

Dielectric and conductivity properties of polyethylene doped with barium titanate particles

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Abstract

The frequency and temperature dependences of dielectric permittivity and electric conductivity of high-density polyethylene with the addition of monodisperse barium titanate particles are studied. It was shown that dielectric permittivity and electric conductance increase with increasing of filler concentration at all temperatures. In this case, conductivity has hopping mechanism described by the Joser theory. The corresponding exponent parameter and activation energy decreases with increasing of barium titanate concentration. The experimental data of dielectric permittivity are compared with the Maxwell-Garnett and Bruggemann theories.

Keywords: barium titanate; high density polyethylene, dielectric permittivity; electric conductivity, composite material.

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1. Introduction

Polymer-inorganic composite materials with high dielectric permittivity and low losses, combining the viscoelastic properties of the binder and the dielectric properties of the filler, are required to create numerous devices. One of the most promising materials of this type is composites based on ferroelectric filler barium titanate. The review article [1] contains data on the permittivity of ceramics based on barium titanate with different grain sizes. When ceramics are prepared with a grain size as small as 0.5-1 μm , dielectric permittivity become significantly enhanced. It equals to 5000 for fine grain (0.5 μm) material, compared with 1500 for coarse grain (50 μm) ceramics at room temperature. The value of 1500 for coarse-grain material is readily understood in terms of an orientational average of the anisotropic dielectric constants which characterize a free single crystal. The value of 5000 for fine-grain microstructures is result of contribution of residual stresses on individual grains. With further reduction in grain size below 0.5-1.0 μm , the value in the tetragonal phase was observed to decrease again. The decrease in dielectric permittivity is explained by changes in crystal structure (i.e., a "pseudocubic" structure, not tetragonal structure).

The practical application of polymer-based composites requires fundamental

understanding of the properties of interactions between components that have a key influence on the macroscopic dielectric properties of composites.

A number of works have been devoted to the study of the dielectric properties of polymer composites based on barium titanate. Particularly, the authors of the work [2] investigated molecular relaxations in PVDF/BaTiO₃ nanocomposites. In dielectric permittivity study, two relaxation processes are identified corresponding to the crystalline, glass transition in the PVDF/BaTiO₃ nanocomposites. Electric modulus formalism is used to analyze the dielectric relaxations to overcome the conductivity effects at low frequencies. As a BaTiO₃ concentration in polyvinylpyrrolidone increased from 0 to 85 wt%, its dielectric constant increased from 7 to 30 with dissipation factors below 0.12 [3]. The ratio between BaTiO₃ and resin and the size of BaTiO₃ particles, were investigated and their related mechanisms were discussed in the work [4]. The BaTiO₃ particle size dependence of the dielectric properties of BaTiO₃/polyvinylidene fluoride composites is explained by space charge effects at the interface between BaTiO₃ and PVDF, and domain configurations (single or multi-domain) of the BaTiO₃ powders [5].

In the work [6], silane treatment is carried out on barium titanate powder. Epoxy and polyvinylidene fluoride (PVDF) polymers are used as matrices for preparation of the composites. Results indicate that the dielectric constant and dissipation factor vary between 18 -140 and 0.01 to 0.09, respectively as the relative ratio of polymer and silane modified filler is varied.

The aim of present work is the study of the effect of monodisperse fraction of barium titanate on dielectric properties of high-density polyethylene.

2. Experiments

We used high density polyethylene (HDPE) as a matrix. Melting and softening points of polymer are 130-135 °C and 80-90 °C, correspondingly. The barium titanate particles with sizes of 600 nm (US, Research Nanomaterials, In.) were added into the fine powder of polyethylene with different concentrations (5 vol. %, 10 vol. %, 20 vol.% and 30 vol.%). Then obtained mixture was shaken in a vortex mixer for 1 hour at room temperature, followed by sonication with dispergator Ultrasonic Cleaner NATO CD-4800 (China) for 4 hours. Disc-shaped samples of composites were obtained by hot pressing at temperature of 165 °C and pressure of 15 MPa. Pressing time after reaching the selected temperature is 15-20 minutes. The diameter and thickness of the obtained films were 4 cm and 80 - 90 µm, respectively. Aluminum electrodes with diameter of 3 cm and thickness of 10 µm are pressed on both sides of the films.

Dielectric measurements were carried out by the Precision LCR Meter 1920 (IET Labs. Inc., USA) over the frequency range of 20 Hz – 1 MHz and at temperatures between 18 °C – 70 °C. In such a case, applied voltage was 0.5 V. Electric capacity C and dissipation factor (the loss tangent) D were recorded by means of this device at different frequencies f . The magnitudes of dielectric permittivity ε were defined as:

$$\varepsilon = \frac{Cd}{\varepsilon_0 S} \quad (1)$$

where ε_0 is the permittivity of free space, d and S are the thickness and the square of the sample, respectively. The real ε' and image ε'' parts of dielectric permittivity and electric conductance σ were calculated by the expressions:

$$\varepsilon' = \frac{\varepsilon}{\sqrt{1+D^2}} \quad (2)$$

$$\varepsilon'' = \frac{\varepsilon D}{\sqrt{1+D^2}} \quad (3)$$

$$\sigma = 2\pi f \epsilon_0 \epsilon'' \quad (4)$$

3. Results and discussion

Figure 1 shows the frequency dependences of the real part of the dielectric permittivity for both pure polyethylene and the composite with different concentrations of barium titanate.

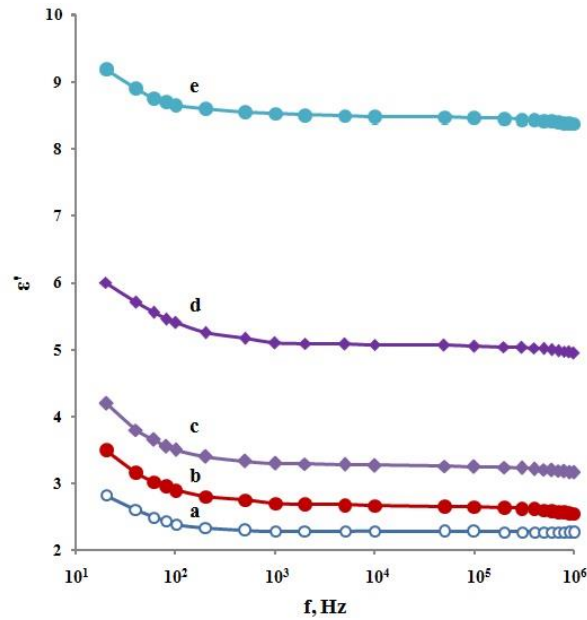


Figure 1. Frequency dependences of real part of dielectric permittivity at 20 °C: (a) pure HDPE, (b) HDPE+5 v.% BaTiO₃, (c) HDPE+10 v.% BaTiO₃, (d) HDPE+20 v.% BaTiO₃, (e) HDPE+30 v.% BaTiO₃.

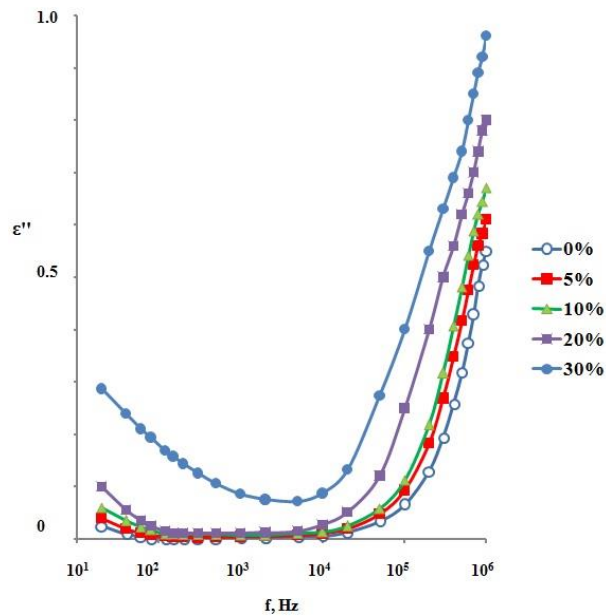


Figure 2. Frequency dependences of image part of dielectric permittivity at 20 °C: (a) pure HDPE, (b) HDPE+5 v.% BaTiO₃, (c) HDPE+10 v.% BaTiO₃, (d) HDPE+20 v.% BaTiO₃, (e) HDPE+30 v.% BaTiO₃.

As can be seen, with an increase in the filler concentration, both real and image parts of the dielectric conductivity increases at all frequencies. In this case, there is a slight decrease in the real ε' component of the permittivity with increasing frequency, which is explained by the delay of dipoles and a decrease in the number of particles involved in polarization. The presence of a significant electrical conductivity of composites at high filler concentrations also leads to the appearance of near-electrode polarization at low frequencies, which occurs in the layer adjacent to the electrode [7]. In this case, an increase in the permittivity at low frequencies is observed. This effect is most observed at high concentrations of barium titanate.

According to Maxwell–Garnett theory [8], scalar dielectric permittivity ε_{eff} of a medium consisted of particles with dielectric permittivity ε_p and the matrix with dielectric permittivity ε_m is

$$\varepsilon_{eff} = \frac{(1 - f_v)\varepsilon_m + f_v\beta\varepsilon_p}{1 - f_v + f_v\beta} \quad (5)$$

where f_v is a volume fraction of the inclusions; β depends on the shape of the inclusions. If the particles are spherical, then

$$\beta = \frac{3\varepsilon_m}{\varepsilon_p + 2\varepsilon_m} \quad (6)$$

and (3) reduces to

$$\varepsilon_{eff} = \varepsilon_m \left[1 + \frac{3f_v \left(\frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m} \right)}{1 - f_v \left(\frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m} \right)} \right] \quad (7)$$

Owing to $\varepsilon_p \gg \varepsilon_m$ then (7) turns into

$$\varepsilon_{eff} = \varepsilon_m \left(1 + \frac{3f_v}{1 - f_v} \right) \quad (8)$$

As can be seen from the last expression (8), the effective value of the dielectric permittivity does not depend on the permittivity of the particle substance.

Note that the Maxwell-Garnett approximation describes well isolated particles that are completely isolated from each other by the material of the medium. Bruggemann proposed the concept of a self-consistent effective medium. The Bruggemann approximation better describes the case where the particles are randomly distributed in the matrix material and agglomerated. The expression describing the two-component system in the Bruggemann approximation can be written as

$$f_v \frac{\varepsilon_p - \varepsilon_{eff}}{\varepsilon_p + 2\varepsilon_{eff}} + (1 - f_v) \frac{\varepsilon_m - \varepsilon_{eff}}{\varepsilon_m + 2\varepsilon_{eff}} = 0 \quad (9)$$

In order to compare the experimental concentration dependences of the permittivity with the theory of Maxwell-Garnett and Bruggemann, we present them at the frequency of 1 kHz as well as theoretical curves on the same Figure 3.

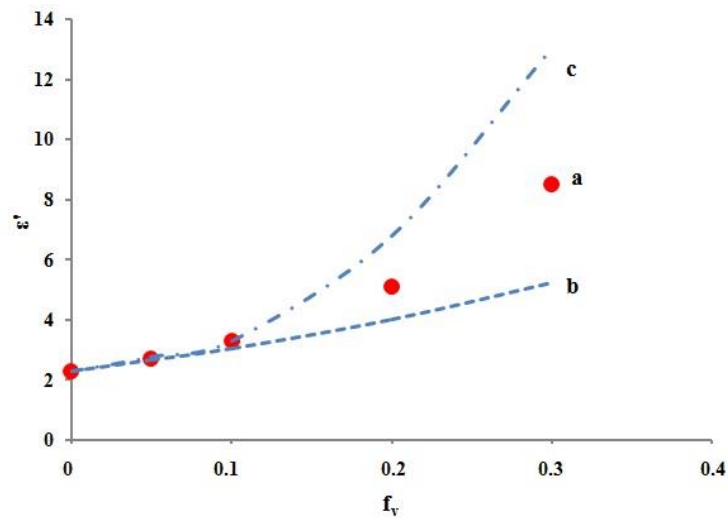


Figure 3. Comparison of experimental data at frequency of 1 kHz with theories: (a) experimental data, (b) the curve according to the Maxwell-Garnett approximation, (c) the curve according to the Bruggemann approximation.

As can be seen, the experimental values are located between the theoretical curves corresponding to the Maxwell-Garnett and Bruggemann theories. This fact indicates to the partial aggregation of barium titanate particles in polyethylene.

Figure 4 shows the temperature dependences of the real part of the dielectric permittivity up to the softening temperature of polyethylene.

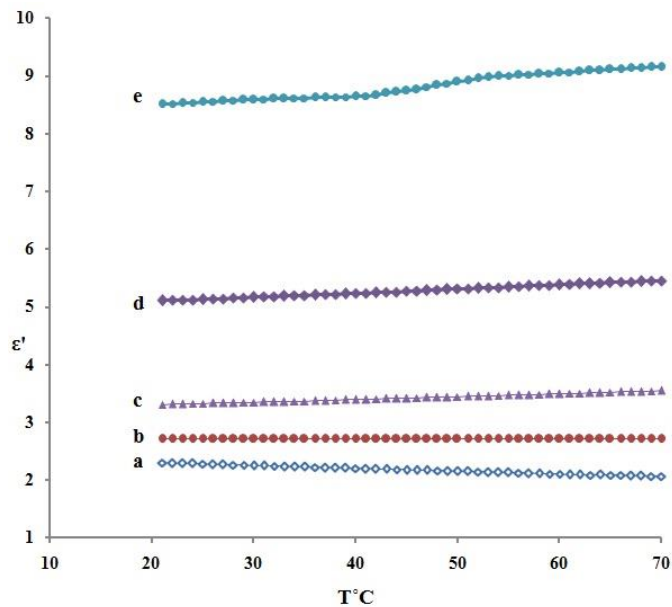


Figure 4. Temperature dependences of real part of dielectric permittivity at frequency of 1 kHz: (a) pure HDPE, (b) HDPE+5 v.% BaTiO₃, (c) HDPE+10 v.% BaTiO₃, (d) HDPE+20 v.% BaTiO₃, (e) HDPE+30 v.% BaTiO₃.

As can be seen, the dielectric permittivity of the pure polyethylene slightly decreases with increasing temperature. Since polyethylene is a non-polar dielectric, such a change in the dielectric permittivity is explained by a decrease in its density and, accordingly, a decrease in

the number of polarized particles. As the concentration of barium titanate particles increases, the ferroelectric component contributes to the permittivity. Therefore, at high filler concentrations, the permittivity increases with increasing temperature.

Frequency dependences of electric conductivity at different concentrations of barium titanate are presented in figure 5. One can see from this figure, conductivity increases with increasing of frequency. In this case, conductivity is more for the composites with more concentration of filler.

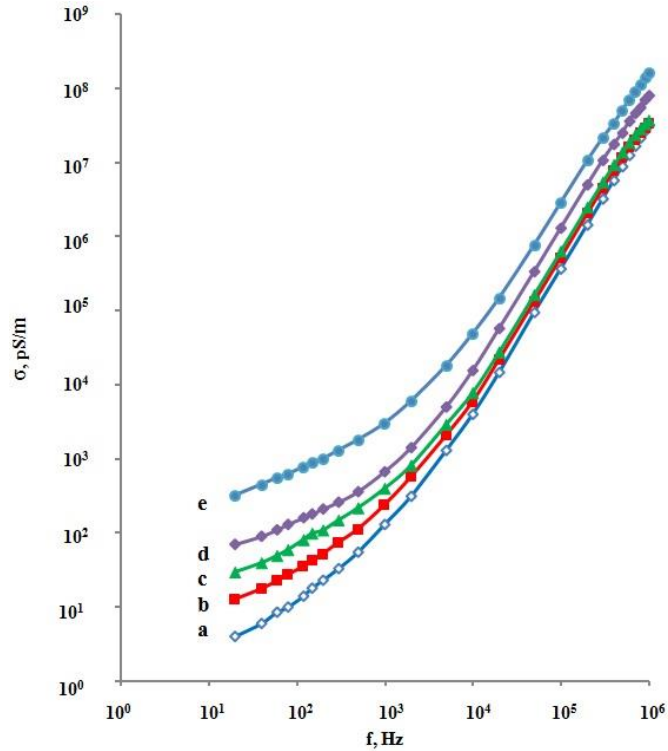


Figure 5. Frequency dependences of electric conductance of samples at 20 °C: (a) pure HDPE, (b) HDPE+5 v.% BaTiO₃, (c) HDPE+10 v.% BaTiO₃, (d) HDPE+20 v.% BaTiO₃, (e) HDPE+30 v.% BaTiO₃.

The frequency dependence of the conductivity of composite materials has a hopping mechanism and can be described by the equation obtained in [9]

$$\sigma = \sigma_{dc} + Af^n \tag{10}$$

where σ_{dc} is the direct current conductivity, A is a constant at given temperature, n is a parameter that varies from 0 to 1 and characterizes the degree of interaction of charge carriers with the matrix material. Conductivity occurs by hops between particles and along defects in the polymer matrix. Since the particles are randomly arranged, isolated conducting paths have a wide size distribution leading to conductance dispersion [10].

An analysis of the frequency dependences of the conductivity of colloids showed that the coefficient n , which characterizes the degree of interaction of carriers with the matrix material, decreases from 0.52 to 0.47 with an increase in the concentration of BaTiO₃ particles from 5 to 30%, which confirms the decrease in the interaction between charge carriers and the matrix material.

Figure 6 shows the temperature dependences of conductivity for both pure polyethylene and colloids.

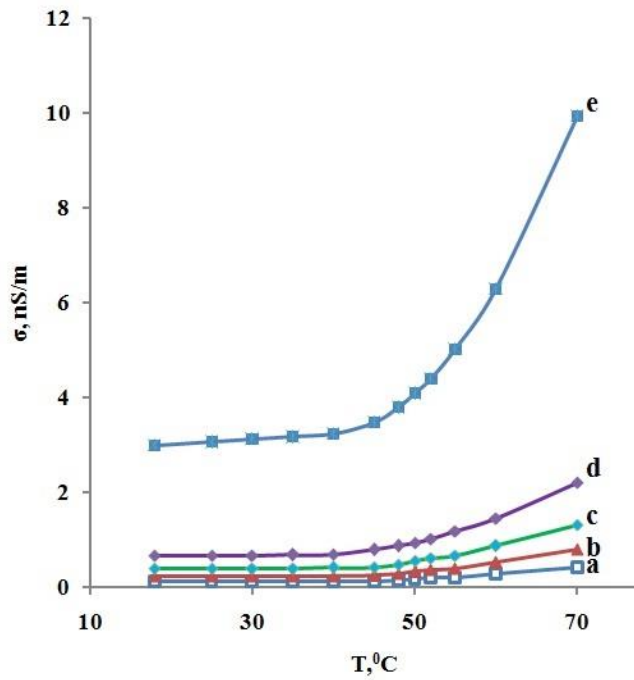


Figure 6. Temperature dependences of electric conductance at frequency of 1 kHz: (a) pure HDPE, (b) HDPE+5 v.% BaTiO₃, (c) HDPE+10 v.% BaTiO₃, (d) HDPE+20 v.% BaTiO₃, (e) HDPE+30 v.% BaTiO₃.

As can be seen, the conductivity increases with increasing temperature. Moreover, with an increase in the concentration of barium titanate, the conductivity increases at all temperatures. At the same time, these dependencies obey the Arrhenius law:

$$\sigma = \sigma_0 e^{-\frac{E}{k_B N_A T}} \quad (11)$$

where σ_0 is the pre-exponential factor, E is the activation energy of electrical conductivity. k_B is Boltzmann constant, N_A is the Avogadro number, T is Kelvin temperature.

From the last expression, it is possible to find the activation energy E of the colloids. The calculated values of the activation energy are given in Table 1. As one can see from this Table, the increase of barium titanate concentration leads to the decrease of activation energy. The value of E consists of the activation energy of the motion of the carriers and the energy necessary for the nucleation of new charges. It is an energy barrier which an ion must overcome to move inside the polymer medium. The larger the E , the harder the ions move within the composite and, accordingly, the lower the conductivity.

	Activation energy
Pure HDPE	121.7
HDPE+5 v.% BaTiO ₃	120.3
HDPE+10 v.% BaTiO ₃	118.5
HDPE+20 v.% BaTiO ₃	117,0
HDPE+30 v.% BaTiO ₃	116.2

Table 1. Activation energy (in kJ mol⁻¹) for the pure polyethylene and the composites.

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