Dielectric properties of oligomeric diisocyanate based composites with barium titanate

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A series of composites is synthesized on the basis of oligomeric diisocyanate with different contents of ferroelectric filler barium titanate ($BaTiO_3$). The dielectric performances of the obtained composites are found to follow extreme dependences on the filler content with a sharp minimum of the dielectric permittivity and maximum of the dielectric loss tangent at $BaTiO_3$ content 30 vol.%. The characterization of the composite layers by confocal microscopy revealed that the observed dependences of their dielectric properties upon the composition are determined by structural changes of the composites, including percolation, formation of a single infinite cluster and structures of matrix-island and chain types at certain critical concentrations.

Keywords: composites, coatings, diisocyanate, barium titanate, dielectric permittivity, dielectric loss, electrochromatography, supercapacitors.

1. Introduction

Production of composite materials with specified dielectric properties is an important task in many fields, including production of protective dielectric layers in various electronic devices, supercondensers, as well as functional layers of sorbents, which increase efficiency of electrophoretic separation of components in capillary columns and microfluidic chips [1–5].

As a composite material is a system of subsequently-interconnected components with various electric characteristics; its dielectric properties (capacitance, permittivity) are determined by respective irreversibly proportional dependences and depend both on a composition of the composite (a component ratio) and on a type of interphase contacts and interactions. In particular, increase in the permittivity ε and decrease in dielectric losses $(\mathrm{tg}\,\delta)$ of the composites with ferroelectric fillers are observed at the most uniform distribution of filler particles in a matrix and at the presence of percolation (a spatial grid of bonds) between the filler particles due to amplification of a synchronized response of the distributed filler to impact by an electric field. The said effects have been studied in the papers [6–11] for the composites based on cyanoethylated ether of polyvinyl alcohol with barium titanate $BaTiO_3$ (which is a ferroelectric having one of the highest values ε), whose dielectric properties have been controlled by optimization of an amount of the input filler and modification of its surface with different additives (disperse oxides [7,8], a fullerenol [9], a graphene [10]), which provide amplification of the inter-phase interactions due to formation of specific function groups. It has been ascertained that dependences of the dielectric properties of the composites on a concentrations of the input additives are often nonlinear with sharp extremums and correlated to a content of certain centers on a filler surface and to uniformity of its distribution in the matrix, wherein an important role is played by fractal characteristics of distribution of the filler particles in the matrix [11].

The present study has applied an approach under consideration to the composites based on an oligomeric diisocyanate, which is promising to be used as a sorbent (model fixed phases) for the electrochromatography [12,13]. The composite sorbents based on fixed phases with particles of the ferroelectric filler distributed therein have a number of advantages in comparison with existing sorbents, including a higher capability of selective separation of components being analyzed and control of an electroosmotic flowrate, a higher stability and persistence in a pH wide range, a highly-developed surface, as well as modificability to enable control of the surface chemical composition in a wide range.

2. Experimental part

The polydimethylsiloxane (PDMS) Sylgard-184 (Dow Corning) 10×10 mm of the thickness 4 mm has been used as the substrates. Their surface was laminated by composite materials based on the oligomeric diisocyanate (Crosslinker CX-100 produced by Cytec, USA, with a molecular weight of $M_n \sim 1500$ and a content of the isocyanate groups 5.6%) with submicron $(500 \pm 20\,\text{nm})$ particles of $BaTiO_3$ (US Research Nanomaterials, Inc. Houston, TX, USA) pre-dispersed therein, with variation of the $BaTiO_3$ concentration in a reaction mixture from 5 to 50% vol. relative to a
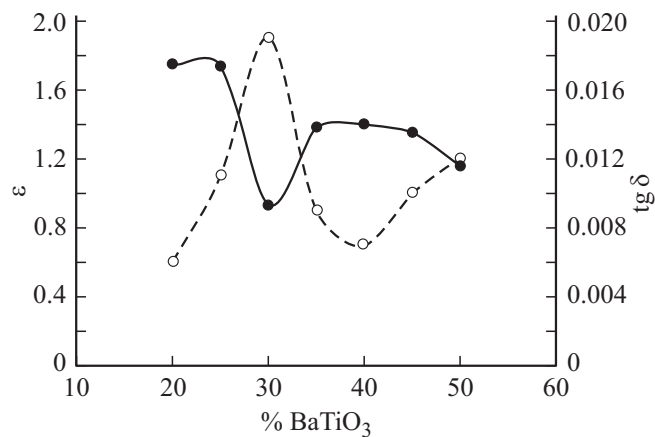
Figure 1. Dependence of the permittivity — a solid line and of the dielectric loss tangent of the composites on the BaTiO$_3$ content — a dashed line.

diisocyanate volume in the reaction mixture. The substrate was laminated using a spinneret for subsequent drying at the temperature of 50°C during 60 min [13–15].

After drying, the produced composite layers of the thickness of $0.2-0.25 \mu m$ were covered by upper electrodes by means of a silver contactol (a current-conducting glue).

The capacitance (C) and the dielectric loss tangent (tg δ) of the produced samples were measured by means of a LCR meter E7-20 (MNIPI, Minsk, Belarus) at the frequency of 1 kHz. The permittivity was calculated by the formula:

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

where C — measured capacitance of the condenser, d and S — a thickness of the composite layer and an area of the electrode surface, respectively, $\varepsilon_0 = 8.85 \cdot 10^{-12}$ F/m — a dielectric constant. Errors of determination of the magnitudes ε and tg δ by averaged data of the measurements for

3−5 electrodes applied to a surface of each of the samples under study, do not exceed 15 and 10%, respectively.

The surface morphology of the produced composite layers of BaTiO$_3$ in the polymer matrix was studied by the confocal laser scanning microscopy using the Leica TCS SP5 confocal laser scanning microscope (Leica Microsystems). The BaTiO$_3$ distribution density calculated by a texture segmentation method (a random field model) [16].

3. Results and discussion

Results of measurements of the dielectric characteristics of the composite layers (Fig. 1) have shown that within the whole studied range of the BaTiO$_3$ content in the polymer matrix the change of the permittivity and the dielectric loss tangent of the produced composites is of an mutually opposite and oscillating type with a prominent minimum ε and maximum tg δ at the BaTiO$_3$ content of 30% mass.

The Fig. 2 shows the microphotographs of the samples of the produced composites, which correspond to changes of their structure. Analysis of the data obtained shows that at the BaTiO$_3$ content of about 15 vol.% there is formation of ordered chain elements of local percolation (Fig. 2, a), while at the filler concentration of 25 vol.% — a matrix & chain structure with primary fragments of an island structure (Fig. 2, b). With increase in the amount of the input BaTiO$_3$ to 35 vol.% (Fig. 2, c), there is increase in the local density of the distribution of the filler particles with formation of the island and island & chain structures corresponding to beginning percolation. With further increase in the filler concentration to 50 vol.% and above, there is agglomeration of the filler particles with formation of large associates and sharp decline of the homogeneity of the composite structure.

An observed sharp minimum of the permittivity and a maximum of the dielectric loss tangent at the barium titanate content of 30 vol.% may be due to the above-discussed disordering of the chain structure as a result of agglomeration of the filler particles to small associates with
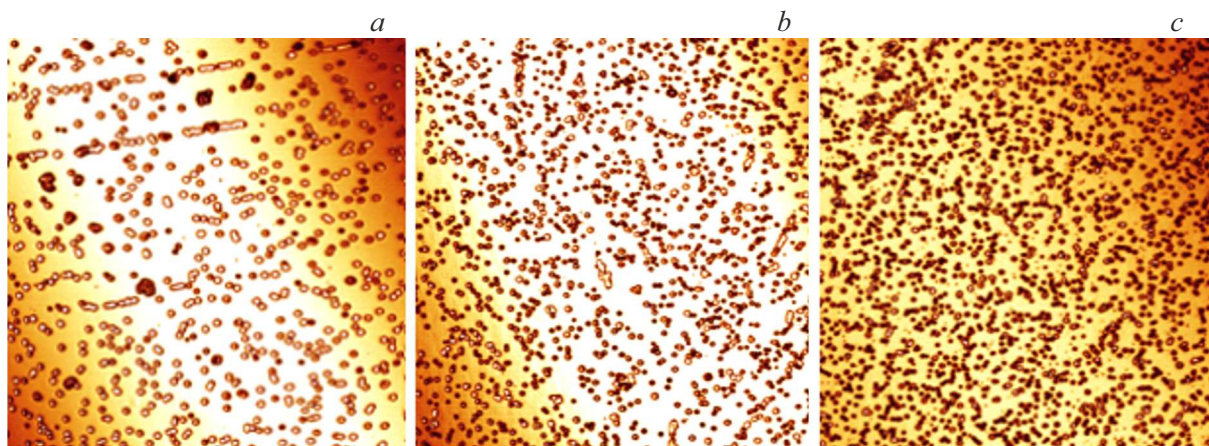
Figure 2. Confocal microphotographs of the surface ($250 \times 250 \mu m$) of the composites based on diisocyanate, with the BaTiO$_3$ content of 15 (a), 25 (b) and 35 vol.% (c).

formation of the island structure as accompanied by the significant decrease in a local percolation degree. It should be noted that percolation is a prerequisite for increase in the magnitude ε and minimization of $\mathrm{tg}\,\delta$ of the composites of this type, which are structured as condensers with a subsequently connection of layers of different materials, whose total capacitance and permittivity depend on values of initial materials of isocyanate and BaTiO$_3$ by an irreversibly proportional law. Such nonlinear dependences of the dielectric characteristics on modification conditions of barium titanate, which make conditions for percolation in the system, have been earlier observed in similar composites based on cyanoethylated ether of polyvinyl alcohol [6–11]. The filler concentration of 35 vol.% corresponds to a transition to formation of a matrix & chain structure in an endless structure as accompanied by beginning general percolation, which corresponds to observed increase in permittivity. At the same time, with further increase in the barium titanate content to $45-50$ vol.%, there is an evident opposite trend due to agglomeration of its particles to large associates.

4. Conclusion

It was ascertained that the dependence of the dielectric properties of polymer & onorganic composites based on the oligomeric diisocyanate and barium titanate with a sharp minimum of permittivity and a maximum of dielectric loss tangent at the BaTiO$_3$ content of 30 vol.%. The nonlinear dependence is correlated to changes of the composite structure, which in increase in the filler content is characterized by formation the matrix & chain structure at the filler concentration of about 15 vol.%, the transition to the island & chain structure (25 vol.%), beginning percolation (35 vol.%) and mass agglomeration of the filler particles ($45-50$ vol.%). The disordering of the chain structure due to the agglomeration of the filler particles, the reduction of their distribution homogeneity and the percolation degree at the filler content of 30 vol.% corresponds to the minimum permittivity, while the beginning percolation at the BaTiO$_3$ concentration of about 35 vol.% — its sharp increase.

The results obtained show controllability of the dielectric properties of the polymer & nonorganic composites, in particular, a change of permittivity from 1 to 2 and the reduction of the dielectric loss tangent to values below 0.01, which is promising for use of materials produced as the model fixed phases (sorbents) providing a higher efficiency of separation of the components in the electrochromatographic capillary columns and microfluidic chips.

Funding

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