

# Investigation of the dielectric properties and defectoscopy of nanocomposites based on silica and polymers reinforced with carbon nanotubes

C S Osokin<sup>1</sup>, M K Eseev<sup>1</sup>, A A Goshev<sup>1</sup>, P Horodek<sup>2,3</sup>, S N Kapustin<sup>1</sup>,  
A G Kobets<sup>2,4</sup>, A S Volkov<sup>1</sup>

<sup>1</sup>Northern Arctic Federal University named after M.V. Lomonosov, Severnaya Dvina  
Emb. 17, 163002, Arkhangelsk, Russia

<sup>2</sup>Joint Institute for Nuclear Research, Dubna, Moscow region, Russian Federation;

<sup>3</sup>Institute of Nuclear Physics Polish Academy of Sciences, Krakow, Poland

<sup>4</sup>Institute of Electrophysics and Radiation Technologies NAS of Ukraine, Kharkov,  
Ukraine

E-mail: m.eseev@narfu.ru

**Abstract.** This work presents the results of experimental studies of the properties of nanocomposites based on silica and polypropylene reinforced with carbon nanotubes by dielectric relaxation and positron annihilation spectroscopy. On the basis of these results the technique of diagnosis and control of the investigated materials are proposed. This work was supported by the project of the Ministry of Education of Russian Federation №3635 "Investigation of the nanocomposites properties at controlled modification of the structure by reinforcement with carbon nanotubes".

## 1. Introduction

Active research of composite materials which include nanostructures such as carbon nanotubes (CNTs) as filler is being conducted widely around the world. Due to the large surface area of CNT and significant differences in the physical properties between nanoobjects and macrostate material, the 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, 3]. There is a particularly urgent task to study strongly nonlinear dependence of the composite properties on the concentration of the filler, which is necessary for the selection of the optimum functional properties of materials (strength, thermal, dielectric and other characteristics). Such dependence was observed in works [4,5], where a sharp increase of electromagnetic waves absorption and dispersion occurred at the concentration of CNTs of about 0.05%. The data on the influence of impurities on dielectric properties of CNTs of different composites at microwave frequencies associated with the search for promising materials for "stealth"-technologies is presented in the literature [6]. These papers [7,8] investigate microwave characteristics at a controlled modification of carbon nanotubes and nanocomposite materials based on them. We were also interested how the positrons will annihilate in the materials reinforced with CNTs. For this purpose, the composite consisted of sintered silicon glue (matrix) was prepared. It was reinforced with multi-walled CNTs at concentrations of 0% and 1% by weight, with an aspect ratio of  $10^2$  by the method of chemical vapor deposition.



We also studied electrical properties of composite based on polypropylene and epoxy matrix considering orientation effects of CNTs. Nanotubes were preliminarily separated in 1:1 acetone-alcohol solution with CNTs concentration of ~0.05% by weight exposed to ultrasound.

## 2. Experimental studies of silica reinforced with CNTs by method of positron annihilation spectroscopy

Positron annihilation spectroscopy (PAS) is a method usually recommended as a successive for detection of open volumes in materials. In the aim of verification of PAS potential application in further studies of our nanocomposites, the measurements of Doppler Broadening of Annihilation Line (DB) were performed. Variable-energy positron beam available at the LEPTA facility [9] at Joint Institute for Nuclear Research in Dubna was used in experiment. This is a small linac which uses frozen Ne as the moderator of positrons emitted from  $^{22}\text{Na}$  isotope. Then it allows them to accelerate to demanded energies within the range between 50 eV and 30 keV and to implant them into the sample in the form of a beam. Controllability of positron energies makes it possible to implant particles at a precise depth. DB measurements consisting of registration of energetic spectrum of gamma quanta emitted in annihilation processes were done using HpGe detector with energy resolution of 1.2 keV at 511 keV. Analysis of obtained spectra results in extracting of so called S parameter. It is defined as the ratio of area under the central part of 511 keV line to the total area below this line. S parameter represents a quantity related to the amount and size of free volume. More information about the method is presented e.g. here [10,11].

In Figure 1 the S parameter depending on the energy for reference sample without CNTs (circles) and sample containing 1% of CNTs (squares) are presented. It should be noticed that differences between these dependencies are well visible. The values of S parameter for specimen containing CNTs are much lower. Similar tendency was observed by Chen et. al. [12]. In this case the decreasing S parameter was explained as the presence of additional carbon nanofiber particles which have no free volume.

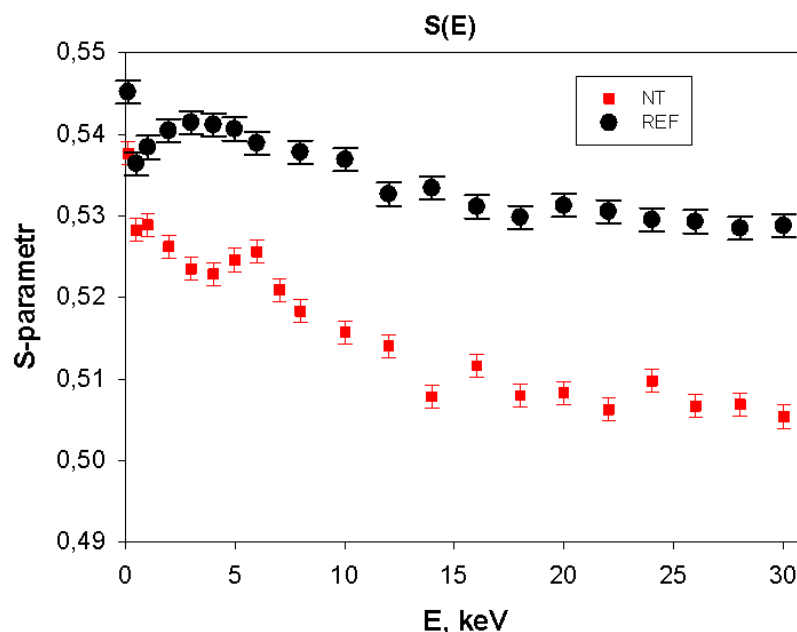


Fig. 1. The dependence of S-parameter of annihilation on positron energy for ceramic samples. Squares (NT) stand for CNTs concentration of 1%, and circles (REF) stand for the sample without CNTs

## 3. The frequency dependence of the polypropylene nanocomposite electrical properties

Electrical characteristics of the samples were studied by the dielectric relaxation spectroscopy method [2,3], 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 range of 0.01 Hz - 1 MHz. The

measured values were permittivity  $\epsilon$  and conductivity  $\sigma$ . The study of electrical properties of composites was accomplished using broadband dielectric spectrometer Novocontrol concept 80.

Composites, which were parallel layers of polypropylene with CNTs as filler, were placed in capacitor parallel and perpendicular to the plates. Data on the electrical properties were also compared with layered polypropylene without CNTs and polypropylene without preferred direction.

Figures 2 and 3 show samples conductivity and permittivity dependence on the frequency of the field. It can be seen that addition of CNTs enhances orientation properties of the sample.

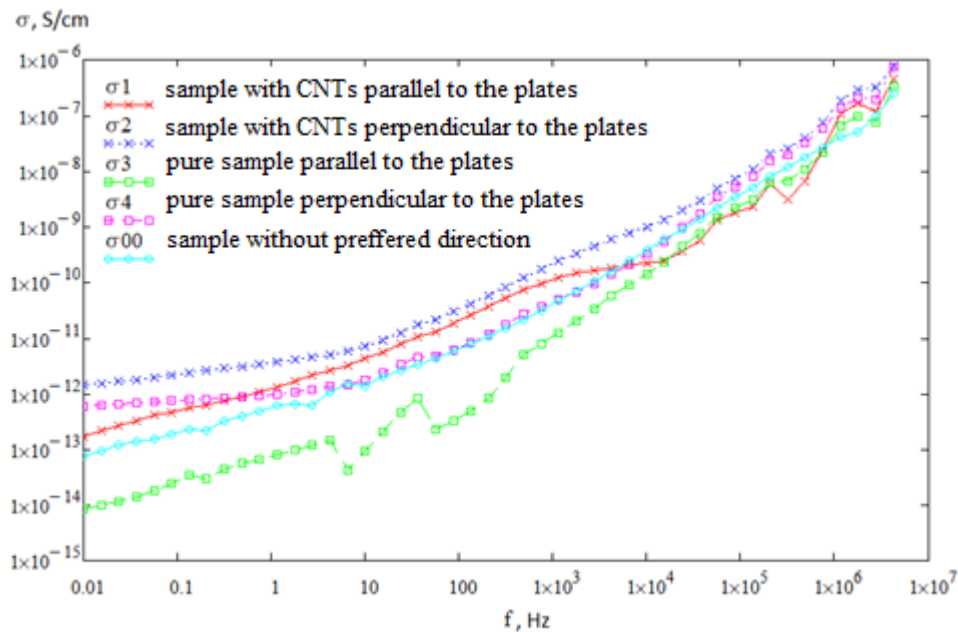


Fig. 2. Conductivity of samples:  $\sigma_1, \sigma_2$  – polypropylene with CNTs parallel and perpendicular to plates;  $\sigma_3, \sigma_4$  – pure polypropylene parallel and perpendicular to plates;  $\sigma_{00}$  – polypropylene without preferred direction

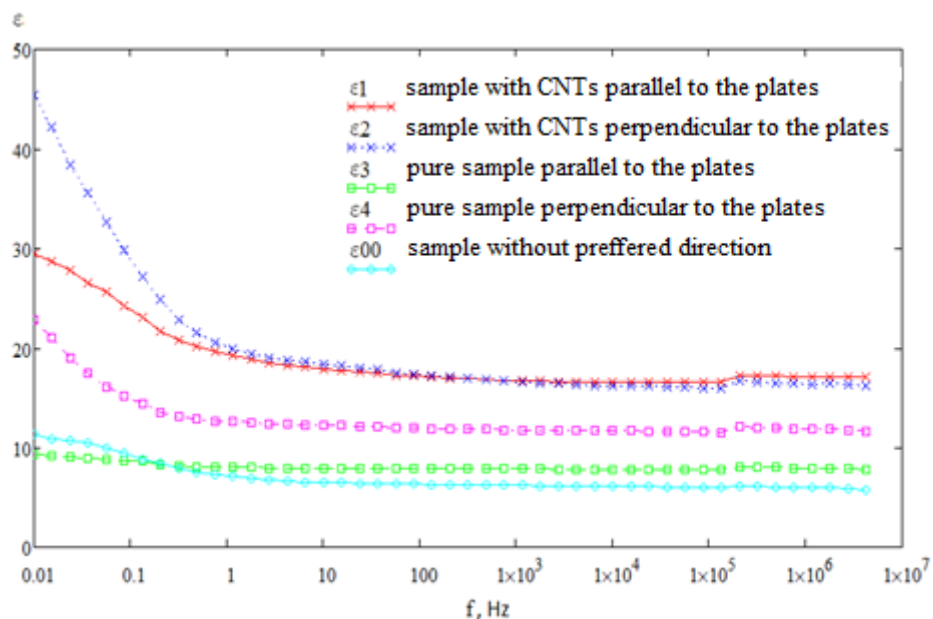


Fig. 3. Permittivity of samples:  $\epsilon_1, \epsilon_2$  – polypropylene with CNTs parallel and perpendicular to plates;  $\epsilon_3, \epsilon_4$  – pure polypropylene parallel and perpendicular to plates;  $\epsilon_{00}$  – polypropylene without preferred direction

The results obtained may find application in relatively simple studying of composites for the presence of preferred direction respectively to the electrical properties.

#### 4. The frequency dependence of the epoxy nanocomposite electrical properties

The samples for these series of experiments were epoxy reinforced with carbon nanotubes at different concentrations – 0%, 0.05%, 0.2% and 0.5% by weight. A part of samples was placed in the capacitor with a constant field and voltage of 30 kV during the solidification of epoxy. The other part solidified freely without electric field. All samples then were studied by the dielectric relaxation spectroscopy method mentioned above.

Figure 4a shows the frequency dependence of the conductivity of samples which solidified freely. The lines with rectangles stand for samples placed in the installation in the position in which they solidified and the lines with triangles stand for samples turned at angle of 90 degrees to its solidification position. The black, red and blue lines stand for concentrations of CNTs – 0%, 0.05% and 0.5% respectively.

It can be seen that the conductivity greatly increases for the samples, which were turned, especially in the low frequency area. It can be explained by the inhomogeneous distribution of CNTs in samples obtained during the solidification in gravitational field. The CNTs, deposited on the bottom of the sample, open the conductivity channel. The graphs also show clear dependence on CNTs concentration.

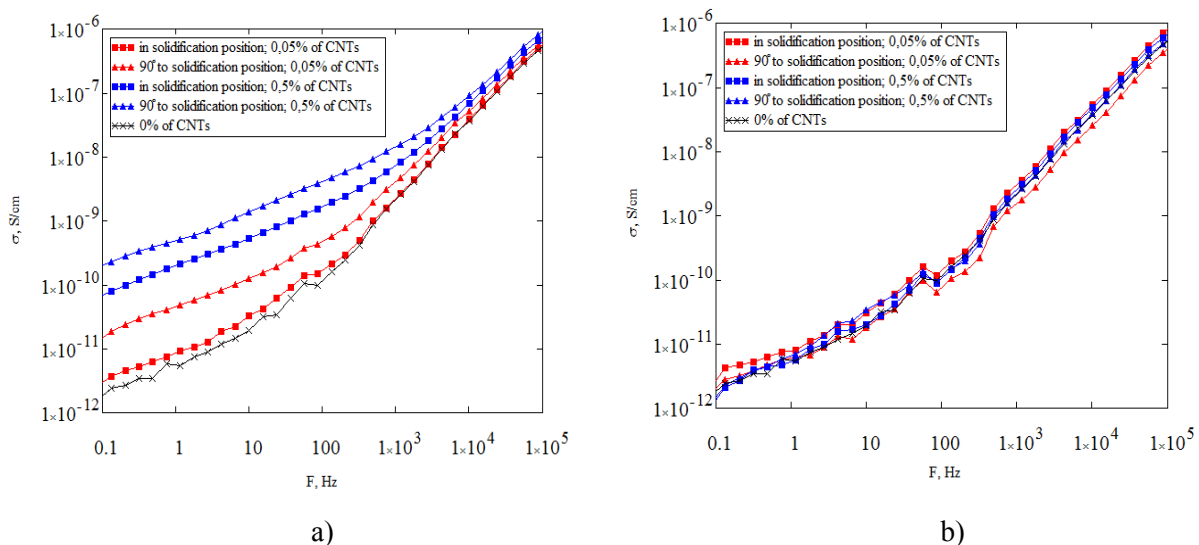


Fig. 4. The conductivity of a) freely solidified samples; b) samples solidified in electric field; Squares stand for samples in the position in which they solidified, rectangles stand for samples turned at the angle of 90 degrees to its solidification position; black – 0% of CNTs, red – 0.05% of CNTs, blue – 0.5% of CNTs.

Figure 4b shows the frequency dependence of the conductivity of samples which solidified in constant electric field. The lines designations are the same as the previous ones.

Here we cannot see any clear rotational or even concentration dependence of samples conductivity. Consequently the conclusion can be made that the distribution of nanotubes in the samples which solidified in electric field is more homogeneous.

## 5. Conclusion

- The results obtained show orientation dependence of electrical properties of the polypropylene samples with CNTs layers.
- On middle and low frequencies conductivity and permittivity of samples with CNTs considerably exceed respective characteristics of pure propylene samples.
- The electric field results in more homogeneous distribution of CNTs in epoxy sample during the solidification process.
- The results obtained show the possibility to detect CNTs in different samples using positron annihilation spectroscopy methods.

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