Magnetic Applications of Polymer Gels

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SUMMARY: In this paper we report results of both, material preparation and magnetic characterisation, on $CoFe_2O_4$ particles of nanometric size formed by in-situ precipitation within polymer gels. The size of the particles was controlled within a very narrow volume distribution and its average value was shifted from 2 to 10 nm. The existence of nanoparticles showing, at room temperature, coercive field values between 500 and 900 Oe and saturation magnetisations of about 500 emu/cm^3, suggest to use these systems to get magnetic recording media with ultra high density. Poly(vinyl alcohol)(PVA) and Polystyrene (PS) films were prepared from this nanocomposite material. After a magnetic field treatment nanoparticles within the PVA films are free to rotate in response to an applied magnetic field. This PVA based nanocomposite film portends a new class of magnetic material with very little or no electrical and magnetic loss.

Introduction

The design and synthesis of materials with nanometer dimensions are the subject of intense current research[1)]. Materials with nanoparticles exhibit novel electronic, optical, chemical and magnetic properties due to their extremely small dimensions[2)].

The critical point in obtaining nanosized materials is to prevent particles from aggregation[1,3)]. By use of polymer gels it is possible to stabilise, isolate and characterise a mesoscopic form of $CoFe_2O_4$. The formation of this magnetic material shows typical structure characteristics on the nanometer scale, and can be controlled by the polymeric gel matrix that acts as a spatially restricted microenvironment and molecular template for inorganic mineralisation[4-6)].

Potential applications exist for these magnetic materials in information storage, generator, electronic circuitry, sensor and electrical transformers[7-12)].

The present study deals with the preparation and characterisation of PVA and PS films with a new type of nanocomposite magnetic material, which: i) presents mechanically free-rotor nanoparticles and ii) can be used as a magnetic recording media with ultra high density.

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Experimental

Crosslinked polystyrene sulfonic acid sodium salt (Scientific Polymer Products, Inc.) was exchanged with Co(II) and Fe(II) (molar ratio 2:1) from an aqueous solution of the respective chlorides, followed by thorough washings to remove excess of physisorbed ions. The gel was then exposed to a 0.5 M aqueous solution of NaOH at 60ºC which causes precipitation of the corresponding hydroxide and the conversion to oxide. The gel was thoroughly washed with distilled water to neutral pH and dried. The same procedure was repeated for 6 times.

In order to obtain PVA based films from the nanocomposite material a two step process was carried out. In a first step, a water ferrofluid was made in the following way: The mineralised gel was roll milled for 4 days. The fine powder obtained was then wet milled for 24 hours by adding the appropriate amount of deionised water. The liquid was centrifuged at 600 rpm 4 times and concentrated in an Amicon 8050 ultrafiltration cell using a YM30 membrane under 36psi N_2 gas. In a second step, the appropriate amount of the water ferrofluid was mixed with an aqueous solution of PVA (Aldrich). Polymer films were prepared by pouring the solution into glass plates and allowing the water to evaporate at room temperature. Films were dried under vacuum at 50ºC for 24 hours.

PS based composite materials were obtained by mixing the appropriate amount of the mineralised gel, in fine powder form, with polystyrene (BASF) in a Haake Rheocord 9000 unit coupled to a Rheomix 600 mixer with two roller rotors at 200ºC. The materials obtained were pressed in a hot press to obtain thin samples.

Iron and cobalt content of the samples were determined by inductively coupled plasma mass spectroscopy (ICP-MS) with a PolyScan 61E Thermo Jarrel ASH spectroscope.

Wide Angle X-ray Diffraction (WAXD) patterns from the mineralised gel were obtained at room temperature using a Philips Geiger X-ray diffractometer operating in the 2θ range between 2 and 72 degrees at a rate of 1°/min, using Ni-filtered CuKα radiation.

The mineralised gel was studied by transmission electron microscopy (TEM). The dry gel was embedded in a Spurr resin and ultra micro sectioned prior to analysis with a Hitachi H800-MT microscope.

Magnetic characterisation of the samples (mineralised polymer, ferrofluid and polymer films) was done using a SHE-SQUID magnetometer and a sealed Kevlar sample holder.

Results and Discussion

The lattice constants deduced from the WAXD patterns of the mineralised polymer gel (dried state) are consistent with those of $CoFe_2O_4$ (see Fig. 1). The average diameter of the $CoFe_2O_4$ particles was 10 nm as determined from the widths of the peaks using the following equation[13]:

$$\langle d \rangle = \frac{1.38762}{FWHH \frac{\pi}{180} \cos\left(2\theta_{peak} \frac{\pi}{360}\right)}$$

where <d> is the average particle diameter, FWHH is the full width at half height of the main peak and $2\theta_{peak}$ its position.

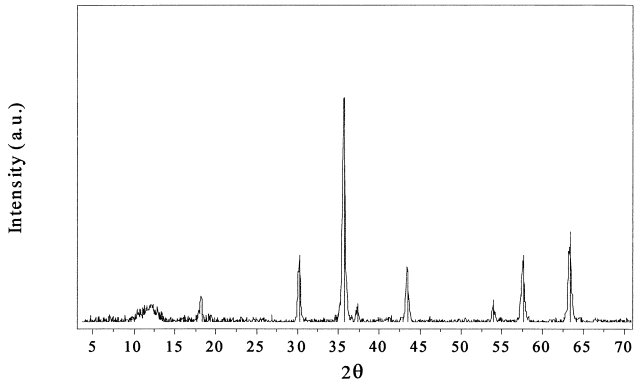

Figure 1. X-ray diffraction pattern of the mineralised polymer gel (dried state). Vertical lines stand for the theoretical positions and relative intensities of the inverse spinel $CoFe_2O_4$ diffraction peaks.

The TEM microphotographs reveal magnetic particles cubic or spherical in shape but some needle like shape particles are found. The magnetic particles do not seem to be aggregated.

The characterisation of the mineralised polymer gel by ICP-MS reveals an oxide content of 12.4 wt%.

The low field (1 kOe) magnetisation (M) vs. Temperature (T) measurements for the zero-field-cooled (ZFC) and field-cooled (FC) cases, reveal the existence of irreversibility phenomena commonly associated with metastable magnetic states (see Fig. 2). To detect the blocking temperature, T_B, the maximum in the ZFC curve, which corresponds to the blocking of the magnetic moment of the particles with random orientations of the anisotropy direction,

it was necessary to apply larger fields (5 kOe in Fig. 2). The broad maximum in the ZFC at 5 kOe is due to the broad distribution of energy barriers and relaxation times of the magnetic moments of the particles.

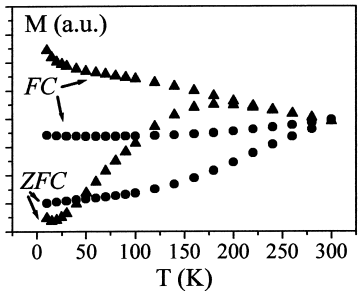

Figure 2. Magnetisation (M) vs. Temperature (T) curves for the field cooled (FC) and zero field cooled (ZFC) cases for the mineralised polymer gel sample (dried state) in an applied field of 1 kOe(●) and 5kOe(■).

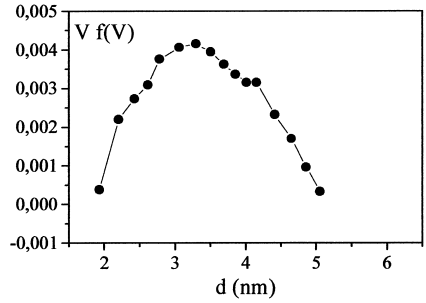

Figure 3. Volume distribution of the magnetic particles inside the mineralised polymer gel, deduced from the ZFC and FC data

The ZFC magnetisation, $M_{ZFC}(T)$, of a set of independent particles is given by[14]:

$$M_{ZFC}(T,H,t) = \frac{m_o H}{2T}\int_0^{V_B(T,t)} dVf(V)V^2$$

where H is the applied magnetic field, t is the experimental resolution time and V_B (T,t) denotes the blocking volume at any T and t. That is, at a given temperature T, particles with a volume $V<V_B$ are superparamagnetic while particles with volume $V>V_B$ are blocked in the initial states. In real systems it is always very difficult to have independent particles, but the above formula may be used, however, if the dipolar interaction between particles is much lower that the magnetic anisotropy field[15]. This is in fact our case. The volume distribution may be deduced, therefore, from the analysis of the $M_{ZFC}(T)$ curve and is represented in Fig. 3. As can be seen, the diameter of the particles is comprised between 2 and 5 nm. These values are lower than those deduced by TEM and by WAXD, suggesting that the magnetic core of the particles corresponds to only one fraction of the total crystallographic volume.

The M(H) curve at room temperature (300 K) for the mineralised resin dispersed in a PS film is presented in Fig.4. This sample shows hysteretic behaviour with a coercive field of about 820 Oe. The magnetic data together with the fact of having a dispersion of nanometric

particles with a narrow size distribution suggests that this material may be used for high recording applications[15].

The situation is very different for the PVA-based composites. While the volume distribution of the particles deduced from the ZFC and FC data is identical to the above mentioned samples, the M(H) curves (see Fig. 5) differs markedly.

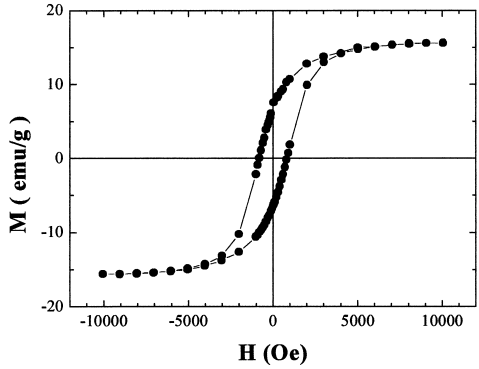

Figure 4. Isothermal magnetisation curves at T = 300 K for the mineralised polymer dispersed in a PS film.

After applying a magnetic field treatment to the PVA-based composites[16] it is possible to obtain a rapid variation of the Magnetisation vs. Magnetic field near the zero field value, as it occurs for free-rotor magnets[16]. The rapid variation of the magnetisation near zero field is better observed in the derivative dM/dH vs H shown in Fig. 6, as well as in the large reduction of the coercive field which is only of 100 Oe.

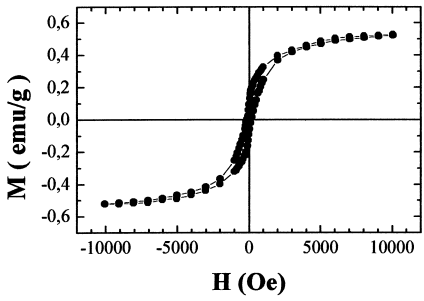

Figure 5. Isothermal magnetisation curves at T = 300 K for the ferrofluid dispersed in a PVA film.

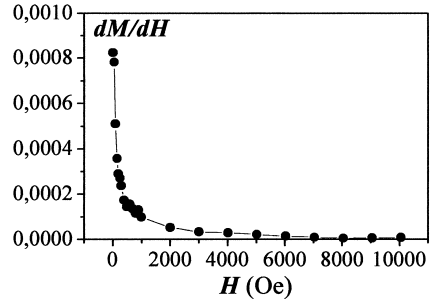

Figure 6. Derivative dM/dH as a function of the applied field, H.

At low field values there is a much faster variation of the magnetisation with the applied field than in the case of the PS-based nanocomposites. This effect may be related to the polymer matrix. In the magnetisation process, particles with their easy axis not aligned with the applied field are affected by a torque that may break the bonding between the magnetic nanoparticles and the matrix. This torque may liberate some particles, which become free to rotate and to follow without delay small magnetic fields.

Conclusions

Our method of preparation is extremely powerful in getting nanometric particles with a narrow size distribution. The magnetic data of the $CoFe_2O_4$ nanoparticles dispersed in PS films suggest that these materials may be used for high recording applications. The application of a magnetic field treatment to the PVA-based nanocomposites, produces free-rotating particles with extremely low magnetic losses. This suggests uses in sensors, switches and electrical transformers.

Acknowledgements

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