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Investigations on ferrofluid-conducting polymer composite and its application

R.P. Pant*, S.K. Dhawan, N.D. Kataria, D.K. Suri

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

Abstract

The study describes the synthesis and characterization of ferrofluid-conducting polymer composite materials and its thin films. The results of our measurement for the film grown under the influence of with and without magnetic field are quite interesting and encouraging for the electromagnetic interference shielding purpose. Change in the physical properties were correlated by analyzing the spectral features of the films.

Keywords: EMI; Conducting polymer; Microwave

1. Introduction

Ferrofluid-polymer composite materials are the dispersion of magnetic and non-magnetic particles in the host polymer matrix. The composites of ferrofluid with non-magnetic particles with size in the micron range show quite unusual behavior [1]. Skjeltrop directly observed the crystallization of magnetic holes forming different lattice according to the direction of the field [2]. In our earlier studies on ferrofluid-composite, the frozen alignment of magnetic particle in the field direction exhibit quite interesting results [3]. Thus, the composites of ferrofluid behaves like many body system with dipole interaction that can be controlled by external magnetic field as per their utilization.

In the recent past, the conducting polymers have acquired importance because of their technologically viable applications in electromagnetic interference (EMI) shielding, opto-electronic devices, sensors, etc. [4,5]. The electromagnetic wave constitute two components as electric field (E) and the magnetic field (H) which is at right angle to each other. The ratio over E to H factor (impedance) has been exploited in the shielding purpose. Taking this into an account, we have synthesized ferrofluid-conducting polymer composite with a non-conducting polyvinyl alcohol (PVA) polymer matrix. This composite material has been used to prepare various sets of composite films on a glass substrate by using spinning technique [6]. In order to see the shielding effectiveness of the composite film a microwave absorption measurement has been carried by placing the sample in a wave guide cell. To understand the physical properties of the composite material and its thin films, these have been characterized for their spectral characteristics, crystalline phase analysis, particle shape and size distribution. Orientation of the domains and also surface morphology of the samples and the size distribution has been determined. A possibility of the future direction and development has been described to realize the full potential of this technology to industry.

2. Experimental

A water-based ferrofluid having Fe_3O_4 solid magnetic particles of the size range 20–100 Å having saturation magnetization ~100 G has been used. Conducting polymer polyaniline (PANI) was synthesized by using chemical oxidative polymerization by taking monomer and oxidant ammonium per sulfate in 1:1 mole ratio at 2–5°C. The stirring of the reaction mixture was carried

*Corresponding author. Fax: +91-11-572-6938.
E-mail address: rppant@csnpl.ren.nic.in (R.P. Pant).

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out for 4–6 h. On completion of the polymerization the reaction mixture was filtered and washed with double distilled water. An aqueous solution of PVA was used as a host matrix. Conducting polymer was then added to viscous and bubble free solution of PVA of 1:10 ratio to homogenize the stock solution. Thereafter, different concentration of water base ferrofluid was added and the mixture was homogenized by ultrasonification. This solution was used for the preparation of thin films on a glass substrate using spinning technique under the influence of with and without magnetic field. Three different category of films were prepared (i) only PVA (sample a); (ii) PVA with PANI (sample b) and (iii) PVA with PANI and 0.5 ml ferrofluid, without field (sample c) and with the influence of magnetic field ~500 G (sample d). The physical size of the magnetite particle and the orientation of the domains were characterized by using scanning electron microscope (Leo SEM 440). The size distribution and the crystallinity were determined by using transmission electron microscope (JEM-200 CX). The microwave absorption measurement as an EMI potentiality were carried by placing a sample on a wave guide cell in the signal range 18–26 GHz.

3. Results and discussion

The formation of conducting polymer occurs by generation of cation radicals or polarons which on further coupling gives rise to bipoloraons. Fig. 1 shows the UV visible absorption spectra of the composite material. The conducting polymer polyaniline (PANI) shows absorption bands at 320, 420 and 820 nm, where as ferrofluid composite shows absorption bands at 365, 440 and 890 nm respectively. This shows that the interaction of polyaniline with the ferrofluid has taken place and leading to shift in the absorption bands. In the present system ferrofluid particles interact with the conducting polymer and form a composite material. Since, PANI has environmental stability due to non-degenerate ground state and structurally this polymer differs from other polymers in the sense that the nitrogen hetero atom present in polyaniline is the part of the polymer backbone. The presence of NH group in polyaniline gives the polymer a chemical flexibility. This NH is capable of interacting with other chemical reactive groups of PVA and ferrofluid by way of interactions and coordinating themselves with the conducting polymeric backbone.

In a nano-phase material the particle size, crystallinity and its distribution always plays crucial role in making devices. There are various techniques to determine the particle size distribution like transmission electron microscope, X-ray diffraction, viscosity magnetization and log normal distribution. In the present work, we have used the TEM measurement technique. Fig. 2 shows the representative electron micrograph of stock solution of ferrofluid-polymer composite and corresponding electron diffraction pattern. The inter planar spacings calculated from the diameter of the diffraction rings perfectly match with the crystalline phase of Fe_3O_4 (JCPDS card No. 19-629) and the orthorhombic phase of polyaniline conducting polymer [7]. However, very broad band which corresponds to the PVA is also seen. This confirms the three phase composite system of the stock solution. It is seen that the size and shape of the particles are almost spherical in shape for both ferrofluid and PANI and their average diameter is ranging between 50–150 Å and 0.1–0.4 μm respectively. The black contrast correspondence to the host PVA polymer and the particles are embedded uniformly in the polymer matrix.

The surface morphological investigations of composite films were performed by using scanning electron

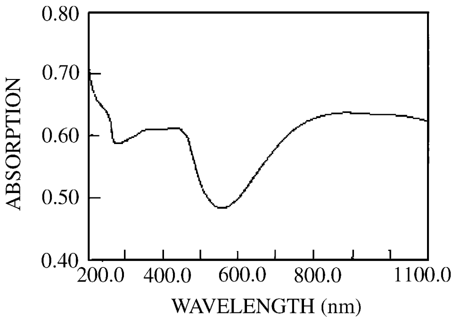

Fig. 1. UV-visible spectrum of ferrofluid-polymer composite material.

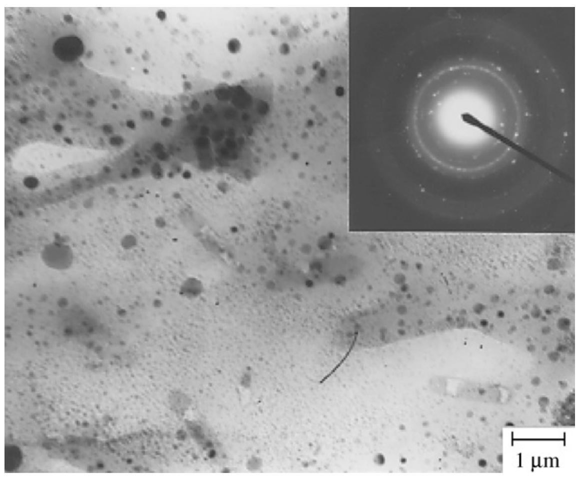

Fig. 2. Transmission electron micrograph and corresponding electron diffraction (inset) of ferrofluid-polymer composite.

microscope. The micrographs were recorded at magnification 30,000 and by keeping the accelerating voltage 10 kV. Fig. 3 shows the scanning electron micrograph of PVA-PANI film (sample b) which indicates the irregular shape with random distribution of particles lying in the range 0.1–0.3 μm. Fig. 4 shows the surface morphology of the ferrofluid-composite film (sample c) in which it is quite interesting to see the increase in particle dimension and the size distribution lies in the range 0.4–0.7 μm. On application of external magnetic field ($\sim$500 G) the surface morphology shows that the particle have formed like a hillock and tending to form elongated in the direction of the applied magnetic field with size range of the order of 0.5–1.5 μm (sample d, Fig. 5).

The electromagnetic radiation interference is one of the unfortunate byproducts of the rapid proliferation of electronic devices. These are undesired conducted or radiated electrical disturbance including transients, which can interfere with the operation of electrical or electronic equipments. Keeping this in mind a possibility has been explored using ferrofluid composite for the EMI shielding effectiveness. The microwave absorption studies of the samples was carried out in the K band range. The sample was placed in a specially designed wave guide cell to monitor the absorption properties of the composite material. The net absorption was monitored from the reflectance, internal reflectance and the transmission measurements. The measured values are the net effect of microwave on the properties of composite material. Table 1 shows the microwave absorption of the composite films and the relative absorption. The observed data reveals that the composite materials has the property of microwave absorption. The relative shielding effectiveness calculated for the sample c shows less value (1.12 db) as compared for the sample d (1.30 db). This shows that the orientation of the domains improves the EMI shielding property of the material because magnetic vector of the radiation is also encountered. The value of microwave absorption prepared for the films having 1.0 ml ferrofluid is also included in this table which reveals that by increasing the ferrofluid concentration the shielding property of the material slightly improves. The relative absorption, however, increases from 0.18 to 0.22 db for the films with increased concentration of ferrofluid from 0.5 to 1.0 ml respectively. In view of this, a planned study is to be carried out for the improvement in the shielding effectiveness by using this composite material. Also, a suitable conductive polymer which is compatible to ferrofluid and other conducting particles are to be explored.

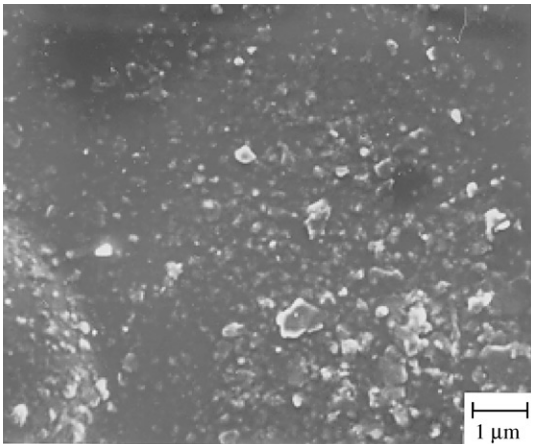

Fig. 3. SEM micrograph showing the morphology of PVA-PANI film (sample b).

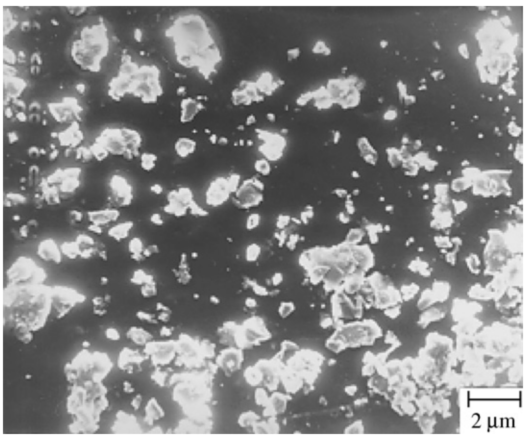

Fig. 4. SEM micrograph showing the morphology of ferrofluid-composite film (without field, sample c).

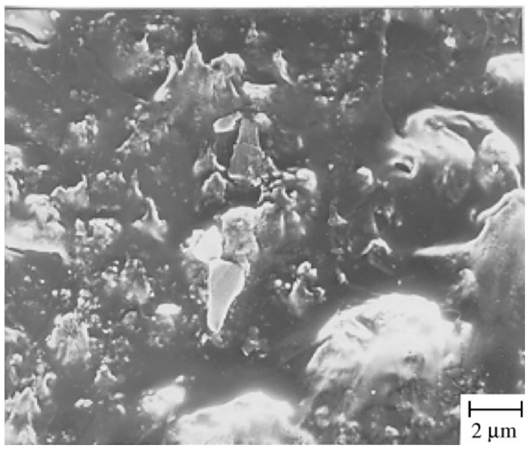

Fig. 5. SEM micrograph showing the morphology of ferrofluid-composite film (with field, sample d).

Table 1
Microwave absorption measurement of ferrofluid–polymer composite films at 24.4 GHz

Sample details	Input power empty cell (db)	Microwave absorption (db)		Relative absorption (db)
		With field	Without field	
PVA	5	—	0.12	—
PVA + PANI	5	—	1.05	—
PVA + PANI + FF(0.5 ml)	5	1.30	1.12	0.18
PVA + PANI + FF(1.0 ml)	5	1.35	1.13	0.22

4. Conclusion

The present study has shown that the polymerization techniques of ferrofluid-composite materials have potential for the EMI shielding. Ordered orientation further improves the shielding effectiveness. The uniform size agglomerates are formed due to the superparamagnetic behavior of the particles. On selection of the ferrofluid, and conducting polymer the property of the composite may improve many fold for its application.

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References

[1] A.T. Skjeltrop, Phys. Rev. Lett. 51 (1983) 2306.
[2] A.T. Skjeltrop, J. Appl. Phys. 57 (1985) 3285.
[3] R.P. Pant, Rashmi, R.M. Krishna, P.S. Negi, K. Ravat, U. Dhawan, S.K. Gupta, D.K. Suri, J. Magn. Magn. Mater. 149 (1995) 10.
[4] S.K. Dhawan, D.C. Trivedi, J. Electromagnetic Compatibility 1 (1991) 124.
[5] Jones, Scott A "EMI protected aircraft" US patent No. 5,670,742 (1997).
[6] R.P. Pant, V.K. Sankarnarayanan, V.N. Ojha, D.K. Suri, J. Magn. Magn. Mater. 201 (1999) 27.
[7] S.V. Warhadpande, M.C. Gupta, Ind. J. Chem. 31A (1992) 43.