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Comparative study of dielectric properties of polymer based composites containing barium titanate modified with different kinds of nanotubes

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The effect of modification of barium titanate ($BaTiO_3$) submicron particles by the deposition of different kinds of nanotubes (carbon single- and multiwall, as well as comprising potassium polititanate $K_2Ti_6O_{13}$) upon dielectric properties of composites obtained by incorporation of thus modified $BaTiO_3$ into cyanoethyl ester of polyvinyl alcohol as a polymer binder is studied. The introduction of all the applied nanotubes in relatively small amounts (below 0.1 vol.%) provides a growth of the dielectric permittivity of the composites due to the improvement of their structural uniformity, while the addition of higher amounts of carbon nanotubes results in percolation with an abrupt increase of electrical conductivity due to the formation of conducting pathways comprising networks of interconnected nanotubes. The permittivity of the studied composites is found to grow with an increase of fractal dimension and decrease of lacunarity characterizing a non-uniformity of filler distribution in the polymer binder.

Keywords: polymer composites, barium titanate, nanotubes, dielectric permittivity, fractal dimension, lacunarity.

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Introduction

Polymer-based composite materials having high permittivity (ε) together with low dielectric loss find wide application in modern electronics [1–12], in particular, for creating functional layers in high-power capacitors [1–9], and flexible and expandable electronic devices [10,11]. To improve the designated performance of this type of materials, it is necessary both to use components (binder and filler) with high permittivity and to control interphase interactions between them [2,6–9,12] with one of the promising approaches that implies introduction of composite carbon nanotubes as a texturing agent [9]. We have shown earlier that the permittivity of composite materials based on cyanoethyl ether of polyvinyl alcohol (CEPA) and ferroelectric $BaTiO_3$ filler that had one of the highest permittivities (25–35 and higher than 4000, respectively) among polymers and inorganic substances even at the optimum relation of components didn't exceed 60–100, however, it may be increased significantly due to modification of the filler surface, in particular, due to the introduction of nanocarbon additives — shungite carbon [13], graphene [14,15] and fullerenol [16]. Potential utilization of multiwall carbon nanotubes together with nickel and copper oxides to make high-performance electrode materials for supercapacitors was demonstrated in [17], where the achievement of desired electrical properties (in particular, capacitance) was based on the formation of a system of carbon–metal and carbon–oxygen–metal bonds between nanotubes and oxide matrix. In [18], a similar approach was used for materials that included nickel oxide and reduced graphene oxide associated with the carbon nanotube system and featured improved capacity properties due to a highly-developed surface, porous ion transfer channels and percolating electron conduction channels.

A series of our works [19,20] found that the main factors defining the improvement of dielectric properties is the increase in polymer matrix filler distribution homogeneity achieved due to the enhancement of interphase interactions between them and characterized numerically by the change of fractal characteristics of composite microstructure. With reference to the above-mentioned studies, this work investigates the possibility to control the structure and dielectric properties of similar composite materials due to filler modification by various types of nanotubes that were presumably capable both of bonding with filler particles and polymer and of forming conduction channels in the material.

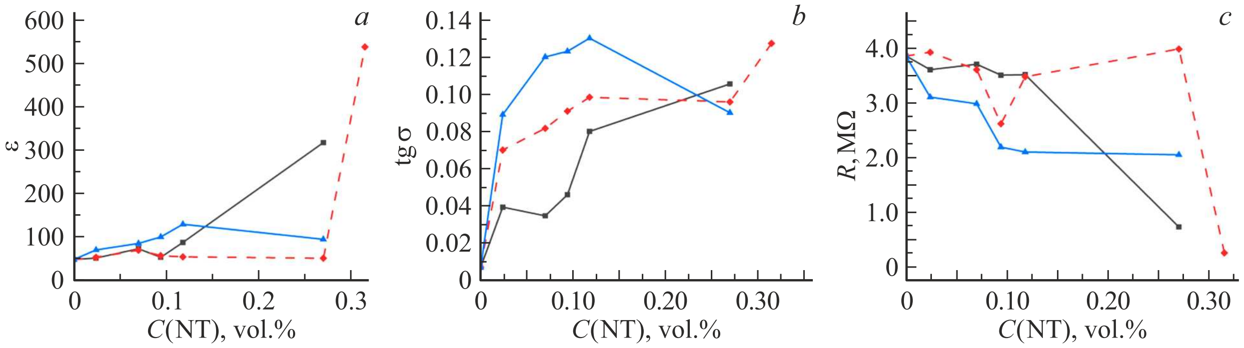

Figure 1. Dependence of the permittivity (*a*), dielectric loss (*b*) and resistance (*c*) of composite materials on the content of MWCNT (---♦---), SWCNT (—■—) and $K_2Ti_6O_{13}$ based nanotubes (—▲—). Lines on the diagram are shown for clarity.

1. Experiment

Ferroelectric $BaTiO_3$ filler (Fuji Titanium, Japan, particle size about $0.5\,\mu$m, permittivity $\varepsilon \sim 4400$) was modified by three types of nanotubes:

1) multiwall carbon nanotubes (MWCNT-2, Boreskov Institute of Catalysis, Siberian Branch, RAS, Novosibirsk, diameter $d \sim 12$ nm, length $L \sim 5\,\mu$m, specific surface $S_{sp} = 260 \pm 5\,m^2/g$);

2) single-walled carbon nanotubes (SWCNT TUBALL, OCSiAl, Novosibirsk, $d = 1.6 \pm 0.4$ nm, $L > 5\,\mu$m, $S_{sp} = 500-1000\,m^2/g$);

3) $K_2Ti_6O_{13}$-based nanotubes ($d \sim 10$ nm, $L > 1\,\mu$m, $S_{sp} \approx 300\,m^2/g$) synthesized by means of hydrothermal treatment of $TiO(OH)_2$ in KOH solution in accordance with the procedure described in detail in [21].

Nanotubes were deposited from water suspensions in amounts corresponding to 0.02–0.40 mg of nanotubes per 1 g $BaTiO_3$, with boiling followed by complete desiccation. Modified $BaTiO_3$ was introduced into the binder — cyanoethyl ether of polyvinyl alcohol CEPA (PB paste, Shanghai Keyan Phosphor Technology Co, Ltd., China, permittivity $\varepsilon \sim 27$). After drying, the content of $BaTiO_3$ in composite materials was approx. 34 vol.%.

For electrical measurements, composite material layers about $50\,\mu$m in thickness (measured using a dial thickness gauge made by NPF „Zavod Izmeron“) were applied to glass substrates covered with aluminum foil. Then, electrodes made of the Kontaktol Silver conductive paste were applied to the sample surface and dried, and then dimensions were measured and area was calculated for further electrical measurements.

Electrical properties of the samples were measured using the E7-20 LCR meter (made by MNIPI, Minsk, Republic of Belarus) by connecting the instrument terminals to the aluminum substrate and three Kontaktol electrodes with measured data averaging. Measurements were conducted at frequencies from 25 Hz to 1 MHz. Directly measured properties included resistance, dielectric loss angle tangent and capacitance that was used to calculate permittivity by the following equation:

$$\varepsilon = \frac{C \cdot d}{\varepsilon_0 \cdot S}, \tag{1}$$

where C is the measured condenser capacitance , d and S are the composite layer thickness and electrode surface area, respectively, $\varepsilon_0 = 8.85 \cdot 10^{-12}$ F/m is the dielectric constant.

Structure of composite materials was studied by the scanning electron microscopy method at the Engineering Center, Saint Petersburg Institute of Technology (TU), using the Tescan Vega 3 system. The following fractal microstructure characteristics of composite materials were calculated using the data obtained by the box-counting method (based on partitioning of the analyzed microphotograph into cells with counting structural elements within the cells and analysis of filler particle distribution over cells with different sizes) in accordance with our technique [16,17]:

— fractal dimension defined as the slope coefficient of the log-log dependence of the mean number of centers of mass of filler particles N in cells on the cell size x in microphotograph partitioning ($\ln N$ vs. $\ln x$);

— lacunarity is a parameter that characterizes inhomogeneous filling of space with studied objects

$$\Lambda = \left(\frac{\sigma}{\mu}\right)^2,$$

where σ and μ are the standard deviation and mean number of centers of mass of filler particles in the studied cells, respectively.

2. Results and discussion

Dependences of electrical properties of the fabricated composite materials on the amount of nanotubes deposited on the filler are shown in Figure 1.

The findings show that, when small (up to ~ 0.1 vol.%) amounts of nanotubes are introduced, a growth of ε is observed up to the maximum at 0.07 vol.% for MWCNT and SWCNT and up to 0.12 vol.% for potassium polytitanate

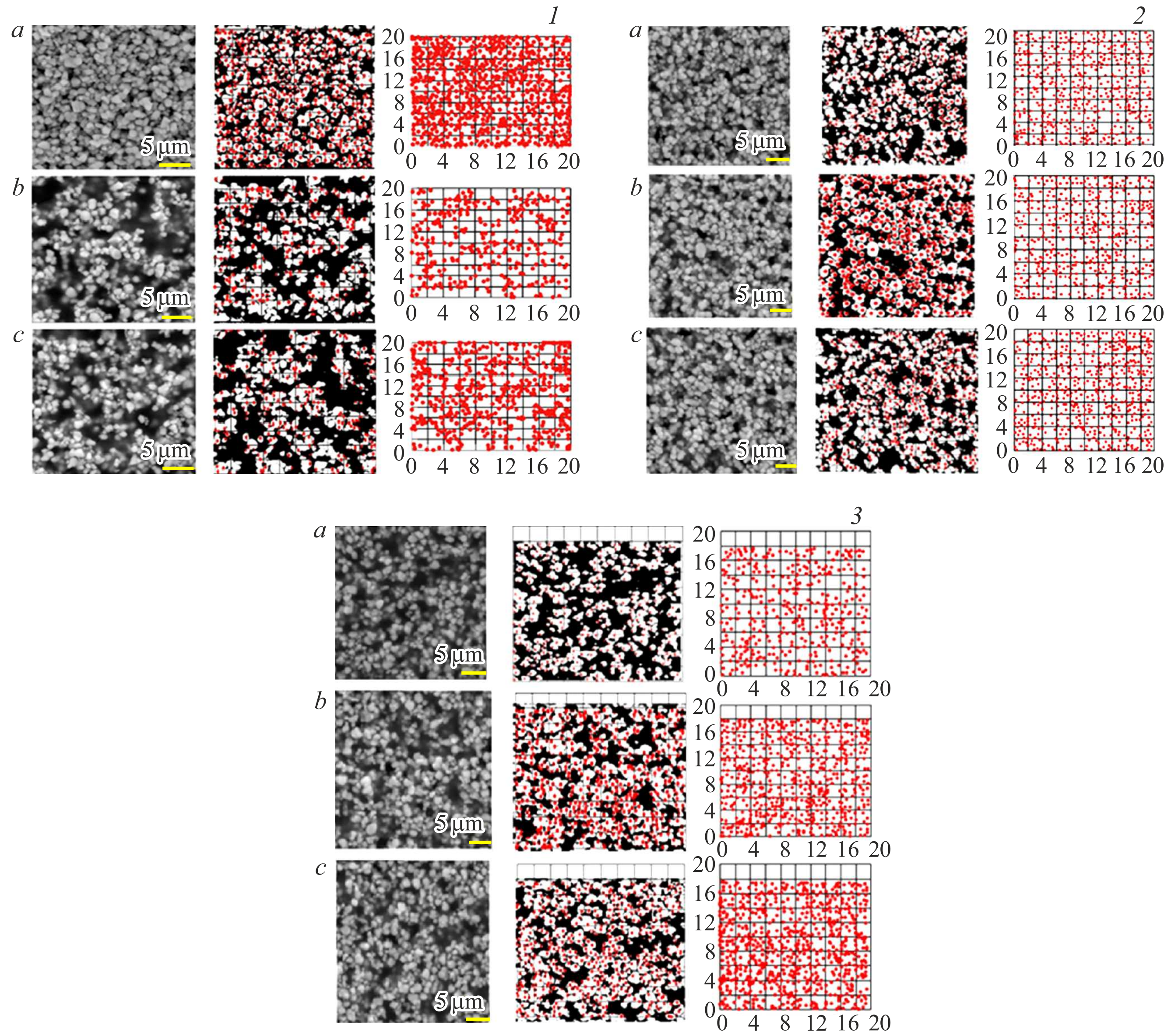

Figure 2. Electronic microphographs (left), binarized representation indicating the centers of mass of particles (in the center) and distribution of centers of mass of particles in $20 \times 20\,\mu$m square cells (right) for composite materials: *1* — with the content of MWCNT 0.07 (*a*), 0.12 (*b*) and 0.27 vol.% (*c*); *2* — with the content of SWCNT 0.12 (*a*), 0.27 (*b*) and 0.36 vol.% (*c*); *3* — with the content of $K_2Ti_6O_{13}$ based nanotubes 0.12 (*a*), 0.27 (*b*) and 0.36 vol.% (*c*).

nanotubes with relatively small growth of dielectric loss and decrease in resistance. When higher amounts of MWCNT and SWCNT are introduced, significant growth of permittivity together with sharp reduction of resistance take place, which may be caused by percolation due to formation of a conductivity channel network consisting of intersecting nanotubes. For SWCNT, smooth growth of electrical properties is observed starting from 0.1 vol.%, and when MWCNT is introduced, the growth is much sharper and starts from ~ 0.27 vol.%. The observed differences may be due to the fact that metallic type of conductivity prevails for MWCNT, but both metallic and semiconductor types of conductivity are possible in SWCNT, therefore the growth of conductivity is caused by just a part of nanotubes introduced into the composite material, which leads to a smoother dependence, while for MWCNT, threshold concentration, where conductive channels are formed, may be relevant. In addition, a sharper growth of conductivity when SWCNT is introduced may be attributable to their longer length compared with MWCNT, which facilitates the emergence of through conductivity channels at lower nanotube concentrations in the material. When $K_2Ti_6O_{13}$-based nanotubes are introduced in the amount of approx. 0.1 vol.%, much higher permittivity (up to 130) is observed compared with the introduction of SWCNT and MWCNT in the same amount ($\varepsilon \approx 70$), however, in this case, dielectric loss tangent grows (up to 0.19 compared with 0.07 and 0.04 for MWCNT and SWCNT, respectively). Moreover, unlike

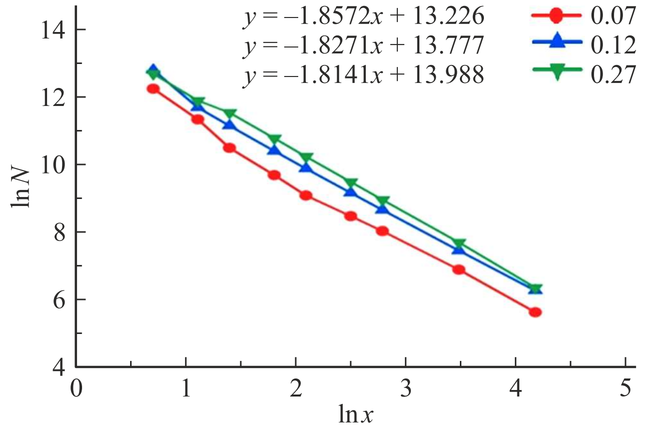

Figure 3. Log-log dependences of the mean number of filler particles in square fragments of microphotographs on the fragment side and approximating equations for composite materials with the MWCNT content of 0.07, 0.12 and 0.27 vol.%.

composite materials containing MWCNT and SWCNT,when the amount of $K_2Ti_6O_{13}$ nanotubes increases to more than 0.2 vol.%, permittivity decreases a little without significant change of resistance, which is attributable to the absence of conductive properties in potassium polytitanate in the given conditions [22] and, respectively, of percolation.

Electronic microphotographs of the fabricated composite materials containing different amounts of MWCNT with partition into 20 × 20 μm square cells are shown in Figure 2. Images recorded during partitioning into fragments with other dimensions are similar. Dependences of the mean number of particles in cells on the cell size used for calculation of fractal dimension and lacunarity are shown in Figure 3.

Fractal dimensions and lacunarities calculated using the analysis of obtained data in accordance with the technique described above are shown in the table.

Comparison of the obtained data with the permittivity of composite materials (Figure 4) shows that in all cases the permittivity grows as the fractal dimension increases and lacunarity reduces.

Thus, it was found that modification of $BaTiO_3$ by all described types of nanotubes in the optimum amounts facilitated the improvement of dielectric properties of composite materials due to the increase in uniformity of filler particle distribution in the polymer matrix and structural order of material in general, in particular, due to the increase in the degree of self-similarity of its microstructure. Uniform distribution of ferroelectric filler particles modified by conductive nanotubes facilitates formation of the ordered „microcapacitor“ system (conductive particles separated by dielectric layers — $BaTiO_3$ and polymer) in the material due to which permittivity of the whole composite material grows considerably.

Conclusions

The obtained results demonstrate that dielectric properties of polymer-inorganic composite materials may be controlled through modification of ferroelectric filler particles by various types of nanotubes that have structuring effect on the material. Depending on the number of introduced nanotubes, an increase in the permittivity without significant growth of conductivity and dielectric loss due to an increase

Fractal dimensions and lacunarities (with cell size of 20 μm) of composite materials fabricated by modification of $BaTiO_3$ with different amount of nanotubes

Content of nanotubes, vol.%	Multiwall		Content of nanotubes, vol.%	Single-wall		$K_2Ti_6O_{13}$	
	Fractal dimension	Lacunarity		Fractal dimension	Lacunarity	Fractal dimension	Lacunarity
0.07	1.86	0.09	0.118	1.62	0.14	1.87	0.11
0.118	1.83	0.20	0.27	1.64	0.12	1.87	0.14
0.27	1.81	0.28	0.36	1.67	0.10	1.81	0.19

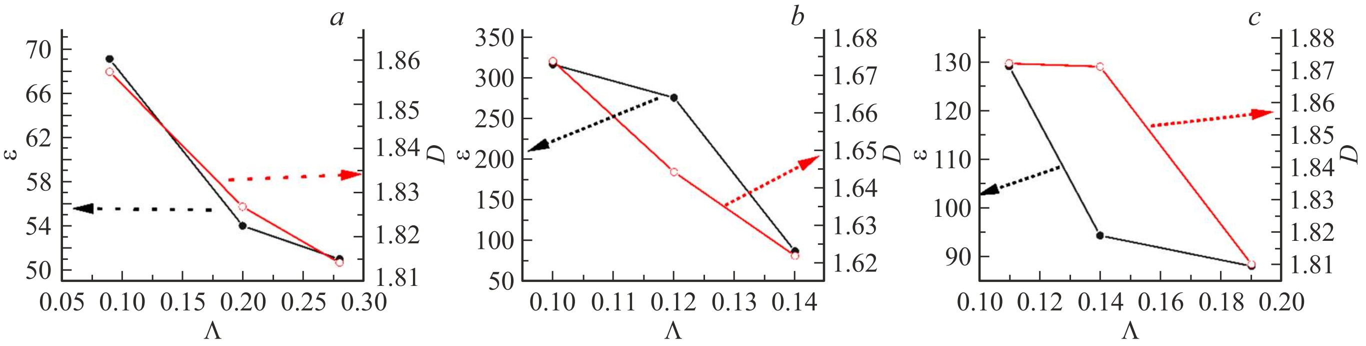

Figure 4. Dependences of permittivity (●) and fractal dimension (○) of composite materials on the content of MWCNT (*a*), SWCNT (*b*) and $K_2Ti_6O_{13}$-based nanotubes (*c*).

in the uniformity of filler particle distribution in the matrix as well as a sharp growth of conductivity and permittivity due to percolation at relatively high concentrations of carbon nanotubes forming the conductivity channels are possible. In general, the proposed approach based on the filler surface modification and comprehensive study of the interaction between fillers and binder, including the analysis of the fractal microstructure characteristics of a material, has good prospects for optimization of various composite material fabrication techniques and forecasting target properties of composite materials.

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Conflict of interest

The authors declare no conflict of interest.

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