PREPARATION OF POLYMER MAGNETIC MICROSPHERS AND INVESTIGATION OF THEIR MAGNETIC PROPERTIES

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The polymer magnetic microspheres (PMMS) have been prepared on the basis of collagen and polysterene by introduction of magnetite nanoparticles. The curve of magnetization of PMMS is very close to the theoretical one, calculated on the basis of Langeven equation. Magnetic properties of PMMS remain unaltered for a long time (two years and more), that can be indicative for a rigid fixation of nanoparticles in polymer matrix and for stability of their concentration. With application of transmission electron microscopy it has been shown, that nanoparticles are separated from each other and are not capable to aggregate. Magnetizing of PMMS arises according to Neel mechanism. Orientation of magnetic moments of nanoparticles in the externally applied magnetic field occurs by its rotation inside nanoparticles.

1. INTRODUCTION

Magnetic nanoparticles embedded in non-magnetic matrices like polymers have widely investigated [1-4]. Such objects have specific properties and a big perspective of their application in nanoelectronics [5]. Magnetic nanostructures have been used to advantage for high-gradient magnetic separation, high-density magnetic recording of information, pigmentation, microwave coatings, ferrofluids, for magnetic cooling et cetera. Instruments and devices are made on their base [5-8].

In [9-10] there have been first given polymer microspheres (PMS) synthesis, including one magnetic nucleus in size 0.1-200 µm. Such PMS are of big practical use in medicine and biology, for drug delivery, water purification, isolating of biology substances, cells, pursuance of fermentative reactions et cetera [6-8]. From one side such systems have a big values of initial magnetic susceptibility, from the other side - non- zero values of residual magnetization and coercive force, that limit their usage in some fields. Systems are composed from polymer matrix and magnetic nanoparticles have no such disadvantages. They can be repeatedly used without remagnetization. In further description we will call such systems polymer magnetic microspheres (PMMS).

Magnetic properties of PMMS are determined by magnetic properties of magnetite nanoparticles and their concentration in PMS. As PMMS are isotropic magnetic medium, their magnetization does not depend on the direction of applied magnetic field being suitable objects for magnetic phenomena investigation. PMS are diamagnetic and do not influence on PMMS magnetic properties. PMS has a high dielectric constant. For instance, for polystyrene ε=2.5-2.6 at 10^6 Hz at T=293K . After embedding nanoparticles into PMS such composition has specific electric and magnetic properties at high frequences electromagnetic field. Small quantity of magnetic nanoparticles and their sizes make PMMS physically small system with properties distinct from massive object [11].

Magnetic nanoparticles have been previously investigated. In [12] there have been obtained nanoparticles distribution on size. Synthesis was carried out by method of chemical deposition of two-valence and three valence salts of Fe with alkali excess. It is shown that nanoparticles distribution in size can be described with big accuracy of histogram that is assymetrical and flat from side of big size nanoparticles.

In [13] there have been investigated magnetite nanoparticles morphology and it is shown that chemical

composition of nanoparticles on the surface and inside are different. It is established that magnetic properties on the nanoparticle surface are more slight.

In [14] chain magnetization of magnetite nanoparticles with magnetic dipole-dipole interaction is investigated. There have been obtained the equation for magnetization of these systems.

In [15] there have been investigated structure and some physical properties of polymer magnetic microspheres and it is shown that nanoparticles agregation in polymer matrix does not take place.

This paper is the continuation of a series of our works dedicated to the investigation of structure and properties of magnetite nanoparticles being in polymer matrix. It deals with the study of magnetite nanopaticles magnetic properties in PMMS. To determine magnetic characteristics of PMMS in this paper magnetization and magnetic susceptibility of PMMS are investigated and attempts to explain magnetization mechanism is make out.

2. EXPERIMENT
Prepare PMMS for investigation

PMMS were prepared on the base of collagen and polystyrene with embedding of magnetite nanoparticles. PMMS have three size with very narrow deviation: 255 ± 1.5, 179 ± 1.5, 46.9 ± 7.3 μm. Nanoparticles of magnetite were embedded in PMS by the two ways:
a) just during the time of synthesis of PMS b) by the method of treatment of prepeared porous polymer microsphers with two and three valent salt of Fe with after deposition of magnetite nanoparticles. The process of deposition go by the influence of abundance of alkali. In this case nanoparticles take plases in pores of microsphers. The full description process of nanoparticles synthesis and some their physical properties are discribed in certificates [16, 17]. In this work we used four kind of magnetic nanoparticles, obtained in different carrying medium with different average diameter: 9.5 ± 0.1, 7.7 ± 0.1, 7.3 ± 0.1 and 5.5 ± 0.1 nm. The method of obtaining conditions of magnetic nanoparticles are discribed in [18].

Determination diameter of PMMS

Diameter of PMMS was determined by the help of light microscope at different magnifies: 100, 160 and 256. The value of magnify depend on kind of carrying medium: liquid or gaseous. We measured diameter of 250 PMMS and made statistic analysis.

Statistic analysis of diameters of PMMS showed, that synthesized microspheres have distribution by the sizes (the root-mean-square deviation $\sigma = 22.683$), which is more gently sloping from the big side of PMMS (assimetrik coefficient $\varepsilon = 0.383$) and polydispersiya coefficient of distribution K= 1.057. Microphotography and histogram of collagen PMMS distribution on the their sizes are shown on Fig.1 and Fig.2.
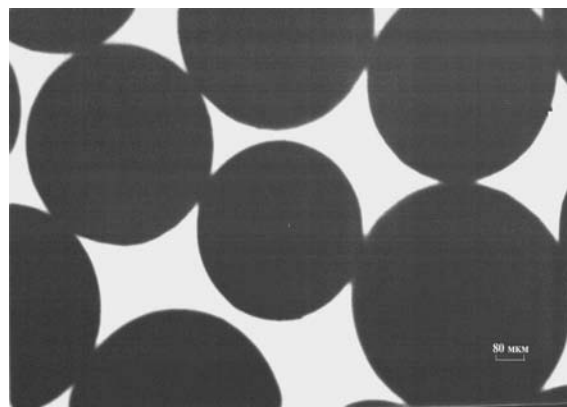

Fig.1 Microphotography of PMMS

Diameter of PMMS depends of properties of carrying medium (molecular mass, polarity, viscousity et cetera). The carrying medium in this work at synthesis, storing and investigation of PMMS are ethanol in water and glycerin in water. The sizes of microsphers become more bigger after penetration molecule of medium in pored PMMS. The measuring of dependence of the average size PMMS on the time of staying in medium glycerin – water = 4 : 1 has shown, that diameter of PMMS is increasing with increase of time and at big time go out to plateau (fig.3).

We measured dependence of the average size of PMMS on the time in medium glycerin-water with different concentration of water: 4 : 0.1; 4 : 0.5; 4 : 1.5; 4 : 2. The final average sizes for these mediums were : 305.5 ± 1.6; 307.5 ± 1.7; 308.9 ± 1.7; 313.4 ± 1.7 μm accordingly.
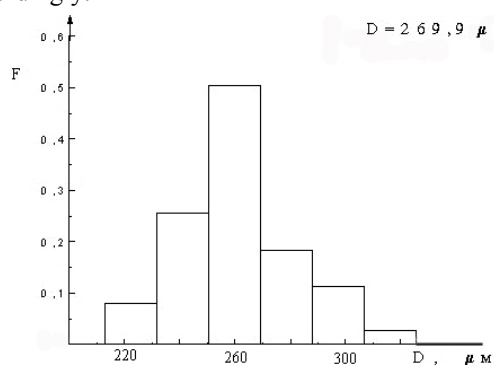

Fig.2 Size distribution histogram of PMMS

These sizes were depended on concentration of water in medium and were reaching during 30 – 48 hours. That's why all measuring of physical characteristics of PMMS were perfomed after passing 48 hours, that is after PMMS reached final sizes.

Magnetization measurement.

To investigate magnetic properties of nanoparticles in polymer matrix (PMMS) and to confirm the fact that nanoparticles do not aggregate in polymers as was proved by electron-microscopic investigation of PMMS section [15] we carried out PMMS magnetization measurement. The magnetization measurement was perfomed on vibration magnitometer perfomed on the base of electromagnet FL-1.
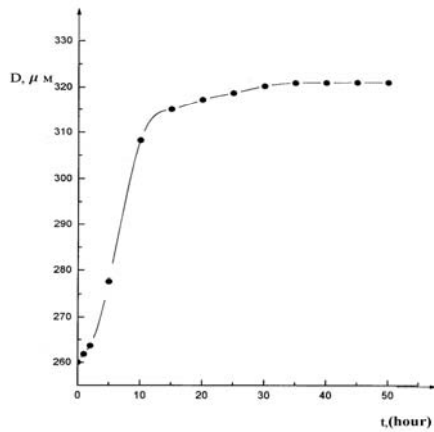
Fig.3 Diameter PMMS as a function of time in medium
glycerin-water at ratio 4 : 1

Magnetic field value varies up to 10^4 A/m . Magnetization determination was carried out according to the method given in [19]. The error was less than 3%.

In Fig.4 there have been shown PMMS magnetization curve obtained at volume concentration of magnetite nanoparticles φ_m=0.0098 at room temperature.

Magnetic susceptibility measurement of individual PMMS

To measure magnetic susceptibility we set up device similar to the given in [20]. Magnetic susceptibility of individual PMMS is determined on PMMS speed measurement in viscous medium in nonuniform field of ferromagnetic cyllinder placed into uniform magnetic field. For determination magnetic susceptibility we used formulas from [20].
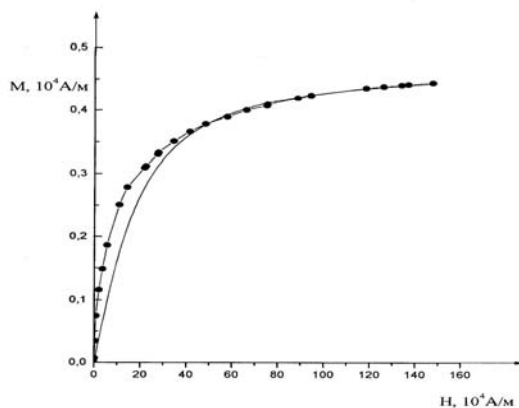

Fig.4 Experimental and calculated (unbroken) curves of
magnetization PMMS at nanoparticles concentration
φ_m=0.00984

Measurement of magnetic susceptibility of individual PMMS was carried out at room temperature at different intensities of magnetic field: 2.4, 50.0 and 206,84 kA/m. All these values of magnetic field are on the linear section of the dependence of magnetic field value on electric field intensity value in electromagnet coil FL-1. To fulfill the requirement of uniformity and small PMMS motion speed in gradient magnetic field (Reynolds number ~ 10⁻

3) as a viscous medium we use glycerin-water medium in the 4:1 ratio. Viscosity of this medium is equal to η = 38,85 mPa/s. It is measured at room temperature with viscosimeter VPJ-3, internal diameter of its capilary is 0.99 mm, viscosimeter constant is 0,777 mm/s.

3. INVESTIGATION RESULTS AND DISCUSSION

As it is seen from fig.4 PMMS magnetization curve at magnetite nanoparticle concentration φ = 0.0098 is characteristic of superparamagnetic mediums. Magnetization saturation is equal M=4.034 kA/m, initial magnetic susceptibility is equal χ_0 = 0.026. Average maximum and minimum diameters of magnetite nanoparticles defined from formula [13, 21] on the base of magnetization data are equal 3.78, 7.80 and 1.86 nm, respectively. Magnetic diametrs determined from data on the sample magnetization curve and obtained from electron microscopy data are in agreement.

Theoretical curve of magnetization plotted on the basis of Langeven equation is given on Fig.4(unbroken curve). As it is seen from Fig. 4 experimental and theoretical curves of magnetization are close to one another. It can indicate that magnetic diameters of nanoparticles are found properly on the basis of in method presented in [21] and magnetite nanoparticles in polymer matrix are isolated and placed at a certain distance, i.e. nanoparticles do not aggregate.

Periodical investigation of magnetite nanoparticles concentration in PMMS and their magnetic properties each 6 month show that their magnetic properties is remained constant during observed time interval. It points out that nanoparticles under the investigation are rigidly fixed in polymer matrix and their concentration does not changed by the time. Rigid fixing of nanoparticles in polymer matrix defines that their magnetization occurs according to Neel mechanism. Orientation of magnetic moment of nanoparticles in external magnetic field is carried out by the rotation inside the nanoparticles. Evaluation of relaxation time shows that it is equal to 7.028· 10^{-12}s. As the process duration of PMMS magnetization measurement is much more than relaxation time of nanoparticle magnetic moment, each nanoparticle is like a superparamagnetic one. We measured magnetic susceptibility of 120 individual PMMS, which average size is 269.9 μm at magnetite concentration φ_m=0.0098 at H=206.84 kA/m, its value has been chosen particularly for this nanoparticle concentration in polymer matrix and viscosity of carrying medium. Average value of magnetic susceptibility of one PMMS is equal to 4.79·10^{-3}. Histogram of PMMS number distrribution according to values of their sizes is given on Fig.2. Agreement of PMMS distribution histograms with the diameter and logarythmic values of magnetic susceptibility calculated by method of $\chi2$ criteria is equal to 95% that can be identified the correlation of magnetic susceptibility with PMMS diameter. On this base we plotted dependence of PMMS magnetic susceptibility on their diameter (Fig.5). Prelimenary, by method of 4-D and Q-criteria there have been rejected random values of magnetic susceptibility for all PMMS diameter values [22]. To explain this dependence (Fig.5) we supposed that PMMS consist of

disks of different diameter. Disk thickness is equal to the distance between magnetite nanoparticles and consequently these disks consist of only one layer of nanoparticles. Thus, general magnetic moment of PMMS is equal to the sum of disk magnetic moments of different diameter. Magnetic moments of disks, in turn, consist of magnetic moments of sum of magnetic moments of chains, arranging along the diameter and lines parallel to disk diameters.

Magnetic moment of nanoparticle chains depends on the magnetic moment of each individual particle and quantity of nanoparticles in the chain which in turn depend on the interaction force between the particles and value of external magnetic field [23]. At big values of magnetic field and small quantity of nanoparticles in chains (because of small concentration or small diameter of PMMS) magnetic moment of chain is determined by total amount of nanoparticles in it, i.e. all nanoparticles take part in magnetization. At small values of magnetic field intensity magnetic dipole-dipole interaction plays an important role in the magnetization chains [14]. In this case energy of dipole-dipole interaction is more than energy of magnetic dipole interaction with external magnetic field.
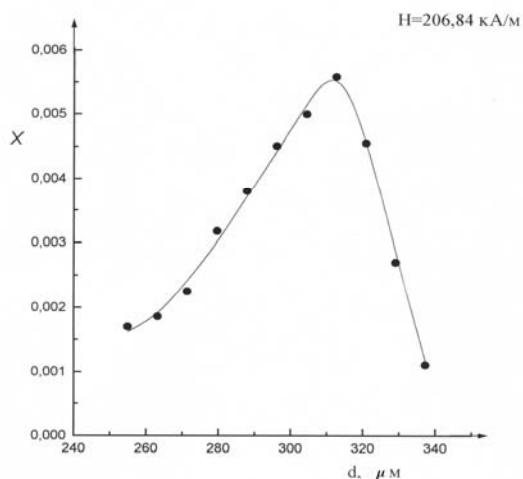

Fig.5 Magnetic susceptibility as a function of diameter PMMS

Therefore at small values of magnetic field intensity and big amount of magnetite nanoparticles in the chain (because of nanoparticles concentration is increased or PMMS diameter is increased) the part of nanoparticles in neighboring chains form closed subsystems with total zero magnetic moment, so nanoparticles amount taking part in the magnetic moment is decreased. In this case chain length also decreases and it brings the decrease of magnetic moments of each individual chain and each individual cross-section. As a result PMMS total magnetic moment decreases. As we suppose PMMS magnetization of small diameters (d=294.22 μm, see Fig.5) occurs at the expense of chain magnetization resulting from magnetite nanoparticles arranged along the line of external magnetic field. Nanoparticles chains with magnetic dipol-dipol interaction magnetize by method of parallel remagnetization. With the increase of PMMS diameter up to value 294.22 μm there have been taken

place increase of nanoparticles amount in chains and values of magnetization and magnetic susceptibility are increased respectively. Initial magnetic susceptibility of PMMS, which we calculated by formula [14] is equal to $1.698 \cdot 10^{-3}$, that correlates with the experimental values obtained from measurements of individual PMMS magnetic susceptibility with small diameter (d=223.2 μm, $\chi = 1.68 \cdot 10^{-3}$, d=232.3 μm, $\chi = 1.92 \cdot 10^{-3}$) Fig.5, initial section.

Dependence of PMMS magnetic susceptibility on magnetite concentration at small values of concentration was investigated to confirm above-mentioned mechanism of magnetization. We investigated dependence of PMMS magnetic susceptibility on magnetite concentration at φ_m= 0.0007, 0.0001, 0.003, 0.008 and 0.01 and magnetic field H=50 kA/m. The investigations shaw that at small concentrations of magnetite PMMS magnetic susceptibility is increased with concentration growth and this dependence can be described by linear formula:$\chi = 0.69 \cdot \varphi_m - 0.52 \cdot 10^{-3}$. It confirms our suggestion that at low concentrations all nanoparticle chains formed from magnetite nanoparticles take place in magnetization process. Concentration increasing leads to the grouth of nanoparticle amount in chains and consequently to the increasing of magnetic susceptibility.

At big diameters of PMMS (d>294.22 μm) and constant concentration the amount of magnetite nanoparticles localized in microsphere diameters is increased. The amount of magnetite nanoparticles with average diameter d=5.48 nm being in PMMS with diameter 304.36, 314.51 and 324.1 μm determined on the base of PMMS magnetite concentration data (φ_t =0.013) is equal to 17913, 18510 and 19076, respectively. The amount of magnetite nanoparticles in external magnetic field confined in the chain at H=206.8 kA/m calculated by the formula [23] is equal to 16310, 14310 and 13096, respectively. As it seen at big diameters of PMMS there has been taken place decrease of nanoparticle amount in chains that brings about the decrease of chain magnetic moments and then magnetic susceptibility of PMMS.

Thus analysis of studies under the investigation shows that magnetic nanoparticles are uniformly distributed over PMMS. Nanoparticles size of magnetite does not change during PMMS synthesis. Magnetic diameters of nanoparticles determined from PMMS magnetization curve and calculated from corresponding geometric diameters are in agreement. PMMS have superparamagnetic properties. Magnetic characteristis of PMMS are defined by magnetic nanoparticles characteristics and their concentration. PMMS magnetization arises from to the orientation of total magnetic moment consisting of PMMS magnetic moment of discs sums and they consist of magnetic moments of magnetite nanoparticles chains arranged along the diameter and lines parallel to PMMS diameters. At PMMS small diameters and big magnetic fields all nanoparticles of magnetic chains take part in magnetization, but at PMMS big diameters and small magnetic field formation of closed dipole subsystems is occurred and therefore PMMS magnetization is decreased.

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