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Heating of polyacrylamide ferrogel by alternating magnetic field

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ABSTRACT

Ferrogel based on polyacrylamide network with embedded maghemite nanoparticles with mean number average particle diameter 12 nm was synthesized by radical polymerization in water-based ferrofluid. The network structure of ferrogel was characterized by Flory–Rehner theory and it was shown that the embedded particles were substantially larger than the mesh size. It prevented the translational movement of particles in the ferrogel. The immobilization of particles was confirmed by dynamic light scattering. The adhesion of macromolecular chains to the particles was determined by calorimetry using thermochemical cycle. The enthalpy of interfacial adhesion was found several orders of magnitude higher than the energy of dipoles in typically applied magnetic fields. Despite the difference in the mobility of particles in ferrofluid and ferrogel the comparative study of their heating in alternating magnetic field, however, revealed their close similarity. In both cases it was governed by superposing of Neel and Brownian relaxation mechanisms.

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1. Introduction

The heating of the liquid systems with dispersed magnetic nanoparticles by alternating magnetic field is among the most promising medical applications of magnetic nanomaterials. It opens way to the local hyperthermia of tissues in cancer therapy [1–4]. Therefore, the magneto-induced heating of ferrofluids is extensively studied experimentally and theoretically [5–10]. The mechanism of heating involves the dissipation of the magnetic energy during reorientation of magnetic dipoles in the alternating field according to the basic mechanisms of Neel and Brownian relaxation. In case of Neel relaxation the magnetic moment of a particle changes its direction inside the crystalline lattice. In case of Brownian relaxation a particle with its dipole rotates in the alternating field as a whole [5–10]. Meanwhile, there are magnetic dispersions in which the movement of magnetic particles is restricted. For instance, it takes place if ferrofluid is placed in a biological tissue and magnetic particles are absorbed by its structural elements. Another example of a liquid system with the restricted mobility is ferrogel, which is an advanced biocompatible and biomimetic material prospective for bioengineering and biomedical applications. Ferrogel structure comprises two substructures which are: (i) the polymeric cross-linked network swollen in water, (ii) the magnetic subsystem of embedded magnetic particles. Both subsystems cross-influence each other and it

makes ferrogels tunable and versatile materials. The magnetic behavior of ferrogel depends not only on the magnetic subsystem but also on the properties of the polymeric network. There are several studies [11–14] which report the influence of the gel network on the relaxation of the dipoles in the magnetic field. It was shown that the cross-link density of a gel strongly affect the superposing of Neel and Brownian relaxation of magnetic particles.

One of the interesting aspects of the magnetic behavior of ferrogels is their heating with alternating magnetic field due to the power losses by dipole relaxation. What would be the relation between Neel and Brownian relaxation mechanisms in the specific ferrogel structure? The resolution of this question depends on the mobility of MNPs embedded in polymeric network of ferrogel. There are at least two factors which govern the mobility of MNPs in the network. One is the relation between the MNP diameter and the mesh size of the network. If the MNPs are smaller than the mesh size, then the particles can move inside the network. In the other case they can only rotate at their location being entrapped in the network. The second factor is the affinity of the MNP to the polymeric subchains which constitutes the network of the gel. Strong adhesion of macromolecules to the surface of MNPs can prevent their rotational mobility as MNPs become tightly bonded to the network. Both factors can vary depended on the nature of MNPs and polymeric gel. Therefore, their estimation is very important concerning the mechanism of magnetic losses in ferrogels.

The present research is a comparative study of the heating by the alternating magnetic field a ferrofluid and a ferrogel, which contained the same MNPs. The objective was to estimate the restrictions which the gel network imply on the mobility of MNPs

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and how it affected the magnetic losses in the alternating magnetic field. We took maghemite MNPs synthesized by laser target evaporation. This type of MNPs was exhaustively characterized in our previous studies [15,16]. Polyacrylamide was taken for the gel network. The polymeric gels of polyacrylamide are well-characterized in numerous studies [11–13] and are extensively used in biomedical applications due to their biocompatibility. In the present study we have characterized both the mismatch between the MNPs dimensions and the mesh size of gel network and the adhesion of polymer to MNP surface.

2. Experimental part

2.1. Synthesis and characterization of MNPs

Iron oxide ($\gamma\text{-Fe}_2\text{O}_3$) magnetic nanoparticles (MNPs) were made by laser target evaporation (LTE) – the method of high temperature physical dispersion based on the evaporation of a solid pellet by the laser beam with consequent condensation of vapors in the gas phase [17,18]. Transmission electron microscopy (TEM) was performed using JEOL JEM2100 microscope. The produced MNPs were spherical and non-agglomerated. Particle size distribution (PSD) was lognormal with median value 11.4 nm and dispersion 0.423 (Fig. 1).

$$\text{PSD}(d) = \frac{2.462}{d} \exp\left(-0.5 \left(\frac{\ln \frac{d}{11.4}}{0.423}\right)^2\right) \quad (1)$$

The chemical composition of MNPs determined by the electrochemical Red-Ox titration using an automatic titrator TitroLine (Schott Instruments) was close to Fe_2O_3 . The crystalline structure of MNPs was analyzed using Bruker D8 Discover X-ray

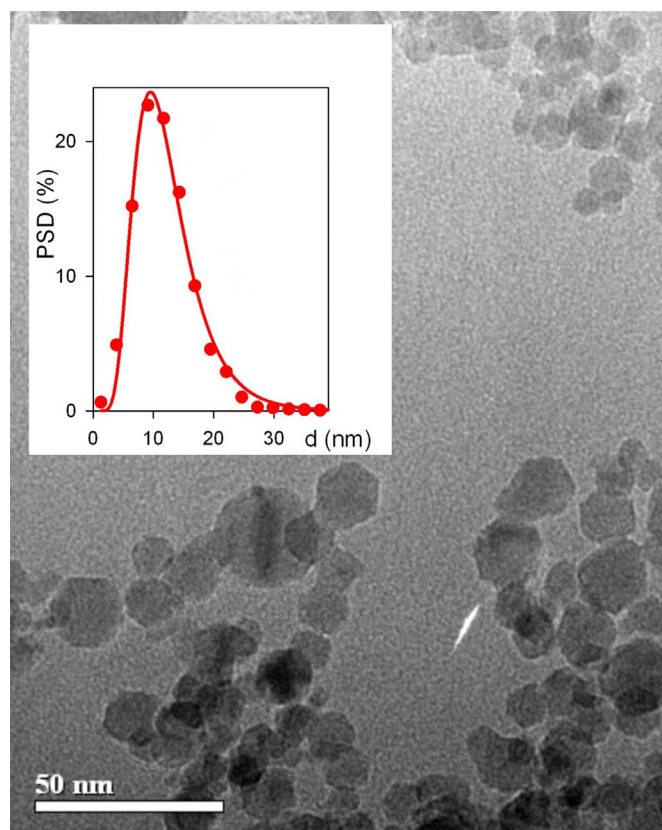


Fig. 1. TEM image of MNPs. Inset – particle size distribution.

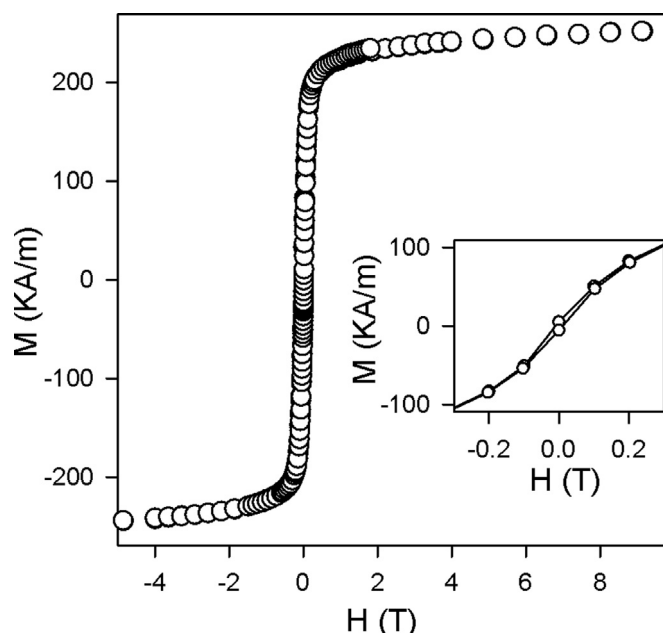


Fig. 2. Hysteresis loops of MNPs at 300 K.

diffractometer. It corresponded to maghemite. A detailed discussion on the crystalline and chemical structure of LTE MNPs was provided in our previous report [15]. Hysteresis loops for air-dry MNPs at 300 K were obtained using squid magnetometer MPMS XL7 (Quantum Design). Saturation magnetization of MNPs was 252 KA/m. The magnetic behavior of MNPs in low fields was close to superparamagnetic (Fig. 2).

2.2. Synthesis of ferrofluid, ferrogel and model composite

Ferrogels were synthesized by radical polymerization of acrylamide in ferrofluids of LTE $\gamma\text{-Fe}_2\text{O}_3$ MNPs. Suspensions of MNPs were prepared in distilled water with the addition of an electrostatic stabilizer sodium citrate in 5 mM concentration. Ultrasound treatment was done using Cole-Palmer CPX-750 ultrasound processor at a 300 W average power output level. Suspensions in an initial concentration 15% (by weight) were treated by ultrasound, and the diminishing of an average hydrodynamic diameter of aggregates in suspension was monitored by the dynamic light scattering. The stock suspension was then diluted with 5 mM sodium citrate solution to prepare ferrofluids with concentration of MNPs 5.0%, 9.1%, 10.9%, 13.0%.

Weighted portions of acrylamide (AppliChem, Darmstadt) were dissolved in ferrofluids with MNPs concentrations 10.9% and 13.0%. In each case monomer concentration was 1.6 M. Cross-linking agent – methylenediacylamide was added to the mixture in 16 mM concentration to provide network density 1:100, which is the average number of cross-links per number of monomer units in linear subchains. Ammonium persulfate in 3 mM concentration was used as an initiator. Polymerization was performed in PE probe tubes (diameter 10 mm) at 80 °C for 2 h. Upon the polymerization gel cylinders were removed from the probe tubes and washed in distilled water for 2 weeks with water renewal every 2 days until constant weight of the gel samples was achieved. As the gel samples swelled, the final concentration of MNPs changed with respect to the initial concentration established in the synthesis. Finally, the concentration defined by the thermogravimetric analysis became 7.4% and 10.5% of MNPs in ferrogel by weight.

Model binary composites of polyacrylamide filled with MNPs were prepared for the determination of the enthalpy of interaction

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