

STRUCTURE AND DIELECTRIC PROPERTIES OF NANOCOMPOSITES ON THE BASIS OF POLYETHYLENE WITH Fe₃O₄ NANOPARTICLES

A.M.MAHARRAMOV^a, M.A.RAMAZANOV^{a*}, R.A.ALIZADE^b,
P.B.ASILBEYLI^b

^a*Baku State University, Z.Khalilov str.23, Baku, Azerbaijan, AZ 1148*

^b*Institute of Physics, Azerbaijan National Academy of Sciences
33, H.Javid ave., Baku, Azerbaijan, Az-1143*

Have been studied structures and dielectric properties of nanocompositions on the basis PE+Fe₃O₄. It was found that the coagulation of Fe₃O₄ in polymeric matrix depend on nanoparticles concentration and supramolecular structure and crystallinity degree of polymer. It is assumed the change of permittivity of magnetic nanocomposition on the base PE+Fe₃O₄ that is in dependence of constant magnetic field treatment and supramolecular structure of polymeric matrix, is linked with differences in the diamagnetic anisotropy.

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1. Introduction

At the last time nanocompositions on the basis of polymers and nanomagnetics widely applied in radio technics, television, communication technics, storage devices, computer technics due to their relatively new superparamagnetic, magnetic resistant, operating, high coercive force and other unique properties [1-4].

The structural polymeric nanophase materials have specific peculiarities and properties that differ of properties of compounds in normal phase; such as other mechanical and electrophysical characteristics in various frequency range including microwave range. The polymeric matrix stabilizes active nanoparticles, its properties is on principle differ from the properties of atoms and molecules of its massive samples.

The properties of nanocomposites are defined by chemical nature of polymeric matrix, structure of interphase bordures, its share in nanocomposites is huge, and also interactions of nanoparticles with polymeric matrix.

These materials are a matter of huge interest in term of theoretical analysis of its structure and properties as well as in term of its practical application.

Such kind nanocomposites are superparamagnetics since at low concentration in polymeric matrix the direction of nanoparticles axes of light magnetization are suddenly distributed. At high concentration of nanoparticles in matrix they contact each other and form infinitive conductive cluster and as result the nanocomposite has got the ferromagnetic properties.

Theoretically and experimentally found that Fe₃O₄ nanoparticles in polymeric matrix under the constant magnetic field undergo the polarization. The polarization of nanomagnetite depends on external field, environment of polymeric matrix, electric properties (polarity, permittivity, activation energy of electrons and etc.), nanomagnetite size, metallic properties (number of valent electrons, energy of binding).

In presented work is studied the dependence of theoretical and experimental values of permittivity of nanocomposite PE+Fe₃O₄ from Fe₃O₄ nanoparticles concentration.

*Corresponding author: mamed_r50@mail.ru

2. Samples and methods of experiments

The magnetic polymeric nanocomposites were obtained by following: the nanoparticles of Fe_3O_4 with size 4-10 nm was added at stirring to solution of PE in trichloroethylene at 343 K. The reaction mixture is mixed at temperature 343K till emulsion formation, and then added water and separated Fe_3O_4 , contained PE, then dried in evacuated vessel. From compound were obtained the samples of nanocomposites by hot pressing method at melting point of PE under the pressure 15 MPa during 10 minutes with further cooling to ambient temperature at different rates.

Microstructures of composites PE+ Fe_3O_4 were studied on scanning atomic and magnetic force microscope (AFM, MFM).

Measurement of permittivity(ε) and dielectric loss tangent $\text{tg}\delta$ for nanocompositions PE+ Fe_3O_4 were implemented on frequency range 100-10⁶ Hz and in temperature interval 30-140°C on device E7-20.

3. Experimental and theoretical results

Earlier in [5] has been shown that at low volume of magnetite nanoparticles in polymeric matrix, the permittivity can define as:

$$\varepsilon_{HK} = \frac{\varepsilon + 2}{3} \varepsilon \cdot \left(1 + \frac{1}{3} \frac{\varphi}{\varepsilon_0} \cdot \frac{d_{\max}^2}{V_0 kT} \right) \quad (1)$$

where ε - permittivity of polymeric matrix, φ - volume concentration of magnetite nanoparticles in polymeric matrix. Permittivity of nanocomposite and dipole moment of nanomagnetite is a linear function of nanomagnetite concentration. The theoretical and experimental data of dependence of value of permittivity of PE+ Fe_3O_4 from concentration is given on Fig.1. As it is seen from Fig.1, the dependence of theoretical value of permittivity from concentration changes linearly whereas the value of experimental dependence changes with extremum. The change of experimental value of permittivity of nanocomposite is evidently connected with threshold value of filler.

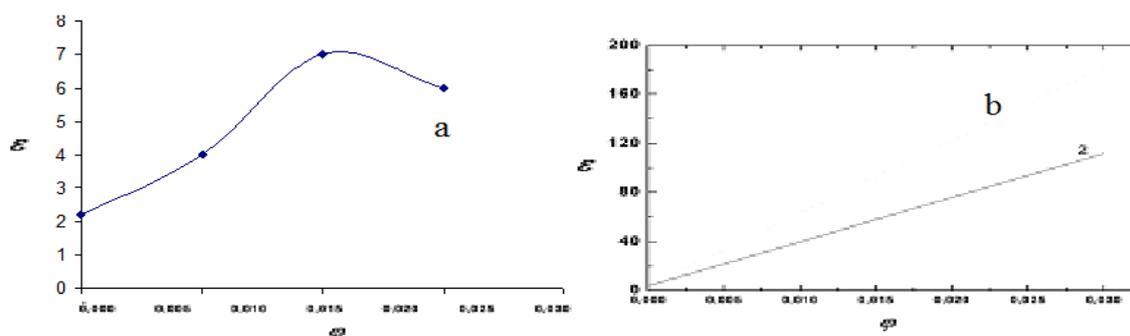


Fig.1 Dependence of permittivity of nanocomposite PE+ Fe_3O_4 from concentration:
a) experimental, b) theoretical

The values of the dielectric loss tangent $\text{tg}\delta$ of the polymer matrix and magnetite nanoparticle is given by:

$$\frac{\text{tg}\delta_2}{\text{tg}\delta_1} = 1 + \frac{1}{3} \frac{\varphi}{\varepsilon_0} \cdot \frac{d_{\max}^2}{V_0 kT}$$

The law of energy conservation for the polarization of magnetite nanoparticles that are in reciprocal-perpendicular electrical (E) and magnetic (H_0) fields in nanocomposite is describing as:

$$\frac{1}{2} \varepsilon_0 E^2 + \frac{1}{2} \mu_0 H_0^2 = \frac{J \cdot E \cdot t}{\frac{4\pi}{3} r^3} + \frac{1}{c} E \cdot (H + H_0)$$

Where – term of left part of equation – the sum of energies of external electric and magnetic fields, I term of right part is a evolving heat at currency (defined by Joule-Lance low), II term – vector of Umov-Poyting. The solution of equation is:

$$d(t, E, H_0) = \frac{1}{3} \varepsilon_0 r^3 E \cdot \ln \left(\frac{6\pi c t l}{r^2} + 1 \right) \cdot \left(1 + \frac{\mu_0}{\varepsilon_0} \left(\frac{H_0}{E} \right)^2 - \sqrt{\frac{\mu_0}{\varepsilon_0}} \frac{H_0}{E} \right) \quad (2)$$

As it seen at $H_0=0$ and $H = \sqrt{\frac{\varepsilon_0}{\mu_0}} E$ we got the expression for nanoparticle dipole moment, we described and analyzed earlier. At $0 \leq H \leq \sqrt{\frac{\varepsilon_0}{\mu_0}} E$ the value of multiplier is less than unity and at $H = \frac{1}{2} \sqrt{\frac{\varepsilon_0}{\mu_0}} E$ it has got the minimal value. From equation (2) it is seen that the part of energy of external magnetic field is dispersed (the Bio-Savare law). When the energy of external magnetic field is $\frac{1}{2} \mu_0 H_0^2 < \frac{1}{4\pi c} E H_0$, then occur the decreasing of electric dipole moment (occur depolarization of magnetite nanoparticle). For minimal value of nanoparticle dipole moment we got $d = \frac{3}{4} d_{\max}$. Beginning with $H > \frac{1}{2} \sqrt{\frac{\varepsilon_0}{\mu_0}} E$ the value of electric dipole moment increases and at $H = \sqrt{\frac{\varepsilon_0}{\mu_0}} E$ and reach the value as at absence of magnetic field ($H=0$). Beginning with $H > \sqrt{\frac{\varepsilon_0}{\mu_0}} E$ the increasing of dipole moment continues.

At external magnetic field the dipole moment of nanoparticle that is perpendicular to the plane of electron movement is trying to form up with direction of magnetic field. And this by-turn orient the plane of electron movement along external electric field (due to the reciprocal perpendicularity of electric and magnetic field) which means that the increasing of polarization of magnetite nanoparticles. At Figure 2 is shown the dependence of permittivity of nanocomposite (theoretical) from nanoparticle concentration treated at different strengths of magnetic field. As it seen in dependence of value of magnetic field the permittivity increases. Have been studied the values of resistivity, permittivity and dielectric loss tangent of magnetic nanocomposites on the basis $PE+Fe_3O_4$ at various content of nanomagnetite in dependence of temperature and frequency.

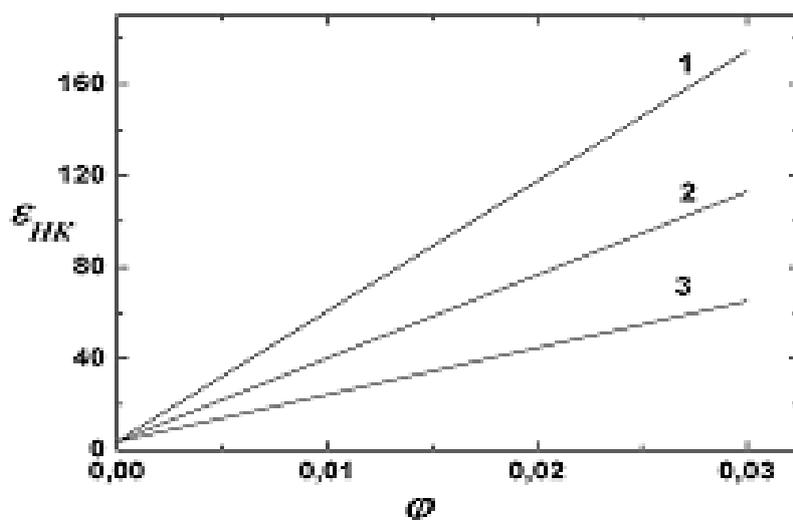


Fig. 2 The dependence of permittivity of nanocomposites from concentration of nanomagnetite.
 $H = 4,1 \cdot 10^5$ A/m -1, $H = 0$ and $H = 2,7 \cdot 10^5$ A/m -2, $H = 1,3 \cdot 10^5$ A/m -3.

It was found the permittivity and dielectric loss tangent of nanocomposition depending the temperature gradually increase and then at temperature of decomposition of polymer crystalline phase spontaneously increase. The sharp rising of ϵ , $\text{tg}\delta$ at temperature of decomposition of polyethylene crystalline phase in our opinion is connected with rising of distance between nanoparticles (Fig.3, Fig.4). Also it is seen that increasing of nanoparticles concentration decomposes the structure of polymer i.e. with raising of concentration of filler the decomposition of crystalline phase of polymer increase.

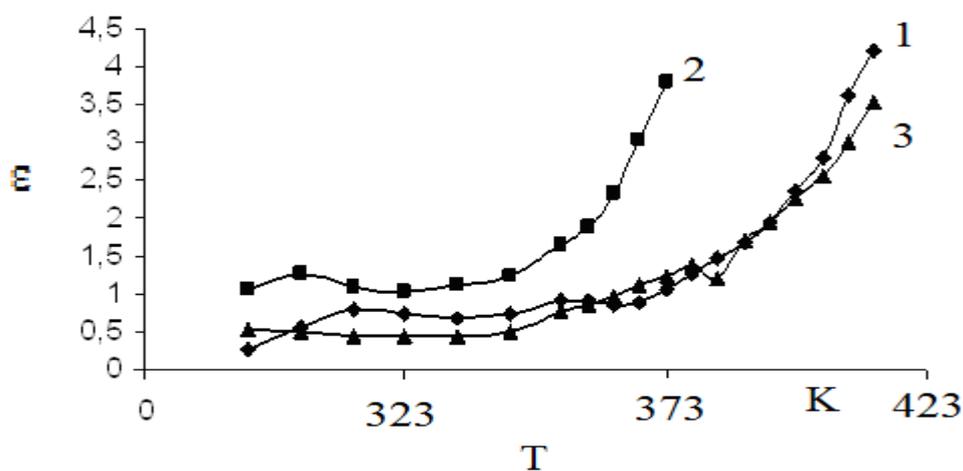


Fig.3. Dependence of permittivity of nanocomposite from temperature
 1. PE+5 ml Fe_3O_4 , 2. PE+10 ml Fe_3O_4 , 3. PE+ 15ml Fe_3O_4 ,

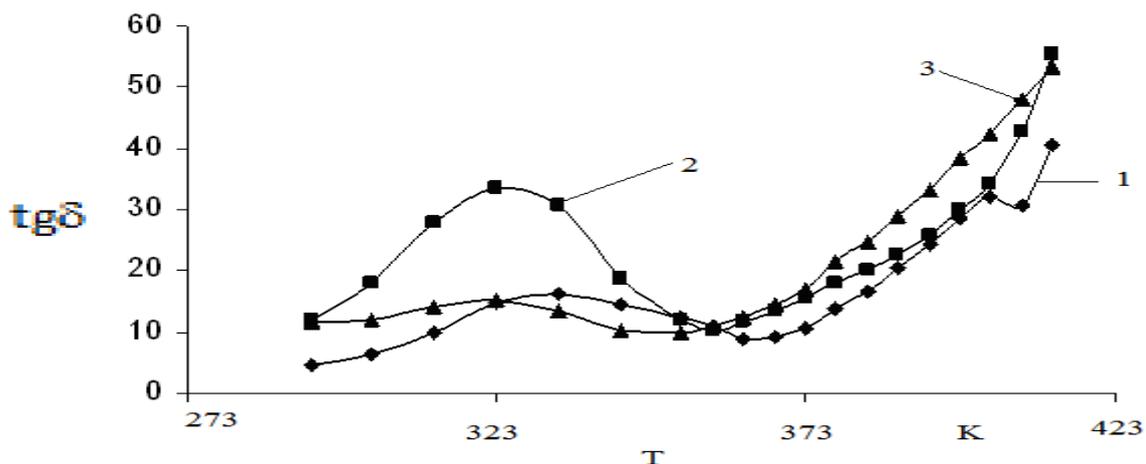


Fig.4 Dependence of dielectric loss tangent from temperature for nanocomposite
1. PE+5 ml Fe_3O_4 , 2. PE+10 ml Fe_3O_4 , 3. PE + 15ml Fe_3O_4

Studied the values of permittivity and dielectric loss tangent of magnetic nanocomposite on the basis PE+ Fe_3O_4 at different content of nanomagnetite in dependence of frequency of measurement. From Fig.5 and Fig.6 it is seen that increasing of frequency lead to declining of ϵ and $tg\delta$. Decreasing of ϵ and $tg\delta$ with frequency rising is explained by decelerating of dipoles and decreasing of particles number, participating in polarization, i.e. with deterioration of polarizing process. It should be noted that at low concentration of Fe_3O_4 at high frequency range observed the increasing permittivity in comparison with samples with high concentration of Fe_3O_4 .

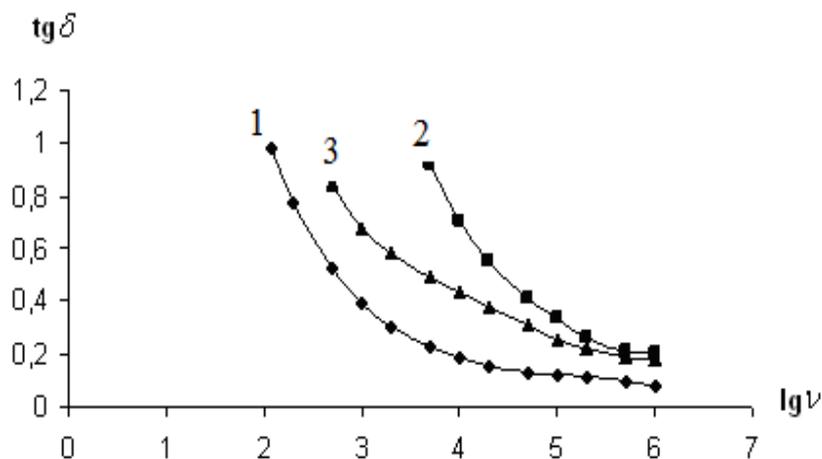


Fig.5. Dependence of dielectric loss tangent from frequency for nanocomposites
PE+ Fe_3O_4 : 1. PE+5% Fe_3O_4 , 2. PE+10% Fe_3O_4 , 3. PE+15% Fe_3O_4

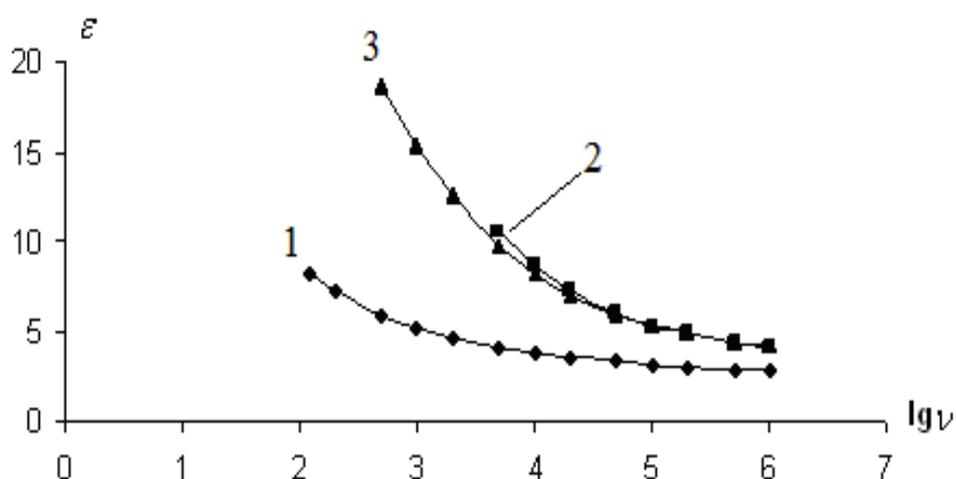


Fig.6 . Dependence of permittivity from frequency for nanocomposites PE+ Fe_3O_4 :
1. PE+5% Fe_3O_4 , 2. PE+10% Fe_3O_4 , 3. PE+15% Fe_3O_4

At low concentration of Fe_3O_4 and, consequently, at little sizes of ferrofiller particles the volume density of defects is considerably lower than in the samples with big sizes of nanoparticles Fe_3O_4 , that reflected not only in dielectric, but also in other electrophysical properties. From experimental data follow that in nanocomposites PE+ Fe_3O_4 the change of permittivity in dependence of frequency is conditioned by low frequency polarization. The monotonic change of permittivity in dependence of temperature by-turn has got relaxing character.

Studied the influence of constant magnetic field on permittivity and dielectric loss tangent. It is shown that after polarization of nanocomposite PE+ Fe_3O_4 under the influence of constant field the value of dielectric loss decline whereas the permittivity rise. The regularity of change of permittivity (Fig.8) and dielectric loss tangent (Fig.7) from frequency monotonously decline, i.e. has got relaxing character. The change of permittivity and dielectric loss tangent after treatment of nanocomposites in constant magnetic field by our opinion is connected with polarization of magnetic particle, and as a result here occur the disordering of structure (excitation of macromolecules, local polarization).

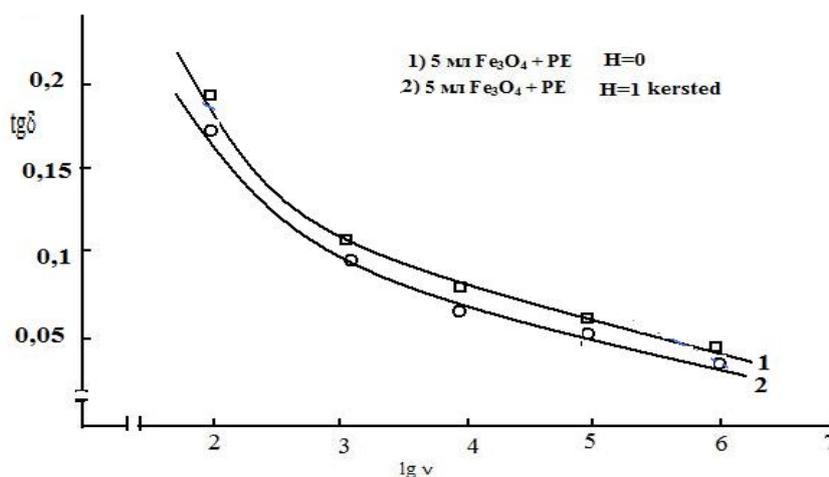


Fig.7 Dependence of dielectric loss tangent from frequency of measurement of nanocomposite PE+ 5% Fe_3O_4 before and after polarization in magnetic field.

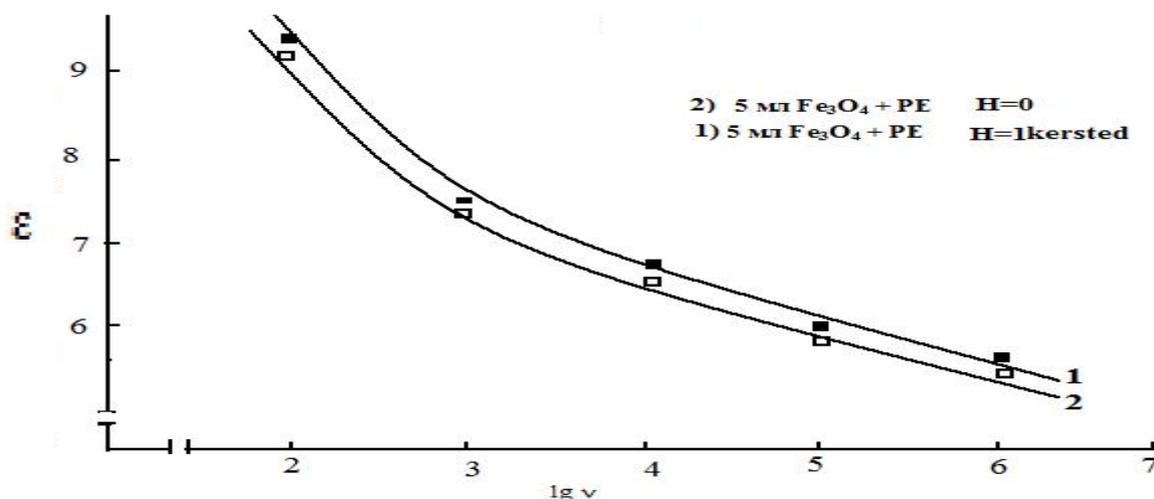


Fig.8 Dependence of permittivity from frequency of measurement of nanocomposite PE+ 5%Fe₃O₄ before and after polarization in magnetic field.

Obviously the changes of permittivity and dielectric loss tangent in dependence of frequency at the same magnetic fillers can be connected with declining of interaction between neighboring molecules of polymeric matrix and interphase action. It is also possible that the magnetic field of polymer molecule can partially orient, and as result decline the potential barrier of shear acts and decrease the value of inductive capacity of nanocomposite. Declining of permittivity from frequency is connected with deterioration of polarization process in nanocomposite. At Figure 9 is given the AFM image of nanocomposite PE+Fe₃O₄ before and after treatment in constant magnetic field. From Figure 9 it is seen that after polarization in constant magnetic field the morphology of nanocomposite strongly change, i.e. occurs the ordering the surface structure elements.

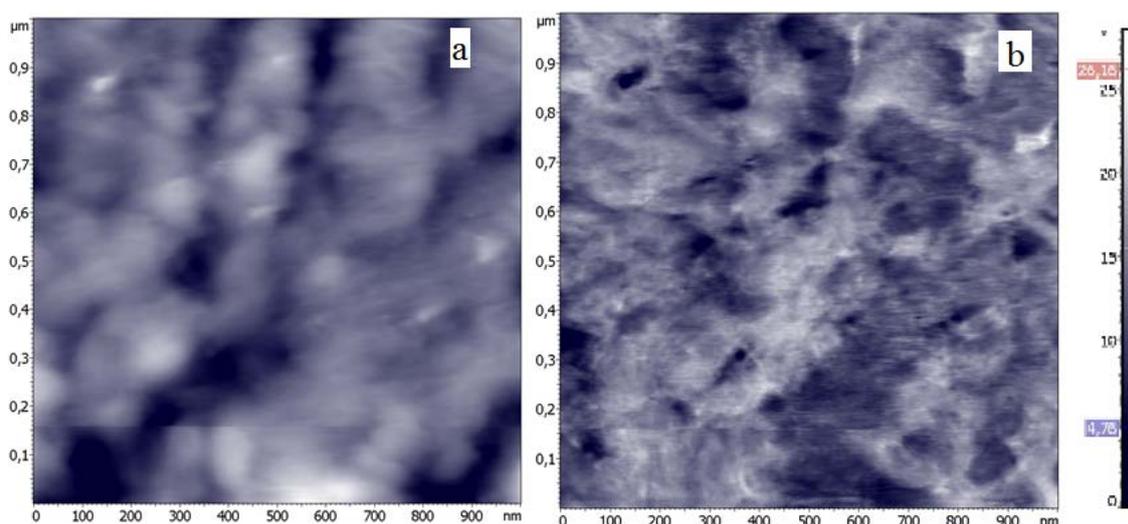


Fig.9 AFM image of nanocomposite surface PE+ Fe₃O₄
a) Before treatment in constant magnetic field, b) after polarization in constant magnetic field

At Figure 10 are given AFM and MFM images of nanocomposite PE+Fe₃O₄. As it is seen from picture the roughness of surface elements of nanocomposite PE+Fe₃O₄ is sharply different. It is also seen that magnetic diameter of Fe₃O₄ coagulants differ from real size of nanoparticles. Therefore, the magnetic size of nanoparticles increased strongly during depolarization under the influence of a constant magnetic field.

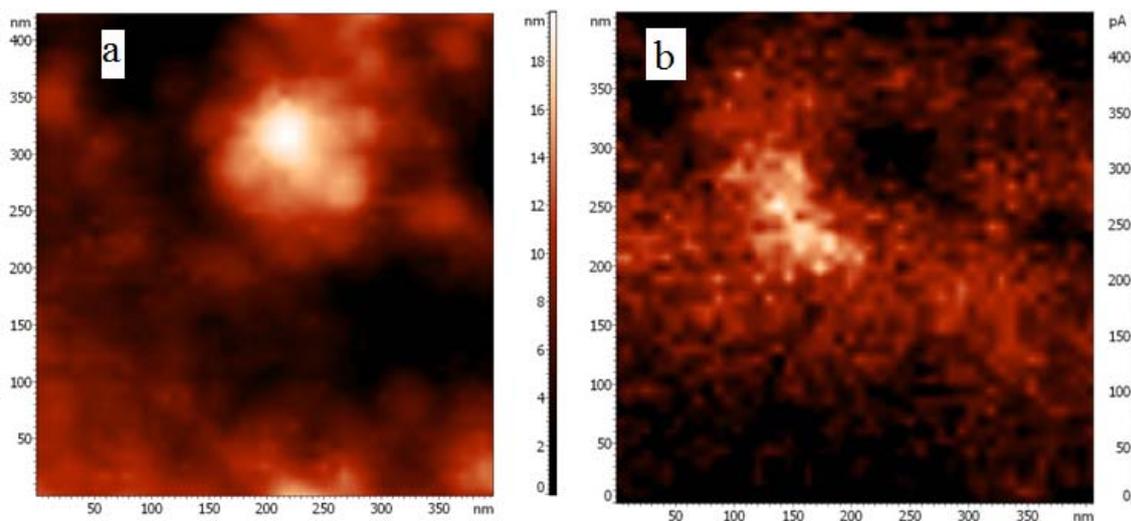


Fig.10. AFM(a) u MFM(b) images of nanocomposite PE+ Fe₃O₄.

4. Conclusion

Was found the coagulation of Fe₃O₄ nanoparticles in polymeric matrix (PVDC, PE) depend on nanoparticles concentration as well as supramolecular structure and crystallinity degree of polymer. It is assumed the change of permittivity of magnetic nanocomposition on the base PE+Fe₃O₄ that is in dependence of constant magnetic field treatment and supramolecular structure of polymeric matrix, is linked with differences in the diamagnetic anisotropy.

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