

Paper for control**STRUCTURE AND MAGNETIC PROPERTIES OF NANOCOMPOSITES ON THE BASIS PE+Fe₃O₄ и PVDF+ Fe₃O₄**M. A. RAMAZANOV*, R. A. ALI-ZADE^a, P. B. AGAKISHIEVA^a*Baku State University**^aInstitute of Physic NAS of Azerbaijan H.Javid Str. 33, Baku Az-1143*

The structures and magnetic properties of nanocomposites have been studied on the basis PE + Fe₃O₄ and PVDF + Fe₃O₄. It was established that coagulation Fe₃O₄ nanoparticles in polymeric matrix depends on its concentration as well as supermolecular structure and crystallization degree of polymer. It is supposed that change of nanocomposite specific magnetization depending of magnetic field intensity and type of polymeric matrix, is connected with a diversity of diamagnetic anisotropy, supermolecular structure and crystallization degree of polymer PE and PVDF. Theoretical calculations show that geometrical (d_{0r}) and magnetic (d_{0m}) diameter of nanoparticles linearly depends on its geometrical diameters and these results harmonize with experimental data.

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*Keywords:***1. Introduction**

Last decade the composites on the basis of polymers and ferromagnetic are widely used in radio engineering, TV, communication engineering, storage devices, computers, because their relatively high magnetic and exploitation properties [1-3].

Polymeric compositions – materials composed of magnetic particles, other functional fillers and polymeric matrix, in which these particles are definitely situated. The matrix defines the structure of formed nanoparticles ensemble (size distribution of nanoparticles, distance between them, its shape, orderliness etc.), and the structure of formed nano-composite defines the properties of nanocomposite. Polymeric matrix stabilizes active nanoparticles, the properties of these nanoparticles principally differ from its atomic, molecular and massive examples.

The nanocomposite properties are defined by chemical nature of polymeric matrix, structure of interphase border, the part of which is huge as well as interaction between nanoparticles and polymeric matrix.

They have great interest from the point of view of theoretical analysis of its structure and properties as well as practical application.

In case with low concentration of nanoparticles in the matrix, nano-composites are superparamagnetic, due to the directions of light magnetization axes are distributed random. High concentration of nanoparticles in the matrix results to react each other and form infinite conductive cluster, and the nanocomposite gets ferromagnetic properties.

In this article the size of magnetite nanoparticles was studied in polymeric matrix. The size of magnetite nanoparticles has been defined by magneto-granulometric method and AFM scanning. The results of different methods are harmonized well. It is established that size of magnetite nanoparticles dependences its concentration in polymeric matrix and polymer crystallization rate.

2. Experimental method and examples

Magnetic polymeric nanocomposites prepared in dimethylformamide solution of PVDF nanoparticles supplemented with Fe_3O_4 . The size of nanoparticles was 4-10 nm. The reaction mixture is mixed at temperature 343K till emulsion formation, and then added water and separated Fe_3O_4 , contained PVDF, then dried in evacuated vessel. The samples of nanocomposite were obtained by hot pressing method at PVDF melting point under 15 MPa pressure during 10 minutes with further cooling to room temperature at different rates.

In trichloroethylene solution of PE nanoparticles of Fe_3O_4 are added at temperature 343 K.

Preparation and physical properties of PMNC are described in [4, 5].

Micro structures of composition PVDF+ Fe_3O_4 have been studied by AFM method.

Magnetization of PMNC samples, prepared on the polymeric basis (PVDF) and (PE) at different concentrations of magnetite was studied by Domenically method.

3. Results

The magnetization curves of PMNC on the basis PVDF with volume concentration of magnetite nanoparticles $\varphi_m = 0.011$ are shown in Fig.1. The magnetization of the sample has super magnetic character as seen in Fig.1. It is known that magnetization of the medium can be described by Langeven equation:

$$M(H) = M_s \cdot \varphi_m \int_0^\infty f(m) \cdot L\left(\frac{mH}{kT}\right) \cdot dm \quad (1)$$

where $L\left(\frac{mH}{kT}\right) = \text{cth}\left(\frac{mH}{kT}\right) - \frac{1}{\frac{mH}{kT}}$ - function of Langevin, $f(m)$ - function of distribution of

magnetite nanoparticles on magnetic moment, φ_m - concentration of magnetite nanoparticles in the medium. Magnetic moment of magnetite nanoparticles is defined as $m = M_s \cdot V_i$, where M_s - magnetization of saturation of massive magnetite which is equal 491,6 kA/m, V_i - volume of magnetite nanoparticle.

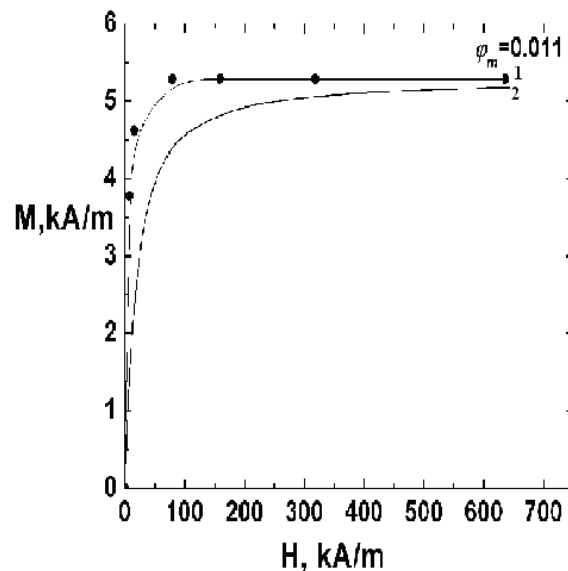


Fig.1 The magnetization of the sample PVDF+Fe₃O₄(10%), obtained by experimental method (curve 1) and calculation method (curve 2).

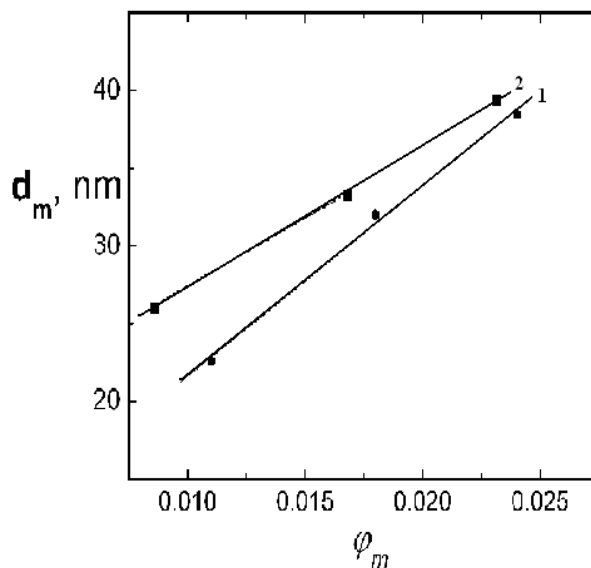


Fig. 2. The dependence of magnetic diameter of nanoparticles agglomerates on its concentration in polymeric matrix: 1-PVDF+Fe₃O₄, 2- PE+Fe₃O₄

For definition of the magnetite nanoparticles in the medium was used Langevin equation at high magnetic fields $M'_s = \phi_m \cdot M_s$, where M'_s - magnetization of saturation of sample.

Applying expansion of Langeven function at low magnetic fields $L\left(\frac{mH}{kT}\right)\Big|_{H \rightarrow 0} = \frac{3mH}{kT}$ and

definition average magnetic moment $\bar{m} = \int_0^{\infty} m \cdot f(m) dm$:

$$M(H) = M_s \cdot \phi_m \frac{3\bar{m}H}{kT}.$$

By the definition initial magnetic perception of the medium is $\chi_0 = \left(\frac{dM(H)}{H}\right)\Big|_{H \rightarrow 0} = M_s \cdot \phi_m \frac{3\bar{m}}{kT}$, then we can define maximum magnetic diameter (d_{mag}^{\max}).

$$d_{mag}^{\max} = \left(\frac{72\chi_0 kT\mu_0}{M_s^2 \phi_m}\right)^{1/3}.$$

Applying the data of magnetic measuring (χ_0, ϕ_m), we defined maximum magnetic diameter of nanoparticles at various concentrations in polymeric matrix.

The dependence of magnetic diameter of nanoparticles coagulant from its concentration in polymeric matrix is shown in Fig.2. The dependence of d_m from ϕ_m is linear, with increasing concentration increases magnetic diameter – it means nanoparticles coagulate can be observed in Fig.2. However the coagulation of the particles depends not only on its concentration, but also depends on supermolecular structure and degree of crystallization. Change of the supermolecular structure of PVDF is stronger than the one for PE.

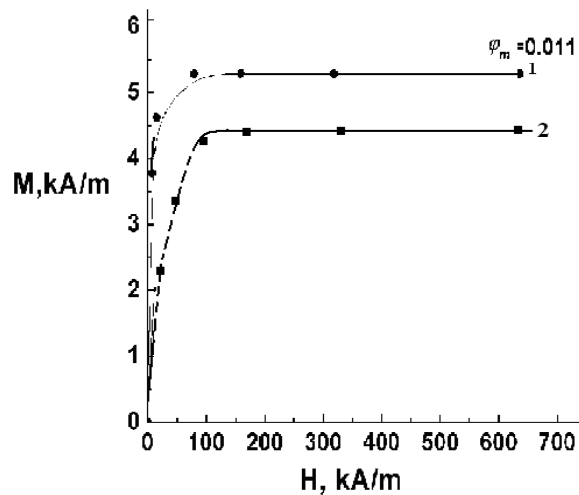


Fig.3 The magnetization of the sample PVDF+Fe₃O₄(curve 1), PE+ Fe₃O₄(curve 2).

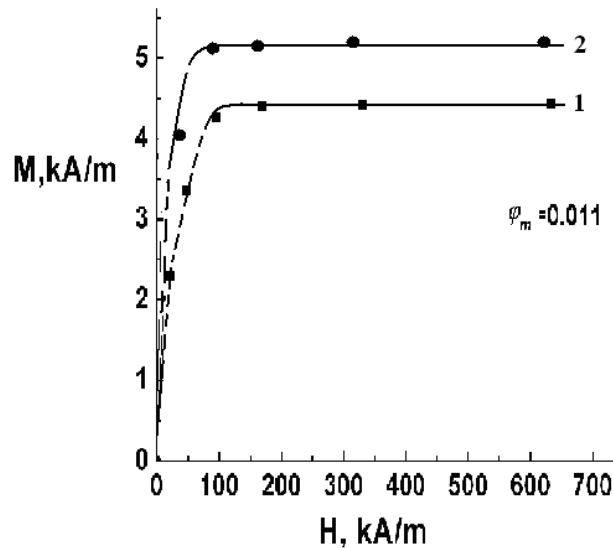


Fig.3 The magnetization of the sample PE+ Fe₃O₄ in various cooling regimes.
1. $\beta=30\text{deg/min}$ (BO) 2. $\beta=4\text{deg/min}$ (MO)

The values of magnetic diameters are various for the same concentration of nanoparticles in PVDF and PE ($\varphi_m=0.017$) as seen in Fig.2

The curves of magnetization PMNC on the basis PVDF and PE with part per volume concentration of magnetite nanoparticles $\varphi_m = 0.011$. The magnetization of the sample PVDF+Fe₃O₄ and PE+Fe₃O₄ has super-paramagnetic character (Fig.3,4). Specific magnetization for nanocomposite on the basis PVDF is higher than the one for PE basis. It should be noted PVDF and PE have got diamagnetic properties – they are diamagnetic. However magnetic properties of C-F and C-H bonds in macromolecules PVDF and PE are different [6]. Magnetic perception depends on supermolecular structure of polymer and crystallization degree. Change of specific magnetization depending on magnetic field and polymeric matrix type can be link with difference of diamagnetic anisotropy, supermolecular structure and crystallization degree of polymeric matrix PVDF and PE.

It is established experimentally that specific magnetization of Fe_3O_4 nanoparticle in the polymer also depends on temperature-duration regime of polymer crystallization (Fig.4). The value of specific magnetization of $\text{PE}+\text{Fe}_3\text{O}_4$ changes depending on temperature-duration regime of polyethylene crystallization, it means specific magnetization of $\text{PE}+\text{Fe}_3\text{O}_4$ increases with declining of temperature-duration regime of polyethylene crystallization as seen in Fig.4. The analysis of magnetization curves shown (Fig.4) the maximum size of nanoparticles coagulants forms in various cooling regimes of polymer (1. $\beta=30$ deg/min (BO) 2. $\beta=4$ deg/min (MO)) are equal correspondingly 21 nm, 15,7 nm. May be the size of magnetite nanoparticles coagulants depends on the rate of polymer cooling. In case with great cooling rates it forms small size coagulants.

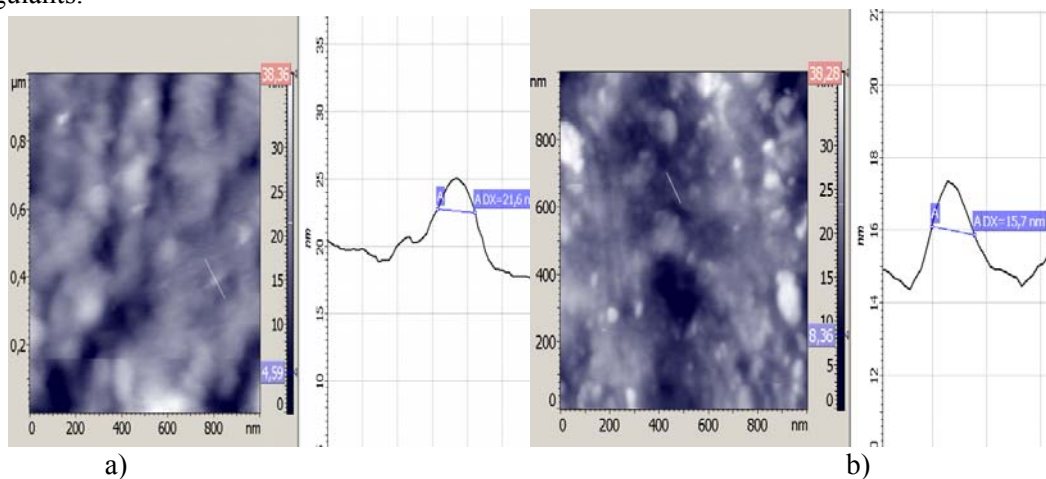


Fig..5 AFM image of nanocomposite surface $\text{PVDF}+\text{Fe}_3\text{O}_4$ and size of Fe_3O_4 nanoparticles a) $\beta=4$ deg/min b) $\beta=30$ deg/min.

The Fe_3O_4 nanoparticles sizes, topography of distribution of nanoparticles in polymeric matrix for the samples, obtained in regimes $\beta=4$ deg/min and $\beta=30$ deg/min. As it shown on the pic.5 size of Fe_3O_4 nanoparticles, formed in various cooling regimes of polymer (1. $\beta=30$ deg/min 2. $\beta=4$ deg/min) are equal correspondingly 21 nm and 15 nm as seen in Pic.5.

The analysis of properties of nanocomposite surface $\text{PE}+\text{Fe}_3\text{O}_4$ and histogram of values of elements images are shown in Pic.6. The mean-square surface roughness of nanocomposite is approximately 15-30 nm as seen Pic.6. AFM scanning shows that nanoparticles Fe_3O_4 are equally distributed in polymeric matrix. It should be noted in forming of nanocomposite properties play a great role interphase interactions between matrix and filler. Microscopic heterogeneity of polymeric matrix structure is made conditional by peculiarities of interactions of matrix and filler in composite crystallization process.

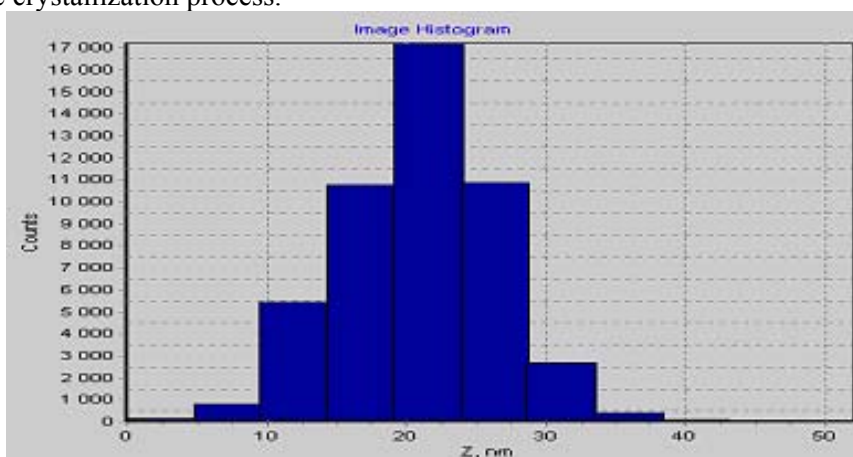


Fig. 6. Analysis of properties of nanocomposite surface and histogram of values of elements images .

There is change of structural micro heterogeneity for crystallized polymers PE and PVDF as a result of interactions on the border, which is differ from micro heterogeneity in polymeric matrix and changes of structural micro heterogeneity for PE and PVDF are various.

The scans of PE+ Fe₃O₄ nano-composition obtained by atomic-Force Microscope and Magnetic Force Microscope. Here magnetic addition is taken as volumes quantity $\gamma_m=0,025$ is shown in Fig.7

The investigations of the magnetite conglomerate composed of nanoparticles have shown that its geometrical size obtained by AFM is sufficiently smaller than the geometric size obtained by MFM. It was found experimentally the magnitude of coefficient K by experimental way and this is appropriate with experimental results. Thus it was found that a coagulation of Fe₃O₄ nanoparticles in polymeric matrix varies depending not only on the volumetric quantity of nanoparticles but also on the surface-molecular structure and crystallization degree of the polymer.

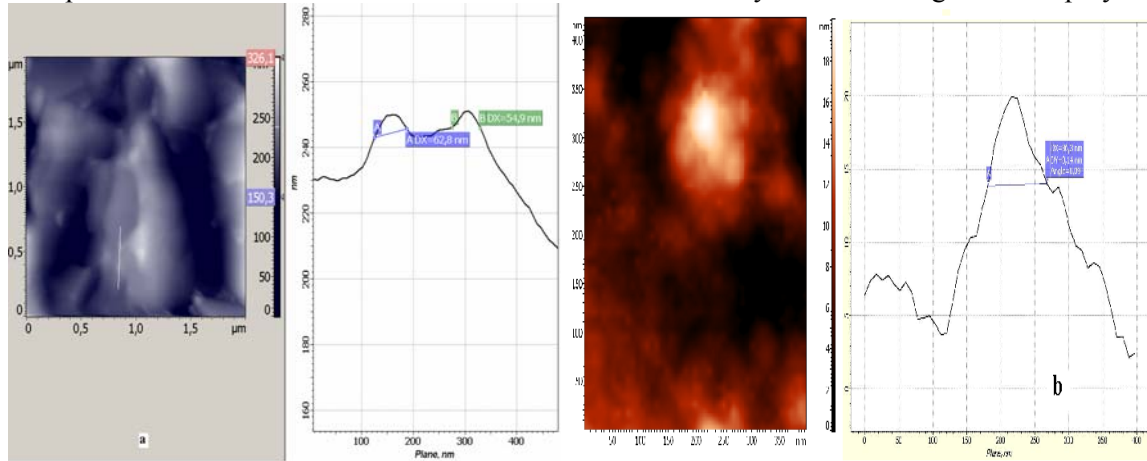


Fig.7. 2D scans and sizes of PE+ Fe₃O₄ nanocomposition with $\gamma_m=0,025$ volumetric quantity of magnetic addition. a) AFM scan b) MFM scan

We had proved theoretically earlier, that surface interphase layer of magnetite nanoparticles has no magnetic properties [7]. Thickness of interphase layer is directly proportional to the diameter of nanoparticle. Geometrical (d_{0t}) and magnetic diameter (d_{0m}) of nanoparticles are connected to each other by equation $d_{0m} = K \cdot d_{0t}$. Then magnetic volume of conglomerate consisting of n nanoparticles can be defined as follow:

$$\frac{1}{6} \pi d_{0t}^3 n^3 - \frac{1}{6} \pi d_{0m}^3 n^3 = \frac{1}{6} \pi d_{0t}^3 n^3 (1 - K^3) = V_t (1 - K^3)$$

If present the conglomerates of n nanoparticles, as one nanoparticle, then magnetic volume can be defined as:

$$\frac{1}{6} \pi d_t^3 - \frac{1}{6} \pi d_m^3 = \frac{1}{6} \pi d_t^3 (1 - K^3) = V_t (1 - K^3)$$

The right sides of these equations are equal. It means that the magnetic diameter of nanoparticles coagulants also linearly depends on its geometrical diameter. Thus the results obtained for magnetic diameter of nanoparticle coagulant are also acceptable for its geometrical size.

4. Conclusions

It was established that coagulation of Fe_3O_4 nanoparticles in polymeric matrix depends on its concentration as well as supermolecular structure and crystallization degree of polymer. The change of nanocomposite on the basis $\text{PE} + \text{Fe}_3\text{O}_4$ and $\text{PVDF} + \text{Fe}_3\text{O}_4$ specific magnetization depending of magnetic field intensity and type of polymeric matrix, is connected with a diversity of diamagnetic anisotropy, supermolecular structure and crystallization degree of polymer supermolecular structure and crystallization degree of polymer PE and PVDF. Theoretical calculations have shown, that geometrical (d_{0l}) and magnetic (d_{0m}) diameter of nanoparticles linearly depends on their geometrical diameters and these results harmonize very well with experimental data.

Acknowledgement

The authors acknowledge the financial support in the frame of the project BSU 50/50

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