MICROWAVE ABSORPTION STUDIES ON FERROFLUID-CONDUCTING POLYMER COMPOSITE

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ABSTRACT

In this communication**,** preparation and characterization of nano-crystalline magnetic particles, their polymer composites prepared by varying doping level of conducting polymer, filler loading graphite in PVA and their microwave absorption studies have been discussed. The electromagnetic interference effect of super-paramagnetic particles (Fe_3O_4, $MnZnFe_2O_4$, $CoFe_2O_4$) of ferrofluid in polymer matrix in relation to conductivity of the composites were studied. The measurement of shielding effectiveness (SE) was carried out in X and K band microwave region. It is observed that the shielding effectiveness increases with the increase of doping and filler loading. Samples were analyzed by XRD, SEM and TEM techniques. The correlation of shielding effectiveness and electrical conductivity is discussed. The results suggest that the role of ferrite in electrically conducting matrix have higher SE. This paper focuses on applications of nano-particles and their composites towards the new technology.

INTRODUCTION

The electromagnetic radiation interference is one of the unfortunate by-product 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 components. The nano-structured materials have attraction for microwave radiation absorbing and shielding materials in the GHz frequency range due to their unique chemical and physical properties. The volume to weight ratio of shielding material is very important in microwave absorbing materials for lightweight and strong absorption properties [1]. The use of plastic materials to the housing of computer and electronic devices has been growing very rapidly due to their advantages over metals, like light weight, design flexibility, low cost and easy to mass production. As such plastic casing of electronic equipment do not provide protection from external field [2]. Composites with discontinuous conducting fillers, such as metal particles, metal flakes, carbon particles, carbon fibers are extensively employed in electromagnetic interference (EMI) **s**hielding [3]

Ferrofluids are the colloidal dispersion of nano-size 2-10 nm magnetic particles in some suitable carrier medium. Ferrofluid – polymer composites materials are the dispersion of ferro-ferrimagnetic with other non-magnetic particles in a host matrix. These composites behave like a many body system with dipole interaction which can be controlled by external magnetic field. The electromagnetic wave constitutes of orthogonal electric (E) and magnetic (H) field and the ratio over E to H factor (impedance) has been exploited in the shielding purpose. Taking this into account, we have synthesized ferrofluid polymer composite with a non-conducting polyvinyl alcohol (PVA) polymer matrix. The present investigation deals with the shielding effectiveness of the ferrofluid -PVA polymer doped by filler graphite, polyanaline and PANI of high intrinsic conductivity to the polymer matrix. We have studied microwave absorption properties of these composites in relation to the particles size, conductivity and magnetization in X and K band microwave region.

EXPERIMENTAL

Synthesis of Ferrofluid -PVA -Graphite Composite

Ferrofluids $MnZnFe_2O_4$, $CoFe_2O_4$ and Fe_3O_4 are synthesized in aqueous medium by well known chemical co-precipitation method in a controlled pH [4] The saturation magnetization (M_s) of $MnZnFe_2O_4$, $CoFe_2O_4$ and Fe_3O_4 ferrofluid is 130, 140 and 180 Gauss respectively. $MnZnFe_2O_4$ fluids was utilized for making composites by adding sub-micron size of graphite colloidal solution in the ratio 1:1 (3a), 1:1.5 (3b), and 1: 4 (3c) and $CoFe_2O_4$ samples with 1:1 (4), 1:4 (4a) in the polymer matrix respectively by spin coating.

To understand the orientation of domains in polymer matrix two samples of $MnZnFe_2O_4$ were prepared under the influence of perpendicular (3a1) and parallel (3a2) magnetic field, see Fig. 5. The thickness of the films is about 50µm. The shielding effectiveness of composite materials were measured in a specially designed X and K-band wave guide cells. The net absorption was computed from the reflectance, internal reflectance and the transmission measurements.

Synthesis of Ferrofluid- PVA- Polyanaline Conducting Polymer Composite

In another set, Fe_3O_4 was used in making conducting polymer polyanaline (PANI). Various sets of films were prepared under the influence of with and without magnetic field. The conducting polymer polyanaline (PANI) was obtained by chemical oxidative polymerization by taking monomer and oxidant ammonium per sulphate in 1:1 mole ratio at 2-5^0 C. The filtered solution was mixed with the host polymer PVA and homogenized. Thereafter, different concentration of ferrofluid was added and the solution was homogenized. Here the surfactant molecules interact with the conducting polymer via H bonding leading to the formation of composites. The NH group of the polymer interacts with surfactant molecules and provides the chemical flexibility to the system. A possible mechanism of its formation has been discussed.

RESULTS

In a nano-phase materials the particle size and their distribution plays a crucial role. The transmission electron micrograph of synthesized magnetic particles shows that the size of the particles is in the range of 5-15 nm as shown in Fig.1. Almost all the particles are spherical in nature and well disperse. These particles were homogenized in PVA matrix. The conducting ferrofluid polymer composite was obtained and a possible mechanism of its formation has been shown in a schematic diagram in Fig.2. The surfactant molecules attached with the ferrofluid interact with the conducting polymer via H bonding leading to the formation of composite. The NH-group in polymer which interacts with the surfactant molecules provides chemical flexibility to the system. The electrical conductivity of the composites varies from 2.8 x 10^{-5} $\Omega^{-1}cm^{-1}$ to 1.0 x10^{-3} $\Omega^{-1}cm^{-1}$ depending upon the loading level of conducting polymer in the ferrofluid as given in Table 1. In ferrofluid-graphite-polymer composite the electrical resistivity decreases with increase in graphite weight-percent as shown in Table 2. The XRD studies shows presence of spinel phase of ferrite and graphite in the entire sample and a representative XRD pattern is depicted in Fig .3. We have observed that the film grown without magnetic field has line broadening for spinel phase as compared to the film grown under the influence of magnetic field. The difference in crystallite size ~12 nm is obtained for the composite prepared with and without magnetic field. There are different mechanisms by which microwaves can couple to a material and a host of ways that the microwave energy is subsequently lost to the system. The different mechanisms, however, have different dependence on certain properties such as sample microstructure, temperature and frequency. Two main loss mechanisms for non-magnetic materials are dielectric losses and conduction losses. Magnetic materials exhibit conduction losses with additional magnetic losses such as hysteresis, domain wall resonance and electron spin resonance (FMR).

Losses due to the Electric and Magnetic Field

In dielectric materials, the absorption of microwaves is related to the materials complex permittivity as

$$\varepsilon = \varepsilon_0(\varepsilon' - i\varepsilon'') \quad (1)$$

where the imaginary part ε” is the effective relative dielectric loss factor.

In an analogous way to the electric losses, the losses due to complex relative permeability is

$$\mu = \mu' - i\mu'' \quad (2)$$

In ferrites, the loss tangent depends on three main contributors

$$\tan\delta_\mu = \tan\delta_h + \tan\delta_\varepsilon + \tan\delta_r \quad (3)$$

in which $\tan\delta_h$, $\tan\delta_\varepsilon$ and $\tan\delta_r$ are the hysteresis, eddy current and residual loss tangents respectively.

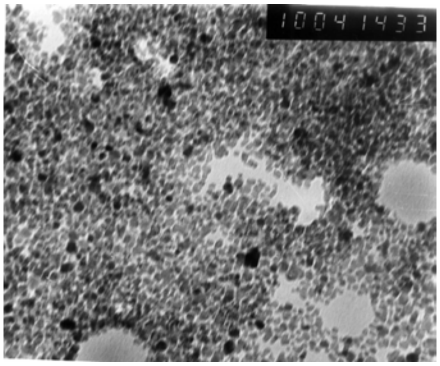

Fig.1. TEM Micrograph of ferrofluid particles formation

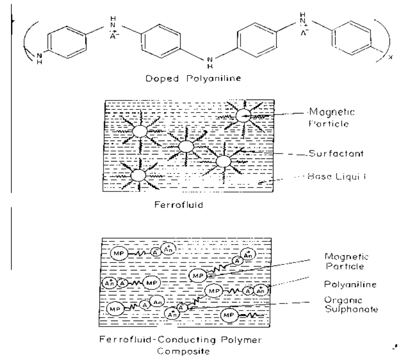

Fig.2. Probable schematic diagram of ferrofluid polymer composites

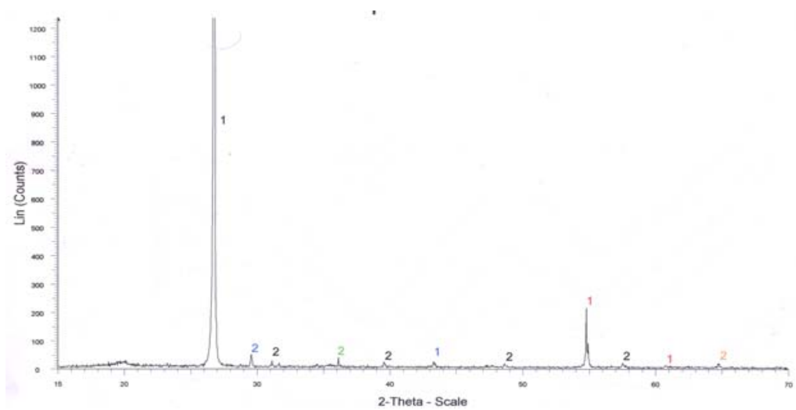

Fig.3. XRD pattern of composite 1) graphite 2) $MnZnFe_2O$ crystalline phase

Table 1 shows the variation of the shielding effectiveness of different compositions of ferrites loaded with colloidal graphite in PVA matrix over the frequency range 8-12 GHz. It is interesting to note the increase in SE due to increase in the graphite concentration in $MnZnFe_2O_4$. Also at higher concentration the system becomes more efficient in shielding and SE increases appreciably for particular frequency range as shown in Fig.4. Similar behavior of SE is observed for $CoFe_2O_4$ - polymer composite. Shielding effectiveness SE verses frequency over X band region of ferrofluid based composites containing different concentrations of graphite as shown in Fig 4.

Table 1. The shielding effectiveness of different compositions of ferrites loaded with colloidal graphite in PVA matrix.

Composition PVA+ferrite+ graphite	**Sample**	**Conductivity $\Omega^{-1}Cm^{-1}$**	**Shielding Effectiveness**					
			8.0 GHz	8.8 GHz	9.6 GHz	10.4 GHz	11.2 GHz	12.4 GHZ
1:1:1($MnZnFe_2O_4$)	3(a)	$1x10^{-8}$	0.0	1.1	1.9	1.5	1.9	7.0
1:1:1.5 -do-	3(b)	$2.4 x10^{-4}$	7.3	6.3	3.1	8.0	7.6	14.0
1:1:4 -do-	3(c)	$3.1 x 10^{-3}$	14.5	10.9	10.2	14.8	13.6	20.6
1:1:1 ($CoFe_2O_4$)	4	$5x10^{-8}$	0.0	0.6	2.3	2.3	1.7	6.4
1:1:4 -do-	4(a)	$6.6x10^{-2}$	11.7	10.2	6.4	11.7	13.1	17.5

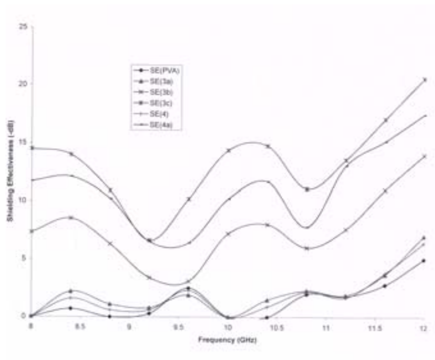

Fig.4: Shielding effectiveness of the composites with varying graphite concentration in $MnZnFe_2O_4$ and $CoFe_2O_4$

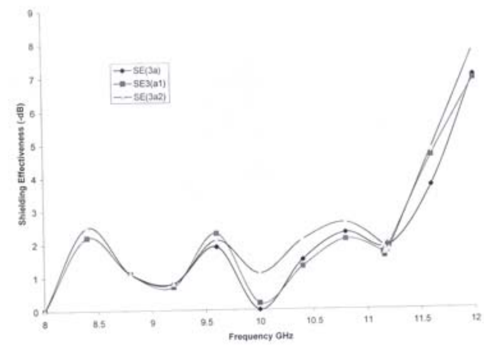

Fig5. Shielding effectiveness of $MnZnFe_2O_4$-graphite-PVA composite without and with ⊥ and || magnetic field

Investigations on different doping level of conducting polymer in relation to microwave shielding effectiveness at 24.4 GHz frequency is shown in Table 2. Further the orientation of magnetic particles in conducting matrix enhances the SE as shown in Fig.5 [5]. This may be due to the orientation of domains remained perpendicular to the direction of wave propagation. The obtained data reveals that the relative SE is higher at particular frequency range.

Table 2 The microwave absorption of ferrofluid – conducting polymer composite films at 24.4 GHz

Composition PVA+PANI+FF	Input Power dBm	Conductivity $\Omega^{-1}Cm^{-1}$	Microwave absorption		Relative absorption
			With field	Without field	
PVA	5	-	-	0.12	-
1:1	5	$10x10^{0}$	-	1.05	-
1:1:1	5	$2.8x10^{-4}$	1.30	1.12	0.18
1:1:1.5	5	$1.0x10^{-3}$	1.35	1.13	0.22

CONCLUSIONS

The observed data reveals that the ferrofluid –polymer- composite material has the properties of microwave absorption due to fast spin relaxation of super-paramagnetic particles distributed in polymer matrix. This kind of composite film may find good applications in microwave absorption devices.

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