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Physical Characteristics of Polymer Magnetic Microspheres

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Abstract

In this study the structure and the magnetic properties of polymer microspheres, filled with magnetite nanoparticles are investigated. Average particle size of magnetite nanoparticles before and after being introduced into polymer microspheres, and the distance between nanoparticles in the polymer microspheres, are measured. Magnetization curve of polymer magnetic microspheres (PMMS) is determined.

The magnetic susceptibility of PMMS with various diameters, and the dependence of PMMS magnetic susceptibility on diameter are determined. Magnetization occurs due to the orientation of PMMS as a magnetic moment. The total magnetic moment of PMMS is the sum of magnetic moments of PMMS sections which consist of magnetic moment chains of magnetite nanoparticles lined up along the diameter and lines parallel to the diameter of the PMMS sections.

Analysis of results showed that magnetite nanoparticles are uniformly distributed all over the microspheres and do not aggregate during PMMS synthesis. PMMS is superparamagnetic. Analysis of the dependence of PMMS magnetic susceptibility on the diameter shows that for small diameters (d $<$ 300 μm), all magnetite nanoparticles in chains are lined up along the external magnetic field. That is, all magnetite nanoparticles in chains take part in the magnetization. However, for large diameters, some parts of chains in sections are transformed into clusters, this reduces the length of chains and decreases the magnetic susceptibility of PMMS.

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1. Introduction

The characteristics of magnetic nanoparticles 3–15 nm in diameter in diffrent mediums have been widely investigated [1-4]. Magnetic nanoparticles have specific properties different from massive magnetic materials.Magnetic nanoparticles, suspended in liquid organic mediums are used in the development and design of apparatus and devices [5,6]. One particular composite material, polymer microspheres filled with magnetic nanoparticles in the form a polymer matrix (PM), is of particular interest. PM has many advantages when compared with liquid materials. With the magnetite nanoparticles firmly fixed in the PM, there is no coagulation of nanoparticles, i.e. magnetite nanoparticles remain fixed and scattered. The PM also acts to stabilize the magnetite nanoparticles, preventing their oxidation and stabilizing other properties over long periods. PM has high dielectric permeability (for example $\varepsilon_{\text{polysterole}} = 2.5$–$2.6$ at 10^6 Hc). Polymer microspheres filled with magnetite nanoparticles are dielectric , and they have specific electric and magnetic properties in high frequency electromagnetic fields. To simplify the present discussion, polymer microspheres filled with magnetite nanoparticles will be referred as polymer magnetic microspheres (PMMS).

The purpose of the present work is to investigate the structure, magnetic characteristics, and magnetization mechanism of PMMS materials.

2. Materials and Methods of Investigation

2.1. Preparation of PMMS

PMMS were prepared by introducing magnetic nanoparticles into the polymer matrix.

Collagen and polystyrene were used as polymer matrix.

Magnetite nanoparticles were introduced into the polymeric microspheres by two methods. In the first method(a), nanoparticles were introduced during the synthesis of polymeric microspheres. In the second method(b), porous presynthesized polymeric microspheres were treated with Fe(II) and Fe(III) salt solutions ,after this treatment magnetite nanoparticles were precipitated.

Method a)-Freshly precipitated magnetite suspension was added to a Gelatin solution of 15% (400ml) by continous stirring. In order to obtain gelatinous microspheres ,first the gelatine solution was dispersed in a nonpolar organic solvent then it was treated with dialdehyde solutions of 1.4-1.75 % and regenerating agents. At last, microspheres were separated.

Method b)- Porous presynthesized polymeric microspheres were introduced into a solution of Fe salts. By adding excess alkali to the solution, magnetite was precipitated. As a result ,magnetite nanoparticles were deposited in the pores of the polymeric microspheres.

Polystyrene-based magnetic microspheres were made as follows. Styrene monomers were polymerized in a magnetic liquid medium by suspension polymerization. In this polymerization technique it was possible to obtain polymer microspheres in the desired size ranges with a narrow size distribution .The surface of polystyrene microspheres thus obtained by this method is electrically neutral. A complete description of the synthesis and the polymerization procedure for PMMS at various magnetite nanoparticle concentrations and their physical properties are given in the following references [7,8]. By chemically modifying the surface of the magnetic microspheres, or using different comonomers, it is possible to obtain magnetic polymeric microspheres having surface characteristics, varying from hydrophobic to hydrophilic. It is also possible to obtain surfaces charged positively or negatively, or to introduce different functional groups. The optimum magnetite –to-gelatin weight ratio varies from 1:0.5 to 1:10. At ratios lower than 1: 0.5 it is difficult to prepare PMMSs due to high solution viscosity and at ratios higher than 1:10 the percentage of magnetite in the microspheres prepared becomes less (less than 2%).

The main statistical parameters of synthesized PMMS are given in Table.

2.2. Determination of Volume Concentration of Magnetite Nanoparticles in PMMS.

Concentration of magnetite nanoparticles was determined by spectrophotometric method [9]. First, PMMS was dissolved in sulphuric acid. Then,5 ml of aliquot was removed from the solution and 10 ml of newly-made 5% sodium tartarate ($Na_2C_4O_6$) and 10 ml of 2% 1,10-phenanthroline monohydrochloride ($NaNH_2OHCl$) were added to this aliquot.Enough water was added to bring the solution up to 100 ml.This solution was set aside for 30 minutes , then its optical density at $\lambda = 516$ nm was measured by a SPECORD UV VIS spectrophotometer.

In order to determine the concentration of Fe in the solutions, a calibration curve was developed from a set of standard solutions with varying Fe^{3+} concentrations.Calibration curve is shown in Figure 1. The relation between optical density and Fe^{3+} concentration can be described by the linear equation

$OD = -0.077 + 7.86\, n_{Fe^{+3}}$, where OD is the optical density of solution, n is the concentration of Fe^{+3}.The volume concentration of Fe ($\varphi_{Fe+3} = V_{Fe}/V_{solution}$) was converted to the magnetite concentration ($\varphi_m = V_{magn}/V_{solution}$) using the formula $\varphi_m = k{\cdot}\varphi_{Fe+3}$, where 0.24 is the ratio between the molecular weights of Fe and magnetite.

Table. Main statistical parameters of distribution of PMMS: (a), (b) – introduction and saturation methods of filling PMMS by magnetite nanoparticles, respectively. $\overline{d}$, $\overline{D}$ - average diameter of magnetite nanoparticles and PMMS, respectively; ε, p_k - coefficients of asymmetry and polydispersity of distribution PMMS in size, respectively.

Samples	$\overline{d}$, nm	$\overline{D}$, μ m	ε	p_k
PMMS, Ia	9.48 ± 0.149	257.5 ± 1.93	0.496	1.059
		171.6 ± 1.57	0.485	1.087
PMMS, IIa	7.7 ± 0.145	246.2 ± 1.5	0.191	1.037
		188.7 ± 1.39	0.014	1.052
PMMS, IIIa	7.3 ± 0.108	251.3 ± 1.69	0.341	1.046
		184.5 ± 1.52	0.401	1.063
PMMS, IVa	5.4 ± 0.073	218.1 ± 0.94	0.284	1.035
		171.6 ± 0.83	0.456	1.027
PMMS, IVb	5.4 ± 0.073	269.9 ± 1.47	0.284	1.029
		201.3 ± 1.25	0.271	1.039

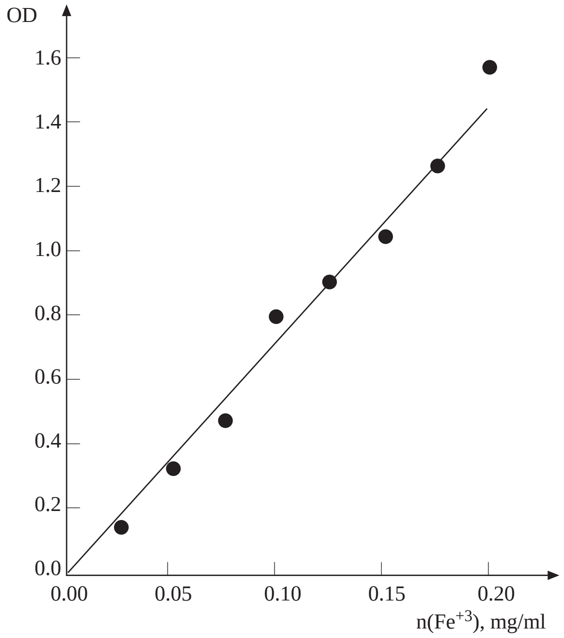

Figure 1. Calibration curve of determination of Fe^{+3} concentration in solutions by spectrophotometric method.

The composition of standard and working solutions and the method of preparation of these solutions are as follows ;

Standard solution: A 0.1 mg/ml Standard solution of Fe is prepared by dissolving 0.7238 g chemically pure $Fe(NO_3)_3{\cdot}9H_2O$ in distilled water. 2–3 ml of HNO_3 ($\rho = 1.40$ g/cm^3) is added for the transition of Fe^{+2} to Fe^{+3}. Common volume of solution is brought up to 1 l.

Working solution: Working solution is composed of the following reagents: 1.5% sodium tartarate ($Na_2C_4O_6$) , 2.2% freshly prepared hydroxylamine hydrochloride NH_2OHHCl (2 g of NH_2OHHCl), 25% sodiumacetate ($NaC_2H_3O_2$) and 0.2% o- phenanthroline (0.2 g).

Fe concentration in the reference solution is 0.01 mg/ml.

2.3. Preparation of PMMS for Investigation by Electron Microscope

PMMS were successively dehydrated in 50, 60, 70, 80 and 96% ethanol, 20 min in each solution, then two times in acetone (1 h each application).

Three mixtures were produced as follows. Beforehand one can prepare first the following mixture: EPON 812 resin, DDSA (dodecenyl succinic acid), and MNA (methylnorbornene-2,3-dicarboxylic anhydride) in the ratio 54:36:24. EPON 812, ethylene carboxylic acid, is a resin frequently used in the fixing of objects for observation under an electron microscope. DDSA and MNA are used as hardeners of the EPON 812 resin. The second mixture was obtained by merging the first mixture with DMP-30 epoxy accelerator (2,4,6-tris (dimethylaminomethyl) phenol) at concentration ratio 57:0.61. A set of third mixtures was obtained by merging the second mixture with the acetone at different concentrations: 1:3, 1:1, 3:1. PMMS was then place in each of the third mixtures (1:3, 1:1, 3:1) and kept for 1 hour at room temperature. Next, the PMMSs were sealed in capsules at 60 °C and stored for a day to cure the resin. Thus, the PMMS were fixed in the hardened resin.

The knives for sectioning the resin-fixed PMMS specimens were prepared as described in [10]. PMMS sections on the order of 50 nm were cut on a LKB 2128 UM IV Microtome. The specimens were cut with an LKB UM IV Ultratome-2128 into 50-nm-thick sections, which were examined on a Philips EM200 electron microscope under 40 000 and 50 000.

2.4. Measurement of PMMS's Magnetic Characteristics

PMMS magnetization was measured by a vibrating sample magnetometer (VSM) in the range 0–16 × 10^5 A/m at room temperature. A standard laboratory magnet capable of producing fields up to 2 Tesla (20,000 Oe or 0–16 × 10^5 A/m) was used. In vibrating sample magnetometry (VSM), a sample is positioned within suitably placed sample coils, and is made to undergo sinusoidal motion, i.e., mechanically vibrated. The resulting magnetic flux changes induce a voltage in the sample coils that is proportional to the magnetic moment of the sample. The applied field may be produced by an electromagnet. The accuracy in the measurement of magnetization is 1%.

Magnetic susceptibility of individual PMMSs was determined by measuring the velocity of microspheres in a viscous fluid in a nonuniform field of a ferromagnetic cylinder placed in a uniform magnetic field. The magnetic field gradient was determined by the method described in [11]. Uniform magnetic field has been created by electromagnet FL-I (producing fields up to 1 Tesla, 10,000 Oe). Basic technical characteristics of electromagnet FL-1 is: nominal electric current - 16 A, nominal electric voltage - 220V, capacity- 2.9kW, changeable shoes - with 100, 80, 50, 20, 10, 5 mm in diameter. Holl detector DX611817A with a sensibility of 187.6μV/μTl was used for the detection of magnetic field value. Also, the dependence of magnetic field value on the electric current value in coil of electromagnet FL-I is known. On the base of the electromagnet FL-I the installation has been created similar to described one in [12]. Magnetic susceptibility of individual PMMS is calculated from the formulas [12]

$$\chi = \chi_0 + \frac{12\pi\eta R_0 D r^5}{t\mu_0 V M_s a^2 (M_s a^2 + 2H_0 r^2)}, H_0 > M_s/2$$

and

$$\chi = \chi_0 + \frac{3\pi\eta R_0 D r^5}{t\mu_0 V \frac{\mu-1}{\mu+1} H_0^2 a^2 (\frac{\mu-1}{\mu+1} a^2 + r^2)}, H_0 < M_s/2,$$

where $\chi_0 = 10^{-6}$ is the magnetic susceptibility of the viscous medium; r is the distance from the axis of the cylinder to the center of the PMMS; R_0 and V are the PMMS radius and volume, respectively; $a = 1.008$ μm is the radius of ferromagnetic cylinder; η is the viscosity of the medium; μ_0 is the magnetic constant;

$M_s = 0.5 \times 10^5$ A/m is the saturation magnetization of the ferromagnetic cylinder; H_0 is the magnetic field; t is time for the PMMS to pass through the distance r; and $D = 86.31$ is the gain parameter.

Magnetic susceptibilities of 120 individual PMMS-IVb samples with magnetite nanoparticle concentration $\varphi_t = 0.013$ were determined. Magnetic susceptibility was measured in the magnetic field, $H = 206.84$ kA/m. Magnetic susceptibility versus diameter for PMMS-IVb (measurements on 120 microspheres) was determined.

The magnetic susceptibility of PMMS-IVb with magnetite nanoparticle concentration $\varphi_m = 0.0007$, 0.001, 0.003, 0.008, 0.01 was determined at $H = 50$ kA/m. Measurements were made in magnetic fields of 2.4, 50, and 206.4 kA/m, which is in the linear part of the dependence of the magnetic field on the electric current through the coils of the FL-I.

A glycerin-water medium in 4:1 ratio was used as viscous carrying medium to obtain uniform and small velocity motion of PMMS under gradient of magnetic field (Reynolds number is equal to 10^3). The viscosity of this medium is 38.87 mPa·s. The viscosity was measured at room temperature by viscosimeter VPJ-3 with the following characteristics: inner diameter of capillary pipe is 0.99 mm, viscosimeter constant is 0.774 $\mathrm{mm}^2/\mathrm{s}^2$.

2.5. Mathematical Processing of Experimental Evidence.

Statistical moments and parameters of distribution, construction of histograms were carried out on the basis of experimental data [13]. First, all experimental data was transformed into dimensionless data. Transition to dimensionless is carried out by the formula: $x = x_{min} + t(x_{max} - x_{min})$, where x_{min}, x_{max} are minimum and maximum value of experimental data, t- is varied within the interval [0, 1]. x may be designed size of PMMS, magnetite nanoparticles, and logarithmic value of PMMS magnetic susceptibility.

Histograms of the distribution of magnetite nanoparticles by size and logarithmic value of PMMS magnetic susceptibility were determined on the basis of electron microscopy data and logarithmic value of PMMS magnetic susceptibility data, respectively. Agreement of two histograms of distribution has been investigated by χ^2 criterion method.

Average, maximum and minimum magnetic diameter of magnetite nanoparticles was determined by formula [14, 15].The magnetic diameter of magnetite nanoparticles was determined by using the magnetization data . First, random values of magnetic susceptibility for certain diameter values of PMMS were neglected by 4 $\overline{D}$ and Q criterion methods.

The number of magnetite nanoparticles localized in the PMMS diameters were calculated based on these particles concentration in PMMS. Number of magnetite nanoparticles lined in the diameter of PMMS is calculated from formula: $N = \frac{D}{2d(k/\varphi_t)^{1/3}}$, where D, d is the diameter of PMMS, magnetite nanoparticles respectively, k is the coefficient of packing, φ_t is the concentration of magnetite nanoparticles.

The programs for statistical analysis, determination of histogram of distribution and carrying out 4 $\overline{D}$, Q and χ^2 criterion methods were written by author in FORTRAN algorithmic language [16]. Programs are realized on IBM compatible computer.

3. Results and Disscusion

In Figure 2a electron microphotography of PMMS-IVb sections with concentration of magnetite nanoparticles $\varphi_t = 0.013$ are presented. As it is shown in Figure 2a magnetite nanoparticles are distributed uniformly all over the polymer microsphere. Average distance between magnetite nanoparticles determined from PMMS-IVb section is equal to 17.4 nm. Diameter of magnetite nanoparticles before and after their filling into the polymer microspheres is equal to $d = 5.44$nm. Histogram of distribution of magnetite nanoparticles in size is shown in Figure 2b. This histogram is constructed according to the diameter data obtained from electron-microscopy investigation of PMMS-IVb sections. The histogram obtained is in good agreement with the histogram, obtained for the sample of magnetite nanoparticles -IV in liquid medium [17].

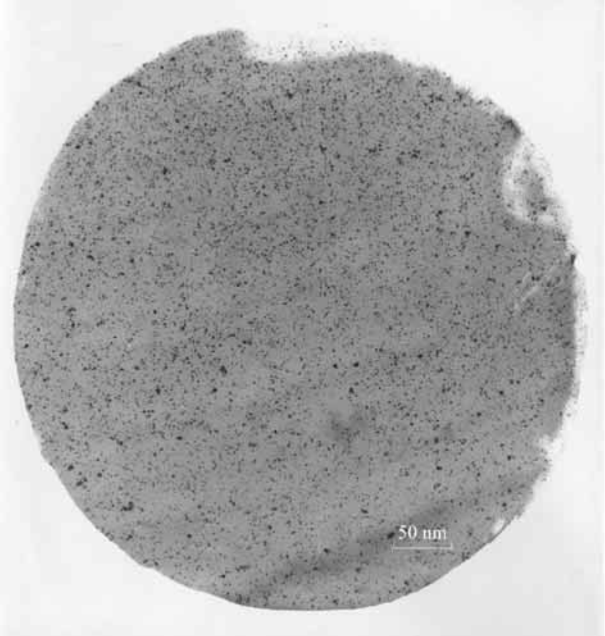

Figure 2a. Electron microphotography of PMMS-IVb section at magnification 50000.

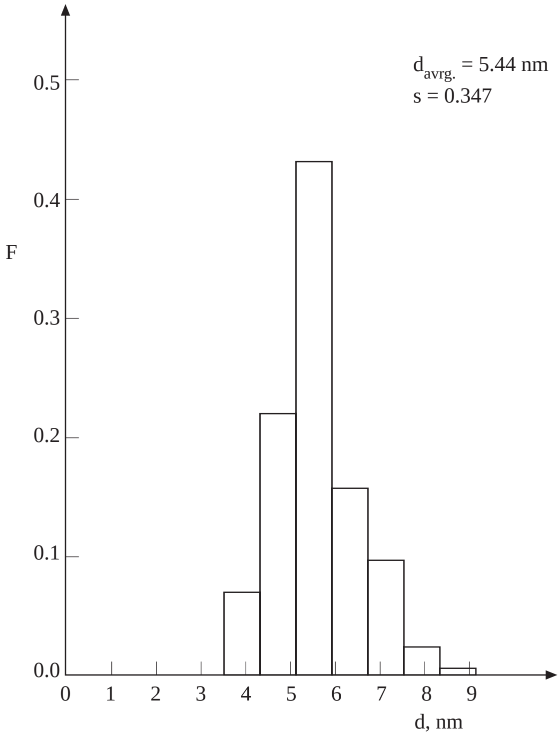

Figure 2b. Histogram of the distribution of magnetite nanoparticles by size.

In Figure 3 magnetization curve of PMMS-Ivb versus concentration of magnetite $\varphi_m = 0.00984$ (line + symbols)is shown.From the figure, the magnetization curve of PMMS-IVb is characteristic for super-paramagnetic medium. As magnetite nanoparticles are fixed hard in the polymer matrix, magnetization of nanoparticles obeys the Neel mechanism. Orientation of magnetic moment of nanoparticles in the external magnetic field is carried out by rotation within nanoparticles. Estimation of relaxation time of magnetite nanoparticles for sample -IV shows, that it is equal to 7.028 × 10^{-12}s. If the duration of PMMS magnetization measurement becomes longer than the relaxation time of magnetic moment, each nanoparticle acts like a superparamagnet.

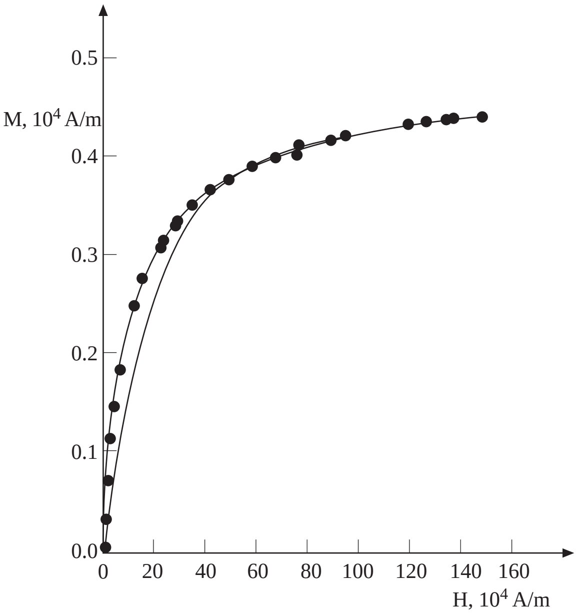

Figure 3. Magnetization curves of PMMS-IVb, obtained at concentration of magnetite nanoparticles φ_m = 0.000984 by vibration sample magnetometry (line+symbols) and calculated by Langevan equation (solid line).

The average, maximum and minimum magnetic diameter of magnetite nanoparticles are equal to 3.78, 7.8 and 1.86 nm, respectively. Magnetic diameters, determined from the corresponding geometrical diameters of magnetite nanoparticles by the formula $d_m = d_g$- 1.68 nm in [15] are in agreement with these values.

Theoretical curve of magnetization, determined by Langevan equation is presented in Figure 3 (solid line). As it is seen from figure, experimental and theoretical magnetization curves are very close to each other.

The average value of PMMS-IVb magnetic susceptibility is equal to 4.79 × 10^{-3}.

The distribution histogram versus logarithmic value of magnetic susceptibility of PMMS-IVb was constructed. Comparison of the histograms of PMMS-IVb distribution on diameter and logarithmic value of magnetic susceptibility showed that they are similar. The agreement is 95%. So, there is a relationship between the magnetic susceptibility of PMMS-IVb and its diameter. The curve showing this relationship is given in Figure 4.

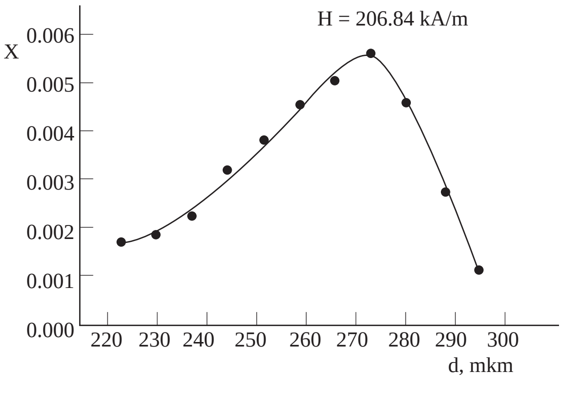

Figure 4. The relationship between the magnetic susceptibility of PMMS-IVb and diameter.

In order to describe this relationship (Figure 4) we suggested, that general magnetic moment of PMMS-IVb consists of the sum of magnetic moments of PMMS sections. The magnetic moment of PMMS sections consists of magnetic moments of magnetite nanoparticles chain lined up along the diameter and lines parallel to diameter of polymer microspheres. Magnetization arises due to orientation of general magnetic moment of PMMS. The value of magnetic moment of chains depends on the number and value of magnetic moment of magnetite nanoparticles. Moreover, the number of magnetite nanoparticles depends on the value of energy interaction between nanoparticles and external magnetic field intensity [18]. For high magnetic fields and small number of magnetite nanoparticles in the chains,the total number of magnetite nanoparticles are determined by magnetic moment of chains. This case is achieved by decreasing concentration of magnetite nanoparticles, or by decreasing diameter of PMMS. At small values of magnetic field intensity and at large number of magnetite nanoparticles in chains, part of magnetite nanoparticles chains are transformed into clusters. In this case, the length of chains is decreased. This as a result causes a decrease in the magnetic moment of chains, sections and PMMS, respectively. This can be attributed to the increasing concentration of magnetite, or increasing diameter of PMMS.

Magnetization of medium with small concentration of magnetite nanoparticles on the base of the model of chain magnetization of magnetite nanoparticles with magnetic dipole-dipole interaction has been investigated in early work of the author [19]. Initial magnetic susceptibility of these systems is calculated from the formula [19]

$$\chi_0 = \frac{1}{3} M_s \varphi_m \frac{m}{kT} + \frac{1}{27} M_s^2 \varphi_m^2 \frac{1}{\mu_0} \ln\left(\frac{V M_s}{m}\right)\left(\frac{m}{kT}\right)^2$$

where M_s- saturation magnetization of massive magnetite, φ_m- volume concentration of magnetite nanoparticles, m – magnetic moment of magnetite nanoparticles, μ_0- permeability of vacuum, V- volume of the sample.

Initial magnetic susceptibility of PMMS-IVb, calculated from this formula is equal to 1.698×10^{-3}. It is in good agreement with experimental value of magnetic susceptibility of individual PMMS-IVb obtained at small diameters of PMMS. At diameters of PMMS $d_{PMMS} = 223.2$, 233.3 μm magnetic susceptibility of PMMS is $\chi_1 = 1.681 \times 10^{-3}$, 1.92×10^{-3} respectively (see Figure 4, initial part of curve).

Investigation of the dependence of PMMS-IVb magnetic susceptibility on concentration of magnetite nanoparticles shows, that at small concentrations of magnetite nanoparticles PMMS-IVb magnetic susceptibility increases with the increase in the concentration of magnetite. This dependence may be described by the linear equation $\chi = 0.69\varphi_m$ - 0.52×10^{-3}.

Calculated and experimental values of magnetic susceptibility at small concentrations of magnetite nanoparticles supports our suggestion that at small concentrations or at $d < 294.22$ μm, all chains of magnetite nanoparticles take part in the process of magnetization. In this case an increase in concentration leads to an increase in the number nanoparticles in the chains. So, magnetic susceptibility of PMMS-IVb is increased, respectively.

At large diameters of PMMS-IVb ($d > 294.22\mu$m, see Figure 4) and at constant concentration of magnetite nanoparticles the number of magnetic nanoparticles, localized in the diameter of PMMS-IVb increases. Number of magnetite nanoparticles with an average diameter of $d = 5.44$ nm, localized in PMMS-IVb with diameters 304.36, 314.51 and 321.13 μm, at a magnetite concentration of $\varphi_t = 0.013$ is equal to 17913, 18510 and 19076, respectively. Number of magnetite nanoparticles in the chain lined up in the external magnetic field, $H = 206.84$ kA/m calculated from formula [14] is equal to 16130, 14310 and 13096, respectively.In this case ,i t is observed that a decrease in the length of chain at large diameters of PMMS-IVb takes place. This leads to a decrease in the magnetic moment and magnetic susceptibility of PMMS-IVb.

The analysis of the investigations showed that magnetite nanoparticles are evenly distributed in PMMS. The size of magnetite nanoparticles does not change during the synthesis of PMMS. This is because the aggregation of magnetite nanoparticles during synthesis of PMMS does not occur. The distribution of magnetite nanoparticles in size does not change during synthesis of PMMS. The magnetic diameters of magnetite nanoparticles, determined from the magnetization curve of PMMS are consistent with the calculated values obtained from corresponding geometrical diameters. PMMS have superparamagnetic properties. The magnetic characteristics of PMMS are determined from the magnetic characteristics of magnetite nanoparticles and their concentrations in PMMS.The magnetization of PMMS at small diameters is due to the orientation of its total magnetic moment. The total magnetic moment of PMMS is the vector sum of magnetic moment of sections and the vector sum of magnetic moment of sections is the sum of magnetic moment of chains of magnetite nanoparticles. In this case, all magnetite nanoparticles take part in the process of magnetization of PMMS. In the PMMS with large diameters, partial transformation of chains to clusters takes place, and magnetic moment decreases, respectively.

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