

Preparation, Structure, and Magnetic Properties of Poly(vinyl alcohol)–Fe₃O₄ Polymeric Nanocompositions

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Abstract—The influence of preparation conditions on the structure of poly(vinyl alcohol)–Fe₃O₄ nanocomposites was examined. The size of single-crystal single-domain particles of the magnetic nanophase (~3–80 nm) and their degree of aggregation during the synthesis of magnetite at high pH values were found to be determined to a considerable extent by the microviscosity of the reaction medium. A dramatic increase in coercivity (9×10^{-4} – 90×10^{-4} T) with an increase in the degree of aggregation is due to the presence of strong interactions between magnetic particles in compact aggregates.

Developing procedures for the synthesis of polymer nanocomposites with a magnetic component, revealing the mechanism of their formation and stabilization, and studying their structure are of great importance for gaining new information on the specifics of magnetic properties of substances in the nanosized state. The use of various polymer matrixes makes it possible to control the morphology of such systems, namely, the particle size, the distance between particles, and their degree of aggregation, with relative ease and over a wide range by varying the synthesis conditions [1–4]. The wide range of variation in structure characteristics presents a good opportunity for controlling magnetic interactions between particles in the nanophase and for studying the effect of these interactions and the size factor on the magnetic properties of nanosystems. In this work, we studied polymeric nanocompositions based on the hydrophilic polymer poly(vinyl alcohol) containing a magnetite (Fe₃O₄) nanophase as a magnetic component.

EXPERIMENTAL

Polymer film nanocompositions containing Fe₃O₄ were prepared in situ via the alkali hydrolysis reaction of a mixture of tri- and bivalent iron salts in the matrix of a chemically crosslinked PVAL gel [5]. The nanocompositions were synthesized as follows. To an acidic (pH ~ 1) aqueous PVAL solution containing a mixture of iron(III) and iron(II) chlorides in the mole ratio 2 : 1, respectively, an aqueous solution of glutaraldehyde as a crosslinking agent was added in an amount sufficient for 5% crosslinking of PVAL macromolecules. In

0.5–1 h, the solution gelled throughout its volume to form a transparent gel colored yellow-brown by iron salts. The water content of such a gel was 97% of the total mass of PVAL and water. Two versions of the synthesis of the Fe₃O₄ nanophase were used. According to the first version, the gel formed (gel I) was treated in a Petri dish with an alkali solution. The second version specified drying a PVAL gel with iron salts at room temperature (gel II). The transparent film formed was lifted from the Petri dish and treated in an alkali solution. The amount of water in the polymer matrix was ~50 wt %. Alkali treatment in both cases led to rapid coloring (from light brown to black) of the polymer gel as a result of formation of the Fe₃O₄ nanophase in the bulk. To synthesize magnetite, an NaOH solution of a rather high concentration (of 5 to 10 mol/l) was used. Otherwise, especially in the case of preparation of nanocompositions with a high Fe₃O₄ content, iron salts could have diffused from the bulk of the polymer gel to the solution.

X-ray diffraction patterns were taken on a Rigaku Geigerflex D/max-RC diffractometer. Electron microphotographs of freeze-fractured surfaces of film nanocompositions were taken with a Hitachi S-520 scanning electron microscope. The average size of Fe₃O₄ crystallites was determined by the standard procedure using the well-known Debye–Scherrer formula from the full width at half the maximum of the most intense X-ray reflection at $2\theta \sim 35^\circ$. Magnetization curves (plots of the magnetization M of a composite versus the magnetic field H) were recorded using a PARC-155 vibrating-sample magnetometer (Princeton Applied Research Corporation) operated at $H \leq 0.45$ T. To obtain magnetization curves for the Fe₃O₄ nanophase, corresponding experimental curves measured for nano-

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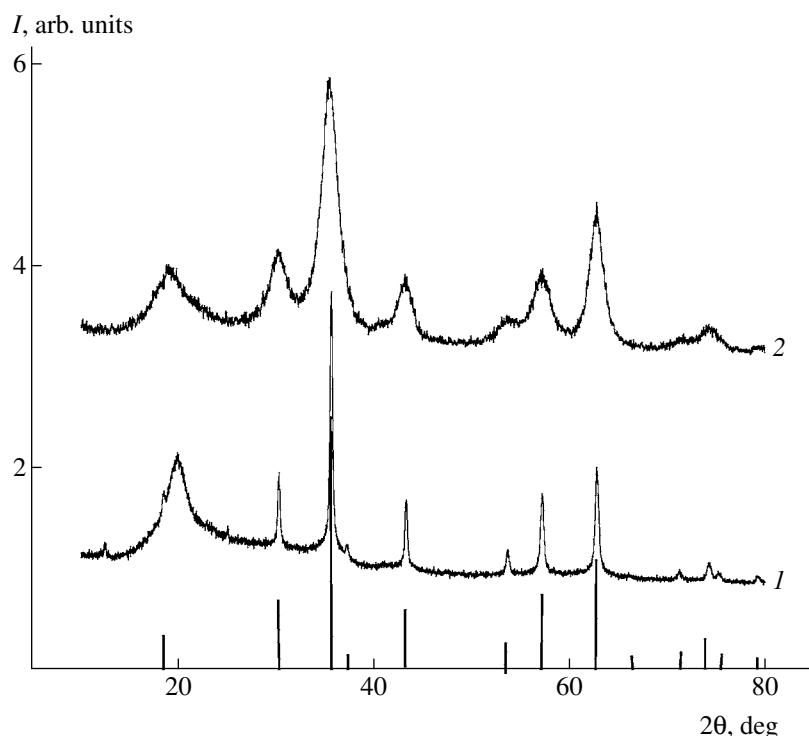


Fig. 1. X-ray diffraction patterns of PVAL-Fe₃O₄ compositions ($c_V = 18$ vol %) prepared from gels (1) I and (2) II in a 10 M NaOH solution and the X-ray stick diagram of Fe₃O₄.

compositions were processed with allowance for the dispersed component in the sample. From the magnetization curves, the value of coercive force H_c (the point of intersection of the curve with the abscissa) was determined. The value of saturation magnetization M_s was calculated by extrapolating the dependence of magnetization on the reciprocal field ($1/H$) to the ordinate in the H variation range of 0.1–0.45 T [6]. The relationship sought was approximated by a power polynomial. The amount of Fe₃O₄ (c_V) in a composition was given in volume percent. The c_V value was calculated from the mass concentration of magnetite c_m , taking into account the density of Fe₃O₄ and PVAL. The value of c_m was determined using thermogravimetric analysis (Mettler TA-4000 thermal analyzer) by examining the residue after sample combustion. The amount of magnetite in gel I compositions could have been as high as 40–45 vol %. The maximum concentration of Fe₃O₄ in gel II compositions was significantly lower (~20 vol %) because of crystallization of iron chlorides in the PVAL matrix upon drying the sample.

To verify the effect of the complexing power of the polymer matrix on the size of magnetite particles formed at high pH values, the Fe₃O₄ synthesis was conducted in a reaction medium containing a mixture of PVAL with the good complexing agent poly(acrylic acid) (PAA) taken in a mole ratio of 0.25. The formation of the Fe₃O₄ nanophase was effected in this case by the alkali treatment of a PVAL–PAA film specimen

with iron salts using the preparation procedure for gel II-based compositions. After completion of the reaction, samples in all cases were washed with water until neutral reaction and dried. To study the structure and magnetic properties of nanocompositions, films ~100 μm thick were used.

RESULTS AND DISCUSSION

Figure 1 shows typical X-ray diffractograms for PVAL–Fe₃O₄ compositions prepared from gels with high (gel I) and low (gel II) water contents. A comparison of the diffraction patterns with the tabulated stick diagram of magnetite indicates that the Fe₃O₄ nanophase is formed as a dispersed phase in the synthesis of the compositions of interest [7]. The presence of a broad reflection at $2\theta \sim 20^\circ$ is due to X-ray scattering by the organic matrix. Figure 2 depicts electron microphotographs of the compositions whose X-ray patterns are given in Fig. 1. As is seen from Figs. 1 and 2, the compositions prepared from gels I and II strongly differ in the character of diffraction patterns and electron microphotographs. The particle size of Fe₃O₄ calculated from diffractograms (D_{XRD} is 57 and ~4 nm for compositions I and II, respectively). The electron microphotograph of the gel-I-based composition distinctly displays dispersed-phase particles whose average size (D_{EM}) is ~120 nm. It is impossible to detect any particles in the electron microphotograph of the gel-II-based

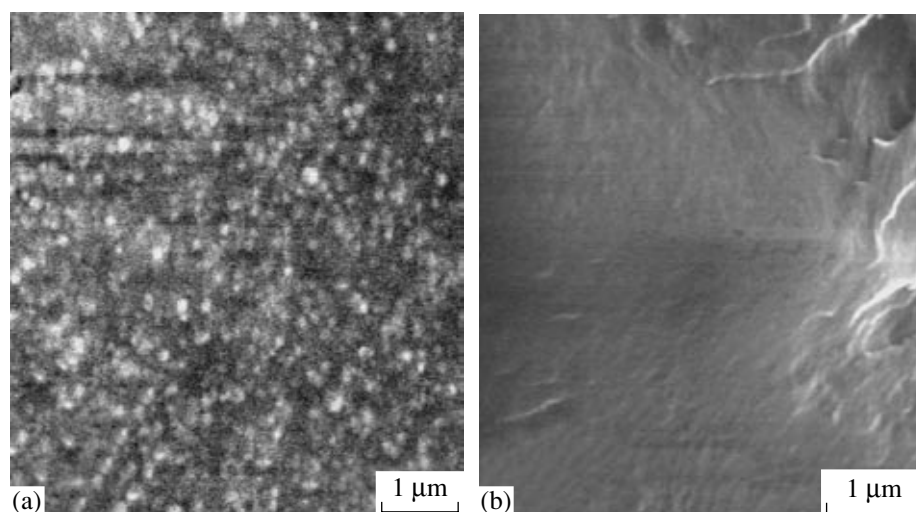


Fig. 2. Electron microscope images of PVAL–Fe₃O₄ compositions ($c_V = 18$ vol %) prepared from gels (a) I and (b) II in a 10 M NaOH solution.

composition. It should be assumed that we determine by the X-ray diffraction (XRD) technique the size of primary particles that can aggregate to form larger secondary particles detectable by the scanning electron microscopy (SEM) technique. The primary particles are undetectable by the SEM technique (probably, except very large entities whose size exceeds ~ 80 nm) because of its insufficiently high resolution, as well as because of electron beam-induced PVAL degradation at large magnifications. The level of aggregation of primary particles can be judged by comparing the size of primary (D_{XRD}) and secondary (D_{EM}) particles. The degree of aggregation, i.e., the number N of particles in an aggregate, was estimated as the ratio between the volumes of secondary and primary particles: $N = (D_{EM}/D_{XRD})^3$. The size of secondary particles for compositions prepared from gel I is ~ 80 – 200 nm.

Table 1. Influence of the amount of water in the reaction medium on the size of Fe₃O₄ particles in compositions with different dispersed-phase contents formed in 5 and 10 M NaOH solutions

c_{H_2O} , wt %	c_V , vol %	c_{NaOH} , mol/l	D_{XRD} , nm
97	18	10	57
	10.5	5	19
	5.5	10	37
	1	5	13
~50	18	10	3
	10.5	5	4
	5.5	10	8
	1	5	3

A decrease in the amount of water in the reaction medium (polymer gel) from 97 (gel I) to ~ 50 wt % (gel II) causes a dramatic decrease in the size of primary particles of the dispersed phase regardless of the composition of the material and the alkali concentration used in the synthesis of Fe₃O₄ (Table 1). The absence of secondary particles from the electron microphotographs of compositions prepared from gel II (a typical SEM image is shown in Fig. 2b) indicates that primary particles in this case either do not aggregate at all or the extent of such aggregation is well below that for the gel I compositions.

An increase in the pH (alkali concentration) and temperature of the reaction medium upon the formation of the magnetite nanophase in gel I leads to an intense growth in the size of primary Fe₃O₄ particles (Tables 2, 3). A comparison of the D_{XRD} and D_{EM} values presented in Table 3 shows that the aggregation number of primary particles formed on the basis of gel I strongly increases with a decrease in their size. Secondary particles in compositions formed at 3°C ($D_{EM} = 130$ nm) contain $\sim 5 \times 10^4$ primary particles ($D_{XRD} = 3.5$ nm). For compositions prepared at 75°C, the value of $D_{EM} = 100$ nm differs slightly from $D_{XRD} = 78$ nm; i.e., very large primary particles do not form compact aggregates as secondary particles. A study of the structure of the compositions at different dispersed-phase formation stages showed that the size of primary particles for gel-I-based specimens can strongly increase during the reaction. For example, in the case of compositions with 18 vol % Fe₃O₄ prepared using a 10 M NaOH solution, D_{XRD} increased at most tenfold, from 5 to 57 nm, as the reaction time was extended from 1 to 24 h. The size of secondary particles changed little under these conditions to ~ 100 – 130 nm, and the aggregation number N of primary particles correspondingly underwent a strong fall

from $\sim 10^4$ to 10. As follows from the data presented in Table 2 and 3, when the PVAL gel with a high water content (gel I) is used as a reaction medium, a strong influence of synthesis conditions on the size of primary magnetite particles is observed. The particle size of Fe_3O_4 can be varied only over a relatively narrow range with the use of the PVAL gel with a low water content (gel II) as a reaction medium. However, it should be noted that the direction of this change remains the same as in the case of gel I, depending on the preparation conditions; i.e., D_{XRD} increases with increases in the pH and temperature of the reaction medium (Table 4).

On the basis of published data [8, 9] and the results obtained in this work, we propose the following mechanism for the formation of the Fe_3O_4 nanophase in a high-pH alkaline medium in reactions directly in the PVAL matrix. The formation of a new phase via the step of generation of a critical nucleus suggests a decrease in the particle size with a rise in the supersaturation of the reaction medium as a result of an increase in the nucleation rate [10]. Such a dependence is observed in the synthesis of a magnetite colloid solution at moderately high pH values (an alkali concentration of ~ 0.7 mol/l) [11].

In contrast, an increase in the alkali concentration (i.e., growth in supersaturation) leads to a strong increase in the size of primary Fe_3O_4 particles in our case (Table 2). This indicates that the most probable mechanism of emergence of the magnetite nanophase at high pH values ($c_{\text{NaOH}} = 5\text{--}10$ mol/l) does not involve the formation of the critical nucleus. An alternative mechanism may involve the formation and subsequent consolidation of an amorphous network of associates of mixed iron(III) and iron(II) hydroxide. This mechanism is discussed in the literature in relation to the preparation of various metal hydroxides, in particular, the iron hydroxide $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ [8, 9]. The consolidation process is accompanied by crystallization of the mixed hydroxide yielding primary Fe_3O_4 particles. In the gel-I-based composition with a dispersed-phase content of $c_V = 18$ vol %, particles with a size of $D_{\text{XRD}} = 5$ nm are formed within 1 h as shown above. Hydroxide crystallization is assumed to be completed by this time, since saturation magnetization already reaches its maximum value of ~ 80 A m²/kg and the amorphous phase must not make a significant contribution to magnetization. Further transformations of primary particles are associated mainly with the processes of their coagulation and coalescence. Secondary particles constitute aggregates of primary entities bound by coagulation contacts. During coalescence as the complete merging of particles, the size of primary particles strongly increases: from 5 to 57 nm in 23 h for the case under consideration. Coagulation by forming a direct chemical bond between particles may develop into coalescence. If a polymer interlayer remains between particles upon their coalescence, such aggregates become

Table 2. Influence of the alkali concentration in the reaction medium on the size of Fe_3O_4 particles in compositions with different dispersed-phase contents prepared from a PVAL gel with a high water content (gel I)

c_{NaOH} , mol/l	c_V , vol %	D_{XRD} , nm
5	1	13
	18	7
	28	12.5
10	1	28
	18	57
	28	30

Table 3. Influence of the reaction temperature on the size of primary (D_{XRD}) and secondary (D_{EM}) Fe_3O_4 particles and on the aggregation number (N) of primary particles in compositions ($c_V = 18$ vol %) formed in a 10 M NaOH solution from a PVAL gel with a high water content (gel I)

T , °C	D_{XRD} , nm	D_{EM} , nm	N
3	3.5	130	5×10^4
20	57	120	10
75	78	100	1

Table 4. Influence of the alkali concentration and the reaction temperature on the particle size of magnetite in compositions with different dispersed-phase contents prepared from a PVAL gel with a low water content (gel II)

c_V , vol %	c_{NaOH} , mol/l	T , °C	D_{XRD} , nm
10.5	10	3	4.4
		20	5.1
		75	5.2
1	10	5	4.2
		20	4.0
		10	4.9
		10	5.7
		5	3.0
		20	
		75	

stable and the size of primary particles in the aggregates does not change.

The particle size decreases as the stabilizing effect of the polymer medium is enhanced [12]. The stabilizing action of the polymer matrix is in general due to intermolecular interaction at the interface in a high-dispersion system, as well as to microviscosity of the reaction medium, which is not related directly to this interaction but exerts a strong influence on the diffusion rate

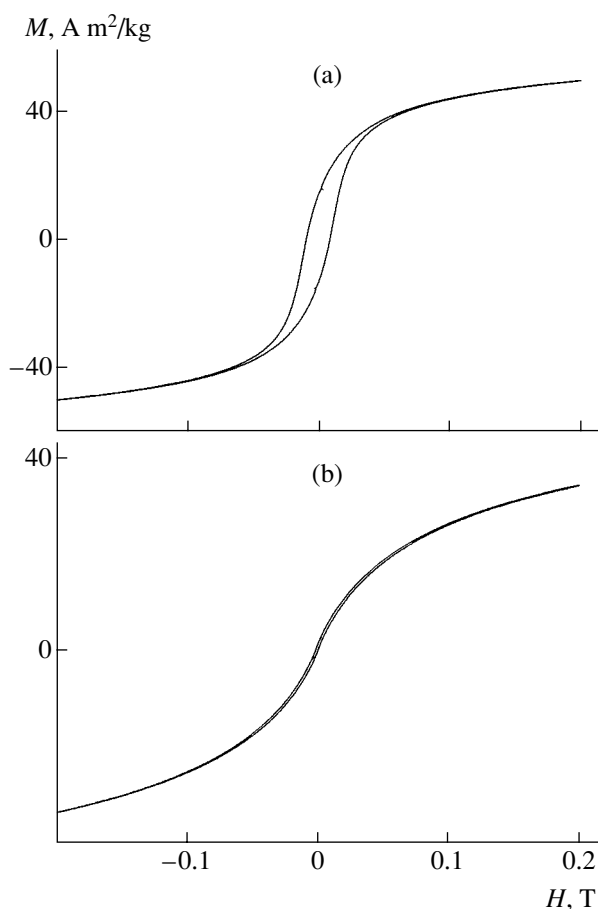


Fig. 3. Magnetization curves of the magnetite nanophase in PVAL-Fe₃O₄ compositions in the (a) presence and (b) absence of aggregation of primary particles ~4 nm in size: (a) the composition ($c_V = 18$ vol %) prepared at 3°C from gel I in a 10 M NaOH solution and (b) the composition ($c_V = 10.5$ vol %) prepared at 20°C from gel II in a 5 M NaOH solution.

of particles. Enhancement of intermolecular interactions facilitates an increase in the density of the polymer shell around particles of the magnetic component. Owing to screening the surface, the aggregation stability of the highly dispersed system increases. A decrease in microviscosity leads to a rise in the mobility of particles, which in turn increases the probability of formation of a coagulation contact. The size of aggregates increases under these conditions, and the coalescence process in these aggregates leads to a growth in particle size.

A considerable increase in the diameter of primary particles from 5 to 12 nm during the formation of the Fe₃O₄ nanophase in a medium that contains PVAL alone or a mixture of PVAL with the strong complexing agent PAA indicates that specific intermolecular interactions at the polymer-particle interface yielding strong coordination bonds are not displayed in the case

of synthesis of the magnetic component at high pH values (alkali concentration ≥ 5 mol/l). This is due to the fact that the bond between PAA carboxylic groups and iron ions does not form at high pH values. The same is obviously true for PVAL, which is a weaker complexing agent as compared with PAA. It should be assumed that the factors that determine the particle size of magnetite in our case are the microviscosity of the reaction medium and nonspecific interactions, such as van der Waals and hydrogen bonding, at the interface. Microviscosity increases with an increase in the polymer concentration in the reaction medium (decreases with an increase in the water content of the polymer gel). Thus, a growth in particle size in the presence of PAA may be explained in terms of the increase in the degree of swelling of the polymer matrix as a result of ionization of carboxylic groups in an alkaline medium, which leads to a decrease in its microviscosity. The strong decrease in particle size in compositions prepared from gel II as compared with those based on gel I must be due to an increase in the microviscosity of the medium and to the enhancement of nonspecific interactions at the interface with a growth in the polymer concentration in the reaction medium. An increase in the microviscosity of the reaction medium may also explain the decrease in the size of primary particles with the lowering reaction temperature.

The probability of formation of a dense coagulation contact between particles must increase with an increase in the collision frequency and the rate of chemical reaction between surface FeOH groups of colliding particles. Since the rate of this reaction and the rate of chemical processes occurring upon coalescence are determined by the pH level in the reaction medium, a rise in the alkali concentration must lead to a growth in the particle size of the dispersed phase (Table 2).

To summarize, the structure of PVAL-Fe₃O₄ polymeric nanocompositions (the size of particles and the degree of their aggregation) is determined to a considerable extent by the microviscosity of the reaction medium, as well as by nonspecific interactions at the interface and the rate of chemical processes occurring during the coagulation and coalescence of the particles. The influence of structure on the magnetic properties of nanocompositions was studied by analyzing magnetization curves for samples prepared under various conditions. The magnetic characteristics (first of all, H_c) depend both on the particle size of the magnetic component and interaction between particles of the magnetic nanophase [13–15]. To reveal the effect of magnetic interactions in an ensemble of particles on the magnetic properties of the Fe₃O₄ nanophase, a comparative analysis of magnetization curves with identical sizes of particles but different patterns of their distribution in the polymer matrix was performed. The magnitude of the size effect could be judged by analyzing the magnetization curves of samples with different sizes of particles that occur well apart and do not form aggre-

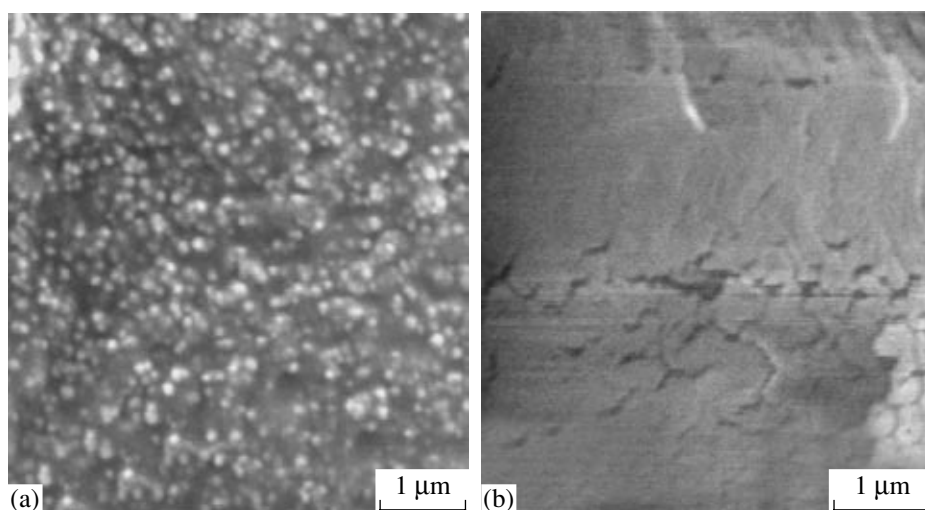


Fig. 4. Electron microscope images of the PVAL- Fe_3O_4 compositions with a primary-particle size of ≈ 4 nm, whose magnetization curves are given in Fig. 3: (a) the composition ($c_V = 18$ vol %) prepared at 3°C from gel I in a 10 M NaOH solution and (b) the composition ($c_V = 10.5$ vol %) prepared at 20°C from gel II in a 5 M NaOH solution.

gates (compositions with a low amount of the dispersed component).

Figure 3 depicts magnetization curves for compositions with close dimensions of primary particles ($D_{\text{XRD}} \sim 4$ nm) but different degrees of aggregation. The degree of aggregation can be judged by analyzing the SEM images of these samples (Fig. 4). The presence of well-developed secondary particles in the gel-I-based composition and their absence from the electron micrographs of the samples prepared from gel II indicates that a high degree of aggregation is observed only in the former case. The coercivity, as follows from the data presented in Fig. 3, in the presence of aggregation of primary particles may be an order of magnitude higher than H_c for the case when aggregation is either absent or its degree is insignificant (90×10^{-4} and 9×10^{-4} T for gel I and gel II compositions, respectively). Such a sharp increase in coercivity, in our opinion, can be explained by the existence of strong interactions between magnetic particles in compact aggregates. It should be pointed out that single-crystal primary particles are single-domain entities, since their diameter is much smaller than the critical domain size for Fe_3O_4 , which is 126 [13] or 80 nm [14] according to various estimates. Interactions in an ensemble of single-domain particles have a noticeable effect on their magnetic characteristics, such as the blocking temperature T_b (temperature of transition from the superparamagnetic to the ferromagnetic state) and the magnetic-moment relaxation time τ [1–3, 13, 14, 16]. The T_b and τ values are closely related to coercivity; therefore, their change may lead to a change in H_c [17, 18].

The manifestation of the size effect is well seen from comparison of magnetization curves for two compositions that have an identical concentration of the dis-

persed component ($c_V \sim 1\%$) but strongly differ in the size of primary particles, 28 and 4 nm, respectively (Fig. 5). Secondary particles in both cases are undetect-

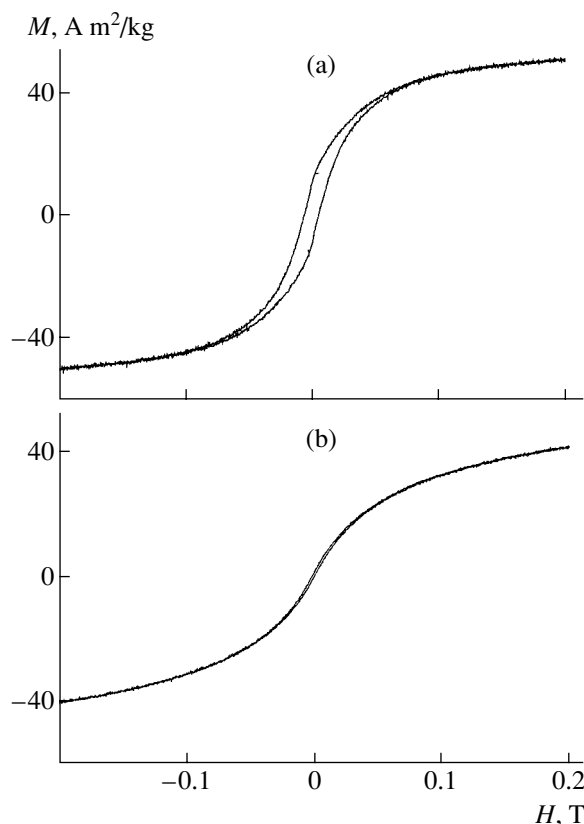


Fig. 5. Magnetization curves of the magnetite nanophase in PVAL- Fe_3O_4 compositions ($c_V = 1$ vol %) with a size of primary particles of (a) 28 and (b) 4 nm prepared in a 10 M NaOH solution (a) at 20°C from gel I and (b) at 3°C from gel II.

able in electron micrographs. As the particle size increases, H_c dramatically increases from 7×10^{-4} to 57×10^{-4} T. Such an increase in H_c is due to a rise in anisotropy energy (the energy barrier of magnetization-vector reversal) of single-domain particles during their growth [15, 19].

The saturation magnetization M_s for the magnetite nanophase in PVAL- Fe_3O_4 compositions in all cases turns out to be lower than that for the bulk magnetite, $92 \text{ A m}^2/\text{kg}$. The M_s value has a tendency to decrease to $\sim 50 \text{ A m}^2/\text{kg}$ with a decrease in the particle size. The decrease in M_s for ferrite nanophases was observed earlier, and it was associated with the surface contribution to nanophase magnetization, which is due to the disordering of the structure of surface layers of magnetic atoms [14, 20–22].

CONCLUSIONS

We have studied the influence of preparation conditions on the structure of poly(vinyl alcohol)-magnetite nanocompositions (size of Fe_3O_4 particles and the degree of their aggregation) formed in situ from a chemically crosslinked PVAL gel. The Fe_3O_4 nanophase is composed of single-crystal single-domain particles whose size varies over a wide range (~ 3 – 80 nm) depending on the synthesis conditions (water content of the polymer gel, pH, temperature, reaction time) for nanocomposites. The stabilizing effect of the polymer matrix at a high pH level is determined to a considerable extent by the microviscosity of the reaction medium, as well as by specific interactions at the polymer/particle interface. The strong increase in coercivity with an increase in the degree of aggregation is due to the existence of strong interactions between magnetic particles in compact aggregates.

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