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Pritom J Bora[1], **K J Vinoy**[2], **Praveen C Ramamurthy**[1,3], **Kishore**[3] **and Giridhar Madras**[1]

[1] Interdisciplinary Centre for Energy Research (ICER), Indian Institute of Science, Bangalore, 560012, India
[2] Department of Electrical and Communication Engineering, Indian Institute of Science, Bangalore, 560012, India
[3] Department of Materials Engineering, Indian Institute of Science, Bangalore, 560012, India

E-mail: praveen@materials.iisc.ernet.in

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Abstract

A solid waste material fly ash cenosphere (FAC) was nickel coated and polyaniline *in situ* polymerized at −30 ± 2 °C in nitrogen atmosphere. A thin film of this composite material was prepared by solution processing and surface morphology/topography was studied. High electromagnetic shielding effectiveness (SE) was obtained for this film; 59 ± 4 μm and 133 ± 4 μm films show an average of 38 and 60 dB SE, respectively, in the frequency range 8.2–12.4 GHz (X-band). Unlike PANI film, the SE of these composite films is high at high frequency. The presence of magneto dielectric microsphere (Ni-FAC) increases the heterogeneity of the composite film in an efficient way for EMI shielding by changing film topography and increasing ac conductivity and permeability.

1. Introduction

In recent times, due to rapid use of radio or microwave frequency in electronics and electrical engineering, electromagnetic interference (EMI) has been a major problem [1, 2]. Intrinsic conducting polymers (ICP) are reported as suitable shielding materials due to many advantages over traditional metallic sheets such as being lightweight, flexible, soft etc [3]. Among the ICPs, polyaniline (PANI) has received special attraction due to the tunable conductivity, adjustable permittivity/permeability, bulk level easy synthesis, low density and non-corrosiveness properties [3–5]. Enhancement of EMI shielding effectiveness (SE) of PANI film at minimum thickness is valuable as SE is directly related to thickness [6].

Fly ash cenospheres (FACs) are solid-waste by-products of power generating thermal plants and are pollutants [7]. Silica (SiO_2) and alumina (Al_2O_3) are the major constituents of FACs [7, 8]. They are formed from hot molten salt at high temperature in the absence of oxygen at room temperature. Typically these are hollow microspheres having low density and nontoxicity with good thermal and dielectric properties. Furthermore, FAC is highly dispersive in the polymer matrix. Metal coated FAC has been reported for many potential applications including microwave absorption [8–10]. In the present effort, FAC was Ni coated and doped in PANI. The thin film of this composite material was prepared and EMI SE was investigated by waveguide method [11] by using a vector network analyzer for X-band frequency (8.2–12.4 GHz).

2. Experimental

2.1. Composite material synthesis and film preparation

FAC was obtained from National Thermal Power Corporation (NTPC), India, with particle size range 10–50 μm, cleaned conventionally and nickel coated by heterogeneous precipitation thermal reduction method [13]. A sufficient amount (2.5 g in 100 ml) of nickel coated FAC or Ni-FAC was dispersed in 1 M HCl solution, following which 6 ml double-distilled aniline was slowly mixed at −30 ± 2 °C. To reduce the freezing temperature of the reaction mixture, 6 M lithium chloride was added. The pre-cooled solution of ammonium persulfhate (APS, 0.6 M) also in HCl and lithium chloride was added at a rate of 3 ml min^{-1} using an external

pump to the aniline solution. The reaction was allowed to proceed for 6 h at −30 ± 2 °C under nitrogen environment. The resulting polyaniline composite (PANI/Ni-FAC) precipitates were washed repeatedly with de-ionized water and deprotonated by stirring in 4 weight % ammonia solution for 8 h at 25 °C. Obtained precipitates (PANI in emeraldine base form) was again washed with de-ionized water and methanol repeatedly and vacuum dried at 50 °C for 12 h.

4 weight % of synthesized PANI/Ni-FAC was added very slowly to dimethyl-propylene urea (DMPU) solution under stirring and further stirred for 6 h. After that, this solution was poured on to special moulds and vacuum dried at 60 °C for 12 h. Thus, the resulting films were acid vapor treated (1 M HCl) under vacuum for 72 h to achieve stable conductivity and dielectric constant. Finally, they were dried under ultra-pure nitrogen. This film was denoted PNiC film. This procedure was repeated again for PANI but this time without Ni-FAC. The average thicknesses of the films were measured by optical profilometry.

2.2. Dielectric and dc conductivity measurements

Complex permittivity and permeability (μ') was obtained by using cavity perturbation technique [12]. Here, sample films were cut at rectangular shape, 2×0.5 cm^2 and placed in the specific positions of the resonance cavity corresponding to complex permittivity (electric field is at its maximum) and permeability, μ' (magnetic field is at its maximum) for the measurements. The height of the cavity is 1 cm and length is 30 cm. It was connected with a vector network analyzer (Agilent, NS230 A) and operated using swept frequency option of the analyzer. The following formula was used for the calculations,

$$\varepsilon' = 1 + \frac{1}{2}\left(\frac{f_0 - f_s}{f_s}\right)\frac{V_o}{V_s} \tag{1}$$

$$\varepsilon'' = \frac{1}{4}\left(\frac{1}{Q_s} - \frac{1}{Q_0}\right)\frac{V_o}{V_s} \tag{2}$$

$$\mu' = 1 + \frac{\left(l^2 + a^2n^2\right)}{2a^2n^2}\frac{\left(f_o - f_s\right)}{f_s}\frac{V_o}{V_s} \tag{3}$$

In equations (1)–(3), V_o and V_s denote the sample and cavity volume respectively. f_0 and Q_0 are resonance frequency and the quality factor of the empty cavity and f_s and Q_s are corresponding parameters for the perturbed case. The length, width, and resonant mode of the cavity are denoted as l, a, and n, respectively.

The dc conductivity was measured by collinear four probe method. The four probe setup was placed on the sample film surface and proper contact was checked by a microscope. It was connected to the Keithley dc current source (Keithley model 6221 ac) and to a nanovoltmeter (Keithley model 2182 A). The delta mode was employed and resulting average resistance (R) was taken and the resistivity (ρ) of the sample with thickness (t_h) was calculated as,

$$\rho = \left(\frac{\pi}{\ln 2}\right)R \times t_h \tag{4}$$

The conductivity (σ) is the reciprocal of the resistivity, therefore, $\sigma = \frac{1}{\rho}$ was calculated.

3. Characterizations and EMI SE results

Surface morphology of the obtained film was studied under SEM at 20 kV (figure 1). The Ni-FAC microspheres were embedded in the PANI matrix and the exposed surface was grafted by thick PANI layer. The procedure followed here results in high molecular weight PANI with long polymeric chain [14]. However, a few small agglomerated regions were also observed due to the some defect bearing Ni-FAC pieces and magnetic dipole interactions between the microspheres. Observed topography as shown in figure 2 of PNiC film consists of a large number of sharp projections. These sharp-projections-like structures could help in electromagnetic interference shielding as conventionally the apex of the cone direction from which anticipated EMI will arrive [15]. The root mean square (rms) surface thickness of this film was obtained as ~0.11 μm.

Obtained complex permittivity ($\varepsilon = \varepsilon' - j\varepsilon''$) details are tabulated in table 1. It was observed that in the presence of Ni-FAC, both the real (ε') and imaginary (ε'') part of the complex permittivity of PANI film increases. The decrease of dielectric loss ($\tan\delta_\varepsilon$) was also observed, obtained $\tan\delta_\varepsilon$ were 0.96 and 0.83 for PANI and PNiC film, respectively.

Obtained permeability (μ') for PNiC film is ~10. The dc conductivity (σ_{dc}) was obtained as 8.4 S cm^{-1} and 15.73 S cm^{-1} for PANI (thickness 52 ± 2 μm) and PNiC film (thickness 133 ± 4 μm), respectively. As in the case of conducting/conjugated polymers polaron/bipolarons are the movable charge species along the chain, the

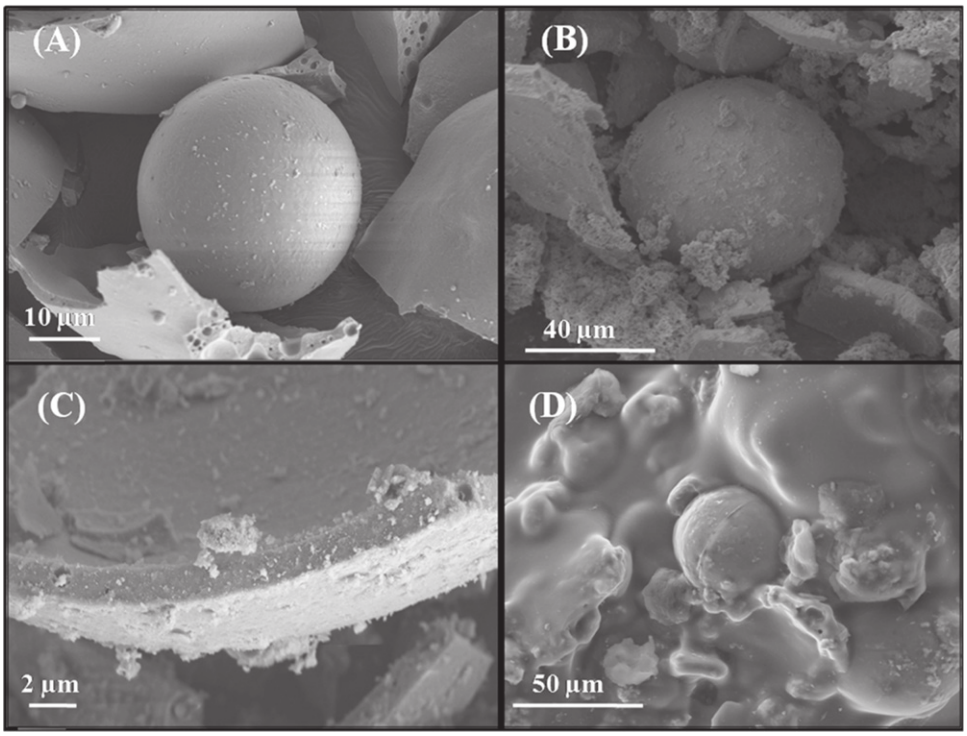

Figure 1. Surface morphology of (A) fly ash cenosphere (FAC), (B) nickel coated fly ash cenosphere (Ni-FAC), (C) Cross sectional view of Ni-FAC, (D) Ni-FAC doped polyaniline (PNiC) film.

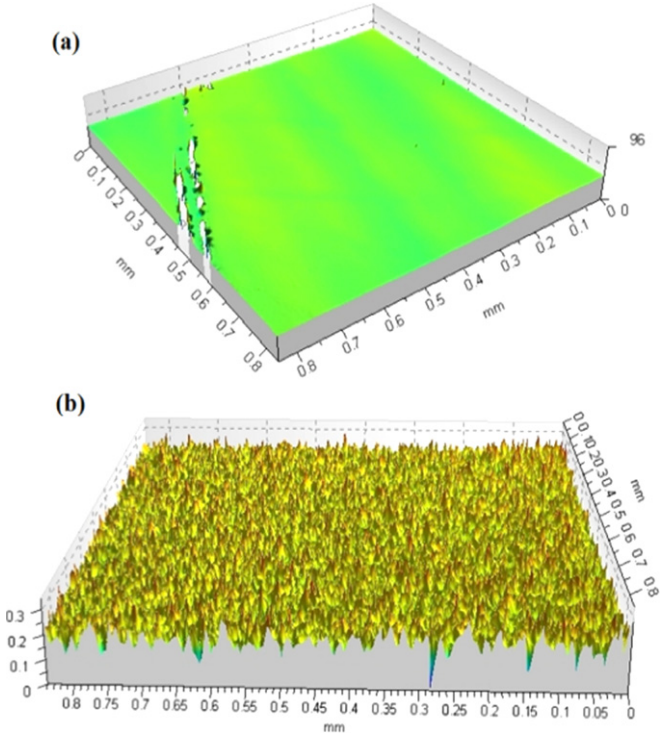

Figure 2. Topography of (a) PANI film and (b) Ni-FAC doped PANI (PNiC) film.

presence of Ni-FAC increases heterogeneity of the system and increases orientation and space charge polarization [16]. Moreover, some polaron/bipolarons are trapped on the surface. Further dielectric loss of FAC constituents also contributes to the total dielectric loss of the PNiC composite. The magneto–dielectric loss occurs due to the three components, namely hysteresis loss (P_h), eddy current loss (P_{ec}) and anomalous losses (P_{anom}) [17]. P_{anom} depends on domain structure, the hysteresis loss and eddy current losses contribute

Table 1. Real (ε') and imaginary (ε'') part of complex permittivity of free standing PANI film (thickness 52 ± 2 μm) and Ni-FAC doped PANI (PNiC) film (thickness 133 ± 4 μm).

Sample (film)	Frequency (GHz)	ε'	ε''	$\tan\delta_\varepsilon = \frac{\varepsilon''}{\varepsilon'}$
PANI	8.7	110	99.2	0.96
	11.7	103	51.9	0.5
PNiC	8.7	140	117	0.83
	11.7	123	56.8	0.46

efficiently in the radio frequency (RF) regions. The hysteresis loss depends on coercivity (H_c) and it is difficult to minimize. The eddy current losses for spherical structure are formulated as [17], $P_{ec} = \frac{\pi B_m^2 d^2 f^2}{20\rho}$, where, B_m, d, f and ρ are the amplitude of magnetic induction, diameter, frequency and resistivity, respectively. Since Ni naoparticles are coated over hollow ceramic microspheres (FACs) and grafted by PANI matrix, there results minimum P_{ec}.

3.1. Electromagnetic interference (EMI) shielding

The EMI attenuation arises due to reflection (R), absorption (A) and multiple reflections (M). The total EMI shielding effectiveness is measured in terms of complex scattering parameter (S-parameter) [3, 11] and it is expressed in dB. Mathematically,

$$SE\,(dB) = -10\log\left(\left|S_{21}\right|^2\right) = -10\log\left(\left|S_{12}\right|^2\right) \tag{5}$$

Where S_{21}, S_{12} is dimensionless. 30 dB SE corresponds to 99% shielding. The factors that affect EMI attenuation are frequency, conductivity, distance between the shielding and interfering source, shield thickness and shield materials. The EMI shielding due to absorption (SE_A) depends on skin depth (δ), total conductivity ($\sigma_T = \sigma_{ac} + \sigma_{dc}$), permeability (μ') and surface scattering as well.

Mathematically [1, 16],

$$\delta = \sqrt{2/\sigma\omega\mu'} = \sqrt{\frac{\rho}{\pi f\mu'}} \tag{6}$$

$$SE_A\,(dB) = 20\frac{t_h}{\delta}\log e = 8.68 t_h\sqrt{\sigma\omega\mu'/2} \tag{7}$$

Where, t_h is the thickness, ω (=$2\pi f$)is the angular frequency and ρ is the resistivity.

Frequency and thickness dependence of SE of the PANI and Ni-FAC doped PANI (PNiC) film is shown in figure 3. It was observed that PNiC films exhibit high shielding effectiveness, especially at high frequency (~12 GHz). For PANI film of average thickness 52 ± 2 μm observed SE is ~17 dB. Interestingly, in the case of PNiC film (average thickness 59 ± 4 μm) obtained average SE value is 38 dB.

While thickness increased to more than twice (133 ± 4 μm), SE increased to ~61 dB above 12 GHz. Thus, this reveals the suitability of PNiC film for EMI shielding at high frequency. Due to the presence of Ni-FAC, resistivity of PNiC film decreases and ac conductivity ($\sigma_{ac} = \varepsilon''\omega\varepsilon_o$) increases (47.6 to 62.1 Sm^{-1}). Further, skin depth (δ) also decreases from ~78 nm to ~63 nm. Conducting PANI surface is supporting normal electric field and embedded Ni-FAC is supporting tangential magnetic and electric field components of incident electromagnetic wave [15]. Since the magneto dielectric microspheres (Ni-FAC) are dispersed optimally, electromagnetic wave has to pass through the space between the microspheres by scattering that results in the increase of SE and it can be expressed as [1, 18],

$$SE\infty - 20\log(b.\,f) \tag{8}$$

Where, b is the microspheres spacing and f is the frequency. As the rms thickness of PNiC film is higher than skin depth by three orders, scattering takes place in high order. In other words, it is an effectively low intense homogenous chiral film. Moreover, the presence of Ni-FAC microspheres decreases the relative mass of PANI in the PNiC film which leads to low loss of reflection loss of electromagnetic radiation at high frequency [19].

4. Summary

In summary, PANI and nickel coated fly ash cenosphere (Ni-FAC) doped PANI composite freestanding films were prepared by solution processing and EMI SE was measured in the frequency range 8–12.4 GHz. Enhancement of SE was observed for PNiC composite film and maximum 61 dB SE was obtained for 133 ± 4 μm

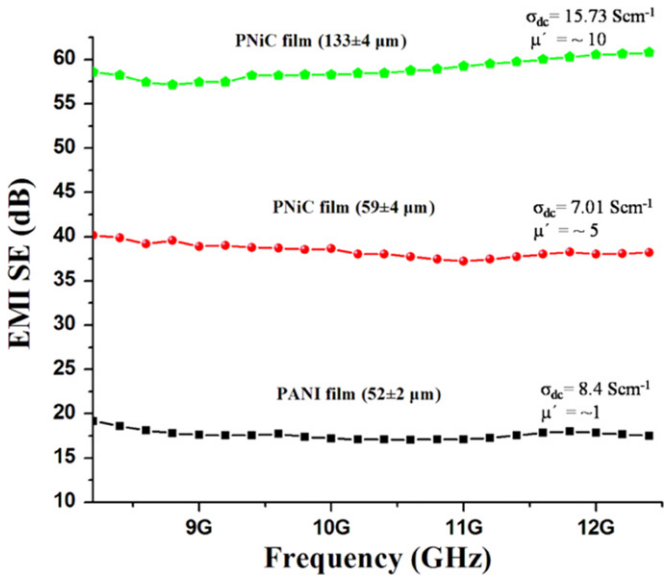

Figure 3. EMI SE of free standing PANI and PANI/Ni-FAC (PNiC) film. The average thicknesses were written inside bracket.

film. Further, unlike PANI film, its shielding effectiveness increases with increasing frequency and thus it shows better SE at high frequencies.

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