EFFECTS OF THE HfO_2 NANOFILLER ON THE ELECTRET PROPERTIES AND STRUCTURE OF THE PE/HfO_2 POLYMER NANOCOMPOSITE

A.S. HUSEYNOVA
Institute of Physics of the Ministry of Science and Education of the Republic of Azerbaijan, AZ1143, H.Javid ave., 131, Baku city, Republic of Azerbaijan
e-mail:aem05@rambler.ru

The effect of electrothermopolarization (ETP) on the structure and electret properties of polymer nanocomposites based on HDPE and hafnium oxide nanoparticles has been studied. It has been established that the physico-mechanical properties of the PE/HfO_2 nanocomposite improve when 3–10% by weight of HfO_2 nanoparticles is introduced into the PE matrix. The appearance of a long-term electret effect in PE/HfO_2 is associated with the inhomogeneity of the nanocomposite structure and the accumulation of a large number of electric charges at the interface. The interaction between the polymer and nanoparticles has been studied. The results of structural changes occurring in the interfacial zone of the PE/HfO_2 polymer nanocomposite are also presented.

Keywords: nanocomposites, polyethylene, hafnium oxide, polymer nanoparticles, electrothermopolarization,electron microscopy.
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1. INTRODUCTION

In recent years, polymer nanocomposites have attracted great interest due to the improvement in the properties of polymers and the expansion of theirapplicationfields. Nanofillers change the supramolecular structure, which largely determines the physicochemical and mechanical properties of the polymer and nanocomposites based on them. The nature of the influence of a nanofiller on the supramolecular structure and properties of polymers is determined simultaneously by the amorphous and crystalline phases, and also plays the role of artificial nuclei for the crystallization of nanoparticles, which leads to a change in the properties of the material [1-6, 10].

It should be noted that, depending on the nature, size, and distribution of nanoadditives, the resulting polymer nanocomposite can be electrically conductive, antistatic, or dielectric. In this regard, the study of the properties of composites obtained by adding metal oxide nanoparticles to polyethylene is of particular interest. The change in the physical properties of polyethylene materials by nanoadditives is mainly due to two reasons: nanoadditive particles act as a source of structuring, and the interfacial layer of the nanoadditive polymer has a large number of charge traps with different activation energies [7–12].

Accordingly, in this work, high-density polyethylene (HDPE) and hafnium oxide nanofiller (HfO_2) were chosen as the polymer matrix, which has improved physical parameters, such as high chemical and thermal stability, and a large band gap (5.5–6 eV), high dielectric constant (22–25), high breakdown strength (3.9–6.7 MV/cm), high neutron absorption coefficient.In technological applications, polymer-based metal-oxide nanoparticles are used in the manufacture of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for surface protectionfrom corrosion, and as catalysts. In the emerging field of nanotechnology, the goal is to create nanocomposites with special properties compared to those of bulk particles.

As it is known, polymers and nanocomposite materials obtained on their basis, after exposure to an external constant electric field at sufficiently high temperatures, are polarized and have electret properties. The main characteristics of the electret material are the magnitude of the electric charge and its stability. They are used in a wide variety of scales, from food processing equipment to special purpose equipment. Physicochemical analyzes of the PE/HfO_2 nanocomposite material were carried out by selecting a special technological mode. The PE/HfO_2 nanocomposite exhibits electrets with a service life that is many times greater than that of pure PE, according to research on their electret properties [13–17].

2. EXPERIMENTAL PART

HDPE polyethylene granules (SOCAR, “Azerikimya” ProductionUnion “Etilen-Polyethylene” plant, 15803-020), CCl_4 organic solvent (Code 141245, 99.5%, CAS Common Chemistry-P.L.C); hafnium oxide (HfO_2) nanoparticles, size 10-20nm, Luoyang Tongrun Info Technology Co., Ltd. China, CAS 12055-23-1, 99%).

Characterization of nanocomposites

SEM analyzes of nanocomposites were made on a JEOL JSM 6610-LV scanning electron microscope at an accelerating voltage of 30 kV.

Polymer nanocomposites were electrothermopolarized (ETP) using an external electric field with a strength of $7\cdot10^6$-$12\cdot10^6$V/m, at a temperature of 373K and then cooling to room temperature for 1 hour. Polymerization provides a strong interaction between the filler and the matrix, which is required in a number of cases. The film thickness is 90–105 μm.

131, H.Javid ave, AZ-1143, Baku
Institute of Physics
E-mail: jophphysics@gmail.com

Synthesis of polymer nanocomposites

PE/HfO_2 polymer nanocomposites were obtained as follows: polyethylene granules were dissolved at room temperature in 60 ml of an organic solvent, carbon tetrachloride (CCl_4), at a temperature of 70C. HfO_2 nanoparticles are added to the polymer solution at various contents and mixed for 5 hours until a homogeneous mixture is obtained. The mixture was transferred to a Petri dish and dried in a vacuum oven for 24 hours. Then, thin films of nanocomposites were obtained from these samples by hot pressing at the melting temperature of polyethylene and a pressure of 15MPa. After hot pressing, the films were cooled in water; the cooling rate of nanocomposite films was 200deg/min.

3. RESULTS AND DISCUSSION

Fig.1 shows the dependences of the surface density of the electret charge (σ) on the lifetime σ=f(τ) for samples of pure PE and nanocomposites based on PE/HfO_2 with different mass content of HfO_2 nanoparticles. It has been established that after ETP, an electret effect is observed in the matrix PE, which is associated with the inclusion of HfO_2 nanoparticles. The lifetime of the surface density of the electret charge for PE and nanocomposites based on PE/HfO_2 was calculated using the following expression:

$$\sigma = \frac{\varepsilon\varepsilon_0 U}{d}$$

where, σ - is the surface charge density, d-is the thickness of the electret, ε-is the permittivity, ε_0-$8.85\cdot10^{-12}$F/m, U- is the charging voltage.

The introduction of HfO_2 nanoparticles can create new traps for electric charge in polyethylene, and this can increase the surface charge density and lifetime. It can be seen that the surface density of electret charges decreases exponentially depending on the lifetime after exposure to discharges. Higher values of σ and relatively higher charge stability is observed for samples of PE/HfO_2 nanocomposites with 5÷10% wt. content of HfO_2 nanoparticles (curve 3, 4, 5). This is due to the presence of deeper traps in the near-surface layers.

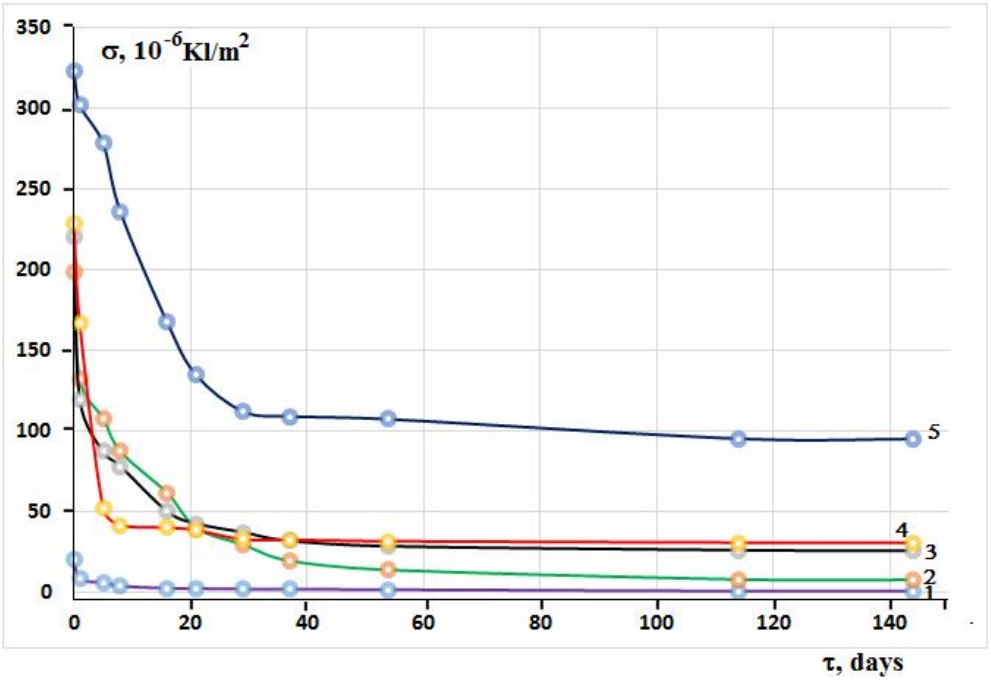


Fig.1. Dependence of the surface density of the electret charge σ on the lifetime τ of compositions: 1. PE; 2. PE/3%HfO_2; 3. PE/5%HfO_2; 4. PE/7%HfO_2; 5.PE/10%HfO_2

In addition, after storage of the electret from a sample of 5÷10wt.%PE/HfO_2 for τ=8÷22 days, the value of σ stabilizes and amounts to $42\div112\cdot10^{-6}$Kl/m^2. This means that the nanocomposite 5÷10wt.%PE/HfO_2 has optimal electret properties. It can also be seen that the surface density of the electret charges of the PE/HfO_2 based nanocomposite is approximately 15 times higher than that of pure polyethylene.

In this work, when studying the electret state, the main attention was paid to the change in the magnitude of the surface charge with time, temperature, and electric field of the ETP, with the structure, relaxation processes of the PE/HfO_2 nanocomposite. The long-term component of the electret effect in PE/HfO_2 is due to in homogeneities of the nanocomposite structure, the boundaries of which are charge traps, which leads to the appearance of Maxwell-Wagner polarization in the entire volume of the nanocomposite.

The change in the electret properties of composites depending on the ETR method is mainly associated with a change in the conditions for stabilization of charges in them and the physical

structure of the matrix. This conclusion correlates well with the results obtained from SEM and electron microscopy (EM) analysis of PE/HfO_2 nanocomposites [17]. Fig.2 shows the EM spectra of PE and a polymer nanocomposite based on PE/HfO_2 depending on the mass content of HfO_2 nanoparticles. Figure 3 shows the SEM spectra of the PE/5%HfO_2 nanocomposite before and after ETP.It should be emphasized that the HfO_2 nanoparticles stabilized with a polyethylene matrix also retained the structural parameters of the nanoparticles contained in the initial dispersion. The study of samples of HfO_2 nanoparticles by electron microscopy (EM) showed that the sample of the dispersion of nanoparticles consists of isotropic nanoparticles. The shape of the particles is uniform, close to spherical.

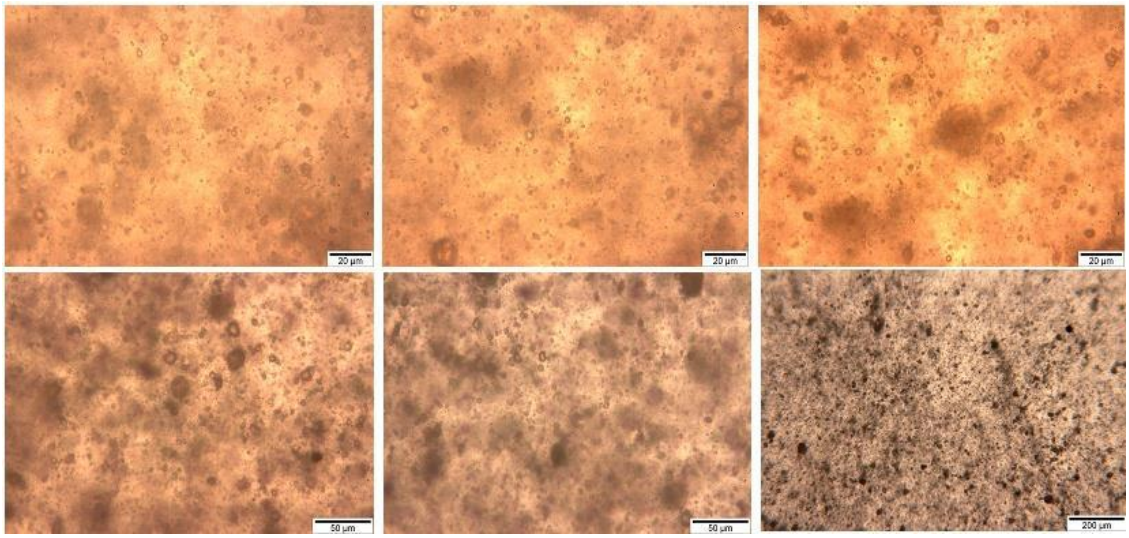
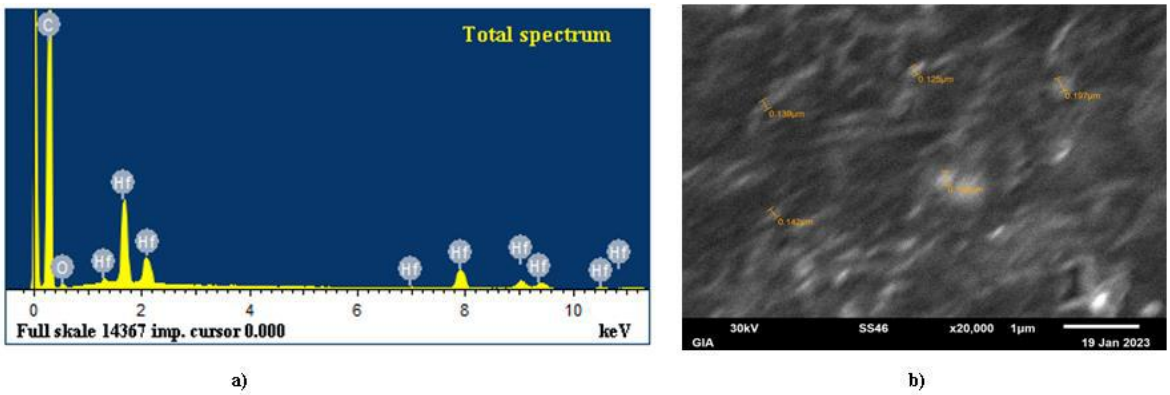


Fig.2. EM images of PE/5%HfO_2 polymer nanocompositesş

Analysis of the EM of the nanoparticles showed that the nanoparticles are uniformly distributed over the volumestabilizing matrix and isolated from each other.

The morphology of the samples and the distribution of HfO_2 nanoparticles in the volume of the polymer matrix were studied using a scanning electron microscope (SEM) (Fig. 3). Elemental analysis in the EMF spectrum also shows (Fig. 3.b) that the resulting nanoparticles are hafnium nanoparticles. Fine crystalline particles can be observed on the surface of Figure 3a. Based on the SEM images, it can be said that the HfO_2 nanoparticles are evenly distributed and aggregated on the surface of the polymer matrix. The average size of iron nanoparticles stabilized in the presence ofpolyethylene is 4,93 nm. Elemental analysis in the EMF spectrum also shows that the obtained nanoparticles are hafnium nanoparticles.



a) b)

Fig.3. SEM images of PE/5%HfO_2 polymer nanocompositesş

RESULTS

Thus, the PE/HfO_2 polymer nanocomposites developed by us represent a new, promising class of electret materials that will undoubtedly be in demand in modern science-intensive technologies. It has been established that with the introduction of 3-10% amounts of HfO_2, the physical and mechanical properties of the PE/HfO_2nanocomposite increase, and the performance of PE products increases.

According to the data of electron and SEM microscopy, in all samples, the nanoparticles are spherical, isolated from each other, and uniformly distributed over the volume of the polyethylene matrix.

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