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Dielectric spectroscopy of a composite of polyvinyl alcohol cyanoethyl ether with graphene-modified ferroelectric barium titanates

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Abstract. The paper presents the results of an experimental study of the dielectric properties of a composite with a polymer matrix based on polyvinyl alcohol cyanoethyl ether (CEPVA) with a filler—ferroelectric barium titanate BaTiO₃ modified with graphene nanoparticles. The behavior of frequency dependences of the components with complex permittivity and electrical modulus indicates the relaxation character of the dielectric polarization with the participation of polar formations of the functional components of the composite under study.

Keywords: dielectric relaxation, electrical modulus, polymer composite, barium titanate, graphene.

Introduction

Polymer-inorganic composites are widely used in various fields of technology due to the combination of the properties of a polymer and a functional filler. CEPVA stands out among other modern polymeric materials (Avanesyan et al. 2009; 2012). It has the highest dielectric constant (ϵ) among modern polymers (up to 25) due to the high number of polar nitrile ($C \equiv N$), carbonyl ($C = O$) and hydroxyl (OH) groups. Polymer-inorganic composite materials with a high dielectric constant may find application in protective dielectric layers in capacitors, displays, electroluminescent light sources, and other electronic devices. Creating flexible optoelectronic devices necessitates materials with high dielectric constants, which can be implemented, in particular, by using polymer composites containing CEPVA as a binder with a filler—ferroelectric barium titanate BaTiO₃ (Alekseev et al. 2006).

Previously, the possibilities of improving the characteristics of composites were studied by modifying the surface layer of the BaTiO₃ filler with Si, Ta, Mg oxides and shungite in order to improve its compatibility with the polymer matrix (Myakin et al. 2011; Sychev et al. 2014). It was found that the modification of the filler allows changing the dielectric constant within wide limits, regulating the interfacial interactions in the system, and also changing the content of active centers on the barium-titanium surface corresponding to the main hydroxyl groups (Bronsted centers) capable of interacting with weakly

acidic hydroxyl groups in CEPVA (Sychev et al. 2016). Creating flexible electronics devices necessitates materials with high dielectric constants, which can be implemented, in particular, by using polymer composites containing polyvinyl alcohol cyanoethyl ether as a binder with a filler—barium titanate modified with graphene (Mjakin et al. 2019).

This article reports the results of an experimental study of the electrophysical properties of a composite based on a CEPVA polymer matrix with a BaTiO₃ filler modified with graphene.

Experiment

The samples were layers of a polymer-inorganic composite deposited through a die onto an aluminum foil specially mounted on a glass slide. A CEPVA solution was used as a polymer matrix, in which a barium titanate BaTiO₃ powder was dispersed, having a dielectric constant $\epsilon = 4000$ and a particle size of the order of 1 μm in a ratio of 1.1 ml of polymer solution per 1 g of solution. filler. The thickness of the layers of the obtained composites varied from 20 to 80 μm . The resulting layers were covered with electrodes of conductive glue on silver (contactol). Electrical measurements in the frequency range $5 \cdot 10^2 - 10^5$ Hz were carried out at room temperature using a specially designed measuring cell and LCR-819 precision meter manufactured by GW Instek, Taiwan.

Results and discussion

Fig. 1 shows the frequency dependence of the capacitance of the sample of the composite under study. The values were determined by the standard formula for a flat capacitor. As follows from the data presented, there is a scatter of the real component of the complex dielectric constant $\epsilon^* = \epsilon' - i\epsilon''$ (ϵ' and ϵ'' are real and imaginary components of ϵ^* , respectively), namely, a decrease in its values with an increase in the frequency of the measuring field.

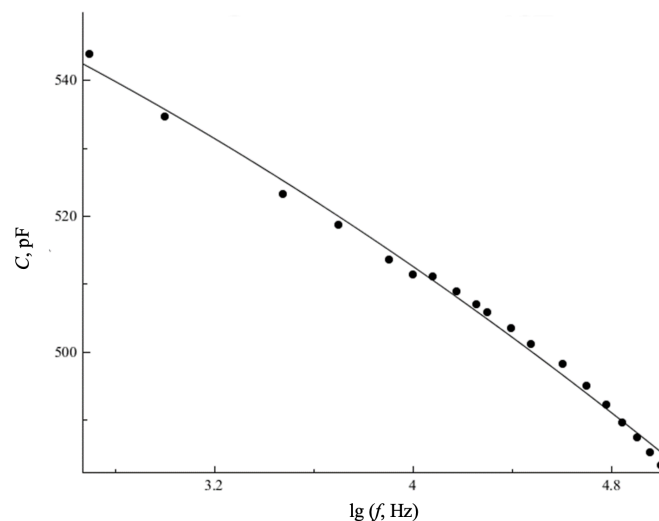


Fig. 1. Frequency dependence of the capacitance of the sample of the CEPVA-modified BaTiO₃ composite

The analysis of the available data (Avanesyan et al. 2009; Borodzyulya et al. 2013) shows that the pronounced dispersion of the experimental dielectric characteristics is due to the presence of functional polar groups in the structure of the polymer binder under study (Fig. 2). The relaxing elements in the structure of CEPVA include OH groups, which, according to IR spectroscopy data, refer not only to the binder material, but also to adsorbed water. The OH group is polar due to the difference in the values of the electronegativity of oxygen and hydrogen atoms, and the density of electronic bonds is shifted towards the more electronegative oxygen atom. Two $2sp^3$ - atomic orbitals of the CEPVA structure are involved in the formation of bonds of the oxygen atom with the C and H atoms. The oxygen atom contains two lone electron pairs, which are located in the $2s$ and $2p$ positions and stimulate the formation of asymmetric polar coordination. The CN group is also polar due to the different electronegativity of carbon and nitrogen atoms. In this case, the density of electronic bonds shifts towards

the more electronegative nitrogen atom. The CN group is distinguished by a pronounced dipole structure, which, due to the presence of a lone electron pair in its structure, can cause the main dielectric response when measured at low frequencies of the electric field.

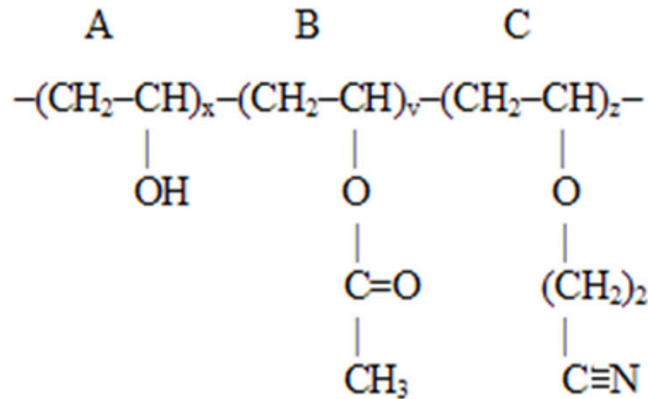


Fig. 2. Structural formula of CEPVA (Borodzyulya et al. 2013)

With increasing frequency, the value of the dielectric loss tangent $\tan \delta$ of the samples decreases (Fig. 3), reaching a minimum at a frequency of about 10^3 Hz. With a further increase in the field frequency, the values of this parameter increase. It is known that CEPVA films, like films made from other cyano-containing polymers, are characterized by significant through conduction. Thus, the results obtained can also be associated with the integral contribution to the dielectric loss of the processes of conduction and relaxation polarization.

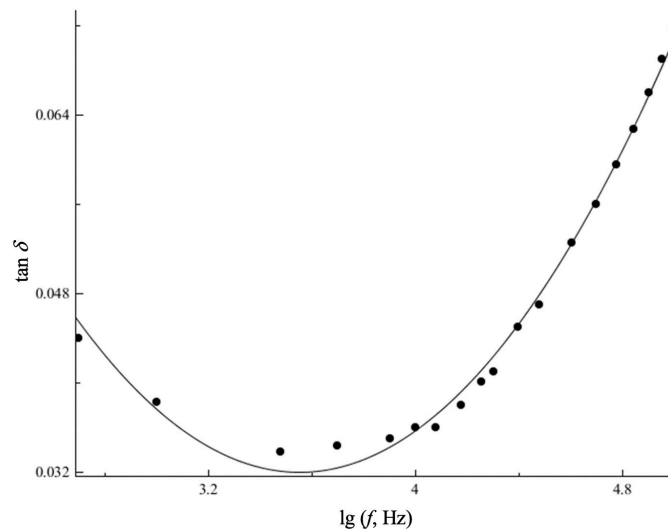


Fig. 3. Frequency dependence of the $\tan \delta$ of the sample of the CEPVA-modified BaTiO_3 composite

The inclusion of graphene nanoparticles leads to a change in the functional composition of the barium titanate surface, associated with a change in the quantitative content of acidic and basic hydroxyl groups, as well as the nature of conjugation of electrons of the lone pair of the hydroxyl group (Sychev et al. 2016). Earlier it was also found (Deb, Ghosh 2010) that the tangent of the dielectric loss angle of the composites under study correlates with the content of surface centers along which water is adsorbed, which determines an increase in this parameter.

In dielectrics, such as, for example, polymer composites, the formation of a space charge can lead to an increase in the local electric field and, as a result, to partial discharges and breakdown. In addition, the accumulation of charge near the electrode causes an abnormally high dielectric constant, which does

not reflect the process of bulk dielectric relaxation, which complicates research in this area. To rationalize the dielectric response of materials with some electrical conductivity, the formalism of the electrical module can be used. This approach makes it possible to interpret the dielectric properties of the sample volume directly with the exclusion of electrode polarization which alleviates the problems caused by electric transport that can mask the dielectric relaxation. The complex electrical modulus M^* is related to the components of the complex dielectric constant and can be represented by the expression (Avanesyan, Salnikova 2017):

$$M^* = \frac{1}{\varepsilon^*} = M' + jM'' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + j \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}, \quad (1)$$

where M' , M'' are the real and imaginary parts of the complex values of the electrical modulus.

The electrical modulus (M^*) can also be expressed as the Fourier transform of the relaxation function $\phi(t)$ (Deb, Ghosh 2010):

$$M^* = M_\infty \left[1 - \int_0^\infty \exp(-\omega t) \left(-\frac{d\phi}{dt} \right) dt \right], \quad (2)$$

where the dependence $\phi(t)$, represented by the so-called Kohlrausch—Williams—Watts function (Williams, Watts 1970), reflects the time process of changing the electric field in the material, described by an extended exponent $\phi(t) = \exp[-(t/\tau_m)^\beta]$, where τ_m is the conductivity relaxation time, and the value of the exponent β indicates the degree of deviation from relaxation of the Debye type. In turn, the relaxation time associated with the process of electric transport can be found from the graph of the dependence of the component M'' on frequency. The value of the parameter τ_m can also be obtained from its temperature dependence as $\tau_m = \tau_0 \exp(E_R/kT)$, where E_R is the activation energy of the relaxation process, τ_0 is the preexponential factor, k is the Boltzmann constant, and T is the absolute temperature.

The data of dielectric measurements of the samples of the layers of the investigated composite made it possible to study the behavior of the components of the complex electrical module. At low frequencies, the value of the parameter M' approaches zero (Fig. 4), which indicates the suppression of polarization near the electrode. At high frequencies, the values of M' are characterized by dispersion and reach a maximum value corresponding to $M_\infty = (\varepsilon_\infty)^{-1}$, due to the process of dielectric relaxation, when the displacement frequencies of localized charge carriers and the external electric field coincide. The behavior of the imaginary part of the electrical module reflects the energy loss of the sample in the electric field (Fig. 5). The frequency range below the maximum values of M'' indicates the region in which the drift of ions over long distances is probable. At high frequencies, their mobility decreases, being limited in space by movement only within the boundaries of the corresponding potential wells. The data obtained can vary with a change in the concentration of the modifier, which is due to some changes in the functional composition of the polymer composite.

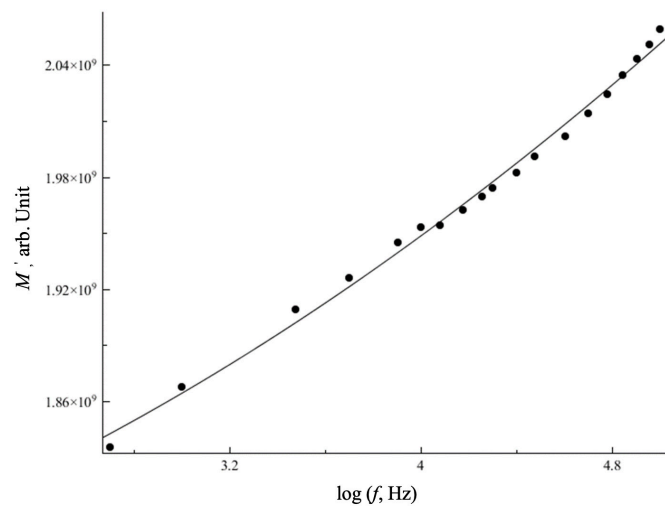


Fig. 4. Frequency dependence of the M' of the sample of the CEPVA-modified BaTiO_3 composite

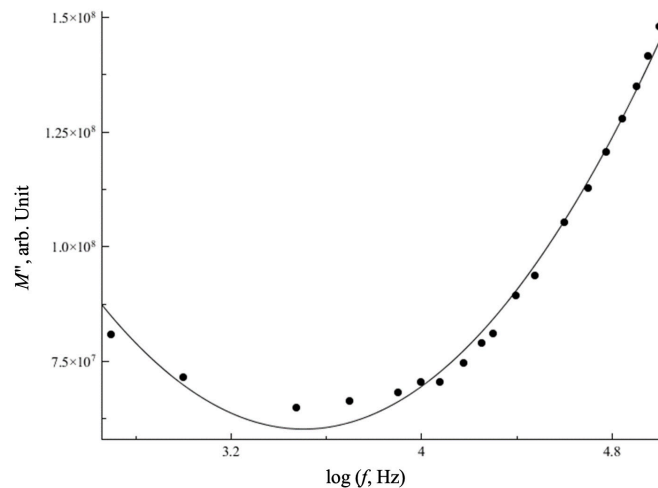


Fig. 5. Frequency dependence of the M'' of the sample of the CEPVA-modified BaTiO_3 composite

Conclusion

Thus, the analysis of the results of dielectric measurements and spectroscopy of the electrical modulus indicates active polarization processes with non-Debye relaxation in the investigated composite. These processes, along with the presence of a filler with a high dielectric constant, are largely associated with the content of polar groups in the CEPVA structure. It can also be noted that the introduction of graphene nanoparticles into the filler of the polymer matrix, i.e., into the ferroelectric BaTiO_3 , has an additional effect on the dielectric properties of the system under study due to the change in the content of basic and acidic centers of the surface.

Conflict of interest

The authors declare that there is no conflict of interest, either existing or potential.

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