Dielectric And Structural Study Of Polymer Composites Based On Polyethylene And Barium Titanate

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Abstract. Structural and dielectric properties of polymeric composites on the basis of polyethylene and a titanate of barium are investigated. It is shown that the studied system can be considered as the composite including electrically isolated spherical particles of filler in a polymeric matrix. Emergence of a maximum of dielectric permeability and loss factor is connected with strengthening of interaction between polar groups of a polymeric matrix and the polarized particles of ferroelectric ceramic $BaTiO_3$.

Keywords: structural and dielectric properties, polymeric composites, dielectric permeability, loss factor.

INTRODUCTION

Over last few years the special care has been given to the development of the polymer composites with high permittivity. Such composites are widely applied in different areas of the modern life (electronics, filtration, medicine, packing etc.). In particular the polymeric systems filled with ferroelectric ceramic powder are used as an additional layer regulating the field distribution in high-voltage insulating constructions.

The introduction of a nonorganic fine aggregate is essentially modified the structure and the composites properties due to formation of the interface nano-layer next to the aggregate particles and interfacial contact [1]. It features the temporal distribution of the local field in some areas of the polymeric system and temperature and frequency dependence of the complex permittivity. The aim of this study is to find the peculiarities of the dielectric relaxation in polymer composites based on polyethylene and barium. The study of the dielectric and thermal properties of complex systems has a great meaning to clarify the electronic process in materials and to understand the nature of their structure [2, 3].

EXPERIMENTAL TECHNIQUES

The polymer composites based on polymer and ferroelectric ceramic have been studied. The low-density polyethylene has been chosen as a subject of the study and the powdered barium titanate $BaTiO_3$ has been chosen as an aggregate.

The samples have been prepared in the form of films and plates (0.3-0.5 mm thick and 20.0 mm in diameter) by pressing with hydraulic press. The pressing temperature has been 170 . The heating time has been 10 minutes, the pressure - 200 kgf/cm2, the hold time - 5 min., the cooling time - 5 min. The dielectric parameters of the samples have been measured with spectrometer "Concept 81" (NOVOCONTROL Technologies GmbH & Co.) in the temperature range from 173K to 323K (accuracy is 0.5K). The measuring voltage supplied to the sample has been 1.0 V.

The relaxation time of the revealed relaxation process was calculated using the Havriliak-Negami approximation [4]:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{\left[1 + (i\omega\tau)^{\alpha_{HN}}\right]^{\beta_{HN}}} \tag{1}$$

where - is the permittivity at the high frequency limit, $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ where ε_s is the static, low frequency permittivity, and τ is the characteristic relaxation time. The exponents α and β describe the asymmetry and broadness of the corresponding relaxation spectra. For β=1 the Havriliak–Negami equation reduces to the Cole–Cole model, for α=1 to the Cole–Davidson model.

Research of the surface structure and definition of element composition of samples was made on the scanning electronic microscope (SEM) of Carl Zeiss EVO 40, under the conditions of low vacuum (table 1).

TABLE 1. Elemental composition of LDPE/BaTiO3 samples.

Element	Nominal concentration	Mass fraction	Weight %	Weight % Sigma	Atomic fraction %
C	12.47	1.3257	24.52	0.41	59.54
O	5.09	1.1464	11.58	0.34	21.10
Ti	5.49	0.9802	14.59	0.38	8.88
Ba	15.93	0.8422	49.31	0.57	10.47
Total			100		

RESULTS AND DISCUSSION

Structural investigation

Electric properties of matrix systems in which there is no physical contact of particles of filler in case of spherical particles can be presented by Bruggeman's equation up to concentration 30 about vol. %:

$$\frac{\varepsilon_f - \varepsilon}{\varepsilon_f - \varepsilon_m}\left(\frac{\varepsilon_m}{\varepsilon}\right)^{1/3} = 1 - \nu_f \tag{2}$$

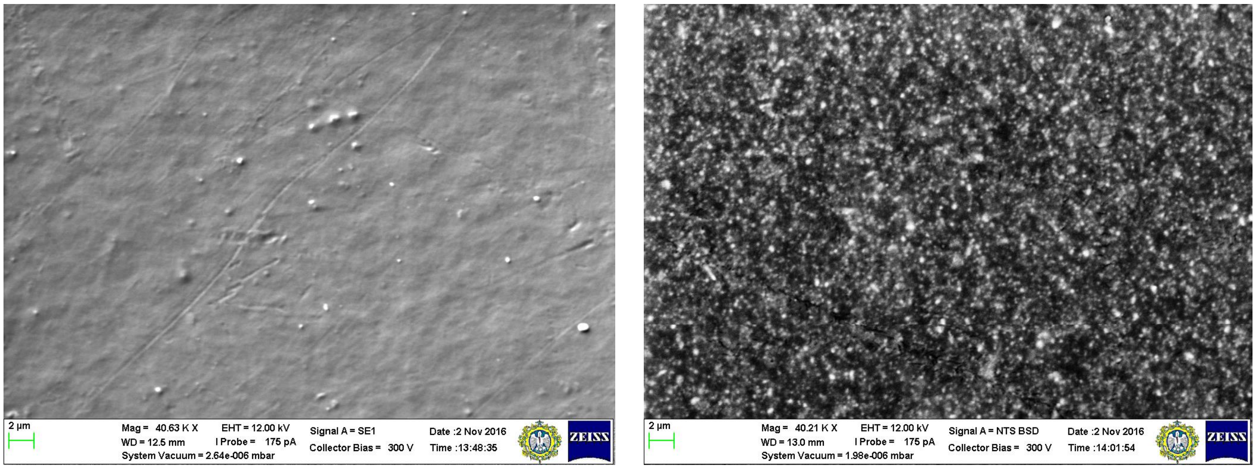
where ε_m – dielectric permittivity of matrix, ε_f – dielectric permittivity of filler, v_f – volume fraction of filler [5, 6].

Values of the parameters entering expression (1) are presented in table 1. Good coincidence of experimental results to a prediction of theoretical model allows concluding that the studied system can be considered as the composite including electrically isolated spherical particles of filler in a polymeric matrix.

TABLE 2. Values of Bruggeman's equation parameters for LDPE/$BaTiO_3$ composite.

ν_f **(vol. %)**	ε	ε_f	ε_m	$f(\varepsilon)$	$1-\nu_f$
0.0	2.14	----	2.14	1.00	1.00
2.0	2.20	1400	2.14	0.99	0.98
8.0	2.35	1400	2.14	0.97	0.92
12.0	2.73	1400	2.14	0.92	0.88
20.0	4.30	1400	2.14	0.79	0.80
Error	± 0.01			± 0.02	

Existence of spherical inclusions in a polymeric matrix is confirmed by results of a research of these systems by scanning electronic microscope (SEM) method (figure 1).



(a) (b)

FIGURE 1. Surface scanning of the polymer composite samples: (a) – LDPE, (b) – LDPE/$BaTiO_3$ composite

Dielectric relaxation

The introduction of $BaTiO_3$ ceramic to the polymer leads to the origin of maximum on the frequency and temperature dependence of dielectric parameters in the medium and low frequency range (figure 2). The location of the temperature maximum of dielectric permeability depends on the concentration of $BaTiO_3$ in the composite (figure 3).

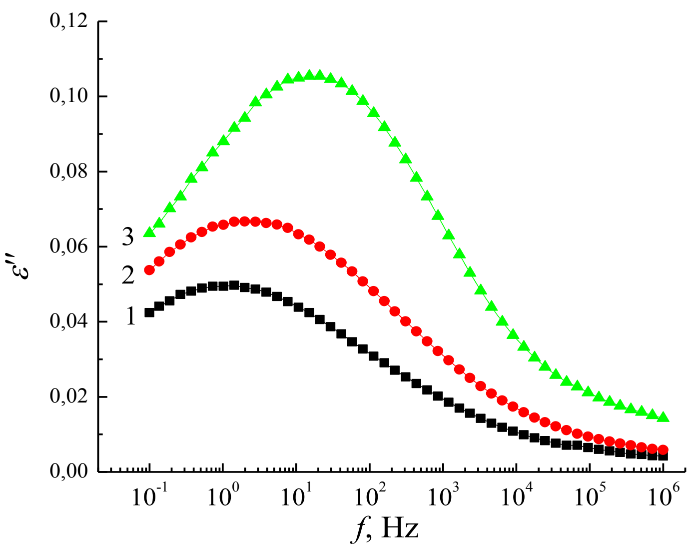


FIGURE 2. Frequency dependence of loss factor ε″ at room temperature. Vol. % $BaTiO_3$: 1 – 8.0, 2 – 12.0, 3 – 20.0

Emergence of a maximum of dielectric permeability and loss factor may be connected with strengthening of interaction between polar groups of a polymeric matrix and the polarized particles of ferroelectric ceramic $BaTiO_3$. This interaction can lead also to growth of energy of activation of polarization processes (figure 4). Besides, in system there are uniformly polarizing areas – domains which dipolar moments for lack of electric field have the disorder character. When imposing the field there is a primary orientation of domains that leads to growth of polarization of a polymeric composite.

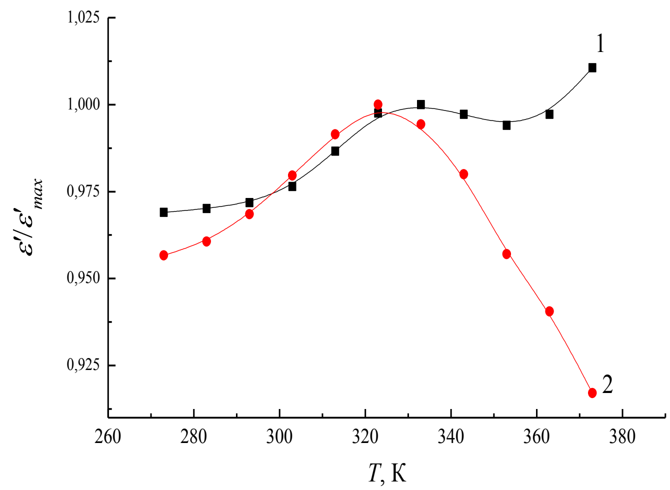


FIGURE 3. Temperature dependence of loss factor ε″ at room temperature. Vol. % $BaTiO_3$: 1 – 12.0, 2 – 20.0

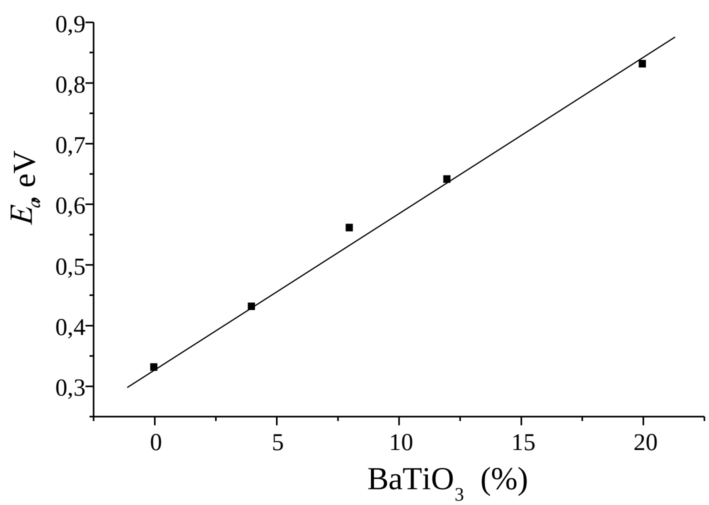


FIGURE 4. Dependence of activation energy on $BaTiO_3$ concentration

The discovered regularities of dielectric behavior in studied systems also may be the result of the existence of monoclinic cell and may be used to identify the monoclinic phase in complex compounds containing barium titanate. As it is known, the transition to the orthorhombic phase in barium titanate is accompanied by change in symmetry and dielectric anomaly. The atoms of Ti and O are displaced along one of the 12 equivalent directions in cubic phase of <110> type (face diagonal). The unit cell takes the shape of the right parallelepiped with b height. The base of the right parallelepiped is a rhombus with sides a = c and obtuse angle β very close to 90%. Such a sell with axial vectors a, b and c is a monoclinic one [7]. In this phase the crystal belongs to the orthorhombic space group of symmetry C2mm. The value of the atoms displacement is of the same order as it is in the tetragonal phase.

CONCLUSION

From the obtained results we can conclude: 1) the studied system can be considered as the composite including electrically isolated spherical particles of filler in a polymeric matrix; 2) emergence of a maximum of dielectric permeability and loss factor is connected with strengthening of interaction between polar groups of a polymeric matrix and the polarized particles of ferroelectric ceramic $BaTiO_3$; 3) the discovered regularities of dielectric behavior in studied systems also may be the result of the existence of monoclinic cell and may be used to identify the monoclinic phase in complex compounds containing barium titanate.

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