Journal of Magnetism and Magnetic Materials 149 (1995) 10–13

ELSEVIER

Journal of magnetism and magnetic materials

XRD, SEM, EPR and microwave investigations of ferrofluid–PVA composite films

R.P. Pant, Rashmi, R.M. Krishna, P.S. Negi, K. Ravat, U. Dhawan, S.K. Gupta, D.K. Suri

National Physical Laboratory, Dr. K.S. Krishnan Road, New Delhi 110012, India

Abstract

Ferrofluid–polymer composite films, prepared under the influence of a magnetic field and without magnetic field, have been studied for their physical characteristics. Results of X-ray diffraction, electron paramagnetic resonance, surface structure and microwave absorption studies are reported in this paper and the experimental data correlated with the crystallite size and relatively cluster size variation in the applied field direction.

1. Introduction

A ferrofluid is a stable colloidal dispersion of magnetic particles. This is due to a delicate balance of attractive and repulsive forces between the particles. In particular, the interaction between magnetic moments in neighbouring particles gives rise to magnetic forces and the surfactant molecules, attached to their surface.

Ferrofluids show a change in their magnetic, thermophysical, mechanical, optical and acoustic properties in the presence of a magnetic field [1]. In this paper, we report the results of our investigations on ferrofluid–polymer composite films prepared under the influence of a magnetic field. The alignment of the magnetic particles in these films is frozen in the direction of the applied magnetic field. The effect of the crystallite size and cluster size of the magnetic particles and the effect of the magnetic alignment is discussed. Data on the steric repulsion encountered by particles are obtained from X-ray diffraction (XRD), scanning electron microscopy (SEM), electron paramagnetic resonance (EPR) and microwave absorption studies.

2. Experimental

A water-based ferrofluid FW-40 from Marpomagna Co., Japan and a polymer–polyvinyl alcohol (PVA) from Loba Chemie, Bombay, were used to prepare composite films. The ferrofluid consists of Fe_3O_4 particles, of mean diameter 8 nm in a water medium [2], and has a saturation magnetization of 400 G and density of 1.359 gm/cm^3. 1 g of PVA was dissolved in 5 ml of double distilled water and then 0.5 g of ferrofluid was thoroughly mixed into it. The mixture was kept for 3–4 h to get it stabilized. This 'Ferrofluid–PVA' solution was used to prepare two sets of films: (a) without magnetic field and (b) under the influence of a magnetic field (500 G) on a glass plate. After drying in air for about 100 h the films were separated from the glass plate using a sharp-edged blade. These films were characterized by various techniques.

The XRD patterns of the samples were recorded on a Siemens D-500 X-ray diffractometer using Cu K_α radiation. Slow scans of the selected diffraction peaks was carried out in the step mode (step size 0.01°, measurement time 2 s). The physical size of the magnetite particles and their clustering behaviour were characterized by a scanning electron microscope (JEOL model JSM-35CF). Electron paramagnetic resonance measurements were carried out at room temperature and liquid nitrogen temperature using an X-band EPR spectrometer (Varian model E-112) at about 9.15 GHz. The microwave transmission loss measurement studies were made in a waveguide cell for microwave signals of 12 and 26 GHz.

3. Results and discussion

Figs. 1 and 2 show the X-ray diffraction patterns of samples (a) and (b) respectively. Both patterns show a very broad peak at $d \simeq 4.5$Å which is due to PVA polymer and other diffraction peaks belonging to the polycrystalline Fe_3O_4 phase. The intensity and d values of the observed diffraction peaks match with the cubic form of Fe_3O_4 (JCPDS data file No. 19-629). A comparison of the two diffractograms indicates a small decrease in the peak width

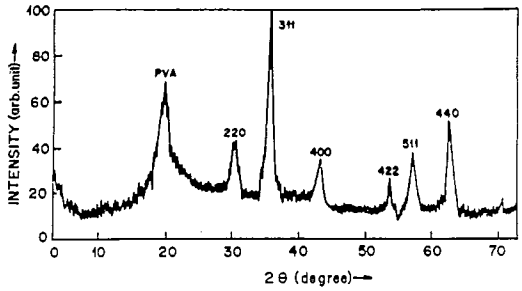

Fig. 1. XRD pattern of the ferrofluid–polymer composite film (a).

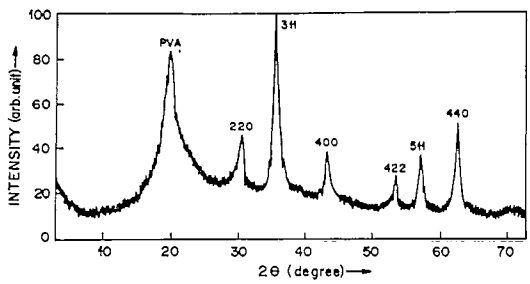

Fig. 2. XRD pattern of the ferrofluid–polymer composite film (b).

of Fe_3O_4 phase in sample (b). In order to measure this change precisely, a slow scan of selected diffraction peaks such as (311), (400), (511), (440) was done. The crystallite size was calculated by using the relation [3]

$$D = \frac{K\lambda}{\beta \cos \theta},$$

where D is the crystallite size, K is a proportionality constant ($= 0.9$), λ is the wavelength of the X-rays used, β is the full width at half maximum (FWHM) of the diffraction peak (in radians) and θ is the Bragg angle. The results of the crystallite size for measurements are given in Table 1. The average crystallite size for the samples (a) and (b) are about 9.0 nm and 10.0 nm respectively. The small increase in crystallite size could be due to crystallographically ordered orientation of individual crystallites in addition to the chain-like clustering of individual domains observed in the SEM micrographs.

The particle size of magnetic ferrofluids in the influence of magnetic field has not so far been measured by XRD to the best of our knowledge. Lesnikovich et al. [4] have measured particle sizes of magnetite using (220) and

Table 1
Crystallite size calculated from XRD data

Ferrofluid–PVA composite film prepared	Crystallite size (nm)				
	(311)	(400)	(511)	(440)	average
(a) without field	9.0	10.5	7.5	10.0	~9.0
(b) with field	10.0	11.0	8.0	11.0	~10.0

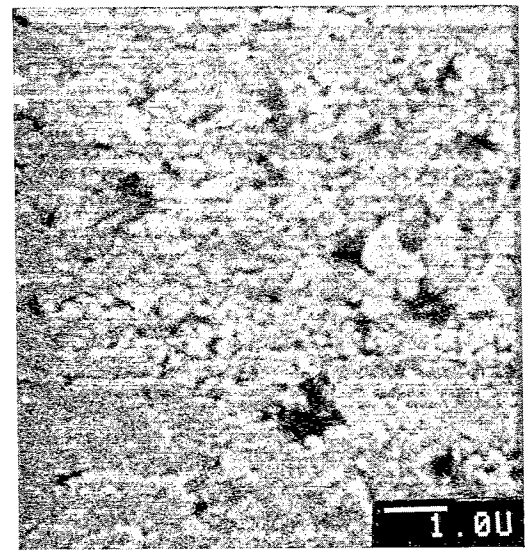

Fig. 3. SEM micrograph showing the morphology of the film (a).

(440) diffraction peaks as 13 nm for a water-based ferrofluid and as 11 nm for a kerosene-based ferrofluid. Sato et al. [5] have also measured the particle size from the (311) diffraction peak for ultrafine magnetite particles prepared by the coprecipitation method and found the range of 11–17 nm.

The surface structure of the composite films, as shown in SEM micrographs (Figs. 3 and 4), were recorded at a magnification of 10000 for samples (a) and (b) respectively. The micrographs were recorded by keeping the accelerating voltage at 15 kV to prevent softening of the films. Agglomeration of magnetite particles has occured in sample (a). The grain size calculated from the micrograph

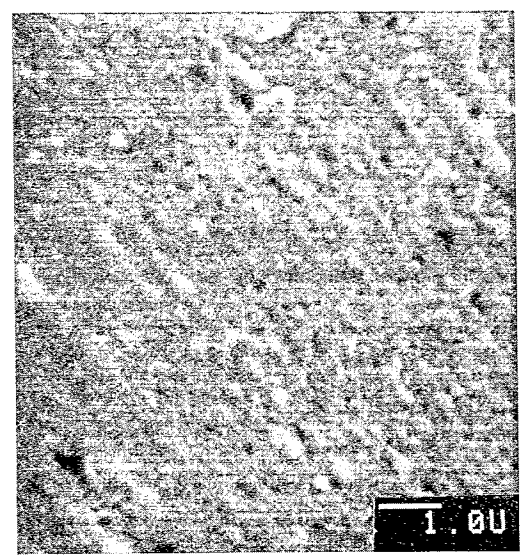

Fig. 4. SEM micrograph showing the morphology of the film (b).

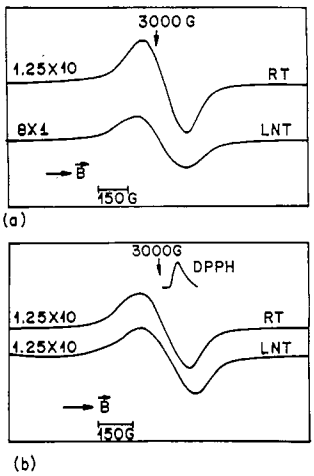

Fig. 5. EPR spectra of ferrofluid–polymer composite film prepared: (a) without magnetic field, (b) with magnetic field.

shown in Fig. 3 is in the range of 100–300 nm, which is larger than the actual particle size of the ferrofluid [2]. The PVA polymer shows a structureless surface when observed by SEM. Ordered and large sized chain-like clustering of magnetic particles has occurred in sample (b) (Fig. 4). A similar kind of discrete needle-shaped aggregation of apparent diameter about 1000 nm, formed parallel to the applied field direction, was observed by Jones and Belfield [6] using an optical microscope. The colloidal dispersion of magnetite–PVA were also characterized by transmission electron microscopy by Yokoi et al. [7] who reported that colloidal particles with diameters of 4–10 nm form chain-like or cluster-like agglomerates. The length of the clusters in our films as measured from Fig. 4 is in the range of 500–2000 nm. Composite films prepared under a smaller magnetic field of 380 G also showed slight orientation indicating that the field was not sufficient to orient all the domains in the field direction.

The EPR spectra of these films were recorded at room temperature (RT) and liquid nitrogen temperature (LNT) and are shown in Fig. 5. A single broad-band EPR signal was observed in both films. Table 2 shows the observed values of linewidth (ΔH) and g factor of both films. In film (b) the linewidth of the EPR signal is greater than that in film (a). This indicates that film (b) (having orientation of the domains) enhances the effective magnetic moment due to the clustering of particles and shows a large linewidth and intensity change of the EPR signal. When these films were cooled to LNT the linewidth of both films increased. The broadening of the EPR signals on lowering the temperature may be due to a change in the spin–lattice interactions between the magnetic ions and the host lattice. It also suggests that, as the temperature decreases, ferrimagnetism starts to collapse and give way to a clustering phenomenon in the composite films [8].

Table 2
EPR data of ferrofluid–polymer composite films

Ferrofluid–PVA composite films prepared	Temperature (K)	Linewidth ΔH (G)	g-factor
(a) without field	300	1143	2.150
	77	1300	2.230
(b) with field	300	1340	2.190
	77	1428	2.230

Table 3
Relative transmission loss of ferrofluid–polymer composite films by microwave absorption

Microwave frequency (GHz)	Waveguide cell, empty (dB)	Waveguide cell with film		Relative transmission loss (dB)
		a (dB)	b (dB)	
12	6.00	6.06	6.08	0.02
26	6.00	6.30	6.37	0.07

The microwave absorption studies were carried out in such a way that the orientation of the domains of the films remained perpendicular to the direction of wave propagation. Table 3 shows the relative transmission loss of the film prepared without and with magnetic field. The observed data reveal that the relative transmission loss is higher at shorter wavelength. Popplewell et al. [9] have shown that ferrofluid composites containing metallic/non-metallic particles have pronounced magnetic dichroism in the 3 mm wavelength range.

4. Conclusions

The present study has thus revealed that the ferrofluid polymer composite films show a change in their behaviour when prepared with and without the influence of a magnetic field. This kind of film may have diverse applications in sensors and other devices. Incorporation of other non-magnetic particles may prove more worthy in their characterstics.

Acknowledgements: The authors are thankful to the Director, National Physical Laboratory for his encouragement and permission to do this work. Useful discussions with Sh. S.U.M. Rao are gratefully acknowledged.

References

[1] S. Chikazumi, S. Taketomi, M. Ukita, M. Mizukami, H. Miyajima, M. Setogawa and Y. Kurihara, J. Magn. Magn. Mater. 65 (1987) 245.
[2] R.V. Mehta, Proc. 5th Int. Conf. on Ferrites, Oxford (IBH, New Delhi, 1989).
[3] B.D. Cullity, Elements of X-ray Diffraction (Addison-Wesley, London, 1959) p. 261.

[4] A.I. Lesnikovich, T.M. Shunkevich, V.N. Naumenko, S.A. Vorobyova and M.V. Baykov, J. Magn. Magn. Mater. 85 (1990) 14.
[5] T. Sato, T. Iijima, M. Seki and N. Inagaku, J. Magn. Magn. Mater. 65 (1987) 252.
[6] G.A. Jones and D.G. Belfield, J. Magn. Magn. Mater. 85 (1990) 37.
[7] H. Yokoi, K. Yagishita and Y. Nakanishi, Bull. Chem. Soc. Jpn. 63 (1990) 746.
[8] R.P. Pant, PhD Thesis, Bhavnagar University (1992).
[9] J. Popplewell, P. Davies and J.P. Llewellyn, J. Magn. Magn. Mater. 65 (1987) 235.