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STRUCTURE AND MAGNETIC PROPERTIES OF NANOCOMPOSITES ON THE BASIS PE+Fe_3O_4 и PVDF+ Fe_3O_4

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The structures and magnetic properties of nanocomposites have been studied on the basis PE + Fe_30_4 and PVDF + Fe_3O_4. It was established that coagulation Fe_3O_4 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 depends 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 the geometrical (d_{0t}) and magnetic(d_{0m}) diameters of nanoparticles linearly depend on its geometrical diameters and these results are in agreement with the experimental data.

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Keywords: PE+Fe_3O_4, PVDF+Fe_3O_4, Magnetic properties, Supermolecular structure, Polymer

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 are composed of magnetic particles, other functional fillers and polymeric matrix, in which these particles are situated. The matrix defines the structure of nanoparticle assembly (size distribution of nanoparticles, distance between them, their shape, ordering etc.), and the structure of formed nanocomposite defines the properties of nanocomposite. Polymeric matrix stabilizes active nanoparticles, the properties of these nanoparticles principally differ from the bulk material.

The nanocomposite properties are defined by chemical nature of polymeric matrix, structure of large interphase part and the interaction between nanoparticles and polymeric matrix.

They are interestimg from the point of view of their structure and properties as well as for practical application.

In case of low concentration of nanoparticles in the matrix, nanocomposites are superparamagnetic, due to the directions of weak magnetization axes, which are distributed randomly. High concentration of nanoparticles in the matrix results to a reaction between them, that form infinite conductive cluster, and the nanocomposite exhibit ferromagnetic properties.

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

2. Examples and experimental method

Magnetic polymeric nanocomposites prepared in dimethylformamide solution of PVDF nanoparticles supplemented with Fe_3O_4. The average size of nanoparticles is 4-10 nm. The reaction is achieved at the temperature of 343K till emulsion formation, and then is added water and after separation of Fe_3O_4, contained PVDF, the mixture is 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 trichloralethylene solution of PE nanoparticles of Fe_3O_4 are added at the temperature of 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. Experimental and theoretical results

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

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

where $L\left(\frac{mH}{kT}\right) = cth\left(\frac{mH}{kT}\right) - \frac{1}{\frac{mH}{kT}}$ - function of Langeven, $f(m)$ - function of distribution of magnetite nanoparticles on magnetic moment, φ_m– concentration of magnetite nanoparticles in the medium. The magnetic moment of magnetite nanoparticles is defined as $m = M_s \cdot V_i$, where M_s – magnetization of satiation of massive magnetite which is equal 491,6 кА/м, V_i – volume of magnetite nanoparticle.

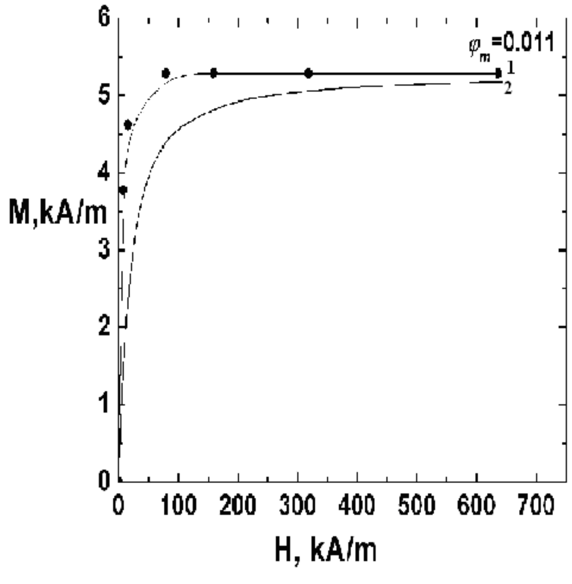


Fig.1 The magnetization of the sample PVDF+Fe_3O_4 (10%), obtained by experimental method (curve 1) and calculation method (curve 2).

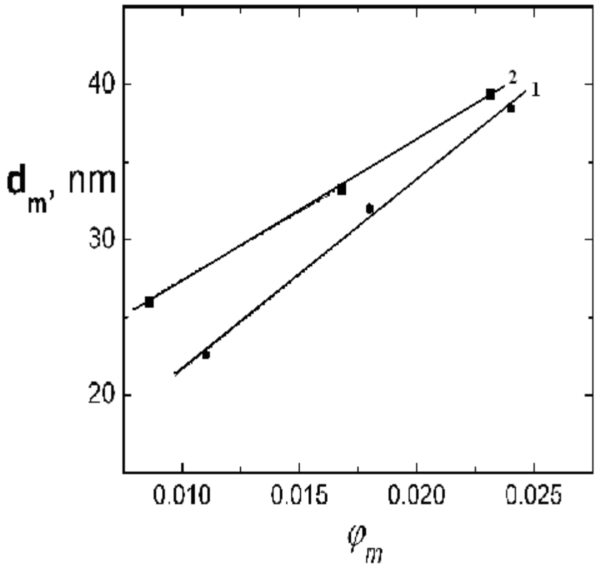


Fig. 2. The dependence of magnetic diameter of nanoparticles agglomerationss on its concentration in polymeric matrix: 1-PVDF+Fe_3O_4, 2- PE+Fe_3O_4

For the definition of the magnetite nanoparticles in the medium was used Langeven equation at high magnetic fields $M_s^{'} = \varphi_m \cdot M_s$, where $M_s^{'}$ - saturation magnetization of the sample.

Applying expansion of Langeven function at low magnetic fields $L\left(\frac{mH}{kT}\right)\Big|_{H\to 0} = \frac{3mH}{kT}$ and definition average magnetic moment $\overline{m} = \int\limits_0^\infty m \cdot f(m)dm$:

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

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

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

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 their 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 larger than the one for PE.

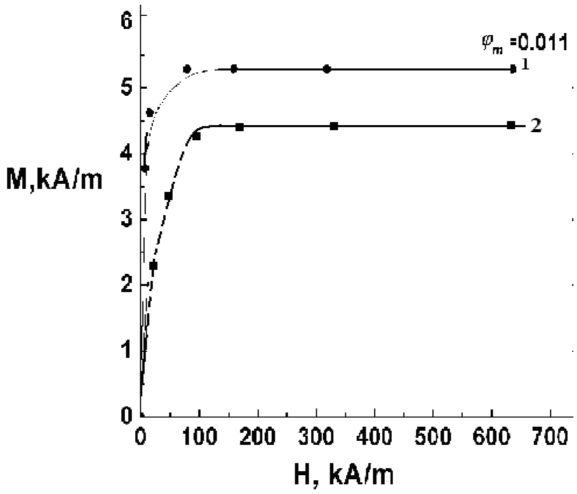


Fig.3 The magnetization of the sample PVDF+Fe_3O_4 (curve 1), PE+ Fe_3O_4 (curve 2).

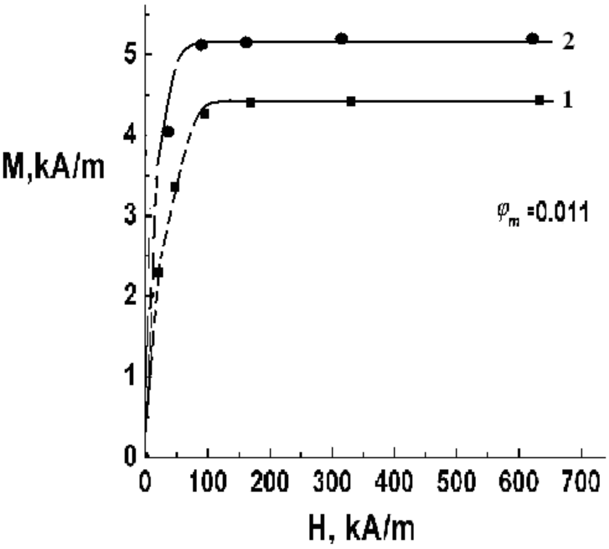
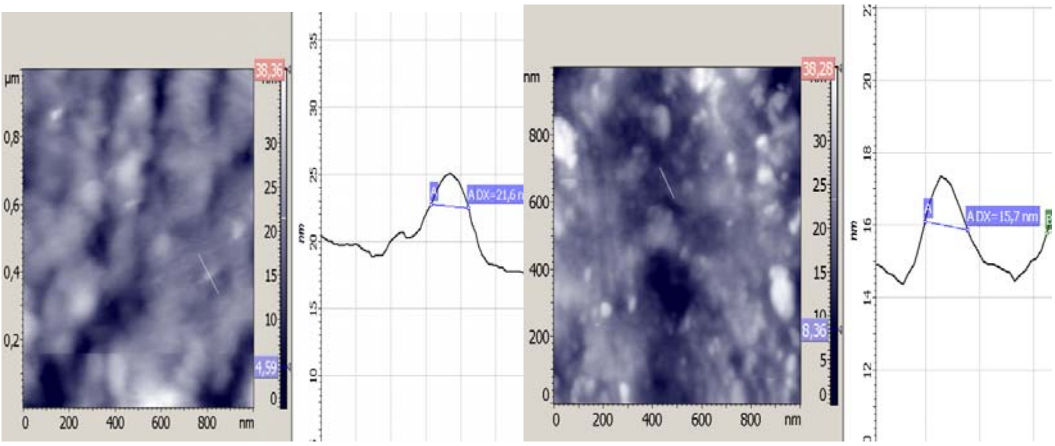


Fig.3 The magnetization of the sample PE+ Fe_3O_4 in various cooling regimes.
1. β=30deg/min (BO) 2.β=4deg/min (MO)

The values of magnetic diameters are various for the same concentration of nanoparticles in PVDF and PE (φ_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 φ_m =0.011. The magnetization of the sample PVDF+Fe_3O_4 and PE+Fe_3O_4 has superparamagnetic 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 $PE+Fe_3O_4$ changes depending on temperature-duration regime of polyethylene crystallization, it means specific magnetization of $PE+Fe_3O_4$ 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. β=30deg/min (BO) 2.β=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.



a) b)

Fig..5 AFM image of nanocomposite surface PVDF+ Fe_3O_4 and size of Fe_3O_4 nanoparticles a) β=4deg/min b) β=30deg/min.

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

The analysis of properties of nanocomposite surface $PE+Fe_3O_4$ 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 conditioned by peculiarities of interactions of matrix and filler during composite crystallization process.

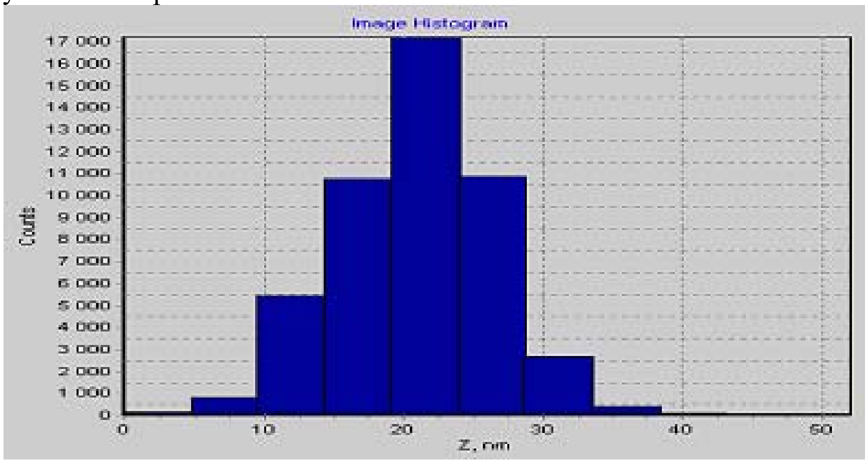


Fig. 6. Analysis of properties of nanocomposite surface and histogram of values of elements images .

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

The scans of PE+ Fe_3O_4 nanocomposition obtained by Aomic-Force Microscope and Magnetic Force Microscope. Here magnetic addition is taken as volumes amount γ_m=0,025 is shown in Pic.7

Investigations the magnetite conglomerate composed of nanoparticles showed that its geometrical size obtained by AFM is sufficiently smaller than the geometric size obtained by MFM. I was find the magnitude of coefficient K by experimental way and this is appropriate with experimental results. Thus it was found that a coagulation of Fe_3O_4 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 polymer.

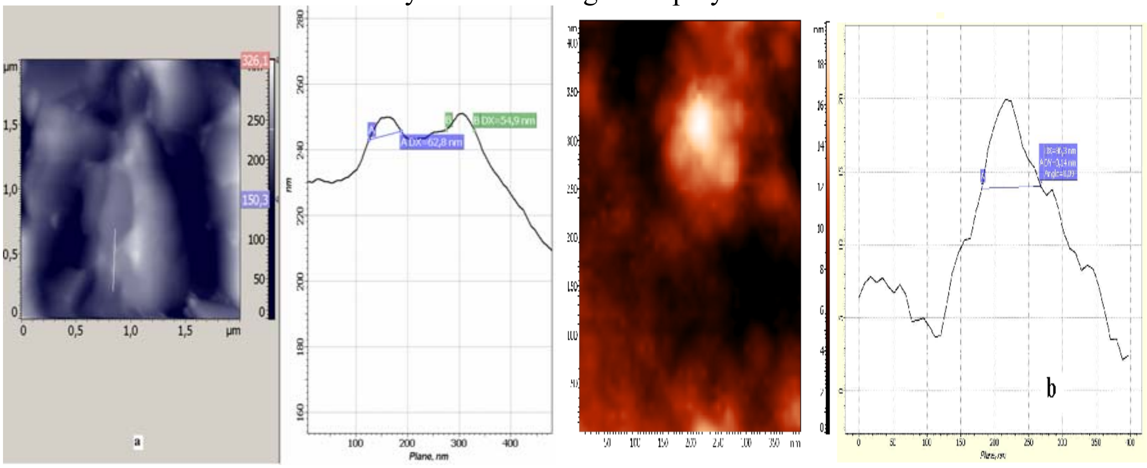


Fig.7. 2D scans and sizes of PE+ Fe_3O_4 nanocomposition with γ_m=0,025 volumetric quantity of magnetic addition. a) AFM scan b) MFM scan

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:

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

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

$$\frac{1}{6}\pi d_t^3 - \frac{1}{6}\pi d_m^3 = \frac{1}{6}\pi d_t^3 \left(1-K^3\right) = V_t(1-K^3) \qquad (4)$$

The right sides of these equations are equal. It means the magnetic diameter of nanoparticles coagulants also linearly depends on its geometrical diameter. Thus the results obtained for magnetic diameter of nanoparticle coagulant are compatible to 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 PE + Fe_3O_4 and PVDF + Fe_3O_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_{0t}) and magnetic (d_{0m}) diameter of nanoparticles linearly depends on its geometrical diameters and these results harmonize very well with experimental data.

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