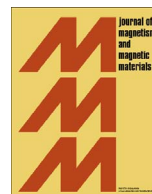




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Multidomain iron nanoparticles for the preparation of polyacrylamide ferrogels

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ABSTRACT

Ferrogels (FG) based on poly(acrylamide) (PAAm) with embedded multidomain iron magnetic nanoparticles (MNPs) were synthesized by radical polymerization in water. Iron MNPs prepared by the electrical explosion of wire were spherical in shape and have an average diameter around 100 nm. MNPs were modified by a surfactant – oleic acid to improve their dispersion in water. DLVO theoretical consideration was done to understand the stability of dispersions. By microcalorimetry it was shown that the oleic layer on the surface of MNPs prevents their interaction with PAAm network of FG. Mechanical testing of the compression modulus and the deformation of FGs in magnetic field show up their prospectiveness as a material for magnetically sensitive MEMS and actuators.

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1. Introduction

Ferrogels (FGs) are a soft type of highly elastic polymer composites which have magnetic particles as a constituent. The particles can be multidomain, single domain or superparamagnetic in nature. Their significant response through controllable deformation in magnetic field has attracted considerable interest for their application as smart materials [1]. Their biological applications, namely, viz. targeted delivery, labeling, radio frequency methods and contrast enhancements in imaging are few examples where size of filler particles are needed to be $\sim 1 \mu\text{m}$ or less [2]. This dimension usually corresponds to multidomain regime of applicable materials like Fe, Ni, Fe_3O_4 etc. To use them in preparation of FGs, a stable concentrated dispersion is required. Making stable aqueous dispersion of multidomain iron magnetic nanoparticles (MNPs) is a challenging task [3]. Moreover, functionalization procedure for these MNPs, post synthesis, further complicates this problem due to high particle aggregation. In present study a room temperature grinding method was employed to modify the surface of Fe MNPs to achieve their stable dispersion. The dispersion was later used in preparation of FGs with poly(acrylamide) (PAAm) network.

2. Experimental section

2.1. Materials

The iron MNPs were synthesized by the electric explosion of wire technique [4]. Surface functionalization of MNPs was carried out under ambient conditions by grinding air-dry MNPs with surfactant, oleic acid. In a typical procedure, 0.5 g of MNPs and 1.5 g of KOH were ground by mixing in agate mortar for 5 min. After homogenization, 4.5 g of surfactant was added followed by grinding for ~ 80 min till highly viscous films are formed. The mixture was washed till neutral pH and then dispersed in distilled water for desired concentration of MNPs. The visual assessment of sedimentation stability of dispersion was ~ 15 –20 min.

FGs were synthesized at room temperature by free radical polymerization of acrylamide (AAm, AppliChem, Darmstadt, Germany). Aqueous solutions of a cross-linker *N,N*-methylene diacrylamide (MDAA, Merck, Schtuchardt, Germany) (48 mM), initiator ammonium persulphate (APS) (50 mM) and aqueous dispersion of MNPs (6.3% w/w) were prepared prior to the reaction. Reactants were used as received. In a typical synthesis procedure, 1 mL of MDAA solution was added to the 0.341 g of AAm and homogenized. 0.3 mL APS solution was added followed by addition of 3 mL of water or dispersion of MNPs or both in specified amount for the preparation of gels with varying MNPs content. Then, 20 μL of catalyst – *N,N,N',N'*-Tetramethylethane-1,2-diamine (Merck) was added to the reaction mixture with vigorous stirring for few seconds. Polymerization took place in poly(ethylene)

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cylindrical tubes for 4 h [5]. The gels were taken out of mold and washed for two weeks with distilled water renewal at a two-day interval. The equilibrium swelling degree (α) of gels was calculated by $\alpha = (m_s - m_d)/m_d$, where m_s is mass of swollen gel and m_d is mass of dried gel. This value was further used in calculation of volume fraction of oleate coated MNPs (ϕ) in swollen FGs.

2.2. Methods

XRD diffractograms were obtained using a diffractometer Bruker D8 Discover in copper radiation ($\text{Cu } K_{\alpha 1,2} \lambda = 1542 \text{ \AA}$) with a graphite monochromator in the diffracted beam. The Rietveld refinement of XRD pattern was performed using *Topas-3* software. Transmission electron microscopy (TEM) was performed were performed using a JEOL JEM2100 microscope operating at 200 kV. Dynamic light scattering (DLS) and zeta-potential measurements were performed using Brookhaven instruments BI-90 Plus Particle Size Analyzer. Bright field optical microscopy was done using BX51 Olympus microscope. Specific surface area of MNPs was measured using Micromeritics TriStar3000 sorption analyzer. Microcalorimetry studies of the enthalpy of interfacial adhesion between PAAm and MNPs were performed using Calvet micro calorimeter of a laboratory construction [6]. Young's modulus was measured using a laboratory setup provided compressive loading of gel samples and optical registration of their deformation. Deformation of ferrogels in magnetic field was monitored by an optical system in a laboratory setup. A magnetic system of NdFeB permanent magnets provided a uniform field 420 mT in the central zone $10 \times 10 \times 10 \text{ mm}^3$ [7].

3. Results and discussion

The structural and magnetic characterization of bare and oleate modified MNPs is shown in Fig. 1.

The room temperature magnetization loop of MNPs shows typical ferromagnetic behavior as visible from high coercivity and retentivity (Fig. 1 and inset a). The (TEM) images of bare MNPs shows that particles have spherical shape and are polydisperse (Fig. 1 inset b). The statistical size distribution analysis was carried out using lognormal distribution function by counting over 1000 particles (inset c). The mean average particle diameter was 65.8 nm. The X-ray diffraction patterns (XRD) of oleate modified

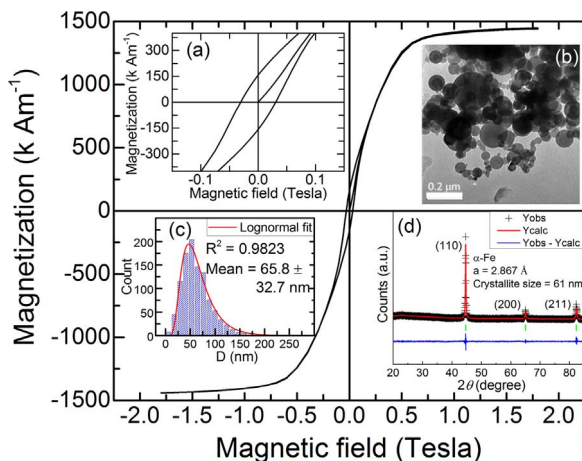


Fig. 1. M-H loop of bare MNPs at 298 K. Inset 1a shows magnified view of magnetization curve. Inset 1b shows the TEM micrograph of bare FPNs. Inset 1c shows size distribution of MNPs from several TEM images. The red curve is lognormal fit on distribution. Inset 1d shows the rietveld refinement of XRD pattern of oleate coated MNPs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

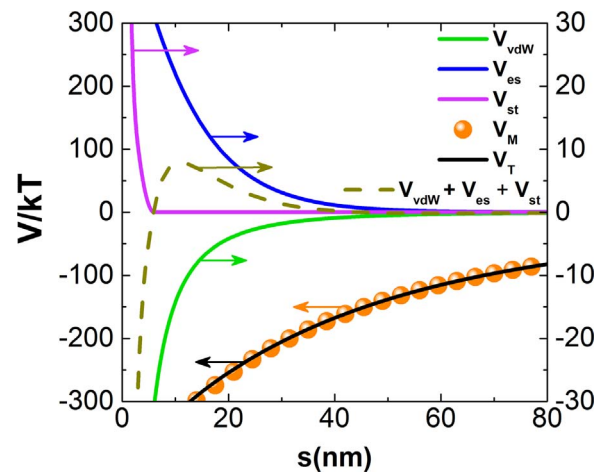


Fig. 2. Normalized interaction energy curves for two identical MNPs as a function of surface-to-surface separation (s). The parameters used for the calculation of energy curves are: the radius of particles, $a=54.5 \text{ nm}$ (from BET measurement; specific surface area of MNPs = $7 \text{ m}^2/\text{g}$), Hamaker constant, $A=2.94 \times 10^{-19} \text{ J}$ [3,8,9], relative permittivity of carrier liquid, $\epsilon_r=80.4$, vacuum permittivity, $\epsilon_0=8.85 \times 10^{-12} \text{ Fm}^{-1}$, ϕ_0 is the surface potential which is approximated here with measured zeta potential, $\zeta = -35 \text{ mV}$, $T=298 \text{ K}$, $k_B=1.38 \times 10^{-23} \text{ J K}^{-1}$, elementary charge, $q=1$, $N_A=6.023 \times 10^{23} \text{ mol}^{-1}$, valency of ions (approximated here with ionized constituents of free surfactants i.e. K^+ and oleate), $z_i=1$, ionic concentration, $c_i=0.001 \text{ M}$, volume of a water molecule, $\nu=0.03 \text{ nm}^3$, volume fraction of coated surfactant, $\phi_p=0.05$, Flory-Huggins parameter, $\chi=0.42$, adsorbed layer thickness, $\delta=3.0 \text{ nm}$ [10], density of surfactant, $\rho=0.895 \text{ g cm}^{-3}$, molar mass of surfactant, $M_w=282.46 \text{ g mol}^{-1}$, vacuum permeability, $\mu_0=1.25 \times 10^{-6} \text{ Hm}^{-1}$ and remanent magnetization, $M_r=157.7 \text{ kA m}^{-1}$ (from Fig. 1). Arrows indicate respective ordinates of curves.

MNPs show Bragg peaks at 44.66° , 65.03° and 82.35° which are characteristic of $\alpha\text{-Fe}$ phase, as shown in inset d. The specific surface area of MNPs was found to be $7 \text{ m}^2/\text{g}$ which corresponds to average diameter of 108.1 nm , which correlates well with TEM results.

The colloidal stability of MNPs dispersion employed in preparation of FGs was qualitatively modeled by extended DLVO approach [3]. Interaction energy curves simulated for current aqueous dispersion are shown in Fig. 2.

The van der Waals interactions were calculated in a classical manner excluding retardation effects. This attractive interaction energy term (V_{vdW}) can be expressed as

$$V_{\text{vdW}} = \frac{-A}{6} \left[\frac{2a^2}{s(4a+s)} + \frac{2a^2}{(2a+s)^2} + \ln \left\{ s \frac{(4a+s)}{(2a+s)^2} \right\} \right] \quad (1)$$

The electrostatic repulsion between coated MNPs due to the charged outer layer of fatty acid was evaluated as:

$$V_e = 2\pi a \epsilon_r \epsilon_0 \psi_0^2 \ln(1 + e^{-\kappa s}) \quad (2)$$

κ is the inverse Debye length and can be written as $(q^2 N_A (\sum z_i^2 c_i) / k_B T \epsilon_0 \epsilon_r)^{-1/2}$. The magnitude of z_i , c_i , and ϕ_p for inverse Debye length calculation were taken in the range of similar studied systems [11,12].

The short range steric interactions among MNPs, imparted by surfactants including osmotic effect and elastic repulsions were taken as [13]

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