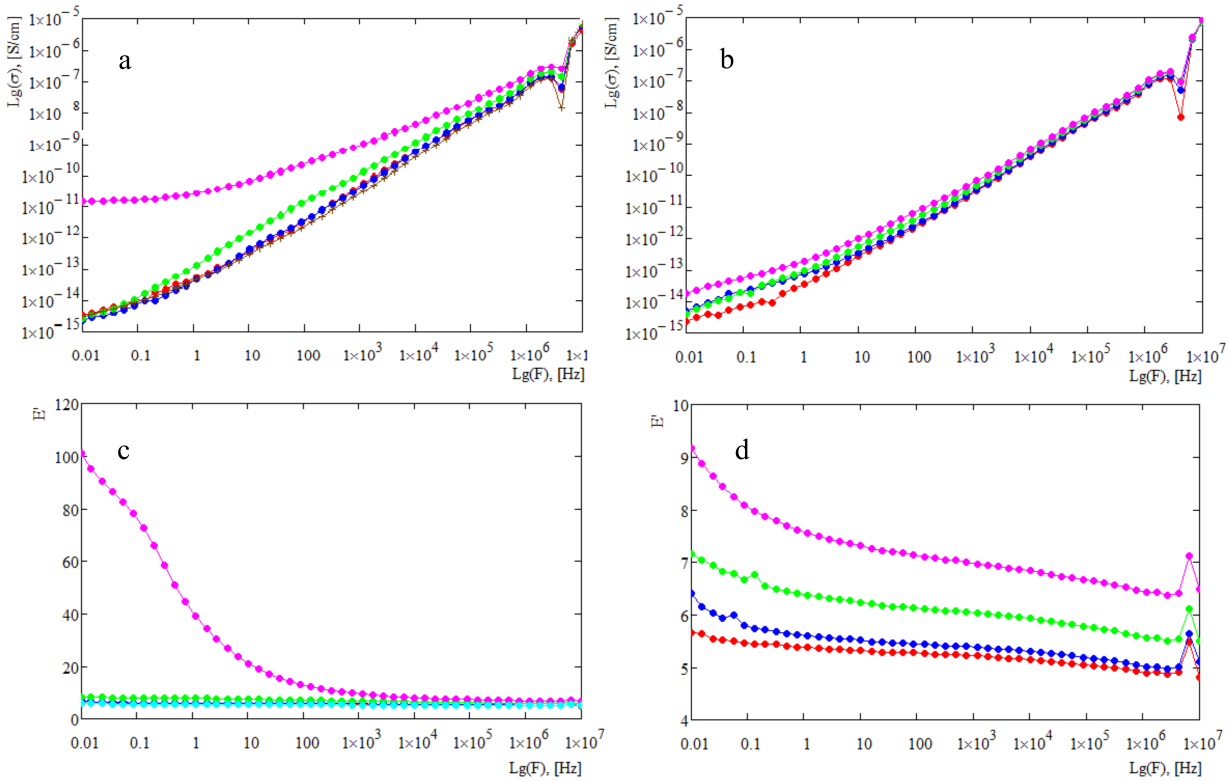

Figure 5. The dependence of the conductivity (a,b) and permittivity (c,d) of the sample on frequency of the alternating electric field.●●● - 0,3%; ●●● - 1%; ●●● - 3%;●●● - 6%; +++ - 0% (CNTs concentration in the composite); (a,c)- samples with CNTs, (b,d) - samples with functionalized CNTs.

The experiment shows that conductivity and permittivity of sample at low concentration changes insignificantly. Considerable change is observed at concentrations >3%. With the growth of CNTs amount in sample both absolute value of conductivity and value of the frequency, at which the transition from constant conductivity value to frequency-dependent value occurs, increases. The addition of functionalized CNTs leads to decrease of conductivity and increase of percolation threshold to more the 6%. The reason for that, as we assume, is in shortening of CNTs during the oxidation. The reason of such huge value of saturation threshold ~6% (figure 5a), in our opinion, is in small aspect ratio of CNTs.

4. Dependence of conductivity on aspect ratio

For the detection of polymeric composite dielectric properties dependence on the aspect ratio α = *L*/*D* (*L*-length, *D* – external diameter of MWCNTs) the CNTs of two types were used in the experiment. Multi-walled nanotubes "*Taunit-MD*" (*NANOTECH*, Tambov) are pictured on figure 6. MWCNTs obtained in our lab by CVD method (CNT_{Lab}) with nickel catalyst [4] are shown on figure 7. The polymeric composites based on epoxy with different percentage of CNTs were prepared using these tubes. The methodic of sample preparation is described in section 1.

Visual method of SEM was used for approximate estimation of the aspect ratio.

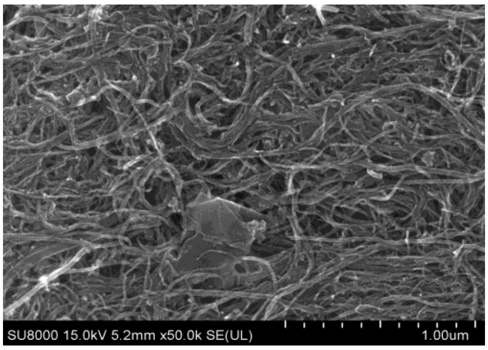

Figure 6. Image of the CNT "Taunit MD" (SEM *Hitachi SU8000*) α ≈ 800.

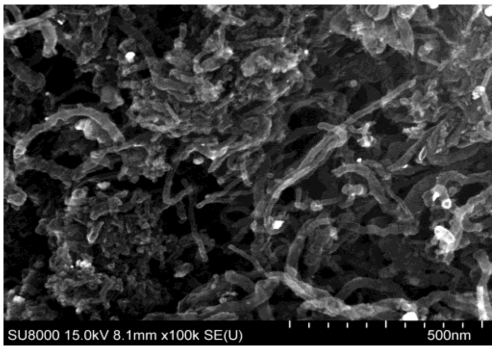

Figure 7. Image of the CNT_{Lab} (SEM *Hitachi SU8000*) α ≈ 14.

The results of experiments are shown on figure 8.

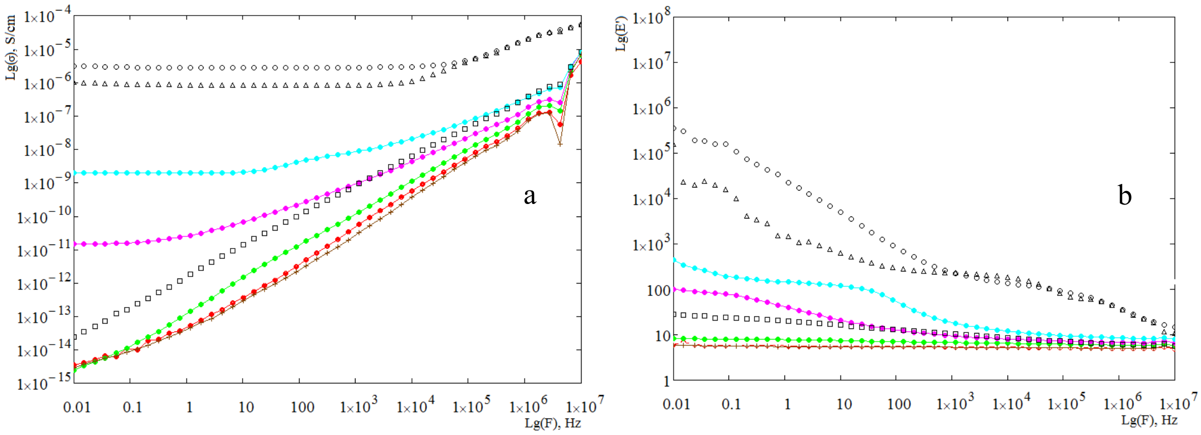

Figure 8.Graphs of the dielectric characteristics of the epoxy composite conductivity (a), the real part of the permittivity (b), on frequency of the electric field: ●●● -0,3%; ●●●- 1%; ●●●- 3%;●●●- 6%; ●●●- 9%, +++- 0% – samples prepared in the laboratory by CVD method. □– 0,06%, △– 0,1%, ○ – 0,3%, – samples with "Taunit-MD".

The measurement of pure tubes outside the polymeric matrix shown insignificant difference in their dielectric properties. Consequently, the difference in dielectric properties of samples could be connected with geometric characteristics of CNTs (aspect ratio). This process is shown on figure 9.

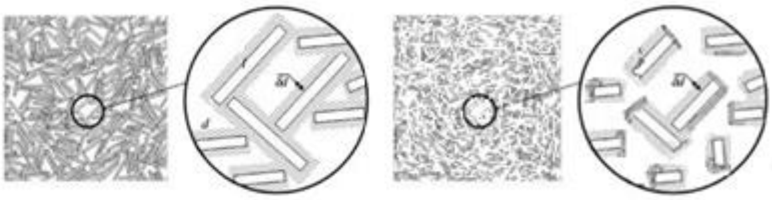

Figure 9. Model representation of CNTs conductivity percolation with different aspect ratio.

On this basis we conducted analytical calculation of percolation threshold on aspect ratio of CNTs by formula:

$$\phi_c = 1 - \exp\left[-\frac{1.4\cdot\left(\frac{\pi}{4}\right)D^2L+\left(\frac{\pi}{6}\right)D^3}{\left(\frac{4\pi}{3}\right)D^3+2\pi D^2L+\left(\frac{\pi}{2}\right)DL^2}\right], \quad (1)$$

where *D* and *L* are diameter and length of CNT. Expending (1) on small parameter $\frac{D}{L} \to 0$ we obtain:

$$\phi_c \approx 0.7 \cdot \frac{D}{L}.$$

In this model the percolation threshold for CNT_{Lab} (with aspect ratio of $\alpha \approx 14$) obtains value of $\phi_c = 5{,}25\%$, and for "Taunit-MD" with $\alpha \approx 800$, $\phi_c = 0{,}0875\%$, which is confirmed in experiment (figure 9). The functionalization of tubes by the acid leads to the change of their aspect ratio. Neglecting the contact resistance connected with the presence of carboxyl groups, we can define the upper boundary of the aspect ratio α less the 10.

5. Conclusions

We formulate main conclusions and results.

- The process of influence of temperature of the solidifier addition into the composite matrix (polymerization temperature) on the dielectric properties of the sample has been considered. The method of decrease of the degree of nanotubes agglomeration in polymeric composite via decrease of polymerization time has been proposed.
- It's been shown that with the growth of CNTs concentration in sample both absolute value of conductivity and value of the frequency, at which the transition from constant conductivity value to frequency-dependent value occurs, increases.
- The influence of CNTs functionalization (in hydrogen peroxide vapors) on dielectric properties of polymer reinforced with them was studied by the dielectric relaxation spectroscopy method. A significant decrease of composites with functionalized CNTs conductivity has been noted. This may be the result of two reasons: shortening (burning) of CNTs during functionalization and deterioration of contact between tubes via screening by carboxyl groups.
- The dependence of dielectric characteristics of composite on aspect ratio of CNTs has been studied. It's been shown, that sample dielectric properties strongly depend on aspect ratio. The dependence between aspect ratio and percolation threshold has been detected.

Acknowledgements

This work was supported by the project the Ministry of Education and Science of Russian Federation №3635 "Investigation of nanocomposites properties with controlled modification of the structure reinforced with carbon nanotubes".

We thank I. Chistyakov and our colleagues from Zelinsky Institute of Organic Chemistry (RAS) for help and assistance.

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