HDPE+Fe_3O_4 MAGNETIC POLYMER NANOCOMPOSITE TECHNOLOGY AND INVESTIGATIONS OF ITS STRUCTURE BY SEM

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The synthesis methods of composite nanomaterials on the base of HDPE polymer matrix and Fe_3O_4 magnetite nanoparticles are developed. The optimal conditions and synthesis process parameters (temperature, concentration of metal-containing compound, time and temperature-time mode of crystallization) influencing on phase composition, nanoparticle dimensions and physicomechanical properties as a whole are established.

SEM-investigations of HDPE+ Fe_3O_4 nanocomposites are carried out. The possibilities of scanning electron microscopy and microroentgenospectral analysis being in investigation methods of material microstructure, definition of quantitative element composition and map construction of element distribution on analytic complex example are shown.

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INTRODUCTION

As a result of gathered scientific data and their analyses it is established that nanocomposite technology can be divided into two methods. The first method is nanocomposite assembly going from bottom with stay of phase increase with the help of surface-active substance. The grinding of massive substance samples takes place in second place. At particle dimensions 1÷20 nm the composite surface has the big excess energy that's why the big attention is paid to nanoparticle stabilization process. As a result of interaction of nanoparticles with inert atmosphere substance, in surface layer the appearance of modified phase is possible. The chemical synthesis of magnetic nanoparticles is carried out by two general methods: the obtaining of particles, the surface of which is covered by surface-active substances or ligands (ex situ), or method where their "hard" stabilization in matrixes (in situ) takes place simultaneously, i.e. nanoparticle stabilization takes place in process of their obtaining. The product, which is constant by its properties, forms in output. In the first method the possibility to operate with nanoparticle surface, for example, the ligand substitution or further surface modification, obtaining of particle monolayers and etc. is saved. The advantage of second method is in the fact that we usually deal with nanomaterial for which the nanoparticle collective properties are especially important. This method we use in our work. The composite material class formed by nanoparticles and organic polymers, as they are attractive ones by technological simplicity, presents the especial interest in this aspect. Because of their plasticity, such materials demonstrate the perspective electric, optic, magnetic and mechanical properties caused by not only individual peculiarities of nanoparticles and polymers but by interactions of interfaces of two materials different by its nature which are inorganic/organic in supramolecular scale.

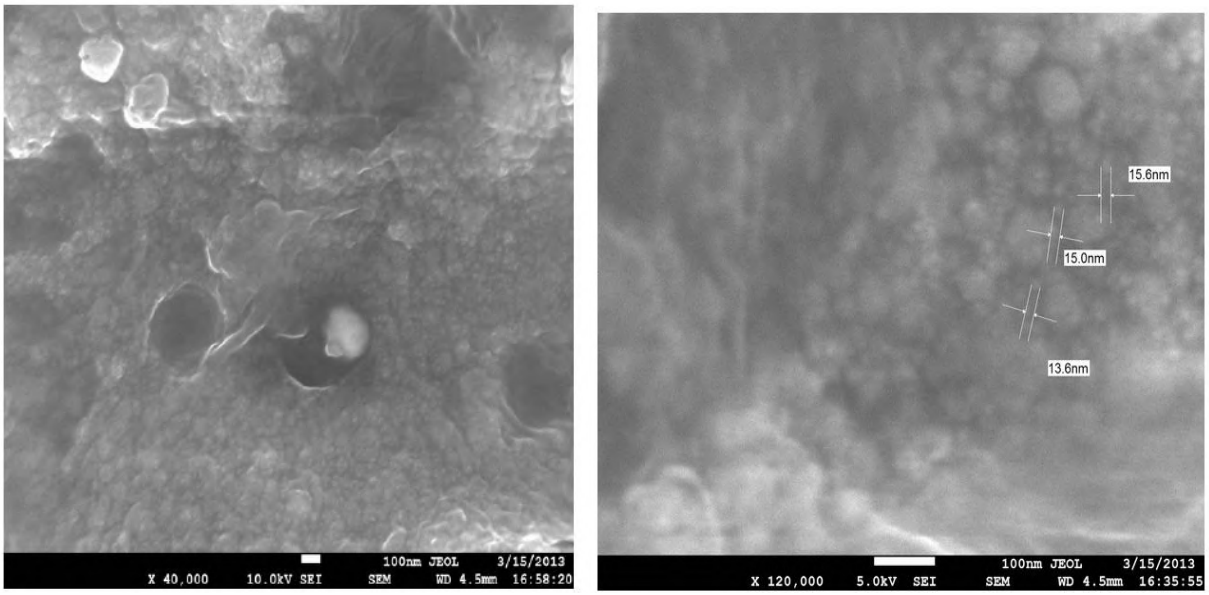
The modern state of magnetic record technology confirms that transition to magnetic nanomaterials allows us to increase the density of record information in 10^3-10^4 times [1,2]. That's why the development of synthesis methods of polymer nanocomposites with magnetic component, investigation of mechanism of their formation and stabilization, the study of their structure has the big meaning for obtaining of new information on substance magnetic property peculiarities in nanostate. The use of polymer matrixes of different types allows us easy regulation of the morphology of such systems and especially the particle dimension and distance between them changing the synthesis conditions [3]. The wide range of structural characteristic changes presents the well possibility for regulation of magnetic interactions between particles of nanophase, study of this interaction influence and dimensional factor on nanosystem magnetic properties.

THE EXPERIMENT TECHNIQUE AND SAMPLE PREPARATION

The nanoparticles and composites with Fe_3O_4 nano-particle addition are obtained by following way in present paper. The magnetic liquid containing the ferric oxide nanoparticles by dimension 3-5nm is obtained by chemical condensation method (colloidal solution of Fe_3O_4 magnetite in water). Further, Fe_3O_4 nano-particles are added in 2% solution of granuled high-density polyethylene (HDPE by 293-285D mark) in carbon tetrachloride CCl_4 and mixture is mixed at temperature 373K up to emulsion formation. After water solution addition HDPE containing Fe_3O_4, which later is dried in vacuum box, isolates. All nano-composite samples are obtained by the same above mentioned method in different concentrations of Fe_3O_4 necessary for us and all described technological factors of their obtaining are supported constant ones for study of concentration change influence of initial reagents on obtained sample properties. The obtained non-transparent film samples which are separeated from Petri cups, are treated by hot pressing method at melting point of polymer matrix under pressure 15Mpa during 10 min with further cooling in different temperature-time crystallization modes: rapid cooling (RC) at temperature decrease rate

β=2000 grad/min („tempering in liquid nitrogen medium“) and slow cooling (SC) at rate β=4 grad/min not without pressure.

Further, HDPE+Fe_3O_4 nano-composite samples in film forms are obtained from above mentioned films with the help of hydraulic press with heated molds at hot pressing. The choice of technological pressing conditions, such as pressure, temperature and enduring time in material melted state is necessary condition at sample obtaining of polymer nano-composite films with different morfology and structural pecularities. The researchers often have methodical difficulties at choice of methods and techniques of investigations by device type and etc. at studyof structural state [4-6]. It is known that scanning electron microsope (SEM) allows simultaneously to research the dimensions and form of nano-particles, distribution of nanoparticles and phases by dimensions, to obtained the phase composition and distribution of chemical elements by its square and square of investigated sample, chemical heterogeneity by section square and also obtain the object image in wide range of enhancement in secondary and reflected electrons. The samples of magnetic polymer nanocomposite HDPE+ Fe_3O_4 in different concentrations 5, 10, 15, 20 vol.% Fe_3O_4 are the investigation objects of SEM by JSM-7600F mark (“Jeol”, Japan).



a) –x40 000 b) – x120 000

Fig. 1. a) is nanocomposite surface structure HDPE+10 vol.% Fe_3O_4 (SC); b) is form and dimensions of Fe_3O_4 in nanocomposite polymer matrix

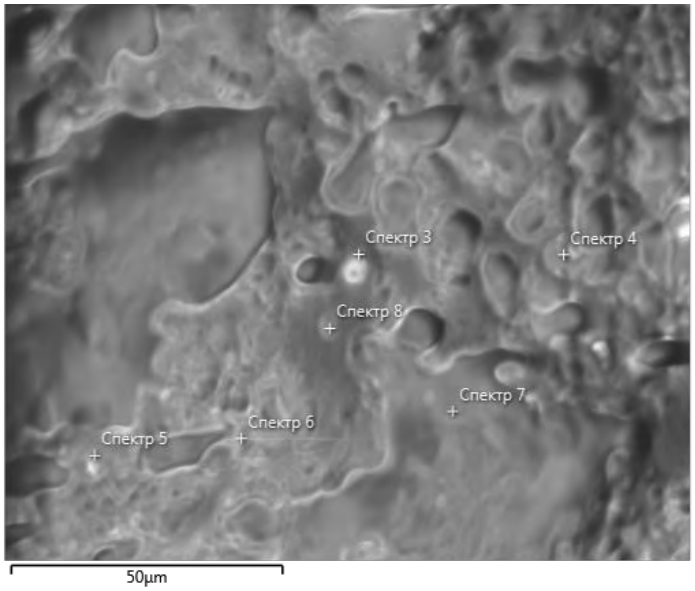


Fig.2. Energy-dispersion microroentgenospectral analysis of nanocomposite HDPE+10 vol.% Fe_3O_4 (SC).

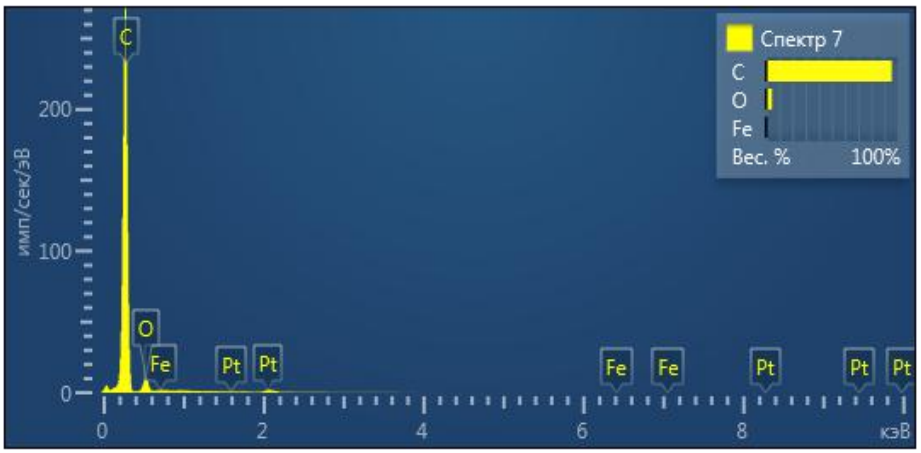


Fig. 3. General form of roentgen spectrum lines showing the element presence in point 7.

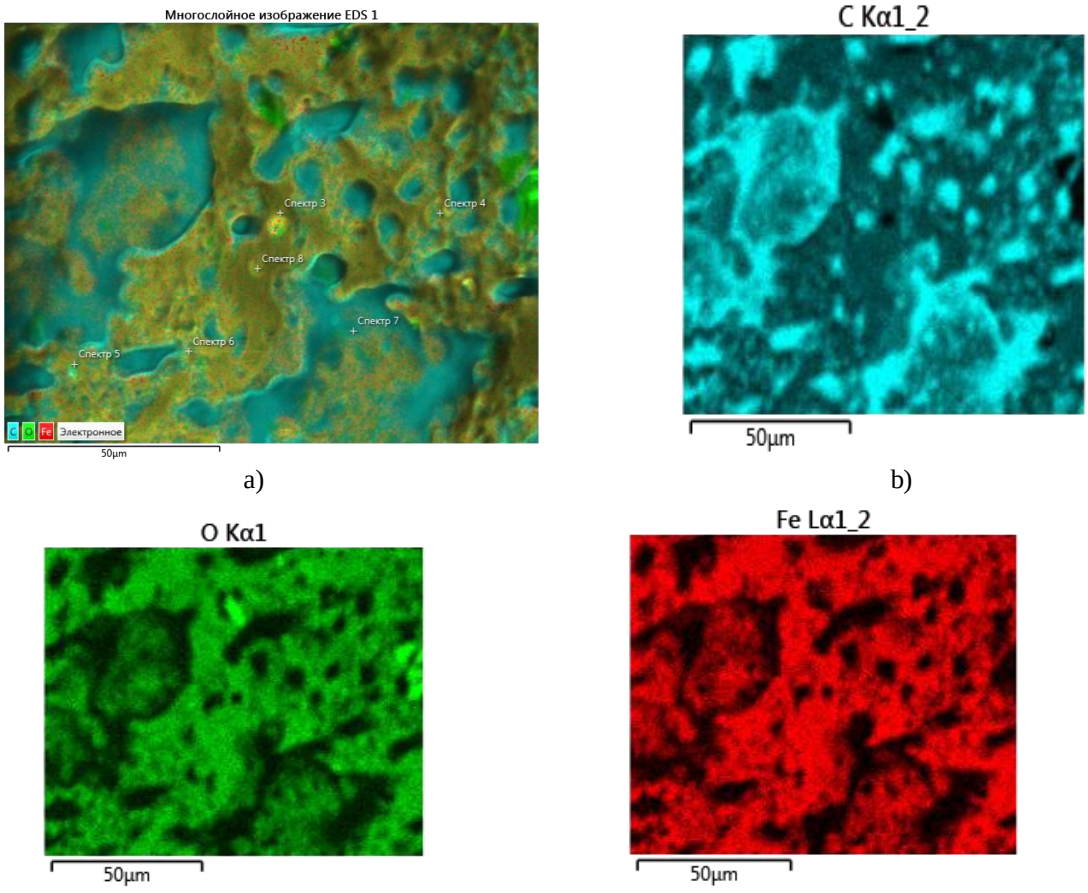


Fig. 4. Many-layered image of HDPE+10 vol.% Fe_3O_4 (MO) nanocomposite sample (a); mapping on this region on C (b), O (c), Fe (d)

RESULTS AND THEIR DISCUSSION

With the help of scanning electron microscopy it is established that magnetite nanoparticles are uniformly distributed in polymer matrix and nanoparticle sizes is 12-28nm in dependence on magnetite nanoparticle concentration (see fig.1). Also, Fe_3O_4 nanoparticle dimensions change with variation of temperature-time mode of polymer crystallization [7-9]. It is known that there are qualitative and quantitative roentgenospectral microanalyses. The quantitative microanalysis is necessary for quantitative determination of element concentration in sample. The qualitative microanalysis allows us to define what elements present in sample. The data of microroentgenospectral analysis can be represented in the form of standard protocols consisting of image of sample microstructure investigation region, table data in height or atomic ratio, spectra and histograms. The microstructure and phase element composition are investigated on sample of HDPE+10 vol.% Fe_3O_4 (SC)

nanocomposite. The sample microstructure investigations are often accompanied by microroentgen analysis, character peculiarity of which is locality: maximal excitation region is equal to 1 μm. This allows us to obtain the information on sample chemical composition in direct chosen region of microscopic dimensions. The microroentgenospectral analyses are carried out with use of energy-dispersion spectrometer in the use mode of secondary electron signals and electron backscattering. The accumulation of whole spectrum takes place in case of energy-dispersion spectrometer, that's why the qualitative analysis is automatically carried out at any measurement. The energy-dispersion spectrometer allows us to carry out the quantitative roentgen microanalysis with choice of analyzed given step region spectra: in the point, on square, on line (see Fig.2).

The quantitative element composition of six point spectra allows us to establish that bright phase consists of carbon (42,53 weight %), oxygen (40, 24 weight %), iron (17, 23 weight %) and dark one consists of carbon (100 weight %). The general form of roentgen spectrum lines showing the element presence in dark phase of point 7 is given on fig.3. The element distribution mapping on surface is carried out for confirmation of phase element composition (see fig.4a, b, c, d). If we impose the chemical element (see Fig.4b, c, d) distribution maps on microstructure (see fig.4a), then we obtain that bright phases consist of three elements C, O, Fe, dark ones consist of C only.

CONCLUSION

Thus the samples of polymer magnetic nano-composites HDPE+Fe_3O_4 obtained firstly by chemical methods, and then by hot pressing method in hydraulic press in different temperature-time modes of crystallization and different content of magnetite nanoparticles. Such films with high content of nanoparticles give the new possibilities for magnetic system formation with high density recording and information storage. Also the possibilities of scanning electron microscopy and microroentgenospectral analysis consisting of investigation methods of material microstructure, determination of quantitative element composition and element distribution map construction on example of analytic complex are shown.

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