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THE MAGNETIC POLYMER NANOCOMPOSITE MATERIALS BASED ON POLYPROPYLENE AND IRON NANOPARTICLES: SYNTHESIS AND STRUCTURE

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In the paper, we report of developing of new nanocomposites based on isotactic polypropylene and iron nanoparticles and investigated its structure by IR, UV spectroscopy, scanning electron microscopy (SEM), atom force microscopy (AFM) and magnetic force microscopy (MFM). IR studies showed that the introduction of nanosized fillers in the polymer matrix does not change its chemical structure, and changes the supramolecular structure of the polymer. SEM studies show that with increasing volume fraction of iron particles changes the supramolecular structure of the polymer and increase the size of the particles in the polymer. AFM studies also demonstrate that the introduction of iron nanoparticles in polypropylene matrix influence on supramolecular structure of polypropylene. MFM analysis have shown that dispersed iron nanoparticles create around themselves a magnetic field, which leads to a change in the morphology of magnetic nanocomposites. Magnetic force microscopy study of the surface of nanocomposites also showed that the nanoparticles distributed in a matrix create domains in the local areas.

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1. Introduction

Composite polymeric materials are a broad class of materials where the polymer matrix combined with components having different chemical nature that ensure the achievement of the desired functional properties. In recent years, interest in the field of composite polymeric materials has increased considerably due to the development of nanotechnology and the use of nano-dispersed fillers. The proportion of the polymer at the interface between the phases increase with the increase of the degree of filler dispersion, and this in turn manifest themselves by appearing of interfacial effects at greater extend. Most researchers, describing the properties of composite polymer materials occurring on interface suggest that the phenomena of energy interface interactions plays the crucial role. Thus, the structuring polymer in the interfacial layer, forming the adsorption layers, sealing or loosening of polymer matrix and also the effect of hardening the polymer in the presence of fillers traditionally associated with interfacial interactions [1-4]. In this context, the study of energy of interfacial contacts in filled polymer systems is very actual and a matter of practical interest, but their realisation methods are quite complicated. From analysis of literature data it is known that there are four factors that determine the properties of filled polymer material: the chemical nature of the components, filler content, the distribution of the filler particles in the polymer matrix and the interfacial interaction, which is characterized by the adhesion of the polymer to the filler surface.

Polymer nanocomposites based on metallic ferromagnetic nanoparticles is a matter of high interest firstly due to possibilities of their use for recording of information with high density, the

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preparation of highly sensitive built-in sensors of weak magnetic fields and spintronics devices, as well as prospects their use as sources of inhomogeneous magnetic field.

This article focused on preparation technology of magnetic thermoplastic polymer nanocomposites based on isotactic polypropylene and iron nanoparticles and study of their structure.

2. Experimental part.

2.1. Materials

The isotactic polypropylene (PP brand Sigma Aldrich P code 1001326963) density of 0,9 g/ml at 250C, refractive index- n20/D 1.49, transition temp - Tg -26 ° C, mol. w.t - average Mw ~ 250000 by GPC, auto ignition temp -> 674 ° F, m.p. – 189^0 C. Iron nanoparticles were prepared by electro explosive technology.

2.2. Research Methods

Infrared spectroscopy (FT-IR).

Nanocomposite structure was studied by IR spectroscopy (spectrometer Varian 3600 FT-IR) at 4000-400 cm^{-1} and room temperature.

UV-spectroscopy.

The UV spectra have been recorded on Spectrophotometer Specord 250 Plus. UV spectra were recorded at 200-700 nm and ambient temperature.

Scanning electron microscopy (SEM).

Distribution of iron nanoparticles in the polymer matrix studied by scanning electron microscopy (SEM, Jeol JSM-7600 F). Scanning was conducted in the SEI mode at an accelerating voltage of 15 kV and a working distance of 4.5 mm.

Atomic force microscopy (AFM).

The morphology of the nanocomposites was studied using atomic force microscopy Integra-Prima (NT-MDT, Zelenograd). For the scan used special silicon cantilevers, fabricated by plasma etching method with a radius of curvature of the needle 20 nm and the resonance frequency of 1-5 Hz. Scan size was 5×5 microns. The measurements were performed in the semi contact microscopy mode in air, was fixed change of oscillation amplitude of the cantilever needle, which determines the surface topography. The scanning speed and the number of scanned lines of the image, respectively 256 and 1,969 Hz.

Magnetic force microscopy (MFM).

Magnetic force microscopy images were obtained with-Prima AFM Integra Prima using a two-pass technique, at a so-called "lifting" mode. Magnetic force microscopy shows the spatial pattern of the magnetic force on the sample surface with the help of MFM probe coated with a thin ferromagnetic film. MFM image obtained using two-pass method. On the first pass determined the relief of the sample using a contact or intermittent-contact regime. On the second pass the probe is lifted and only long-range magnetic forces can affect the probe. At the same time, the MFM image obtained by measuring of the shift of the amplitude or phase of cantilever oscillation, which occurs under the influence of the magnetic force between the sample surface and a magnetized MFM cantilever. Images of magnetic force microscopy contain information about the location of the magnetic domains on the sample surface.

The synthesis of nanocomposites.

The polymer nanocomposite materials were prepared as follows: isotactic polypropylene was solved in toluene at 120^0C. Iron nanoparticles were added to the polymer solution at various volume contents (0.1; 0.3; 0.5; 1; 2; 5%) and stirred for an hour to obtain a homogeneous mixture. The mixture was transferred to a petri dish and dried during the day. Nanocomposites have also been dried in a vacuum oven for 3-4 hours in order to remove the solvent completely. From these samples were obtained the thin nanocomposite film by hot-pressing at the melting temperature of polypropylene and a pressure of 10 MPa. Cooling the film after hot pressing was carried out in water and the cooling rate of films was 200^0/min.

It was also found that the threshold of nanocomposites PP + Fe filling is 5% volume content of iron nanoparticles.

3. Results and discussion

Figure 1 shows the IR spectra of nanocomposites based on polypropylene and iron nanoparticles. As can be seen from the figure 1, after the introduction of iron nanoparticles in a polypropylene matrix the intensity of the absorption bands of many peaks is reduced. The absorption band at 1376 cm^{-1} corresponds to symmetrical deformation vibrations of the CH_3 group, whereas the absorption band at 1459 cm^{-1} - to anti-symmetric deformation vibrations, and absorption band at 2839 cm^{-1} corresponds to the stretching vibrations of CH_2 methylene groups. At the 5% iron content the intensity of the absorption bands at 2839 см$^{-1}$, 1459 см$^{-1}$ and 1376 см$^{-1}$ decreases sharply. IR study demonstrate that introduction of nanosized iron fillers in the polymer matrix does not cause chemical changes in the polymer structure, and only changes the physical structure of the polymer, that revealed itself in IR spectra of the polymer by a decrease of the intensities of the absorption bands.

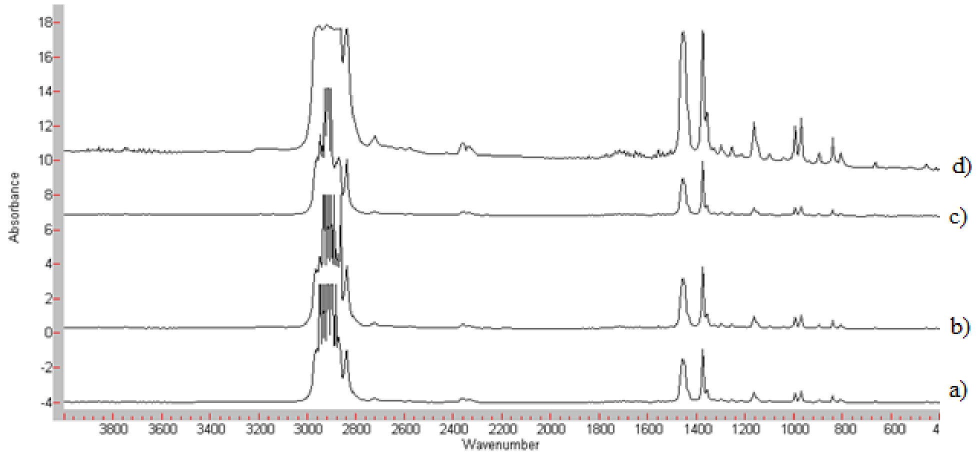

Fig. 1. The IR spectra of PP + 5% Fe (a); PP + 3% Fe (b); PP + 1% Fe (c); (4) pristine PP (d)

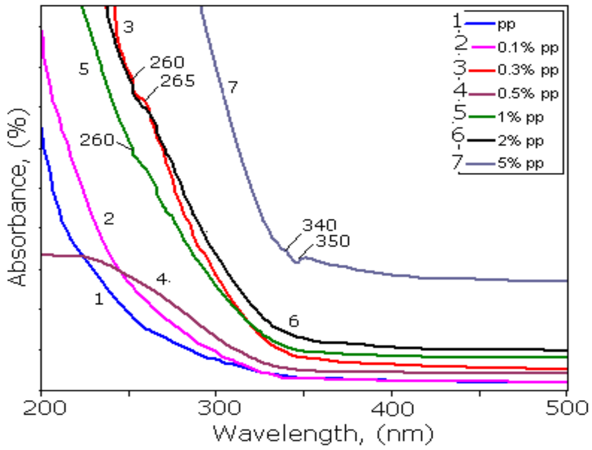

Fig. 2. UV spectra of PP films and nanocomposites based on PP + Fe

Fig. 2 shows UV spectra of the films based nanocomposites PP + Fe with different volume content of iron nanoparticles. As it seen, the absorbance of polypropylene nanocomposite film is very low at small volume content of iron nanoparticles in the polymer matrix. At the 1% iron content of nanoparticle in nanocomposites films was detected the peak at 260 nm wavelength. The increasing of the volume fraction of nanoparticles up to 2%, the intensity peak at 260 nm increases, and there is another peak at 265 nm. With further increasing of nanoparticles up to 5%, these peaks are shifted toward the wavelength of 340 nm and 350 nm. The shift of UV-peaks in the spectrum in the longer wavelengths is explained coagulation iron nanoparticles in the polymeric matrix.

Fig. 3 shows SEM images of pure polypropylene (PP) and nanocomposites PP + Fe. As it is seen from figure, the introduction of nanoparticles in polypropylene matrix changes the supramolecular structure of the polymer. When 0.3% of iron introduced in the polymer, the average diameter of nanoparticles are 24-42 nm. It is found that increasing the volume fraction of iron nanoparticles increases the amount of nanoparticles in the polymer matrix and the size of nanoparticles. Thus, for nanocompositions with 1% iron nanoparticles volume content the average particle size is 47-65 nm, and at 5% volume content - 70-105 nm.

Fig. 4 shows energy dispersive spectrum of PP+Fe nanocomposite and as seen in the polymer matrix prevails mainly iron nanoparticles.

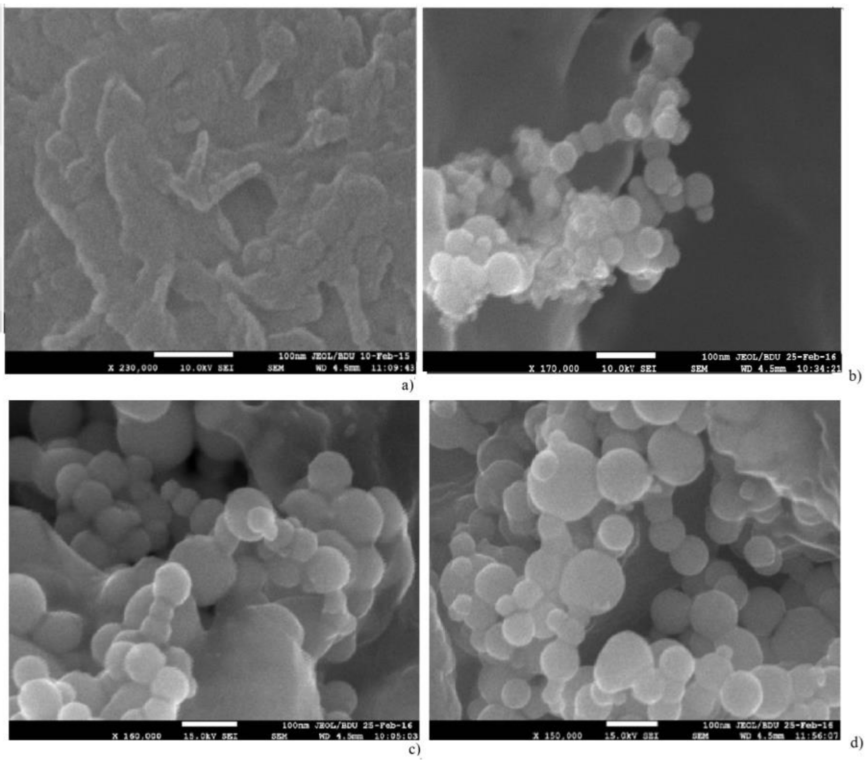

Fig. 3 SEM image of nanocomposites polypropylene + Fe
PP (a), PP + 0,3% Fe (b) PP + 1% Fe (c) and PP + 5% Fe (d)

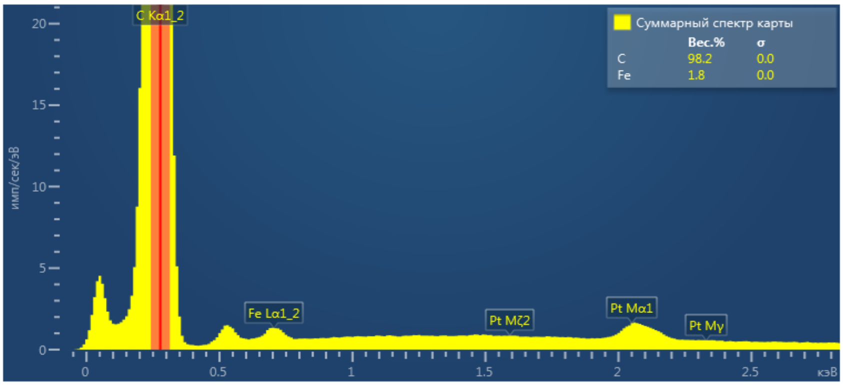

Fig. 4. Energy dispersive spectrum of nanocomposites based on PP + Fe.

Fig. 5 and Figure 6 shows AFM 2D and 3D images of nanocomposites based on PP + Fe with different volume content of iron. As it is seen with the addition of iron nanoparticles in the polymer matrix supramolecular structure varies greatly. This correlates well with the values of the average roughness of the surface of nanocomposites [5-7].

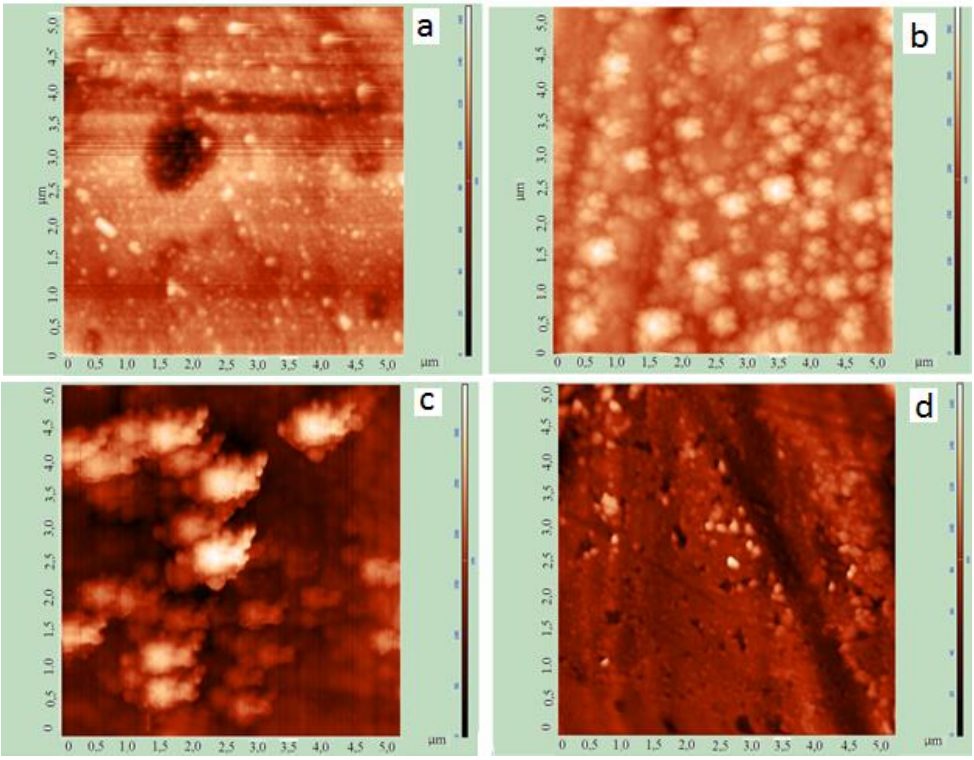

Fig.5 AFM 2D image based nanocomposites polypropylene + Fe
a) PP; b) PP + 0,5% Fe; c) PP + 1% Fe; d) PP + 5% Fe

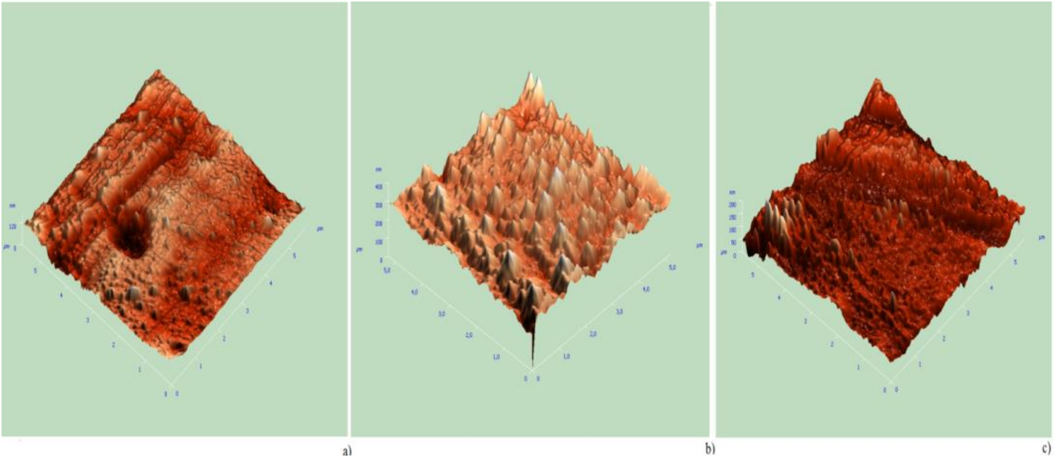

Fig. 6. AFM 3D image nanocomposites based on PP + Fe
a) PP; b) PP + 0,5% Fe; c) PP + 5% Fe

Fig. 7 shows histograms of the surface roughness of the nanocomposites PP + Fe. Thus the average surface roughness of the pure polymer is 80-120 nm; for nanocomposite PP + 0,5% Fe is 100-150 nm; for PP + 5% Fe -100 nm. From this it may be concluded that the introduction of iron nanoparticles in a polymer matrix changes supramolecular structure of nanocomposites substantially, i.e. occurs grinding of the structural elements of polypropylene.

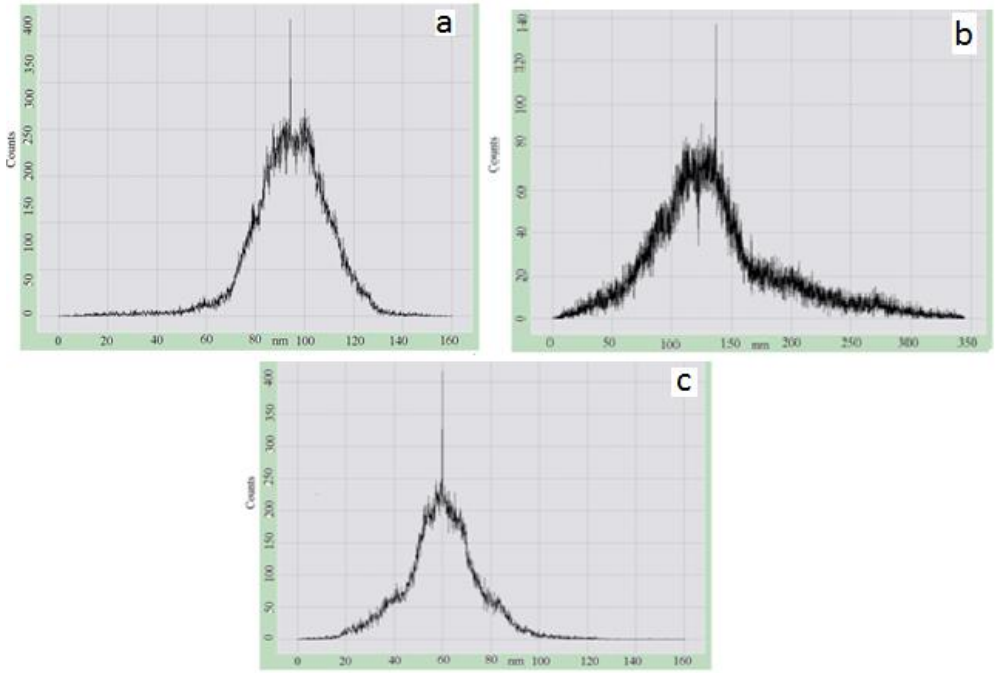

Fig. 7. The histogram of image of RMS surface roughness of nanocomposite:
a) pure PP; b) PP + 0,5% Fe; c) PP + 5% Fe

Fig. 8 shows an AFM and MFM topography of nanocomposite PP + 5% Fe in the scanning area of 18 × 18 microns. MFM images were made in the dynamic mode, using the IMS needles coated with ferromagnetic material. Figure 8 (b) clearly shows the distribution of magnetic signals on the entire surface of the nanocomposite. MFM analysis has shown that dispersed nanoparticles of iron create around themselves a magnetic field, which leads to a change in the morphology of magnetic nanocomposites. Fig. 9 shows the domain structure of magnetic nanocomposites, which was obtained in the mode of dynamic magnetic force microscopy [8].

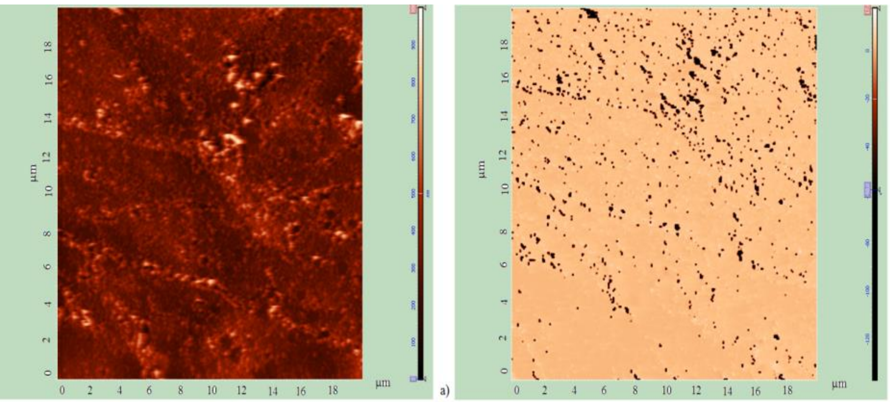

Fig. 8 Atomic force (a) and magnetic force microscopy (b) images of nanocomposite PP+ 5% Fe.

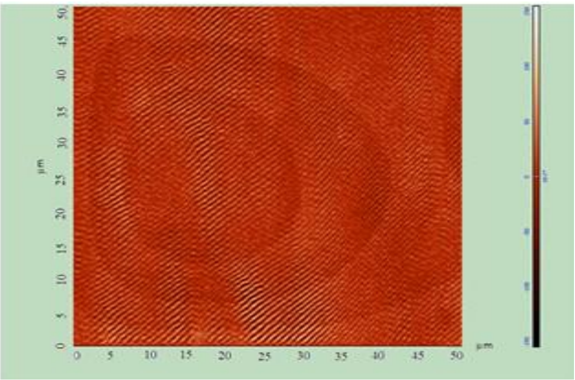

Fig. 9. The domain structure of magnetic nanocomposites based on PP + Fe.

As a result, AFM and MFM research reveal that dispersed magnetic nanoparticles creating around them a magnetic field and change the topography of magnetic nanocomposites. It was also found that the magnetic nanoparticles became magnetized at approaching of magnetic probe and this in turn not allowed to completely approaching of the probe to the surface. As a result, there are the differences between the magnet sizes and the actual geometrical dimensions of nanoparticles. The obtained experimental results correlate with theoretical data very well. Magnetic force microscopy study of the surface of nanocomposites also showed that the distribution of nanoparticles in a matrix create domains in the local areas. The size of these domains ranges 150-400 nm [8].

4. Conclusion

In the presented work, we developed the new nanocomposite structures, based on isotactic polypropylene and iron nanoparticles and investigated its structure by IR, UV spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM) and magnetic force microscopy (MFM). IR studies showed that the introduction of nanosized fillers in the polymer matrix does not change its chemical structure, and changes the supramolecular structure of the polymer. SEM studies show that with increasing volume fraction of iron particles changes the supramolecular structure of the polymer and increase the size of the particles in the polymer. AFM studies also demonstrate that the introduction of iron nanoparticles in polypropylene matrix influence on supramolecular structure of polypropylene. MFM analysis have shown that dispersed iron nanoparticles create around themselves a magnetic field, which leads to a change in the morphology of magnetic nanocomposites. Magnetic force microscopy study of the surface of nanocomposites also showed that the nanoparticles distributed in a matrix create domains in the local areas.

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