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Original article

Magnetic nanoparticles in solid matrices: formation and fixation of structures, induced by magnetic field

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ABSTRACT In this article, the structures formed by the action of the magnetic field to magnetite nanoparticles, embedded into transparent matrices from ferrofluids, were analyzed. As the matrices polyvinyl alcohol and epoxy resin were used, however, the results obtained may be applicable to other media, for example, biological. The data of this work can be useful both for physical investigations of magnetic nanomaterials and for more practical studies, for instance, aimed at solving some environmental problems.

KEYWORDS magnetic fluids, ferrofluids, magnetic nanoparticles, transparent matrices, magnetic nanocomposites

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1. Introduction

Magnetic nanoparticles, in particular, those that are component of the so-called ferrofluids or magnetic fluids (MF), are used in a variety of scientific and technological fields [1, 2]. Among the recently proposed areas of applications, biomedicine [3, 4] and optoelectronics [5–7] can be named. Of particular importance and interest are also ideas related to ecology, for example, in [8], an MF-based technique for eliminating oil spills was considered.

MF, further used as starting substances for obtaining samples, are colloidal solutions, the solid phase of which is a magnetic material, and the diverse fluids can act as a carrier liquid, kerosene or water for instance. These materials are stabilized by applying certain surfactants to the surface of nanoparticles or creating electrical charge on it [2].

For most of MF-related utilizations, the important question is how they interact with the external magnetic field H. It is known that the field forces the colloid nanoparticles to form the extended structures (agglomerates) oriented along the H direction [9]. The characteristics of these objects vary depending on the type of solvent, particle material, surfactant, as well as the conditions of the experiment. One of the convenient ways to study such clusters is their "freezing" in a congealing environment, which was implemented, for example, in [10]. The purpose of the presented study is further development of this approach and demonstration of the peculiarities of the field induced aggregation process in the viscous media.

2. Materials and methods

The samples under consideration were composite materials obtained by infiltration of magnetite (Fe_3O_4) nanoparticles from MF into a transparent medium which are the polyvinyl alcohol (PVA) or epoxy resin. MF was the same as in a number of previous works [10, 11], being an aqueous colloid of magnetite stabilized by a two-layer surfactant with oleic acid molecules or by a charged layer formed on the surface of particles. The particle size was approximately 10 nm.

In the case of PVA matrix, an initial mixture of two aqueous solutions was prepared, one of them was 5 wt. % solution of PVA powder, and another was MF with oleic stabilization, taken at such a concentration as to provide approximately 0.5 vol. % of the magnetic phase in a solid sample. The mixture was stirred at 90 °C, and then treated with ultrasound for one hour. The resulting liquid was applied to a glass substrate and dried.

Since water cannot be used when working with epoxy resin, when fabricating samples with such matrices, ion-stabilized MF was first dried on glass, and then the obtained paste-like precipitate was diluted in a hardener and sonified for one hour. After mixing the hardener with the resin, a short-term sonification of the mixture was also carried out and then it was dried on a glass substrate. The magnetite content was such as to be for the solid matrix approximately 0.25 mg per 1 ml.

In all cases, the liquid mixture was applied to the substrate in such quantities as to finally obtain a sample in the form of a film of 40–70 μm thick. Drying was carried out in magnetic fields oriented in the film plane, or without application of the field. The films have always turned out to be quite transparent; if the field was nonzero, a structure of thin extended objects was visually observed in them.

All samples, both based on PVA and epoxy resin, were fabricated in the fields up to 6 kOe, but special attention was paid to the range from 0 to 1000 Oe, since the saturation field H_s of MF reaches approximately of 1 kOe [9], and the main processes associated with the formation of structures should occur in this interval. This assumption was confirmed experimentally: it was found that the parameters of nanoparticle agglomerates at $H > 1$ kOe change only slightly.

Using a MICRO 200T-01 PLANAR microscope, micrographs were obtained for films, processed further as follows: for each structural element (spherical at $H = 0$ and extended at $H > 0$) in the field of the microscope, its dimensions (diameter d or, respectively, the thickness D and length L) were determined, and then for a given value H, statistics were being accumulated. The number of analyzed objects, N, was of an order hundreds, which made it possible to construct histograms of the distribution of the above values.

In addition, a technique for determining D based on laser probing of the material was used. To do this, a laser beam with a wavelength of $\lambda = 650$ nm was focused on the film (illuminated from the side of the glass substrate), and by finely moving the latter, such a position was chosen where the light diffracted on a separate aggregate. On a screen at some distance away from the sample, a pattern typical of this was observed, containing maxima and minima of diffracted radiation I. Assuming that this case is analogous to the slit diffraction and using the well-known expression $\lambda m = D \sin\theta$, where θ is the angle at the I minimum with the number m, it was possible to determine the transverse size of the selected object. (A similar approach was used to study agglomerates in a liquid medium [12]). Since this method is more time-consuming than the analysis of micrographs, the dimensions of a smaller number of aggregates were evaluated by it.

3. Experimental results

Figure 1 shows micrographs of PVA-based samples fabricated in fields of less or almost the same magnitude as H_s. It is clearly seen that at $H = 0$ inclusions in the polymer matrix are microdroplets whose diameters d noticeably exceed the characteristic size of the individual nanoparticles (Fig. 1a). A relatively small nonzero field leads to the formation of elongated agglomerates, the length of which, L, however, can be easily determined (Fig. 2b). With approaching H_s, the latter, starting from some point, is no longer possible, since the value L for most of agglomerates becomes comparable with in-plane dimension of the sample (Fig. 1c). It should be noted that for weak fields the diameters of the agglomerates turned out to be approximately the same ($D \approx$ 15–20 μm), and, moreover, for $H > H_s$ they also changed insignificantly.

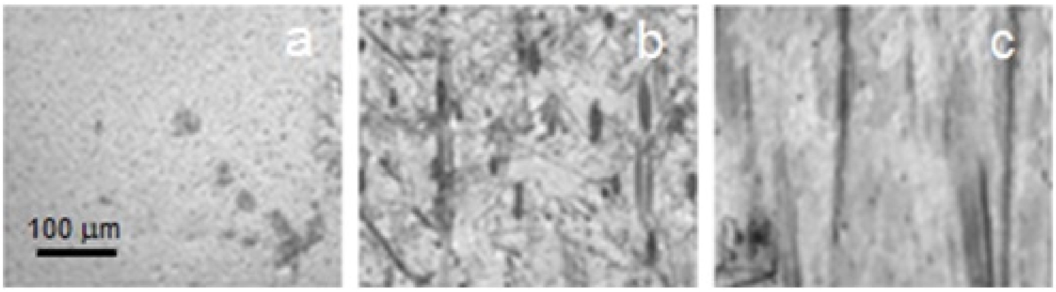

FIG. 1. Micrographs of a sample based on PVA at: a) $H = 0$; b) $H = 40$ Oe; c) $H = 1000$ Oe (the scale is the same for all images)

The same regularities are preserved for composites based on epoxy resin matrices; for example, Fig. 2 shows micrographs of these materials for $H = 0$ and $H \gg H_s$. Here we can note the same presence of microdrops in zero field (Fig. 2a), and "infinitely long" agglomerates at fields of a high strength (Figs. 2b and 2c). It should be emphasized that the D values for different cases may still differ slightly (see Fig. 2c, where the agglomerate with $D \approx 80$ μm is isolated), however, the characteristic size of the order of several tens of microns is typical for almost all extended structural elements. As an exception, we should mention the existence of a certain number of thin objects at $H = 4$ kOe and $H = 6$ kOe (Figs. 2b and 2c).

The statistical properties of the aggregates are illustrated in Fig. 3, which shows examples of histograms of the distribution of d ($H = 0$, Fig. 3a) and L ($H = 40$ Oe, Fig. 3a) in PVA-based composites. These data were obtained by analyzing a number of micrographs with, as already was mentioned, a lot of objects N (in Fig. 3, normalization was performed by the maximum magnitude in the distribution N_0). At $H < H_s$, there were no qualitative differences in the

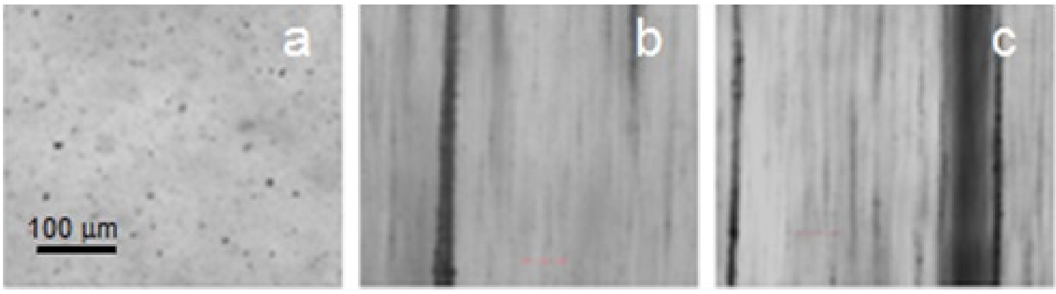

FIG. 2. Micrographs of a sample based on epoxy resin: a) $H = 0$; b) $H = 4$ kOe; c) $H = 6$ kOe (the scale is the same for all images)

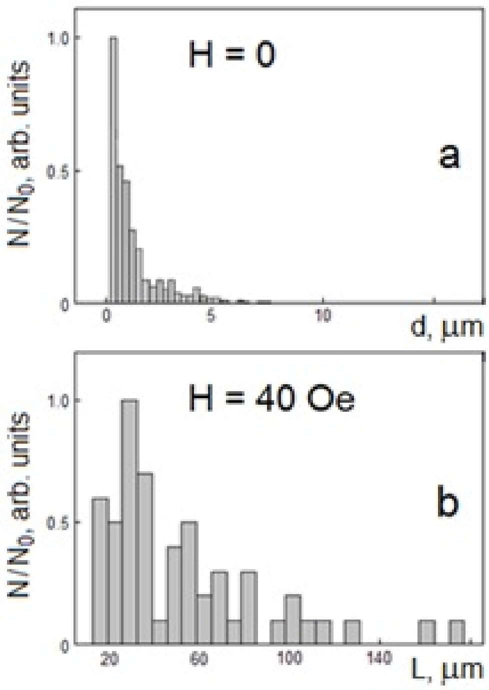

FIG. 3. Histograms of the distribution of the size of agglomerates in a sample with PVA: a) without field; b) in the field $H = 40$ Oe

behavior of histograms for materials with PVA and epoxy resin: with an increase of the field (where the measurement of length was still possible), their shift towards large values of L was recorded.

The laser probing method made it possible to obtain verified data on the thickness of the aggregates. Fig. 4 demonstrates the results of one of the diffraction experiments carried out on an epoxy film fabricated at $H = 4$ kOe. The diffraction pattern, while not ideal, nevertheless allowed us to estimate D. After digitizing the images of the type presented in Fig. 4a, graphs of the dependence of the normalized light intensity on the distance from the beam center along the X direction were obtained. Fig. 4b exhibits the distribution of the relative intensity of diffracted light I/I_0 for one of such a section of the pattern. According to these data, and taking into account geometric parameters of the setup, the values of D were determined. They, slightly differing for different measurements, in order of magnitude amounted to tens of microns in all cases. This gives a useful confirmation of what was obtained earlier, because due to the edge blurring of images, the processing of micrographs is less informative.

4. Discussion

One of the main features of the structures we have considered is that they are formed in a similar way in different environments and under markedly different conditions. Indeed, analyzing the data on the behavior of the magnetic fraction embedded in PVA (Fig. 1) or epoxy resin (Fig. 2), it can be seen that even at very different fields, the thicknesses of agglomerates tend to approximately the same value, and it is observable starting from the smallest H (Fig. 1b). At $H \ll H_s$, large-volume associations of nanoparticles cannot yet occur, and the parameter L, characterizing the extent of the aggregates, remains small. An increase in the field leads to its significant growth and the appearance of long structural elements, although in the interval roughly limited by H_s from above, the presence of a certain number of

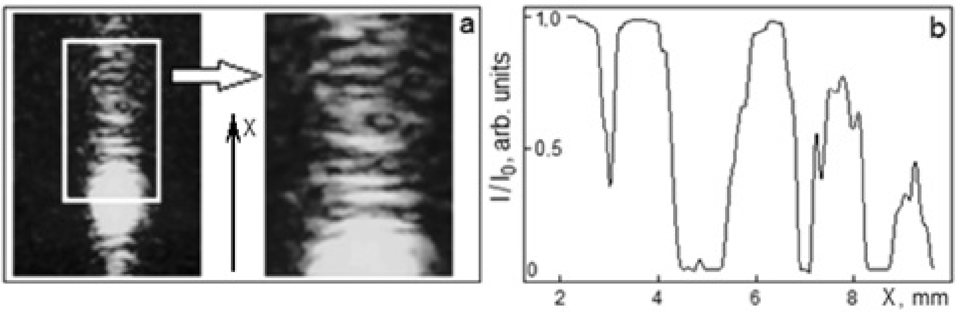

FIG. 4. Diffraction of laser radiation on selected agglomerate (sample based on epoxy resin, $H =$ 4 kOe): a) diffraction pattern at different scales; b) distribution of the relative intensity of diffracted light

"short" aggregates can be noted (Fig. 1c), which reflects the statistical nature of the processes taking place. At $H > H_s$ most of the particles enter into extended column-like systems (Figs. 2a,b), which, by moving the microscope field, can be traced over a long distance, sometimes comparable to the size of the sample.

The suggested mechanism of formation of the structures in our samples may be as follows. The initial state in the preparing of our samples are emulsions (Fig. 1a, Fig. 2a), which is usual when MF is diluted in viscous media [13]. In our case, the size d of most of the microdrops can be estimated as 0.5 μm (Fig. 3a), that is, the number of nanoparticles in each of them should be $\sim 10^4$–10^5. Thus, when the field inducing the magnetic moment appears, not individual particles, as simple models suggest [9], but large objects begin to interact. Already in very small fields, the drops acquire an ellipsoidal shape [13] and start to attract each other, merging into agglomerates of increasing volume and extent. At higher H, maintaining approximately the same thickness D as at the initial stage of growth turns out to be energetically favorable (apparently, from the point of view of minimizing magnetic energy and surface tension energy at the medium-ferrofluid interface). The rate of such a process is determined by the viscosity of the medium and the average size d, i. e., it is obviously much smaller than for conventional MF. In our case, however, the formation of a system of aggregates accomplished long before the transformation of the liquid into a solid matrix, since their appearance (visually observed) has a characteristic time of the order of minutes, whereas the carrier solidifies for about an hour. Therefore, the structures of magnetic nanoparticles related to a specified field are fixed in the matrix as completed.

The presence of defects in the medium may impose certain features on the formation of aggregates. So, in Fig. 1 imperfections that are not related to magnetite are visible and represent a partially crystallized matrix substance (which is typical for PVA [14]). Of course, there are other possible situations - in Figs. 2b,c can be noticed an aggregates with an included "dot-like" objects. During laser probing of samples, they are recorded as irregularities in the diffraction pattern (Fig. 4a).

The results obtained can be extended, with a degree of conditionality, to other media with similar properties, primarily viscous ones. They include biomaterials containing, for example, some proteins, as well as gel-forming or other similar substances. For ecology, petroleum products are very important, in which the behavior of magnetic nanoparticles may turn out to be similar to what was considered in this paper. Understanding of how the structures are arise in them under the action of a magnetic field and what they are, being necessary for the development of theory, may also have practical significance.

5. Conclusion

In this work, a technique for studying agglomerates consisting of magnetic nanoparticles that are fixed in a transparent solidifying medium was considered. It was shown that it allows one to get information about the parameters of these objects, as well as to identify some general patterns of the formation of such structures in a viscous liquid. Statistical properties of agglomerates were obtained, their characteristic sizes were measured, including by laser probing. The possible application of the results was discussed.

References

[1] Oehlsen O., Cervantes-Ramírez S.I., Cervantes-Avilís P., Medina-Velo I.A. Approaches on ferrofluid synthesis and applications: current status and future perspectives. *ACS Omega*, 2022, **7**, P. 3134–3150.

[2] Scherer C., Figueiredo Neto A.M. Ferrofluids: Properties and applications. *Braz. J. Phys.*, 2005, **35**, P. 718–727.

[3] Socoliuc V., Avdeev M., Kuncser V., Turcu R., Tombácz E., Vekas L. Ferrofluids and bio-ferrofluids: looking back and stepping forward. *Nanoscale*, 2022, **14**, P. 4786–4886.

[4] Imran M., Alam M.M., Khan A. Advanced biomedical applications of iron oxide nanostructures based ferrofluids. *Nanotechnology*, 2021, **32**, P. 422001.

[5] Yong Zhao, Yuyan Zhang, Lv R.-Q., Qi Wang. Novel optical devices based on the tunable refractive index of magnetic fluid and their characteristics. *J. Magn. Magn. Mat.*, 2011, **323**, P. 2987–2996.

[6] Dai Q.-F., Deng H.-D., Zhao W.-R., Liu J., Wu L.-J., Lan S., Gopa A.V. All-optical switching mediated by magnetic nanoparticles. *Opt. Lett.*, 2010, **35**, P. 97–99.

[7] Taghizadeh M., Bozorgzadeh F., Ghorbani M. Designing magnetic field sensor based on tapered photonic crystal fibre assisted by a ferrofluid. *Scientific Reports*, 2021, **11**, P. 14325.

[8] Kalaeva S.Z., Morozov N.A., Stradomikiy Yu.I., Makarov V.M., Shipilin A.M., Zakharova I.N. Magnetic fluids for maintaining the cleanliness of surface reservoirs. *ChemChemTech.*, 2006, **49**, P. 91–93 (In Russian).

[9] Chikazumi S., Taketomi S., Ukita M., Mizukami M., Miyajima H., Setogawa M., Kurihara Y. Physics of magnetic fluids. *J. Magn. Magn. Mat.*, 1987, **65**, P. 245–251.

[10] Pleshakov I.V., Prokof'ev A.V., Bibik E.E., Kuz'min Yu.I. Investigation of structures formed by magnetic fluid nanoparticles in polymer matrices by static light scattering. *Nanosystems: physics, chemistry, mathematics*, 2022, **13**, P. 285–289.

[11] Pleshakov I.V., Prokof'ev A.V., Bibik E.E., Nepomnyashchaya E.K., Velichko E.N., Kostitsyna T.A., Seliutin D.M. Spectral characteristics of composite obtained by embedding of magnetic nanoparticles into polymer matrix. *Nanosystems: physics, chemistry, mathematics*, 2021, **12**, P. 279–282.

[12] Prokof'ev A.V., Pleshakov I.V., Bibik E.E., Kuz'min Yu.I. An optical investigation of the geometric characteristics of aggregates formed by particles of magnetic fluid. *Tech. Phys. Let.*, 2017, **43**, P. 194–196.

[13] Zakinyan A.R., Dikansky Yu.I. Effect of microdrops deformation on electrical and rheological properties of magnetic fluid emulsion. *J. Magn. Magn. Mat.*, 2017, **431**, P. 103–106.

[14] Thomas D., Cebe P. Self-nucleation and crystallization of polyvinyl alcohol. *J. Therm. Anal. Calorim.*, 2017, **127**, P. 885–894.

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