

# Magnetoresistance effect in a PE+Fe<sub>3</sub>O<sub>4</sub> based polymer nanocomposite system

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A surface of PE+Fe<sub>3</sub>O<sub>4</sub> based nanocomposite has been investigated by use of Atomic-Force Microscope (AFM) and Magnetic-Force Microscope (MFM). It is shown that sizes of Fe<sub>3</sub>O<sub>4</sub> nanoparticles and intrinsic magnetization increase with concentration of Fe<sub>3</sub>O<sub>4</sub> in polymer matrix. Saturation was observed at low values of magnetic field, as the ferromagnetic nanoparticles possess single domain structure and particles are easily oriented under action of external permanent magnetic field. Also, temporary dependence of resistance of PE+Fe<sub>3</sub>O<sub>4</sub> based nanocomposite was studied for periodical variations of external magnetic field in the interval 0 – 1kOe. The observed variation in magnetic resistance is explained by tunneling of charge carriers, which depends on the mutual orientation of magnetic moments of Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

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A study of nanocomposites based on the ferromagnetic metals and oxides is the area of high interest. In those materials a giant magnetic resistance (GMR) is observed [1]. As shown in [2] the observed large positive magnetic resistance was appeared after preliminary storage of samples in magnetic field and it reaches saturation at lower values of the field. Role of magnetostriction in appearance of giant magnetoresistance (GMR) in nickel-polyarylenphtalide-copper system was studied in [3]. It has been found that GMR phenomenon at the boundary of polymer-nickel is not related to the considerable variation of magnetostrictional deformations as the transverse and longitudinal magnetostrictions on the plane of substrate practically is not varying in the interval of magnetic fields causing junction. Note that, the perfect nature of GMR in polymeric nanocomposite was not finally explained yet.

Fe<sub>3</sub>O<sub>4</sub> nanoparticles were obtained as follows: salts of FeSO<sub>4</sub>×7H<sub>2</sub>O and FeCl<sub>3</sub>×3H<sub>2</sub>O were individually solved in water then solutions were associated in a vessel, stirred by slowly adding of 25% solution of hydroxide ammonium. As a result the thin layer dispersed deposit of Fe<sub>3</sub>O<sub>4</sub> was produced on the bottom of the vessel. To enhance the sedimentation rate the vessel it was equipped with the permanent magnet. The illuminated solution was decanted from the surface of deposited layer and product of sedimentation was washed with distilled water. The

potassium oleate and aqueous solution of sodium dodesulphate were added to the washed deposit under continuously stirring and heating up to 50 °C. A temperature of reaction mixture was raised up to the 90 °C. Peptizing process was carried out during 30 minutes. As a result of processes carried out the Fe<sub>3</sub>O<sub>4</sub> nanoparticles were obtained within of solution.

Polymer magnetic nanocomposites were obtained as follows: nanoparticles of Fe<sub>3</sub>O<sub>4</sub> were added to the solution of polyvinylidenfluoride (PVDF) in dimethyl formamide and the mixture was stirred until the emulsion formation at temperature 343 K. After adding the aqueous solution the Fe<sub>3</sub>O<sub>4</sub> containing PVDF was separated. Then it was dried in vacuum box.

Samples of nanocomposites were obtained by the thermal pressing method at the melting point of polymer matrix under 15 MPa pressure during 10 minutes with further cooling at rate β=30 grad/sec until to room temperature. Sizes of magnetic nanoparticles have been studied by AFM and MFM of Integra Prima type. In the Fig. 1 are presented the AFM images of surfaces of Fe<sub>3</sub>O<sub>4</sub> nanoparticles for various volume contents.

AFM studies showed that sizes of nanoparticles increase with concentration of Fe<sub>3</sub>O<sub>4</sub>. We have proposed that with increasing the content of Fe<sub>3</sub>O<sub>4</sub> nanoparticles in polymer matrix sizes of particles also increase. It leads to increase the probability of formation for larger particles.

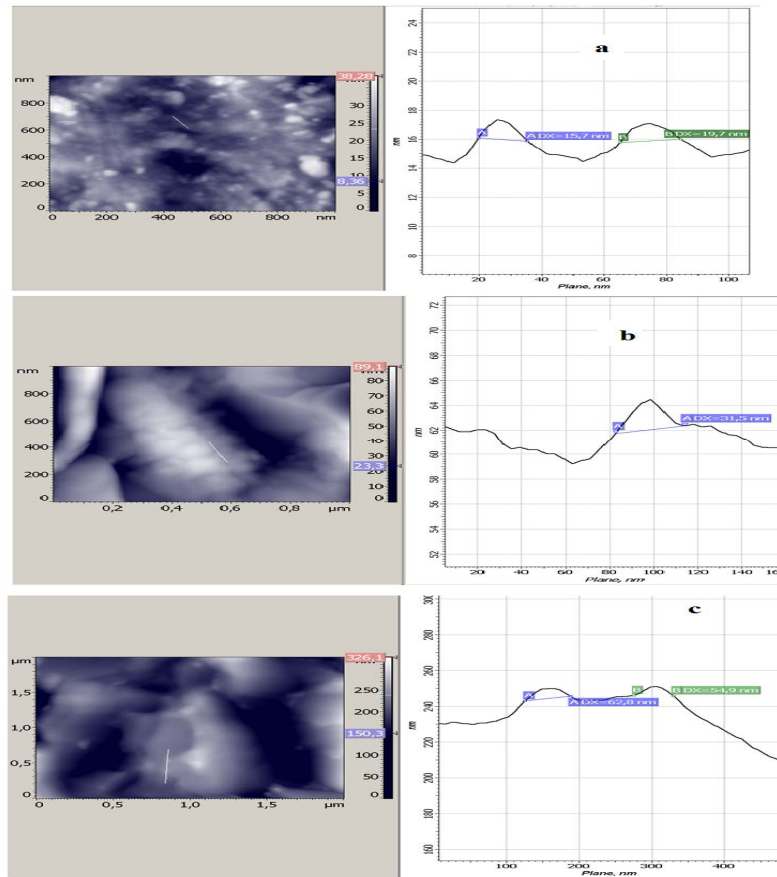


Fig. 1. AFM images of surfaces of PE+Fe<sub>3</sub>O<sub>4</sub> nanocomposites and sizes of Fe<sub>3</sub>O<sub>4</sub> nanoparticles  
 a) PE+Fe<sub>3</sub>O<sub>4</sub> 5 ml, b) PE+Fe<sub>3</sub>O<sub>4</sub> 10 ml, c) PE+Fe<sub>3</sub>O<sub>4</sub> 15 ml.

In Fig. 2 a) and b) the dependencies of intrinsic magnetization of Fe<sub>3</sub>O<sub>4</sub> nanocomposite on the intensity of magnetic field are demonstrated. Has been found that intrinsic magnetization increases with concentration of Fe<sub>3</sub>O<sub>4</sub> in polymeric matrix of polyethylene. At lower values of magnetic field the saturation is observed as the ferromagnetic nanoparticles have single domain structure and particles are easily oriented under action of external

permanent magnetic field. It seems to be due to randomly distribution of orientations of axes for easily magnetization.

At sufficient small sizes the nanoparticles have single domain structure and their magnetic moments are oriented due to external magnetic field. These particles are stabilized by magnetic anisotropy.

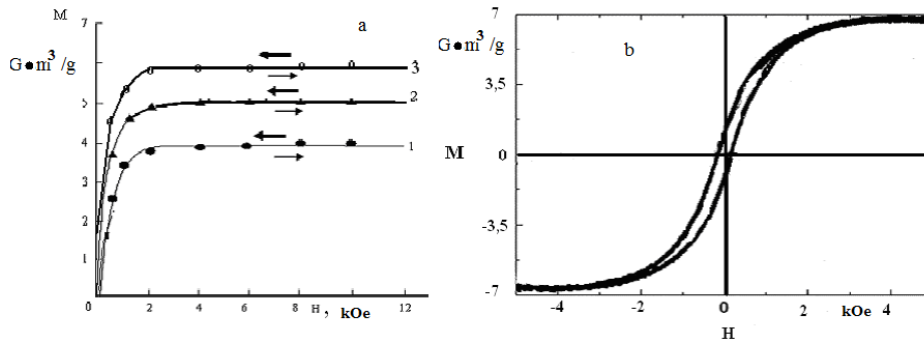


Fig. 2. Intrinsic magnetization as a function of intensity of magnetic field for the PE+Fe<sub>3</sub>O<sub>4</sub> Nanocomposites with different mass contents (MC): a) 1. PE+5% MC Fe<sub>3</sub>O<sub>4</sub>, 2. PE+10% MC Fe<sub>3</sub>O<sub>4</sub>, 3. PE+10% MC Fe<sub>3</sub>O<sub>4</sub> b) PE+20% MC Fe<sub>3</sub>O<sub>4</sub>.

As can be seen from Fig. 2 b) the increase in intrinsic magnetization and saturation are observed with increase in intensity of magnetic field. In the process of demagnetization, i.e. after the magnetizing field has been reduced the residual magnetization is observed. Repeating of cycle in change of magnetic field direction results in observation of hysteresis loop.

It is known that important magnetic characteristics of ferromagnetic materials are coercive force ( $H_0$ ) and residual intrinsic magnetization ( $M_H$ ). From Fig. 2 is seen that with increase in concentration of Fe<sub>3</sub>O<sub>4</sub> in polymer matrix the intrinsic magnetization also increases. An increase of Fe<sub>3</sub>O<sub>4</sub> concentration in polymer matrix of PE leads to the change in properties of nanocomposite, i.e. nanocomposite demonstrates ferromagnetic properties. At sufficient small sizes particles possess single domain structure. Direction of their magnetic moments are defined

by the “game” between orientating action of external magnetic field and stabilizing behavior of either crystalline or geometric magnetic anisotropy. An increase in sizes of Fe<sub>3</sub>O<sub>4</sub> also leads to change in properties of nanocomposite, i.e. Fe<sub>3</sub>O<sub>4</sub> particles enter into multi-domain structure and material gets ferromagnetic properties. In Fig. 3 are presented MFM image of PE+Fe<sub>3</sub>O<sub>4</sub> nanocomposite surface and sizes of Fe<sub>3</sub>O<sub>4</sub> for different contents. Both AFM and MFM studies show that real geometrical sizes are distinctly from the magnetic sizes. These experimental results are in accordance with the theoretical calculation [4].

It was experimentally known that the coagulation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles in polymeric matrix depends not only on the concentration of magnetite nanoparticles but also on the supermolecular structure of polymer.

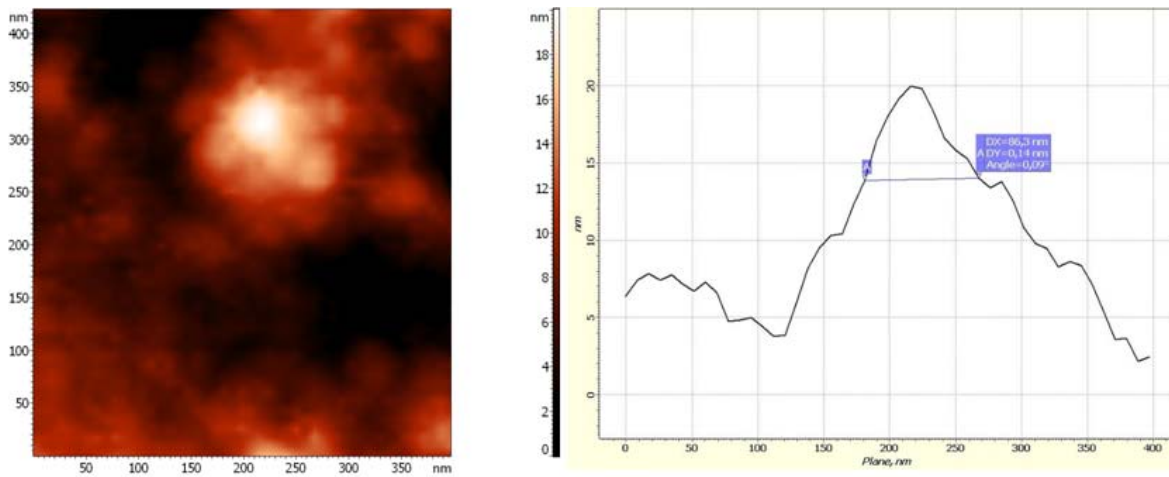


Fig. 3. MFM image of Fe<sub>3</sub>O<sub>4</sub> nanocomposite surface and graph between sizes of Fe<sub>3</sub>O<sub>4</sub> nanoparticles and their contents.

The periodic change in resistance of PE+Fe<sub>3</sub>O<sub>4</sub> nanocomposite has been studied in the absence of magnetic field and when it was present. It has been found that the magnetoresistance effect for nanocomposite decreases with increasing in sizes of Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The periodic change in resistance as a function of time is shown in Fig. 4. Here in the absence of magnetic field ( $H=0$ ) a decrease in resistance is observed. However in the presence of magnetic field ( $H=1$  kOe) magnetic resistance shows increase with time.

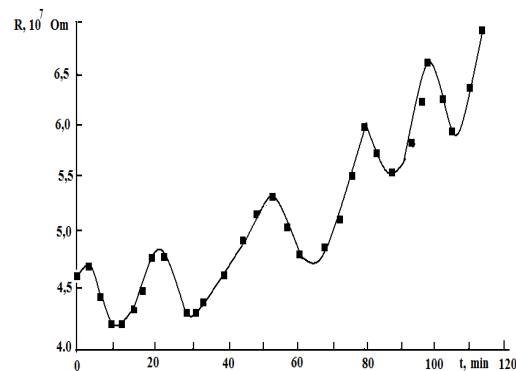


Fig. 4. Magnetic resistance of PE+Fe<sub>3</sub>O<sub>4</sub> nanocomposite as a function of time at periodic change of magnetic field in the interval  $0 \div 1 \text{ kOe}$ .

The observed variation in magnetic resistance can be explained by taking into account the role of ferromagnetic cluster formations composed of nanoparticles surrounded by the superparamagnetic (SPM)  $\text{Fe}_3\text{O}_4$  particles. Mutual orientation of magnetic moments of clusters and SPM particles more probably leads to tunneling of charge carriers and variation in resistance of magnetic composite.

### References

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