Shielding and Dielectric Properties of Ferromagnetic Conducting Polyaniline/PVA Film in 12.4-18 GHz

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Abstract:

The present research work deals with the dielectric properties of polyaniline –nano ferrite composites prepared using chemical oxidative polymerization. The resulting composite possesses the conductivity of 2.5 S/cm and saturation magnetization of 45emu/g. The comparative studies of microwave absorption of ferromagnetic conducting polyaniline composite were carried out by casting in film in poly (vinyl alcohol). The effects of the weight fraction of PANI-Fe_2O_3 composite on the frequency dispersion characteristics of the complex permittivity and the electromagnetic interference shielding effectiveness of conducting polyaniline PANI-Fe_2O_3 composites was studied in the range of 12.4 to 18 GHz.

1. Introduction

The development of electronic equipments have made life easy in one side, they also create a new kind of problems of getting false image, decrease in the efficiency or the short circuiting of the avionic equipment on the other side. This problem mainly arises due to the Electromagnetic interference (EMI). The Electromagnetic field produced by the EMI is the main cause of all these said problems. To over come these problems and to protect the avionic devices, an EMI sheath is required that may enclosed the electronic equipment. However shielding in the frequency range of 12.4 to18 GHz (Ku-band) is more important as the electronic devices which are used commercially like telephone, mobile, computers and TV picture transmission emit electromagnetic radiations in this band. Metals are traditionally used for EMI as they are highly conductive and are capable of reflecting the electromagnetic wave before being transmitting however polymer composites and fiber-reinforced composites containing conductive fillers such as carbon particles, carbon fibers, and dielectric or magnetic loss materials have been extensively used for EMI shielding [1-4]. In recent years, many efforts have been carried out by microwaves engineers, scientist and techno grates to develop EMI shielding and absorbing material using conducting polymers composites as they are light in weight, resistance to corrosion and have flexibility [5]. The most important aspect of conducting polymer composites is their conductivity that can be altered according to the need of the application. Generally, microwave behavior of conducting polymer is critically dependent on dielectric and magnetic properties of the materials. Thus, it is very important to get the expected value of conductivities and permittivity (dielectric constant and dielectric loss) that enhance the microwave behavior of conducting polymer.

The present work deals with the comparative study of different ferromagnetic conducting polyaniline composite to EMI shielding enclosures. The shielding characteristics of materials are based on the reflection and absorption. To make ferromagnetic conducting composites the nano particles of Fe_2O_3 were added in different concentration to the polyaniline matrix. The incorporation of the magnetic fillers reduces the dielectric loss and the values of the dielectric permittivity can be altered to achieve maximal absorption of the electromagnetic energy.

2. Experimental

Ferromagnetic conducting polyaniline-γ- Fe_2O_3 composite was prepared by Chemical oxidative polymerization of aniline in the presence of nanoparticles of γ- Fe_2O_3 in dodecyl benzene sulphonic acid (DBSA) medium. The nanoparticles of the γ- Fe_2O_3 were prepared by the coprecipitaion of Fe^{2+} and Fe^{3+} ion in aqueous ammonium solution maintaining the pH at 10-11.The γ- Fe_2O_3 particles so obtained were mixed in 0.3m solution of DBSA and homogenized by for 2-3 hrs. To this 0.1mole of aniline (An) is added and supersonic stirring continued for 1 hour to form an emulsion. To the above emulsion, oxidant ammonium peroxydisulphate (0.1mole) is added drop-by-drop keeping the temperature of the reactor at -2^0C with vigorous stirring for 5-6 hrs. The green polymer precipitate so obtained is treated with isopropyl alcohol under vigorous stirring for 2-3 hours. The resulting precipitate is then filtered and washed thoroughly and dried at $60-65^0C$ in a vacuum oven.

To cast the film of ferromagnetic polyaniline-γ- Fe_2O_3 composite, the wet form of polymer was mixed in 10% solution of PVA and stirred vigorously for 3hours .The resulting solution was casted in petridish and dried at room temperature. The different samples of PVA film were casted having the polyaniline-γ- Fe_2O_3 weight 5% and 10 % and named as PPVA5 and PPVA10 respectively.

3. Result and discussion:

The oxidative polymerization of aniline proceeds through the formation of radical cations generated by an internal redox reaction, which causes the reorganization of electronic structure, to give two semiquinone radical cations. These radical cations through the coupling reaction lead to the form ion of stable electrically conducting polymer. Incorporation of Fe_2O_3 particles during the process of reorganization of anilinium ion in presence of surfactant DBSA results in the formation of a conductive as well as ferromagnetic polymer. Here DBSA not only help to avoid the phase segregation but also help in functionalization of nanoparticles so that they uniformly suspended in the matrix of polymer and ensure their compatibility with polymer.

3.1 XRD and TEM Studies

The X-ray diffraction patterns of γ- Fe_2O_3, polyaniline doped with DBSA and it composite with γ- Fe_2O_3 are shown in Figure1. The main peaks for γ- Fe_2O_3 are observed at 2θ = 30.2810(d = 2.9493Å), 35.6990 (d=2.5131 Å), 43.4350 (d=2.0817 Å), 53.8050 (d=1.7024 Å), 57.4370 (d=1.6031 Å), 63.0460 (d= 1.4733 Å) corresponding to the (2 0 6), (1 1 9), (0 0 12), (2 2 12), (1 1 15), (4 4 1) reflections which matches with the standard XRD pattern of γ- Fe_2O_3 (PDF No. 25-1402). The peaks present in γ- Fe_2O_3 were also observed in all the compositions of polyaniline complex with γ- Fe_2O_3 which indicates the presence of ferrite particles in the polymer matrix. The line broadening of the peaks in the entire patterns of polyaniline complex indicates about the small dimensions of the iron oxide particles.

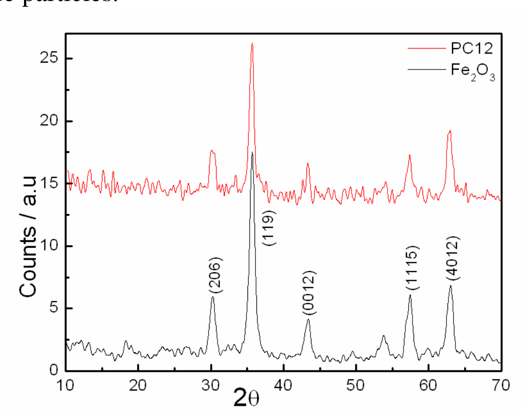

Figure 1: XRD curve of (a) γ- Fe_2O_3 (b) PC12

The average crystallite size of γ- Fe_2O_3 particle can be calculated by line broadening using Scherer's formula

$$D = k\lambda/\beta\cos\theta \qquad (1)$$

where D is the crystallite size for individual peak, λ is the X-ray wavelength, k the shape factor, D is the crystallite size for the individual peak of the crystal in angstroms, θ the Bragg angle in degrees, and β is the line broadening measured by half-height in radians. The average size of γ- Fe_2O_3 particles can be calculated by averaging the crystalline size of all the main peaks and estimated as 8.99 nm for pure γ- Fe_2O_3 and 9.87nm for polyaniline composite with iron oxide having Aniline: γ- Fe_2O_3:: 1:2 (PD12) which is in accordance with the TEM analysis (Figure 2) which shows the uniformly dispersed iron oxide particles of 8-15nm and the agglomerated polymer complex containing 8-13nm size particles of iron oxide.

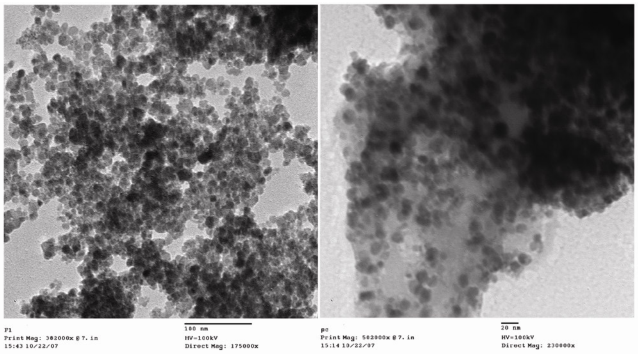

Figure 2: TEM image of (a) γ- Fe_2O_3 having particle size 8-15 nm and (b) PC12 having particle size 8-13 nm

3.2 Magnetic Properties

The magnetic properties of the polyaniline -γ -Fe_2O_3 composite and γ- Fe_2O_3 were explained by using the B-H (Figure 3). The saturation magnetization (Ms) value of the γ- Fe_2O_3 was found to 69.77emu/g at an external field of 10kOe having small value of coercivity and negligible retentivity with no hysteresis loop, indicating the super paramagnetic nature. When these nano ferrite particles are incorporated in the polyaniline matrix in weight ratio of 1:2 (PC12) the magnetization saturation (Ms) value was found to 45emu/g. The retentivity was almost negligible with very small coercivity, indicating the ferromagnetic nature and Ms value increases due to high poly-dispersivity of the γ- Fe_2O_3 in polyaniline matrix that arises by to the fictionalization of nano ferrite particles with the surfactant DBSA that ensure its poly-dispersivity in the polymer matrix and some particle may be elongated outside the matrix due to magneto-dipole interactions leading to higher Ms values of the Polyaniline - γ- Fe_2O_3.

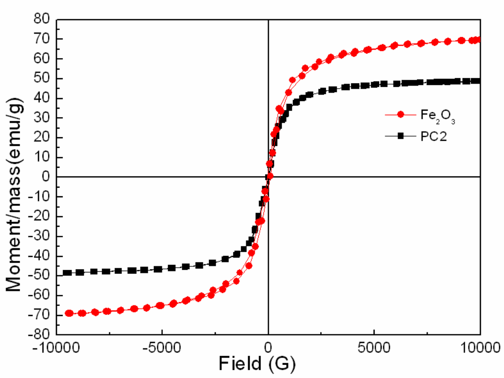

Figure 3: Magnetization curves of (■) γ- Fe_2O_3, (●) PC12

3.3 Shielding and Dielectric Properties

The EMI shielding effectiveness (SE) of a material is defined as

$$SE\ (dB) = -10 \log_{10} (P_t / P_0) \qquad (2)$$

where P_t and P_0 are the transmitted and incident electromagnetic power respectively. For a shielding material total SE is the sum of $SE = SE_R + SE_A + SE_M$, Where SE_R is due to reflection, SE_A is due to Absorption and SE_M is due to multiple reflections.[6]

In two port network S-parameter S_{11} (S_{22}), S_{21} (S_{12}) represents the reflection and the transmission coefficients

$$T = |E_T/E_I|^2 = |S_{21}|^2 = |S_{12}|^2 \qquad (3)$$

$$R = |E_R/E_I|^2 = |S_{11}|^2 = |S_{22}|^2 \qquad (4)$$

$$A = 1 - R - T \qquad (5)$$

Here, it is noted that A is given with respect to the power of the incident EM wave. If the effect of multiple reflection between both interfaces of the material is negligible, the relative intensity of the effectively incident EM wave inside the materials after reflection is based on the quantity as 1-R.

Therefore, the effective absorbance (A_{eff}) can be described as $A_{eff} = (1 – R – T) / (1 – R)$ with respect to the power of the effectively incident EM wave inside the shielding material. It is convenient that reflectance and effective absorbance are expressed as the form of -10 log (1-R) and -10 log (1-Aeff) in decibel (dB) respectively, which provide the SE_A as follows:

$$SE_R = -10 \log (1-R) \qquad (6)$$

$$SE_A = -10 \log (1- A_{eff}) = -10 \log T/(1-R) \qquad (7)$$

Figure shows the Shielding the measured EMI SE of the PVA, PPV5, and PPV10 in the frequency of 12.4-18 GHz. The SE_R and SE_A values calculated by Equations (4) and (5) are found -4.7 dB and -3.0 dB for PVA film at 15.2GHz respectively, while in the case of PPV10 the calculated values of SE_R and SE_A are -5dB and -14.5dB respectively which are much higher than PPVA5. These results suggest that the microwave absorption loss of the PANI/Fe_2O_3/PVA composite is better than the PVA.

The measurement of dielectric properties were carried out through the S parameter obtained through the VNA. The Nicholson-Ross-Weir conversion method was used to obtain the dielectric constant. Figure 4 shows the dielectric constant of PVA, PPVA5 and PPVA 10. It is observed that the dielectric constant value increases with the addition of the Ferromagnetic conducting polymer composite in PVA matrix. It is also observed that ε` is almost constant in the whole frequency range. The increase in the ε` is due to the presence of more charge carriers and polarization or the jumping of charge from one position to another.

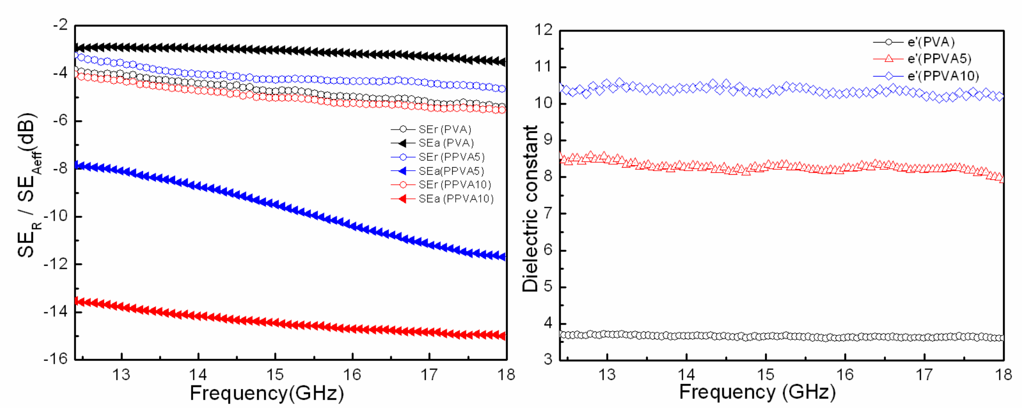

Figure 4: Shielding Effectiveness and dielectric constant curves of PVA, PPVA5 and PPVA10

4. Conclusion:

The Polyaniline-γ- Fe_2O_3 synthesized by the emulsion polymerization has shown ferromagnetic behavior having a magnetization value of 45 emu/g .When PVA film were casted with the Polyaniline-γ- Fe_2O_3 the shielding effectiveness and dielectric constant increases with the increases of weight ratio in the PVA matrix.

5. Acknowledgment

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