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Magnetostriction in ferrogels based on physical and chemical networking with embedded strontium hexaferrite particles

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Magnetostriction in ferrogels based on physical and chemical networking with embedded strontium hexaferrite particles

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Abstract. Magnetostriction of ferrogels based on physical and chemical networking with embedded strontium hexaferrite particles was studied in 420 mT uniform magnetic field. Ferrogel with physical networking was based on natural polysaccharide – guar gum, which gelates due to formation of H-bonds. Ferrogel with chemical networking was synthesized by radical polymerization of acrylamide. Magnetostriction of the physical ferrogel resulted in the increase of length of the gel specimen along the field lines and in the proportional decrease of its width in the direction across the field lines. In case of chemical ferrogel, both the length and the width increased in the uniform magnetic field leading to the increase of the ferrogel volume.

1. Introduction

Magnetostriction is a phenomenon when ferromagnetic materials change their shape or/and dimensions during magnetization in applied magnetic field. It was discovered by Joule in 1842 who had observed the change in dimensions of an iron rod due to magnetic forces [1]. In typical magnetic materials – metals and oxides, the magnetostriction effects are relatively small, and they are, in general, related to crystallographic distortions of lattices [2]. Meanwhile, magnetostriction can be considerably larger in composite materials and especially in polymeric composites with embedded magnetic particles. The underlying reason for large magnetostriction effect is the ability of a polymeric chain to change reversibly its molecular conformation under the force [3], provided by the interaction of magnetic particles with the field and with each other.

Magnetostriction in magnetic polymeric composites had been addressed in a number of experimental and theoretical studies [4-8]. From theoretical point of view, magnetostriction of an amorphous uniformly magnetized elastic composite in constant magnetic field is similar to that of a droplet of ferrofluid There were numerous works in which the deformation of droplets in ferrofluid emulsions were calculated [9-10]. It was shown that a non-compressible uniformly magnetized sphere in a constant magnetic field [4, 9-10] elongates in the direction of field lines and shrinks in the perpendicular direction. The sphere is thus transformed to ellipsoid with its longer axis in the direction of the field. Such a result stems from the minimum of the free energy based on a balance between magnetic energy and surface energy [4]. The elongation of a magnetic composite along the field lines (positive magnetostriction) was experimentally confirmed in several reports [4-7]. It is important, however, to point out that the mentioned theoretical result refers to magnetostriction of i) non-compressible ii) uniformly magnetized composite. If one of these two conditions fails, then there

might be deviations from the predicted behavior. For example, it was shown theoretically [8] that if the condition of uniform magnetization is violated, which is certainly true for disperse magnetic systems, then the negative magnetostriction can also take place due to the alignment of magnetic particles in the elastic composite.

It is also worth noting that the reported results on magnetostriction of magnetic polymeric composites mostly refer to ferroelasts. Meanwhile, there is another type of elastic magnetic composites – ferrogels, which comprise magnetic particles immobilized in polymeric network swollen in liquid [11-16]. Unlike ferroelasts, ferrogels are not subjected to the condition of constant volume at deformation as they can swell or contract in the liquid, which can enter or leave the elastic network. Thus, magnetostriction of ferrogels is an open question as they might not obey both the condition of non-compressibility and that of uniform magnetization. In general, it is quite likely that the magnetostriction behavior of ferrogels is not universal but strongly depends on the chemical composition, particle alignment and their interaction [17-19].

The objective of the present work is to study magnetostriction in ferrogels with different types of polymeric networks but with the same magnetic particle content. As such, we take strontium hexaferrite as a magnetic filler and hydrogels with different types of networking: physical cross-linking and chemical cross-linking.

2. Experimental part

2.1 Characterization of magnetic particles

Strontium hexaferrite (SHF) was a commercial product, purchased from Olkon (Kineshma, RF). It was produced by the industrial sintering method with consequent milling. Figure 1 shows scanning electron microscopy (SEM) image of SHF powder.
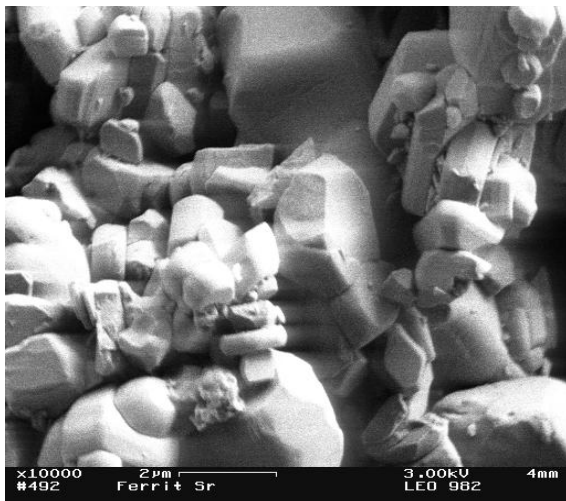

Figure 1. SEM micrograph of strontium hexaferrite particles (Karl Zeiss LEO 982).

SHF particles are polydisperse with particle dimensions varying from 0.1 to 5 μm and irregularly shaped with sharp corners in a majority of cases. A rough estimation of the average size can be done using the specific surface area of the material, which was 3.9 m^2/g, as measured by low temperature nitrogen adsorption (Micromeritics TriStar3000). In quasi-spherical approximation, the average diameter (D) of particles in microns relates to the specific surface area (S) as $D = 6/(S*\rho)$ with ρ denoting the density of particles. Calculation gives 0.3 μm for the lower estimation of average particle size.

The phase composition of the magnetic filler was characterized by X-ray diffraction technique (XRD) using BrukerD8 Discover diffractometer. According to X-ray powder diffraction data, the

crystalline structure consisted of 87% of main phase (hexagonal, S.G. P63/mmc) – strontium hexaferrite $SrFe_{12}O_{19}$ and 13% of hematite Fe_2O_3 (rhombohedric, S.G. R-3c).

Magnetic properties of SHF were measured at room temperature by a vibrating sample magnetometer (VSM). The hysteresis loop is presented in Figure 2. It is noticeable that saturation is not reached even in the field of 17 kOe, which we attribute to the irregular shapes of the particles and internal stress in their structure. A quite high magnetization value of about 52 emu/g at 17 kOe indicates that the size of the particles is large. The observed coercivity about 1250 Oe evidences that the SHF material is magnetically hard.
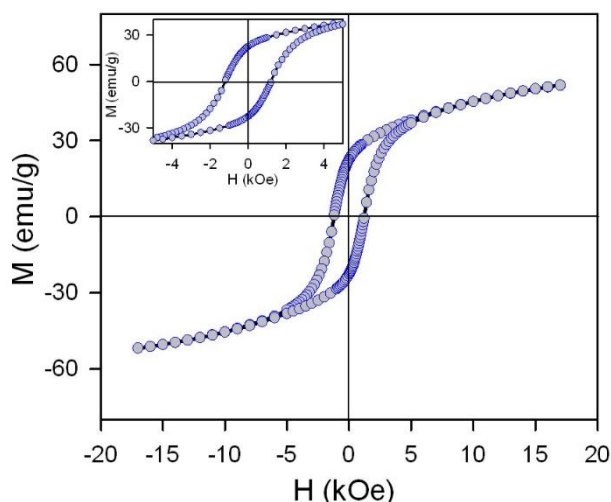

Figure 2. Magnetic hysteresis loop of SHF measured at room temperature; inset shows an enlarged view of the low field range.

2.2. Synthesis and characterization of ferrogels

Ferrogel with physical network was based on natural polysaccharide, viz. guar gum (Sigma-Aldrich, St. Louis, USA). Its average molecular weight was $1.6*10^6$ determined by viscometry. Guar gum among other polysaccharides is known to form physical gels in water solutions even at concentration around 1%. The networking of such gels is provided by intermolecular hydrogen bonds. The stock solution of guar gum was prepared by vigorous stirring of guar gum powder in distilled water for 60 min until visual homogeneity was achieved. Then solution was kept at 90 C for 5 hrs, cooled down to room temperature. SHF was dispersed by ultrasound in a small portion of water. The obtained slurry was vigorously stirred with guar gum solution to prepare ferrogel. Weight fraction of SHF particles in ferrogel was 12.5%. Ferrogel with physical network will be denoted below as FGI.

Ferrogel with combined physical and chemical networking was based on guar gum incorporated into polyacrylamide cross-linked matrix. The synthesis was performed by radical polymerization of monomer – acrylamide – AAm (AppliChem, Darmstadt, Germany) in water solution with methylene diacrylamide (MDAA) as a cross-linking agent. AAm to MDAA molar ratio was 100:1. Initiator of polymerization – ammonium persulfate (APS) was used in 5 mM concentration. SHF was dispersed in water solution of guar gum, which prevented sedimentation of the SHF particles. This suspension was mixed with AAm, MDAA, APS, and water under vigorous stirring. Concentration of guar gum in the reaction mixture was 0.6% by weight. Polymerization took place for 60 min at 70 C. After the synthesis the ferrogel was washed in distilled water for 2 weeks with daily water renewal. Ferrogel with combined networking will be denoted below as FGII. The weight fraction of SHF in ferrogel FGII swollen to equilibrium was 3.70%.

2.3 Testing of magnetostriction

Magnetostriction of ferrogels in a uniform magnetic field was measured using the magnetic system designed and manufactured at JSC "URALREDMET" (Verkhnyaya Pyshma, RF). The design of the magnetic circuit is presented in figure 3.

The magnetic system comprised permanent NdFeB magnets assembled with magnetic conductors. This setup provides vertical uniform magnetic field 0.420 ±0.5% T in the central zone 1 cm^3 where the optical cuvette with ferrogel specimen was placed. Images of the specimen in a magnetic field were captured with an EVS color VEC545 USB camera.
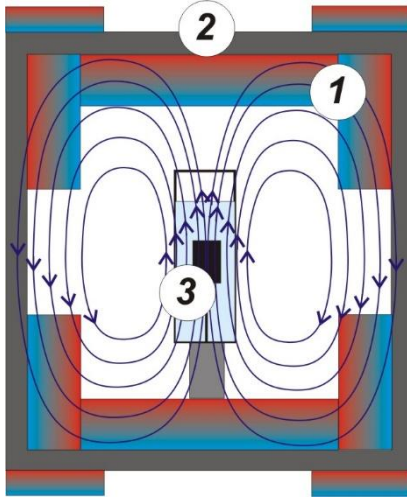

Figure 3. Schematic view of the magnetic system used in magnetostriction experiments. 1 – NdFeB permanent magnets. 2 –magnetic conductor. 3 – optical cuvette with ferrogel sample.

3. Results and discussion

Figure 4 presents the images of ferrogel sample FGI taken in zero field and after exposure to uniform magnetic field 420 mT in the magnetic setup (figure 3) for 170 min. A spherical sample FGI with approximate diameter of 3 mm was pinned by a needle mounted vertically downside at the cap of the optical cuvette Several droplets of water were put in the cuvette to provide saturated water vapor inside and to prevent weight loss of the ferrogel due to evaporation. As the physical gels are typically very soft, the spherical sample has acquired the shape close to ellipsoid in the gravity field, see figure 4 (a), where the minor and major semi-axes of ellipsoid are marked as *a* and *b*, respectively.

In figure 4 (b) it is clearly seen that if the ellipsoidal FGI sample was exposed to a uniform magnetic field, it stretched in the direction of the field. Its major axis extends, and the minor axis shortens. Such deformation is totally consistent with classical consideration of magnetostriction of a non-compressible uniformly magnetized sphere [4].
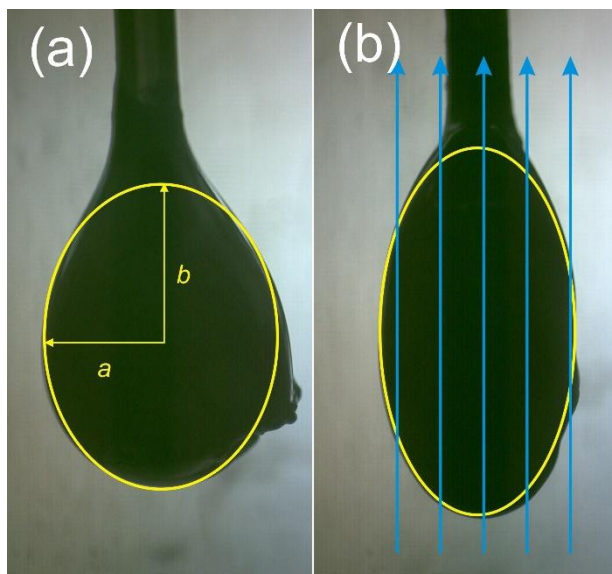

Figure 4. (a) – Image of the FGI ellipsoidal sample in zero field. (b) – The same sample after 170 min exposition to uniform magnetic field 420 mT. Blue arrows show the direction of the field lines. Yellow ellipses present graphical approximation of the shape.

Figure 5 shows the time evolution of the relative magnetostriction of FGI sample. Notably, the total volume of FGI sample calculated using the values of semi-axes of the ellipsoid, remained constant within experimental error all through the duration of the test. Meanwhile, the relative length of the FGI sample along the field lines clearly increased while the relative width of the sample in the direction across field lines decreased. These trends are fitted well by exponent function

$$F(t) = 1 + A(1 - \exp(-\frac{t}{\tau})) \tag{1}$$

where τ denotes relaxation time, which was found equal to 7.36 min both along and across the field lines. Coefficient A that yields the deformation scale was found to be 0.37 (37%) for the longitudinal (along the field) strain and –0.15 (–15%) for the transverse one.

Figure 6 presents time evolution of magnetostriction of the ferrogel with combined chemical and physical networking (FGII) if it was exposed to a uniform magnetic field 420 mT. It is worth mentioning that, unlike the sample FGI, which was kept in the vapor phase during the exposure, ferrogel FGII was immersed in water inside the cuvette. Whereas FGI with physical networking cannot not be placed in water because of its dissolution, a sample of chemically cross-linked FGII does not dissolve.
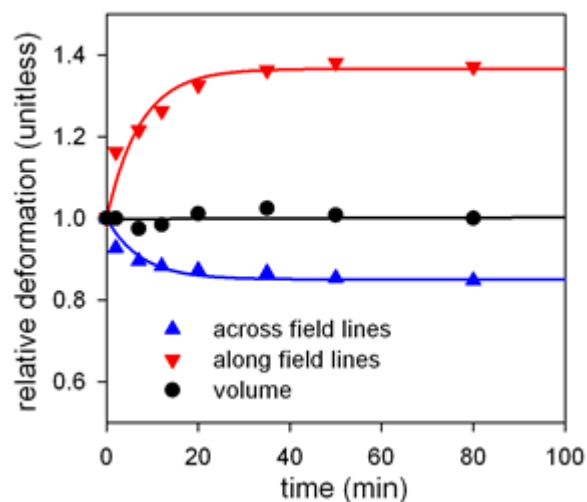

Figure 5. Dependence of magnetostriction of FGI sample in 420 mT uniform magnetic field on the exposure time. Lines correspond to fitting by exponential decay function.
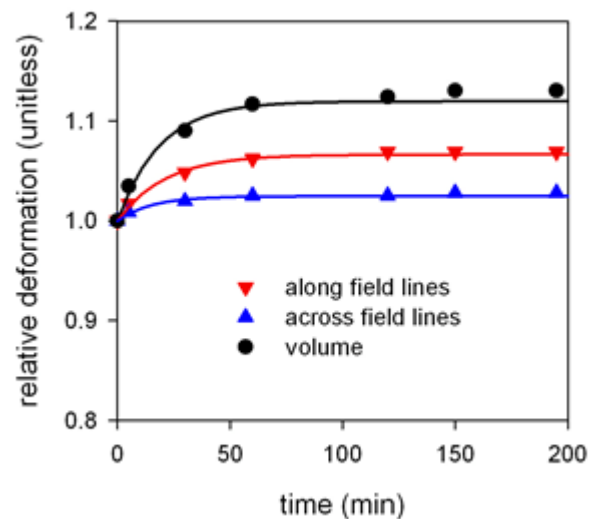
Figure 6. Magnetostriction of FGII sample in 420 mT uniform magnetic field as a function of the exposure time. Lines correspond to fitting by the exponential function.

It is clearly seen that trends in Figure 6 for FGII differ from those of FGI. Both the length and the width of the sample increase. As a result, the condition of constant volume is no longer valid, and the volume increases substantially. The trends are fitted well by exponential decay function of Equation (1), where τ = 16.7 min, i.e., is twice greater than that of FGI. Certainly, it is because chemical network is denser and stiffer than the physical network and, thus, is more resistant to deformation.

In our view, the observed difference between ferrogels with physical and chemical networks might be related to the difference in their swelling. In general, the magnetostriction of a free-hanging sample is the consequence of minimization of its total (magnetic + elastic) energy. If the volume of composite is fixed, like in physical gel FGI, then the only way to minimize the magnetic energy is to elongate along and contract across the field lines.

Meanwhile, if there is an option to change the volume (by means of transporting water in or out of the gel), then the magnetic energy can be diminished also by the volume increase. One possible explanation is that stretching in the transversal direction weakens the lateral repulsion forces between the quasi-chains formed due to the particle attraction along the field direction; in result, the magnetic dipole energy of the sample reduces.

4. Conclusions

Magnetostriction of ferrogels crucially depends on the possibility of their swelling or deswelling in liquid. If swelling of a ferrogel is forbidden (the condition of volume constancy holds), then magnetostriction results in elongation of the ferrogel along field lines accompanied by proportional contraction in the transverse direction. Meanwhile, if swelling is possible, then other scenarios of magnetostriction can take place. In ferrogels with combined chemical and physical networks filled with strontium hexaferrite particles we found that magnetostriction in uniform magnetic field of 420 mT results in the increase of both the length and the transverse size of a ferrogel.

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