

Study of dielectric and structure changes of PE+PbCrO₄ nanocomposite after electric field by ir spectroscopy method

A.S. Huseynova*, F.F. Yahyayev

*Institute of Physics of the Ministry of Science and Education of the Republic of Azerbaijan,
Azerbaijan 131, H. Javid ave., Baku, AZ 1143, Azerbaijan
email: aem05@rambler.ru*

Abstract

In the present work, the dielectric properties and structural changes of the PE+1% PbCrO₄ nanocomposite are studied by IR spectroscopy. It has been shown that the introduction of a sufficient amount of an optimally modified nanoadditive leads to a certain decrease in ϵ_n and an increase in the value of loss tangent ($\text{tg}\delta$) which can be explained by a violation of the homogeneity of the nanocomposite and the formation of defects of different sizes as a result of, ionization processes. An increase in the value of $\text{tg}\delta$ is associated both with an increase in the conductivity of the sample and with structural changes in the polymer. Also, with an increase in temperature, a slight increase in the value of ϵ is observed, which is most likely associated with the occurrence of an additional crystallization process in the polymer. This behavior of the nanocomposite can be associated with thermal stimulation processes - the redistribution of charges at the interface between the particle and the matrix, the accumulation of these charges in deeper traps and, as a result, the creation of an inhomogeneous medium. The value of $\lg\rho_v$ increases until certain temperatures, that is, a positive effect is observed in the nanocomposite sample, which is explained by a decrease in the amount of the space charges in the nanocomposite. Changes in the structure of the PE+1%PbCrO₄ nanocomposite were analyzed using IR radiation. It is shown that structural changes in the IR spectrum after electrothermopolarization are mainly observed at PE wave numbers of 726 cm⁻¹, 73 cm⁻¹, 825 cm⁻¹. Changes in these wave numbers depending on the electrothermopolarization conditions are associated with the activation of CH₂ stretching vibrations in polyethylene.

Keywords: electrothermopolarization, nanocomposite, spectroscopy, dielectric, matrix.

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1. Introduction

Polymer technology has been developing nanocomposite materials with complex properties for many years. Such systems are created either by searching for optimal polymer combinations, or by mixing polymers with nanoadditives of different nature. The introduction of nanoadditions expands the field of application of high molecular weight compounds. It is known that such materials are superior to the polymers they are based on due to their complex

properties. In the acquisition process of nanocomposites, along with the fact that the materials have a low cost, on the other hand, the main components have relatively significant complex properties.

It is also clear that in order to obtain successful and purposeful nanocomposite materials, both the structural elements of the nanocomposite (the shape and size of the particles, their mutual arrangement in the matrix) and also the matrix (the formation of ordered structures of different levels, taking into account the interaction at the interphase boundary, the properties of the nanocomposite materials as a whole and the polymer elucidation of the relationship between the structure, in a word, the upper molecular structure) should be thoroughly studied.

When synthesizing nanoparticles in a polymer matrix, the pores in the matrix play a limiting role for the particle size, and by changing the production technology of the nanocomposite, the relationship between structure and property can be determined by varying the interphase interaction. At the same time, due to the differences of organic and inorganic phases in polymer nanocomposites, the macrosystem behaves differently according to nanosystems. In general, there has been an increased scientific interest in obtaining nanocomposite structures with unique properties by introducing nano-sized particles into polymers, studying their complex physico-chemical properties [2, 4, 6, 10].

Knowing the interaction between the structure, dielectric properties, chemical structure and electret properties of polymers allows choosing the optimal polymers for a specific purpose [8, 13]. In recent years, new nanocomposite materials were obtained and studied by adding nano-additions to high-pressure polyethylene, and interesting results of special importance from both practical and scientific point of view were obtained [9, 11, 12].

Thus, in this study, physico-chemical analysis of PE+1%PbCrO₄ nanocomposite material were conducted, dielectric properties and structural changes were studied through IR spectroscopy. PE+1%PbCrO₄ nanocomposite was found to be an electret with many times higher lifetime than pure PE [13]. New nanocomposite materials obtained by adding nano-additions to high-pressure polyethylene can be considered relevant research objects [1,3,5].

2. Experiments

Obtaining a sample of the nanocomposite is carried out by hot pressing at a polymer melting temperature and a pressure of 15 MPa for 10 minutes, followed by cooling to room temperature under pressure. The hot-pressing process is characterized by three main technological parameters - pressure, temperature and holding time in the molten state. The nanocomposites were preliminarily subjected to electrothermopolarization at a temperature of 373K for an hour. To obtain the samples under study, the composite is first heated to the polarization temperature T_p , then a constant electric polarization field E_p is applied and kept for the time t_p in the field, after which, without removing the field, it is cooled to room temperature. This method of electrothermopolarization makes it possible to vary the energy value and the concentration of injected charges in the nanocomposites in a wide range. The film was cooled to room temperature under the action of an electric field of strength $E_p=7 \cdot 10^6 \text{V/m}$.

Dielectric constant (ϵ), dissipation tangent ($\text{tg}\delta$) and electrical conductivity (ρ) were measured using an IET1920 PRECISION LCR METTER at a frequency of 1kHz-1MHz at a temperature of 293K. The study by IR spectroscopy was carried out on an infrared spectrophotometer SPECORD M-80 in the frequency range 700-4600 cm^{-1} .

3. Results and discussion

To measure the dielectric properties of the PE+1%PbCrO₄ nanocomposite under an alternating electric field, aluminum foil with a thickness of 7 μm was attached to both sides of the sample. The temperature dependence of the dielectric permittivity and the loss tangent and the logarithm of the specific resistance in the indicated type of nanocomposite were studied in the range of 293-450K. To measure the dielectric properties, the samples were placed between electrodes made of stainless steel attached to compressed springs in the measuring core. Measurements were carried out in room conditions with freshly synthesized samples. Knowing the electrical capacity and the geometrical dimensions of the samples, the value of the complex dielectric permittivity ε is calculated by the formula of the planar capacitor:

$$\varepsilon = \frac{Cd}{\varepsilon_0 S}$$

C is the capacity of the samples, d is the thickness of the sample, S is the area of the upper electrode, ε_0 is the electrical constant, the value of which is $\varepsilon_0 = 8.85 \cdot 10^{-12} \text{ Kf}^2/\text{N} \cdot \text{m}^2$.

The temperature of the electric field applied to the nanocomposite varied from 20 °C to 150 °C. The obtained results are given in the form of electric field temperature dependence of dielectric permeability (ε), logarithm of specific resistance ($\lg \rho_v$) and tangent angle of dielectric loss ($\text{tg} \delta$).

In the considered work, the effect of PbCrO₄ nanoadditive on the structure of polyethylene-based nanocomposite was studied.

Determining the dielectric parameters $\text{tg} \delta$, ε , $\lg \rho_v$ have a significant effect on the properties of the surface of the nano additive. At a certain value of the composition of the nanoadditive, the maximum of E_n corresponding to various modifications is related to the maximum homogeneity of the coating. It was also shown that the inclusion of a sufficient amount of optimally modified nanoadditive leads to a certain decrease in E_n and an increase in the value of $\text{tg} \delta$, which can be explained by the disruption of the homogeneity of the nanocomposite and the formation of defects of different sizes, which are the source of ionization processes. This can result in the electrical breakdown of the nanocomposite due to the effect of a strong external electric field. The development of electron and volume charge polarization processes in polymer dielectrics can significantly change the dielectric breakdown process.

From the graph given in Figure 1, it can be seen that the PE+1%PbCrO₄ nanocomposite has two maxima at 305K and 335K. No noticeable change was observed for pure PE. The nature of the dependence of $\text{tg} \delta = f(T)$ for the nanocomposite also changes, as the temperature increases, $\text{tg} \delta$ first increases and then starts to decrease, passing through a minimum in the region close to the melting temperature of the crystallites. Further increase in temperature causes $\text{tg} \delta$ to increase again. Such change of dielectric loss in PE+1%PbCrO₄ nanocomposite is based on full correlation of electrical conductivity of that sample with temperature dependence in alternating electric field.

According to the authors [2,7,10], in some temperature regions, the nature of electrical conductivity and the dependences on it, dielectric loss, during dielectric relaxation and the activation energy of polarization processes can be the same. Such a change in the dielectric properties of polymer nanocomposites indicates that the molecular mobility of the matrix is thermal in nature and is related to the dielectric properties of nanocomposites. Starting from the specific value of the temperature (396K), the value of the loss tangent ($\text{tg} \delta$) continues to increase, which is related to both the increase in the conductivity of the sample and the structural changes of the polymer.

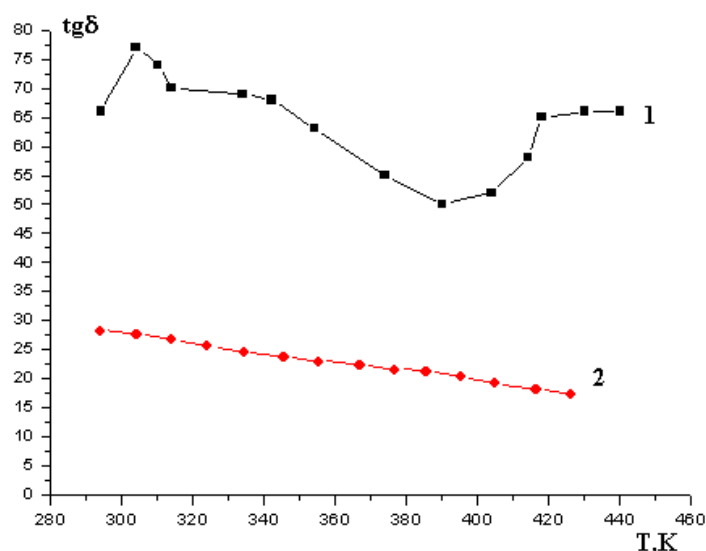


Figure 1. Dependence of dielectric loss angle tangent ($\text{tg}\delta$) on temperature (T) of PE+1%PbCrO₄ (1) nanocomposite and pure PE (2) subjected to electrothermopolarization for 1 hour at temperature $T=373\text{K}$

The graph given in Figure 2 shows the dependence of dielectric permittivity (ϵ) on temperature after electrothermopolarization in PE+1%PbCrO₄ nanocomposite. As can be seen, as the temperature increases, a certain increase in the value of ϵ is observed, which is most likely due to the additional crystallization process taking place in the polymer. At $T=315\text{K}$, ϵ takes its largest value and starts to decrease starting from $T=315\text{K}$. This behavior of the nanocomposite can be related to thermostimulation processes - charge redistribution at the boundary of the particle and the matrix, the accumulation of these charges in deeper traps, and as a result, the creation of an inhomogeneous environment.

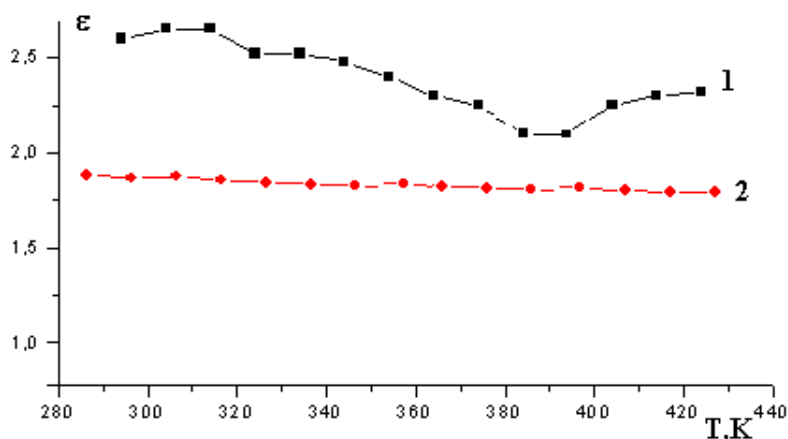


Figure 2. Temperature (T) dependence of dielectric permittivity (ϵ) of PE+1%PbCrO₄ nanocomposite (1) and pure PE (2) subjected to electrothermopolarization for 1 hour at temperature $T=373\text{K}$

As it can be seen, the value of $\lg\rho_v$ increases at certain values of temperature, that is, a posistor effect is observed in the nanocomposite sample. In PE+1%PbCO₄ nanocomposite, $\lg\rho_v$ takes the maximum value at temperature $T=355\text{K}$. The increase in the value of $\lg\rho_v$ is explained by the decrease in the amount of the volume charges in the nanocomposite.

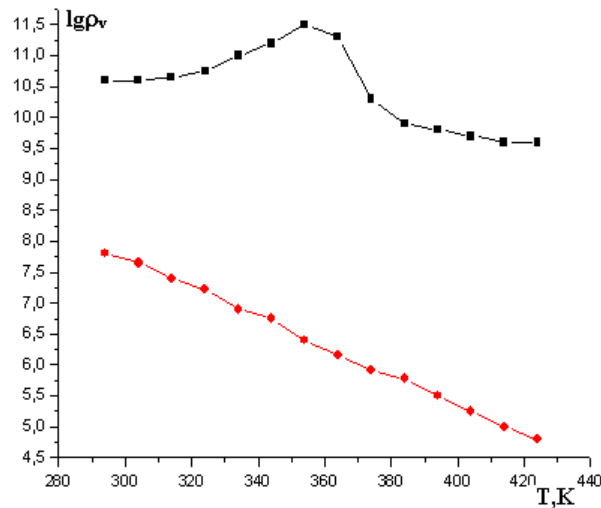


Figure 3. Dependence of logarithm ($\lg\rho_v$) on temperature (T) of specific resistance of PE+1%PbCrO₄ nanocomposite (1) and pure PE (2) subjected to electrothermopolarization for 1 hour at temperature $T=373\text{K}$

One of the hypotheses of the positive effect of nanoadditives on the properties of the polymer matrix is the process of structure formation as a result of the effect of the active phase of the particles in the matrix [1, 3].

One of the possible mechanisms for the formation of transition layers in polymer nanocomposites is the change of the supramolecular structure of the polymer under the influence of nanoadditives, which actively affects the crystallization of the polymer in the volume of the material.

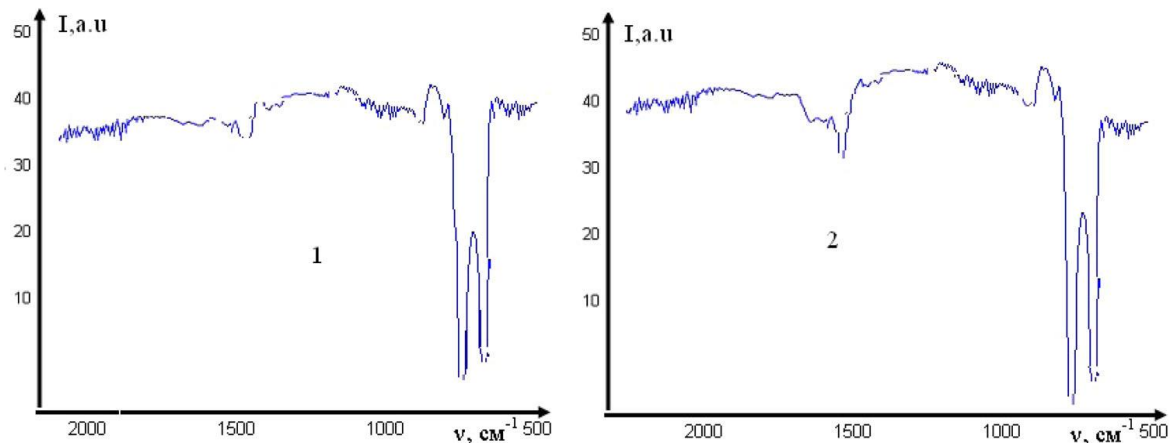


Figure 4. IR spectra of PE+1%PbCrO₄ nanocomposite before (1) and after (2) electrothermopolarization process

The structure change in PE+1%PbCrO₄ nanocomposite was analyzed by IR spectroscopy method in the wave number range of 400-2500 cm⁻¹. It has been shown that PbCrO₄ phase undergoes structural changes in the IR spectrum after electrothermopolarization. Structural changes are mainly observed in polyethylene at frequencies of 726 cm⁻¹, 732 cm⁻¹, 825 cm⁻¹ (Figure 4). Changes in these frequencies depending on electrothermopolarization conditions are related to the activation of CH₂ valence oscillations in polyethylene. After electrothermopolarization, redistribution of doublet

intensities occurs. Differences in the influence of the polarization field voltage on the degree of crystallization of PE and PE+1%PbCrO₄ substances show that nanoadditives changes the structure of the polymer matrix.

The optical density of the C=H group calculated from Figure 4 is shown in Figure 5.

The increase of the optical density of the C=H group depending on the aging time due to the effect of the electric field is the result of breaking the interatomic chemical bonds that form the chain, showing the destructive nature of the field. As can be seen, the rate of optical density increase of PE+1%PbCrO₄ nanocomposite is higher than that of PE. A decrease in molecular weight should be expected since the C=H double bonds formed after the effect of the electric field are the result of breaking of macromolecules (chains). The rate of decrease of molecular weight in nanocomposites is lower than that of pure PE.

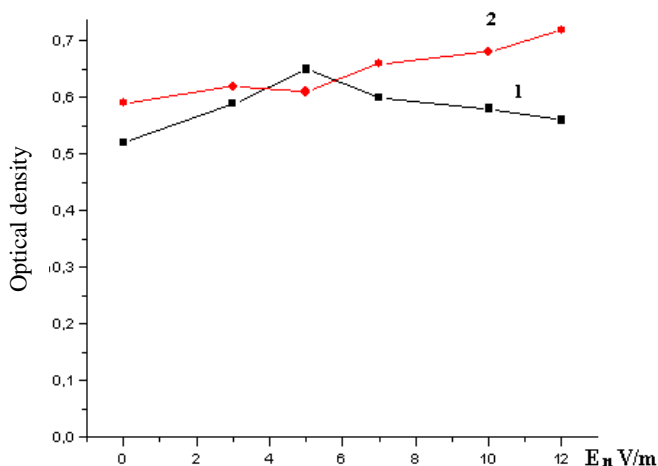


Figure 5. Optical density (D720/730) of pure PE (1) and PE+1%PbCrO₄ (2) nanocomposite subjected to electrothermopolarization for an hour at temperature $T=373\text{K}$ as a function of polarization field (E_n)

The crystallinity degree of polymer nanocomposites strongly depends on the composition, and both the frequencies and intensities of the absorption bands change significantly during the transition from the amorphous state to the crystalline state and vice-versa. Crystal structure samples should be analyzed at temperatures above the melting point of the polymer.

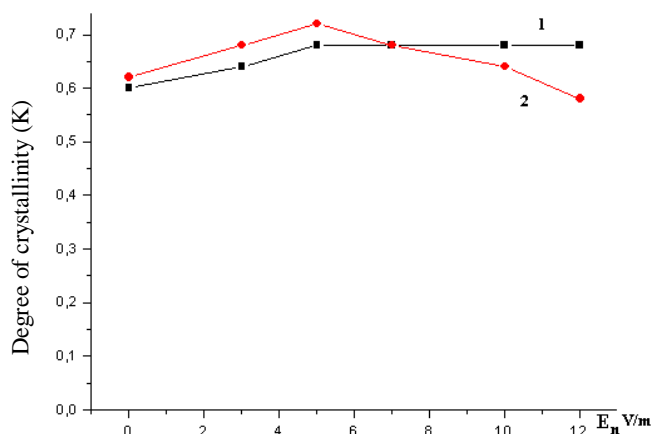


Figure 6. Dependence of the degree of crystallinity (K) on the polarization field (E_n) of pure PE (1) and PE+1%PbCrO₄ (2) nanocomposite subjected to electrothermopolarization for 1 hour at temperature $T=373\text{K}$

Based on the nuclei of crystallization, the molecular chains stack together and form ordered regions called lamellae. Depending on the electrothermopolarization of the PE+1%PbCrO₄ nanocomposite and pure PE, the degree of crystallization is also different. Changes in the PE+1%PbCrO₄ nanocomposite depending on the polarization are associated with the activated CH₂ valence bands in PE. In CH₂, valence bands are activated, and bending vibrations arise.

In this work, the dependence of the electrothermopolarization of the PE+1% PbCrO₄ nanocomposite and pure PE on the crystallinity degree differs. Changes in the PE+1%PbCrO₄ nanocomposite depending on the polarization are associated with the activated CH₂ valence in PE. Valence bands are activated in CH₂, bending vibrations appear.

4. Conclusion

An increase in the amount of $\text{tg}\delta$ can be explained by the violation of the homogeneity of the nanocomposite and the formation of defects of different sizes, which are the source of ionization processes. And this is due both to an increase in the conductivity of the sample and to structural changes in the polymer. Also, with an increase in temperature, a slight increase in the value of ϵ is observed, which is most likely associated with the occurrence of an additional crystallization process in the polymer. This behavior of the nanocomposite may be due to the redistribution of charges at the boundary between the particle and the matrix, the accumulation of these charges in deeper traps, and, as a consequence, the creation of an inhomogeneous medium. The value of $\lg\rho_v$ increases at certain temperatures, that is, a positive effect is observed in the nanocomposite sample, which is explained by a decrease in space charges in the nanocomposite. structural changes in the IR spectrum after electrothermopolarization are mainly manifested at PE wave numbers of 726 cm⁻¹, 732 cm⁻¹, 825 cm⁻¹. Changes in these wave numbers depending on the electrothermopolarization conditions are associated with the activation of CH₂ stretching vibrations in polyethylene. An increase in the optical density of the C=H group depending on the aging time due to the action of an electric field is the result of a break in the interatomic chemical bonds that form a chain, which indicates the destructive nature of the field. Depending on the electrothermopolarization of the PE+1%PbCrO₄ nanocomposite and pure PE, the crystallinity degree changes. Changes in the PE+1%PbCrO₄ nanocomposite after the polarization process are associated with the activated CH₂ valence in PE. In CH₂, valence bands are activated, and bending vibrations arise.

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