

Investigation of structures formed by magnetic fluid nanoparticles in polymer matrices by static light scattering

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ABSTRACT In this work, nanostructured composites in the form of polymer matrices with inclusions of magnetic particles were studied by the method of static scattering of laser radiation. The particles were embedded into polyvinyl alcohol and epoxy resin from magnetite-containing ferrofluid. It is shown that in a magnetic field they form a system of extended aggregates acting as light scatterers and established that optical technique based on this provides important information about the properties of such nanomaterial.

KEYWORDS nanocomposite, magnetite nanoparticles, ferrofluid, polymer matrix.

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1. Introduction

Among many nanostructured materials representing a system of small particles dispersed in an optical matrix, a special place is occupied by those in which the particles consist of magnetically ordered substance [1]. The interest in them is due to the fact that here there is an additional opportunity to control their properties by applying an external magnetic field. Besides, structures created by the field and fixed in a solid medium can be studied by various methods which is important, taking into account that the probing of the texture of such aggregates is still an urgent physical problem.

As an example of a magnet-containing nanocomposite of this type, one can point to a material made by introducing magnetite, Fe_3O_4 , into a transparent polyvinyl alcohol (PVA) matrix [2]. Its samples were obtained in a simple and convenient way – by mixing an aqueous solution of PVA and containing particles water colloid of Fe_3O_4 , i.e. the so-called magnetic fluid (MF). The aim of this work was to study the characteristics of structures formed by a magnetic field in composites prepared by the same approach using the light scattering technique.

2. Experiment

2.1. Samples preparing

The samples were fabricated as films of thicknesses of 40–80 μm by deposition of the initial liquid mixture onto glass wafer, with its subsequent drying in or without external magnetic field H .

In the case of PVA matrix the mixture was prepared by blending of two solutions: 5 wt. % aqueous solution of powdered PVA and water-based MF in such a proportion that provided of about 0.5 vol. % concentration of solid phase in mixture. The MF was the same as in [2] with the colloidal particles of Fe_3O_4 of the diameter approximately 10 nm, stabilized by double layer surfactant with hydrophobic (inner) and hydrophilic (outer) molecules (oleic acid salts). Mixing was carried out at a temperature of about 90°C, and then the resulting liquid was sonified in an ultrasonic bath for one hour.

The samples with the epoxy matrix were made by slightly different way because at this point the use of water as impossible. Here, magnetite-containing ionic-stabilized aqueous MF was dried on glass, and the resulting paste-like precipitate in an amount corresponding to about 0.25 mg/ml per full volume of the matrix substance was diluted in a hardener and sonified for one hour. After mixing with the resin, short-term sonification was also carried out, and then the film was made in the same way as in the case of PVA. For this purpose, commercially available Artline Crystal Epoxy material with high transparency was used.

2.2. Micrography of samples

Micrographs of several samples based on PVA are shown in Fig. 1. The values of H here do not exceed the saturation field H_s of MF, which in order of magnitude is of 1 kOe [3]. At zero field, as can be seen from Fig. 1a, inclusions of MF are present in the sample in the form of dispersed micro-droplet aggregates with dimensions of the order of several microns, composing an emulsion. This is usual for complex environment in which the MF is being embedded [2, 4]. The application of even a small field leads to the appearance of a preferred direction in which extended aggregates are oriented, and their thicknesses d indicate that they arose as a result of the fusion of many droplets. Note that, at least for small fields, not so much the thicknesses of the aggregates depend on H as their lengths, which is well traced from Fig. 1b to Fig. 1d (from 40 to 750 Oe).

Attention should also be paid to the presence of structures that are not related to the MF. They look like some kind of dendrite formations, and in one amount or another are present in all PVA-based films. At higher zoom, it is possible to establish that they consist of many small crystallites. By assumption, these elements are associated with the partial crystallization, typical for polyvinyl alcohol [5]. As it will be seen below, they have not a significant effect on the scattering of optical radiation, which in our case was almost entirely determined by MF-containing objects.

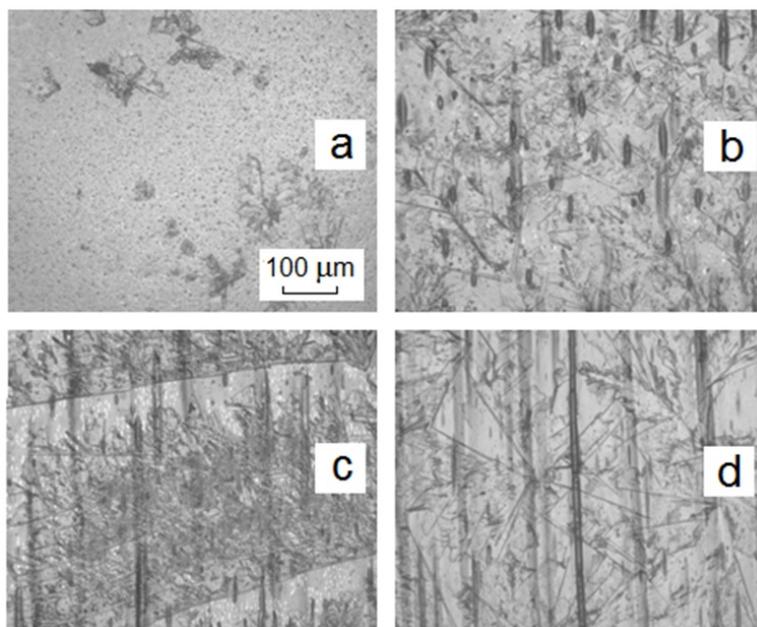


FIG. 1. Micrographs of PVA-based samples for: (a) $H = 0$, (b) $H = 40$ Oe, (c) $H = 115$ Oe, (d) $H = 750$ Oe. The common scale is indicated in the first image

For comparison, Fig. 2 shows examples of microphotographs of samples obtained using an epoxy resin and large fields. In this case, very long columnar aggregates with varying thicknesses are formed, among which, however, those with a diameter of the order of several tens of microns predominate. Of course, there is no here any dendritic structure. The results on light scattering for epoxy-based specimens turn out to be qualitatively similar to those obtained for PVA-based materials.

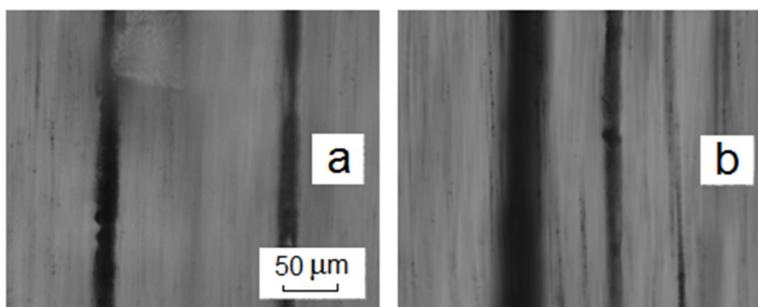


FIG. 2. Micrographs of epoxy-based samples for: (a) $H = 4$ kOe, (b) $H = 6$ kOe

2.3. Light scattering measurements

Static light scattering experiments were carried out according to the standard technique: a semiconductor laser beam ($\lambda = 650$ nm) was directed at the sample (illuminated from the side of the glass plate), which could be positioned in such a way that the direction of the field applied during its manufacture was either parallel or perpendicular to the polarization of the input radiation, and the scattered light was recorded in the plane orthogonal to the plane of polarization by a photodetector mounted on a rotating limb. A polarizer was placed in front of the photodetector, allowing to separate the different components of the scattered light. The measurement consisted in determining the dependence of the scattered light intensity I on the angle between the direction to the photodetector and the optical axis of the system θ , that is, the indicatrix $I(\theta)$ (in experiment the readings of the photodetector U_{ph} , proportional to I were recorded).

The experimental results for PVA-based samples at some values of H are shown in Fig. 3 and Fig. 4 (polarizer in the state of maximum incident light transmission). According to Fig. 2a, which demonstrates the dependence $U_{ph}(\theta)$ at the direction of the laser beam polarization along the field, one can see a rapid increase in the width of the diagram with H increasing from zero to several hundred oersteds (the case of a zero field is not depicted in the figures, since at $H = 0$ the density of the scattered radiation, due to its symmetrical distribution in a large solid angle, greatly reduced). In contrast, when the field is oriented perpendicular to the light polarization, the indicatrix narrows (Fig. 2b). The difference in the widths of these lines becomes very significant already at $H = 500$ Oe, which is illustrated in Fig. 4 representing the functions $U_{ph}(\theta)$ for the two indicated geometries of experiment. An important fact should be noted: at H approaching the saturation field, the change in the indicatrices practically stops, so the function $U_{ph}(\theta)$ measured at $H = 5$ kOe almost coincides with the function $U_{ph}(\theta)$ corresponding to 500 Oe.

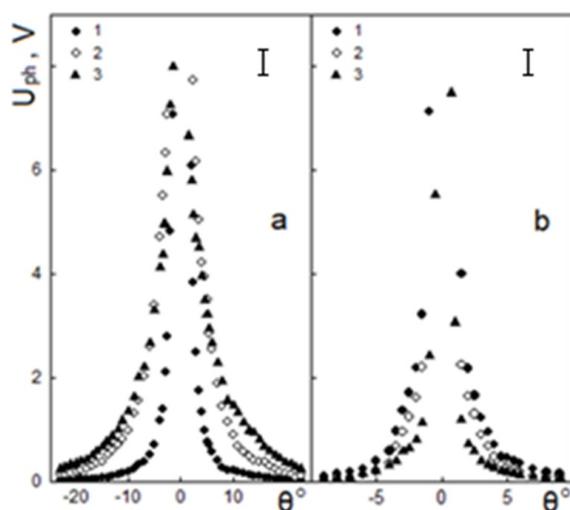


FIG. 3. Light scattering indicatrices of PVA-based samples for parallel (a) and orthogonal (b) orientations of magnetic field and incident light polarization. 1 – $H = 40$ Oe, 2 – $H = 250$ Oe, 3 – $H = 500$ Oe

Since measurements at angles θ close to zero are impossible in scattering experiments, the value of the width of the indicatrix at the half of its maximum intensity was not determined. As a criterion reflecting the properties of the indicatrix, its width $\delta\theta$ at the level $U_{ph} = 1$ V was chosen. Fig. 5 shows the dependences of $\delta\theta$ on H (Fig. 5a), as well as the field dependence of the ratio of the widths measured at parallel and perpendicular mutual orientations of the field and polarization (Fig. 5b).

Obviously, the considered effects can be associated only with the magnetic fraction of the composite. Thus, the dendritic inclusions mentioned above do not make any noticeable contribution to the measurement results, although in some cases a very weak pattern was visually recorded in the scattered radiation, reflecting, apparently, the symmetry of the crystallites.

The degree of polarization of scattered light P , determined from the intensities of its vertical and horizontal polarization components, in all cases, except for the case with $H = 0$, coincided with the degree of polarization of the incident laser radiation with an accuracy of at least 1%. In the zero field, an extremely insignificant depolarization, which, nevertheless, lied outside the error limits, was observed (a decrease in P by 2% from the initial one).

3. Discussion

Since the scattering centers in the samples under study are large objects with transverse dimensions of the order of several tens of microns (Fig. 1, Fig. 2), that is, with $d \gg \lambda$, it is acceptable to consider the obtained results in the framework of the concept of Fraunhofer diffraction. This is additionally confirmed by the fact that, despite the rather

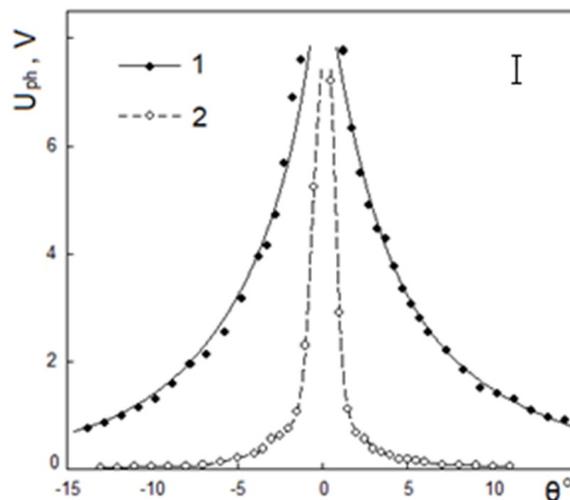


FIG. 4. Light scattering indicatrices of PVA-based sample for parallel (1) and orthogonal (2) orientations of magnetic field and incident light polarization at $H = 500$ Oe

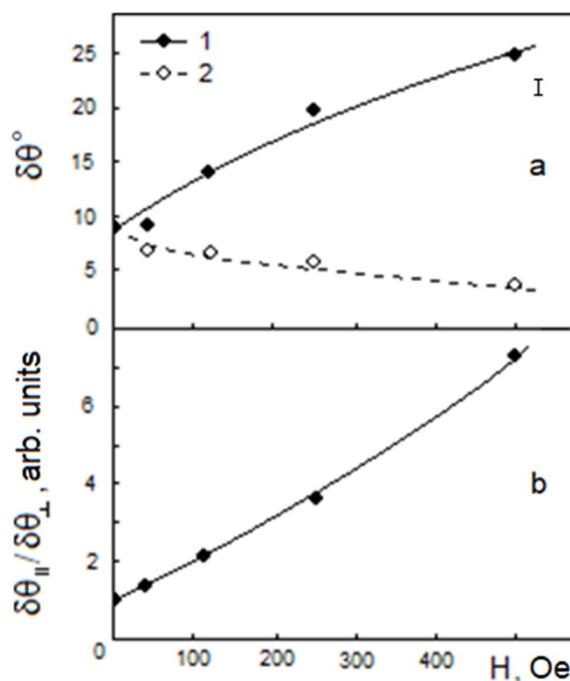


FIG. 5. The width of the scattering indicatrix depending on the magnetic field for different geometries of the experiment: 1 – parallel orientation, 2 – perpendicular orientation (a); the ratio of widths corresponding to these orientations (b)

large width of the indicatrices, for all films manufactured at $H \neq 0$ the value P does not depend on θ and, as mentioned above, does not differ from P of incident light. The classical diffraction pattern from individual aggregates isolated by laser focusing has been observed previously in MF with a complex solvent [6]. In the present work, a similar effect was also recorded, for example, it was clearly manifested on a well-formed structure in an epoxy resin matrix, similar to the one shown in Fig. 2.

Most of the experiments, however, were performed without focusing. Assuming the diameter of the laser spot to be 1 mm and using the images in the microphotographs of Fig. 1, it is possible to estimate the average number of scattered radiation sources in several tens. Consequently, the indicatrix should be a result of summation of a set of diffraction patterns with different parameters. We emphasize that this idea implies a simple scattering. This condition can be considered fulfilled a fairly good, since at small (not much larger than d) film thicknesses, overlapping aggregates practically do not occur. (At the same time, the attenuation of the passing laser beam is quite significant, but this is probably due to the fact that the main contribution to extinction comes not from absorption in magnetic nanoparticles, but namely from scattering). Accordingly, a further increase in the width of the indicatrix, measured when the polarization plane of incident light

coincides with the direction of the field, stops with increasing H . It should be mentioned that the growth of aggregates begins from the emulsion, i.e., they combine mainly microdroplets, in which the field induces a magnetic moment, rather than individual nanoparticles. This state itself ($H = 0$, Fig. 1a) is somewhat different in its effect from all the others in that the shading elements here can be quite small, perhaps, in some part approaching individual particles in size. This is confirmed by a very weak, but still noticeable, dependence of P on θ , suggesting a possible admixture of scattering by the Mie mechanism [8].

Thus, the data of light scattering experiments reflect the internal structure of the studied samples and allow us to draw certain conclusions about their magnetic behavior.

4. Conclusion

It was shown in present work that in a composite nanomaterial prepared on the basis of a polymer matrix with inclusions of nanoparticles of magnetically ordered material, a strongly anisotropic structure appears under the influence of a magnetic field, and its formation is mainly completed close to the saturation field. When using magnetic liquids as a filler, aggregates arising in samples during their manufacture are fixed in a solid medium, representing a system that is convenient to study by optical methods, using, in particular, the light scattering technique.

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