Functional Materials 16, No.2 (2009)

Size distribution of magnetite nanoparticles in a polymer matrix

R.A.Ali-zade, M.A.Ramazanov*, R.Z.Sadykhov

Institute for Physics, National Academy of Sciences of Azerbaijan,
33 Djavid St., Baku Az-1143, Azerbaijan
*Baku State University, 23 Khalilov St., Baku Az-1145, Azerbaijan

Received October 27, 2008

The magnetite nanoparticle size has been studied as a function of the concentration thereof in polymer matrix. The magnetite nanoparticle size distribution has been determined. The magnetite nanoparticle magnetization has been calculated taking into account the magnetic dipole-dipole interaction.

Исследован размер наночастиц магнетита в зависимости от их концентрации в полимерной матрице. Определено распределение наночастиц магнетита по размерам. Вычислено намагничивание наночастиц магнетита с учетом магнитного диполь-дипольного взаимодействия.

Polymeric matrices filled with magnetite nanoparticles (polymeric magnetic nanocomposites, PMNC) are of a considerable scientific and practical interest [1-5]. Such media have several advantages over the liquid ones. The magnetite nanoparticles introduced into a polymeric matrix are in the individual state and their coagulation is impossible. Moreover, the polymeric matrix protects the nanoparticles against a further oxidation, so those may keep their physicochemical properties for a prolonged time.

Those media exhibit a series of unique physical properties, including the superparamagnetism, high magnetic characteristics, giant magnetic resistance, good magnetooptical properties, the specific electric resistance varying within a wide range, etc. [3-7].

It is to note that the function of the polymeric matrix is not reducrd to the stabilization of active nanoparticles having the properties differing fundamentally from those of atoms, molecules, and bulk samples. The matrix defines the structure of the nanoparticle ensemble formed therein (the size distribution of nanoparticles, the spacing therebetween, the particle shape, the arrangement ordering, etc.) that, in turn, defines all the properties of the nanocomposite itself.

In this work, the size of magnetite nanoparticles has been studied as a function of the concentration thereof in the polymeric matrix. The size distribution of magnetite nanoparticles has been determined. The magnetization of the nanoparticles has been calculated taking into account the magnetic dipole/dipole interaction.

The magnetization of PMNC samples obtained using the polyvinilydene fluoride (PVDF) and polyethylene (PE) at different magnetite concentrations has been studied by the Domenicalli technique. The PMNC preparation and physical characteristics ar described in [8].

Fig. 1 shows the magnetization curves for a PVDF based PMNC with the volume concentration of magnetite nanoparticles φ_t =0.098. The sample magnetization is seen to be of superparamagnetic character. It is known that the magnetization of such media can be described using the Langevin equation:

$$M(H)=M_s\cdot\varphi_m\int_0^1 f(m)\cdot L\left(\frac{mH}{kT}\right)\cdot dm \qquad (1)$$

where $L\left(\frac{m_iH}{kT}\right)=cth\left(\frac{mH}{kT}\right)-\frac{1}{\frac{mH}{kT}}$ is the Langevin function; $f(m)$, the distribution function of the magnetite nanoparticle magnetic moment ; φ_m, the nanoparticle concentration in the matrix. The nanoparticle magnetic moment is determined as $m_i=M_s\cdot V_i$, where M_s is the saturation magnetization of bulk magnetite amounting 491.6 kA/m; V_i, the nanoparticle volume. To determine the nanoparticle concentration in the matrix, the Langevin equation for high magnetic fields $M_s'=\varphi_m\cdot M_s$, was used where M_s' is the saturation magnetization of the sample.

Using the Langevin function expansion in low magnetic fields $L\left(\frac{m_iH}{kT}\right)\Big|_{H\to 0}=\frac{3m_iH}{kT}$ and definition of average magnetic moment $\overline{m}=\int_0^1 m\cdot f(m)dm$, we get the maximum magnetic diameter $\left(d_{mag}^{\max}\right)$ of nanoparticles

$$d_{mag}^{\max}=\left(\frac{72\chi_0 kT\mu_0}{M_s^2\varphi_m}\right)^{1/3}.$$

The minimum magnetic diameter of nanoparticles can be determined using the Langevin equation expansion in high magnetic fields:

$$M=M_s\cdot\varphi_m\left(1-\frac{1}{\frac{MH}{kT}}\right)$$

From the magnetization curves, the dependence $M=M(1/H)$ can be obtained and the minimum magnetic diametercan be determined:

$$d_{mag}^{\min}=\left(\frac{24\varphi_m kT}{tg\alpha\cdot\mu_0}\right)^{1/3}$$

where α is the angle between the tangent to the $M = M(1/H)$ line in the point $\lim\limits_{H\to\infty} M\left(\frac{1}{H}\right)$ and the abscissa axis.

Let the magnetite nanoparticle size be distributed according to lognormal law:

$$f(x)=\frac{1}{\sqrt{2\pi}\sigma\cdot x}\cdot\exp\left(-\frac{(\ln x)^2}{2\sigma^2}\right)$$

where $x = d/d_v$, d_v being the nanoparticle average diameter. Let this expression be substituted into (1). Considering the Langevin function expansions in high and low magnetic fields and integrating (1), we obtain for the distribution parameters the following expressions:

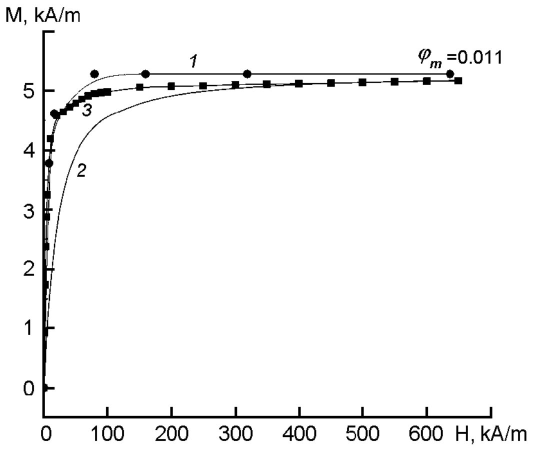

Fig.1. Magnetization curves of a PVDC+ Fe_3O_4 obtained in experiment (1) and by calculation without (2) and with (3) account for the magnetic dipole/dipole interaction.

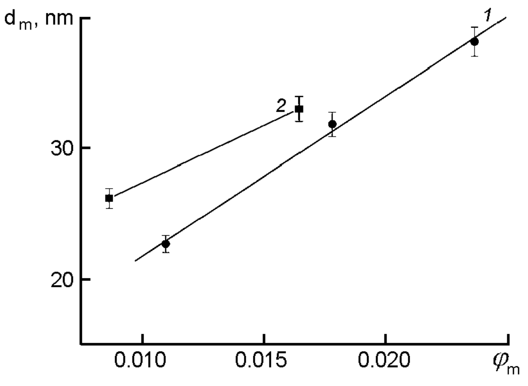

Fig.2. Dependence of the nanoparticle conglomerate magnetic diameter on their concentration in PVDC (1) and PE (2) matrix.

$$d_V=\frac{1}{3}\left(\frac{72\chi_0 kT\mu_0}{M_s^2\varphi_m\left(\frac{3\chi_0 H}{M_s\varphi_m}\right)^{1/2}}\right)^{1/3} \quad \text{and } \sigma=\frac{1}{3}\left(\ln\left(\frac{3\chi_0 H}{M_s\varphi_m}\right)\right)^{1/3}$$

Using the data from magnetic measurements (χ_0,φ_m), the maximum magnetic diameter of the nanoparticles and the logarithmic average diameter of nanoparticles have been determined at different concentrations thereof in the polymeric matrix, Table 1

Table 1: Maximum and minimum diameters of nanoparticles and the lognormal distribution parameters thereof as determined at various nanoparticle concentrations for PVDF+Fe_3O_4 and PE+Fe_3O_4 PMNC samples

Samples	Parameters			
	d_{min}, nm	d_{max}, nm	d_v, nm	σ
PVDF+Fe_3O_4				
φ_m				
0.011	6.3	31.9	24.76	0.25
0.018	11.0	34.4	29.51	0.23
0.023	14.2	38.0	32.36	0.34
PE+Fe_3O_4				
φ_m				
0.008	10.1	26.2	26.7	0.112
0.017	11.0	33.2	30.06	0.258

The regularity of the magnetite nanoparticle size variation with the concentration is seen to be linear: $d_{min}= 659{,}17\times\varphi_m$, $d_{max}= 26{,}12 + 498{,}62\times\varphi_m$, $d_v=17{,}85+636{,}24\times\varphi_m$. Among these dependences, the angular coefficient in the $d_{min}=d_{min}(\varphi_m)$ one is higher than in others. The small nanoparticles are coagulated stronger than those of medium and large size. The angular coefficient for medium-size nanoparticles is within the range between those for d_{min} and d_{max} ones.

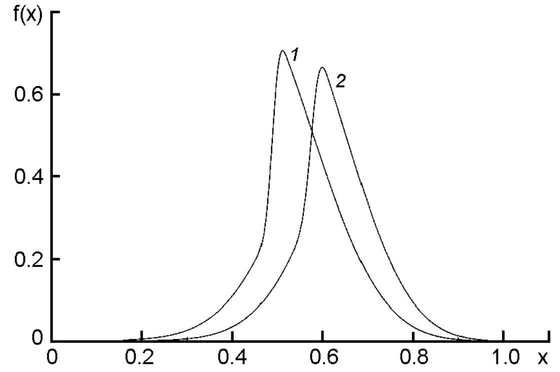

Fig.3. Magnetite nanoparticle distribution in PVDC matrix at concentration 0.011 (1) and 0.018 (2).

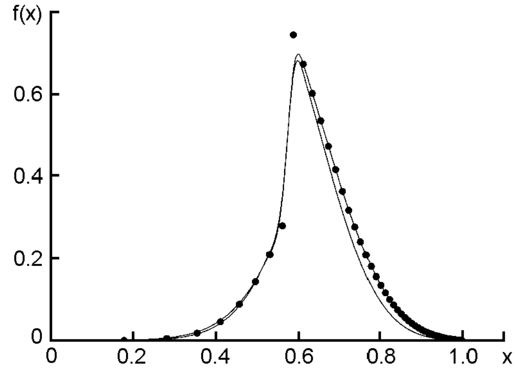

Fig.4. Magnetite nanoparticle distribution in PVDC and PE matrices at concentration 0.018.

In Fig.2, presented is the maximum magnetic diameter of magnetite nanoparticle aggregates is shown as a function of their concentration in the polymeric matrix. The d_m (φ_m) is seen to be linear, the magnetic diameter grows as the concentration increases, that is, the coagulation of nanoparticles occurs. However, the coagulation depends not on the concentration thereof only but also on the polymer physicochemical properties (viscosity, electric characteristics, etc.).This dependence is heavier for PVDF than for PE. It is seen in the Figure that the magnetic diameters are different in PVDF and in PE, the nanoparticle concentration being the same (φ_m =0.017).

The regularity obtained is confirmed by the coagulation theory, too. It is known that when the nanoparticles are coagulated, their concentration decreases [9] as $\frac{dn}{dt} = -k_0 \cdot n^2$, k_0 being determined as $k_0 = \frac{8kT}{3\eta}$, η is the medium viscosity.

By definition, $\varphi_t = \frac{V_t}{V}$, where V_t , V is the solid phase and medium volume, respectively. Since $V_t = N \cdot V_0$ and $n = \frac{N}{V} = \frac{\varphi_t}{V_{0t}}$, the latter differential equation can be written in the form

$$\frac{dV}{dt} = -k_0 \varphi_t$$

The solution is $V_{0t} = k_0 \cdot \varphi_t + V_0$. In the latter expression, let us pass to d_{0t}

$$d_{0t} = d_0 \left(1 + \frac{2k_0 \varphi_t t}{\pi d_0^3} \right)$$

The nanoparticle aggregate diameter is seen to be a linear function of concentration, that is consustent with the result obtained before (see Fig. 2).

In the latter relation, let the critical time be introduced determined as $t_{cr} = 1/(2k_0 \varphi_t / \pi d_0^3)$. The critical time evaluation for the PDVF sample has shown that it is 9.5; 6; 5 μs at the concentration φ_t=0,098; 0,155; 0,187, respectively. As the magnetite nanoparticle concentration in a polymer matrix decreases, the critical time reduces.

The concentration of the solid nanoparticle phase (φ_t) was determined as follows. The PMNC mass consists of the polymer mass and nanoparticle one: $m_{PMNC} = m_{PM} + m_{\mathrm{Fe_3O_4}}$, where $m_{PMNC} = \rho_{PMNC} V_{PMNC}$, $m_{PM} = \rho_{PM} V_{PM}$ $m_{\mathrm{Fe_3O_4}} = \rho_{\mathrm{Fe_3O_4}} V_{\mathrm{Fe_3O_4}}$. By definition, $\varphi_t = \frac{V_{\mathrm{Fe_3O_4}}}{V_{PM}}$, then we get $\varphi_t = \frac{\rho_{PMNC} - \rho_{PM}}{\rho_{\mathrm{Fe_3O_4}} - \rho_{PM}}$.

We have shown before that the surface layer of a magnetite nanoparticle is not magnetitic [10]. The non-magnetitic layer thickness is in proportion to the nanoparticle diameter. The geometric (d_{0t}) and magnetic (d_{0m}) nanoparticle diameters are related together as $d_m = K \cdot d_t$ (K = 0.154 for the magnetite nanoparticle samples under study). Then the magnetic volume of an aggregate

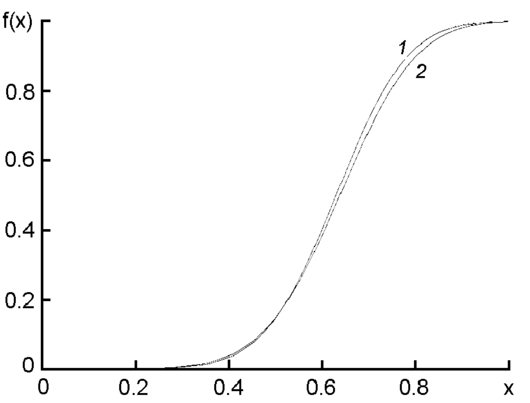

Fig.5. Dependence of the frequency accumulation on the nanoparticle size.

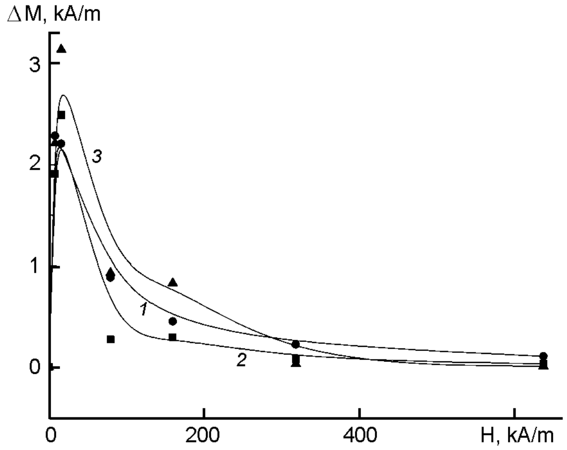

Fig.6. Difference between experimental and calculated curves of magnetite nanoparticle magnetization in polymeric matrix as a function of the magnetic field strength.

consisting of n magnetite nanoparticles can be determined as

$$\frac{1}{6}\pi d_{0t}^3 n^3 - \frac{1}{6}\pi d_{0m}^3 n^3 = \frac{1}{6}\pi d_{ot}^3 n^3 \left(1-K^3\right) = V_t(1-K^3)$$

If an aggregate of n nanoparticles is considered as one nanoparticle, then its magnetic volume is determined as

$$\frac{1}{6}\pi d_t^3 - \frac{1}{6}\pi d_m^3 = \frac{1}{6}\pi d_t^3 \left(1-K^3\right) = V_t(1-K^3)$$

The right-hand sides of both expressions are the same. Thus, the magnetic diameter of the nanoparticle aggregates depends on their geometric diameter also linearly. So the above results for the magnetic diameter of the aggregate are valid for its geometric size, too.

The lognormal distribution parameters for PMNC samples PVDC+Fe_3O_4 and PE+Fe_3O_4 are presented in the Table. The regularity of magnetite nanoparticle size variation as a function of concentration thereof is seen to be linear and similar to that found above (see Fig.2).

In Fig.3, presented are the size distribution curves for magnetite nanoparticles in PVDC at concentrations φ_m =0.011, 0.018. it is seen that when the concentration increases, the average particle size grows but the distribution character remains unchanged.

Fig. 4 presents the magnetite nanoparticle distribution in PVDC and PE matrices at 0.018 and 0.008 concentrations. The nanoparticle diameters are the same in both cases in spite of different concentrations.

Fig. 5 shows the frequence accumulation curve as a function of the nanoparticle size at concentrations φ_t=0.098, 0.155. It is seen to be S-shaped and the nanoparticles of larger sizes make the main fraction of the dispersed phase.

In Fig.1, demonstrated is the magnetization curve calcilated using (1) taking into account the lognormal distribution. In low magnetic fields, the experimental magnetization curve is seen to differ from the calculated one. That difference as a function of the magnetic field shtength is shown in Fig. 6. It is seen to have a maximum at a certain field strength and decreases at a further field increase. Fig. 7 shows the maximum difference between the experimental and calculated magnetization characteristics as a function of the magnetite nanoparticle concentration. The dependence is seen to be quadratic.

In spite of low concentrations, the nanoparticles are rather large and, accordingly, a high magnetic moment. Thus, the magnetic dipole/dipole interaction is to be taken into account in the expression for magnetization (1). The interaction energy was taken in the form [11]

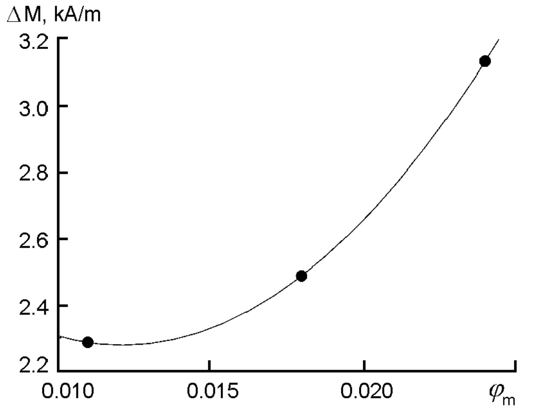

Fig.7. Maximum difference between experimental and calculated magnetization curves as a function of magnetite nanoparticle concentration.

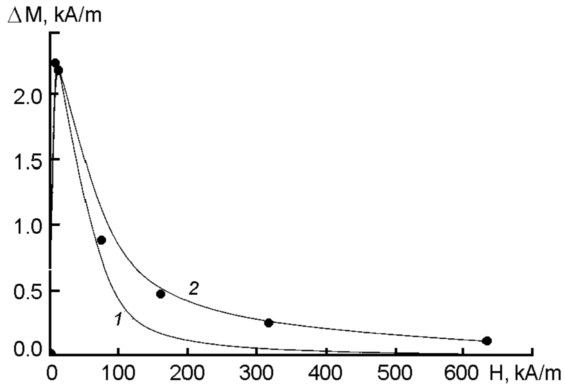

Fig.8. Difference between experimental and calculated magnetization curves and additional item as a of the magnetic field strength.

$$E_{d-d}=-\frac{m^2}{4\pi\mu_0 r^3}\left(cth\frac{mH}{kT}-\frac{1}{\frac{mH}{kT}}\right)^2$$

The expression for magnetization was obtained taking into account the magnetic dipole/dipole interaction ($E_{d\text{-}d}$) [12]. The aditional item for that case was found as [11]

$$\Delta M=\frac{1}{3}M_s^2\varphi_m^2\frac{1}{\mu_0 H}\ln\left(\frac{VM_s}{m}\right)\left(cth\frac{mH}{kT}-\frac{1}{\frac{mH}{kT}}\right)\left(-\frac{mH}{kT}\mathrm{csc}h^2\frac{mH}{kT}+\frac{1}{\frac{mH}{kT}}\right) \qquad (2)$$

The consideration of the expression obtained has shown that it has a maximum at $mH/kT = 1.54$ and decreases as the magnetic field increrases. The dependence of the additional item on the nanoparticle concentration is quadratic, too.

Fig. 8 shows the difference between the experimental curve and the calculated one with the additional item (2) as a function of nanoparticle concentration. The curves are in a good agreement. The calculated magnetization curve taking into account the dipole/dipole magnetic interaction (Fig. 1) agrees well with the experimental one.

Thus, it has been shown that when the magnetite nanoparticles are introduced into a polymeric matrix at a high concentration, their coagulation takes place. The conglomerate size depends linearly on the nanoparticle concentration as well as on the polymeric matrix properties. Although the concentrations are rather low and the nanoparticle size is large (accordingly, the magnetic moment is high), the dipole/dipole magnetic interaction is to be taken into account when calculating the magnetization of such media.

This work has been supported financially by CRDF (Grant AZEI-3113-BA-08).

References

1. F.Mirzaleyrat, L.K.Varga, *J. Magn. Magn. Mater.* **215-216,** 253 (2000)
2. Kai Liu, L.Zhao, D.Klavins *J.Appl. Phys.* **93**, 7951 (2003)
3. A.E.Varfolomeev, A.V.Volkov, D.Yu.Godovsky, G.A.Kapustin, *Pis'ma Zh. Eksp. Teor. Fiz.* **67**, 37 (1998)
4. A.V.Kimel, R.V.Pisarev, A.AQ.Rzhevsky et al., *Fiz. Tverd. Tela* **45**, 269 (2003)
5. S. Honda. *J. Magn. Magn. Mater.* **165**, 153 (1997).

6. USSR Author`s Cert. 1486515 (1989).
7. USSR Author`s Cert. 1567623 (1990).
8. A.M.Magerramov, M.A.Ramazanov, R.Z.Sadykhov, R.A.Ali-zade, *Nanotekhnika* **4**, 11 (2005)
9. R.A.Ali-zade, *Neorg. Mater.* **42**, 1215, (2006)
10. E.D.Schukin, A.V.Pertsov, E.A.Amelina, Colloid Chemistry, MGU Publ. (1982) [in Russian].
11. R.A.Ali-zade, *Fizika* **5,** 37 (1999).
12. S.V.Vonsovskiy. Magnetism. Magnetic Properties of dia-, para-, ferro-,antiferro- and ferrimagnetics, Moscow, Nauka (1971) [in Russian].

Розподіл наночасток магнетиту за розмірами у полімерній матриці

Р.А.Алі-заде, М.А.Рамазанов, Р.З.Садихов

Досліджено розміри наночастинок магнетиту залежно від їх концентрації у полімерній матриці. Визначено розподіл наночастинок магнетиту за розмірами. Обчислено намагнічення наночастинок магнетиту з урахуванням магнітної диполь-дипольної взаємодії.