Lightweight Polyaniline-Cobalt Coated Fly Ash Cenosphere Composite Film for Electromagnetic Interference Shielding

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Thermal power plant's solid environmental waste fly ash cenosphere (FAC) is cobalt coated chemically and functionalized by *in situ* synthesis of polyaniline (PANI) under nitrogen atmosphere at -30 ± 2 °C and characterized by various techniques. The electromagnetic interference shielding effectiveness (EMI SE) of free standing PANI/Co-FAC (PCC) films prepared by solution casting indicates an appreciable shielding. The most effective average EMI SE of ~ 30 dB was obtained for 89 ± 3 μm thicker flexible film over the frequency range of 12.4-18 GHz (Ku-band). Mechanistically, EMI shielding due to absorption was found to be dominant. The obtained shielding effectiveness due to absorbance (SE_A) of PCC film is nearly two times higher than PC film. The microwave conductivity (σ) of PCC film (157-184 Sm^{-1}) is much higher than PC film (118-142 Sm^{-1}). Moreover, the high EM attenuation constant (α) value of PCC film indicates excellent suitability of EMI shielding due to absorption.

Keywords: polyaniline, cobalt, fly ash cenosphere, EMI shielding, dielectric
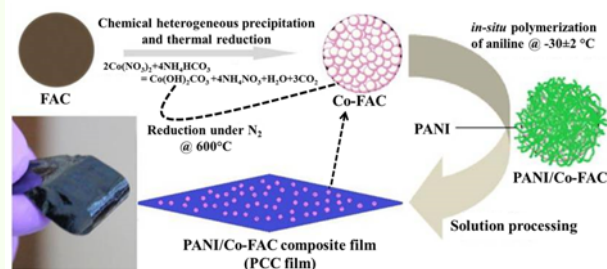
1. INTRODUCTION

In recent years, due to the development of electronic systems and telecommunications electromagnetic interference (EMI) is as a major problem.[1-5] The microwave frequency range 12.4-18 GHz is known as Ku-band. The importance of this frequency range is that it offers users more flexibility as it enables smaller antenna.[4] The Ku-band frequency range is used for many potential applications e.g., satellite communications, broadcasting, military and aerospace applications. Thus the probability of electromagnetic interference (EMI) is higher in this frequency range and the need of newer shielding materials is increasingly felt.[2,4] Efforts are continuously required to replace traditional metallic sheet based shielding materials by carbon based polymeric materials. Intrinsic conducting polymers (ICP) has many advantages including light weight, low density, flexibility and low cost.[1-3] Joo *et al.* investigated the thickness dependency of total shielding efficiency of various ICP films (100-800 μm). The work looked at the pronounced thickness effects for shielding effectiveness (SE) of PANI and PPY films along with weak temperature dependency.[6] In a related activity, they studied the multilayer films of various thicknesses by sandwiching a lossy dielectric between two sheets of the same thickness.[7]

In case of EMI shielding materials, the synergetic effect of magnetic and electrically conductive ingredients has been investigated.[2,5] Lately, to have a better degree of EMI shielding efficiency, core-shell structure has received considerable attention along with conducting polymers.[5-9] Fly ash cenosphere (FAC), an environmental pollutant solid

waste product in power generation plants, shows properties such as light weight, low density, nontoxic, and good insulation.[10-13] Metal coated FAC, an important core-shell composite, has been proposed for wider applications including EMI shielding as it possesses microwave absorbing properties.[12-19] Fu *et al*. reported that magnetically active $CoFe_2O_4$ coated hollow microspheres (FAC) behave like microwave "blackbody" in certain range (4-18 GHz).[19] In an another study, the microwave absorption of barium-ferrite-coated FAC at 2-18 GHz was found to display maximum reflection loss −15.4 dB for 3 mm thick powder pressed sample.[20] Recent investigation shows the controllable EMI shielding property of conducting polymer/cobalt nano-composite.[21] The microwave absorption property of polypyrol-Co nanocomposite was reported by Luo *et al*.[22] Under optimal conditions, they reported the average reflection loss was ∼ 10 dB for 4 mm thicker powder pressed sample in the frequency range 2-18 GHz.[22] Singh *et al*. studied the EMI shielding property of PANI-FAC composites in the frequency range 12.4-18 GHz. According to their result, the average EMI shielding effectiveness of PANI-FAC composites (PANI to FAC ratio 1:1) was reported ∼ 30 dB (shielding due to absorption was ∼ 20 dB and shielding due to reflection was ∼ 10 dB) for 2 mm powder pressed sample.[23] In the present investigation, magnetically active PANI/Co-FAC core-shell composite were synthesized and EMI SE are measured in thin film keeping in interest at minimum thickness with better flexibility.

2. EXPERIMENTAL PROCEDURE

The fly ash cenospheres were (particle size range 5-50 μm) cleaned by conventional acid and base treatment. It was cobalt coated by chemical heterogeneous precipitation thermal reduction method.[24] Optimally, 2.5 weight % of Co coated cenosphere (Co-FAC) was dispersed in anilinium ion and *in situ* synthesis of PANI/Co-FAC composite was carried out under nitrogen atmosphere at −30 ± 2 °C according to the procedure adopted in the literature.[25] Similarly, PANI-FAC composite was also synthesized under same condition for comparison. Obtained PANI/Co-FAC composite powder was solution processed for film preparation. Typically, 4 weight % of the synthesized composite was added very slowly to dimethyl-propylene urea (DMPU) solution under stirring for 5 h. In the next step, this solution was poured on to special moulds and kept in vacuum oven at 70 °C for 12 h. Thus obtained films were 1 M HCl acid vapor treated for 72 h to achieve stable conductivity. Finally, ultra-pure nitrogen was passed for drying and purification. Prepared, PANI/Co-FAC and PANI-FAC composite were named as PCC and PC film respectively. The average thicknesses of as prepared films were measured by using optical profilometry, obtained thicknesses were 91 ± 3 μm and 89 ± 3 μm for PC

and PCC film respectively. Obtained root mean square (rms) roughness for PC and PCC film was found as 0.17 ± 0.03 μm and 0.14 ± 0.05 μm, respectively.

3. RESULTS AND DISCUSSION

The surface morphology of chemically prepared Co-FAC composite and its elemental results are as shown in Fig. 1(A). No magnetic element was found in these FAC particles, as reported earlier,[13] silicates and alumina are observed to be the major constituents. Mostly uniform coating of Co nanoparticle was observed. However, in some regions agglomeration is also seen (particularly in defect bearing FAC). The chemical linkage which connects the shell and core are Si-O-Co and Al-O-Co respectively.[24] The X-ray diffraction patterns of Co-FAC and PANI/Co-FAC core-shell composites are shown in Fig. 1(B). In Co-FAC core shell three peaks at $2\theta = 44.82°$, $55.52°$ and $77.21°$ (less intense) are observed, which corresponds to (111), (200) and (220) planes of face cantered cubic (fcc) structure of cobalt.[23,26] Using Scherrer formula,[26] from the full width half maxima (FWHM) of (111) plane, crystallite size is calculated to be as ∼ 26 nm. In the X-ray diffraction pattern of composites, both the Co and FAC diffraction peaks were observed along with PANI diffraction peaks which were observed at ∼ 15° and ∼ 25°. This is due to the lower coherence length and the periodicity parallel and perpendicular to PANI chains respectively.[27] The magnetic properties of the composites were shown in Fig. 1(C). The obtained hysteresis loops indicating that both Co-FAC and PANI/Co-FAC are typically soft ferromagnetic materials. The saturation magnetization (M_s) and coercivity (H_c) of Co-FAC was found to be 45.06 emu/g and 186.25 G respectively. In case of PANI/Co-FAC composite obtained M_s was 20.98 emu/g with negligible change in H_c (184.25 G). To investigate the nature of dispersion of the Co-FAC in PANI matrix, the composite samples were analyzed by FESEM and elemental mappings were carried out (Fig. 2). These images suggest a homogenous dispersion of Co-FAC in PANI matrix. Few small agglomerated regions are noticed (due to defect bearing FAC and magnetic dipole interactions) which affect the surface topography of the film and these might help in EMI shielding.

The electromagnetic interference shielding effectiveness (EMI SE) is the logarithmic ratio of incident (P_I) to transmitted (P_T) power of radiation i.e.[1,2]

$$SE(dB) = -10\log\frac{P_I}{P_T} = SE_R + SE_A + SE_M$$

where, SE_R, SE_A, and SE_M represents EMI shielding due to reflection, absorption and multiple reflections respectively. The unit of EMI SE is dB and 20 dB SE corresponds to 99% shielding.[1,2] The role of multiple reflections can be
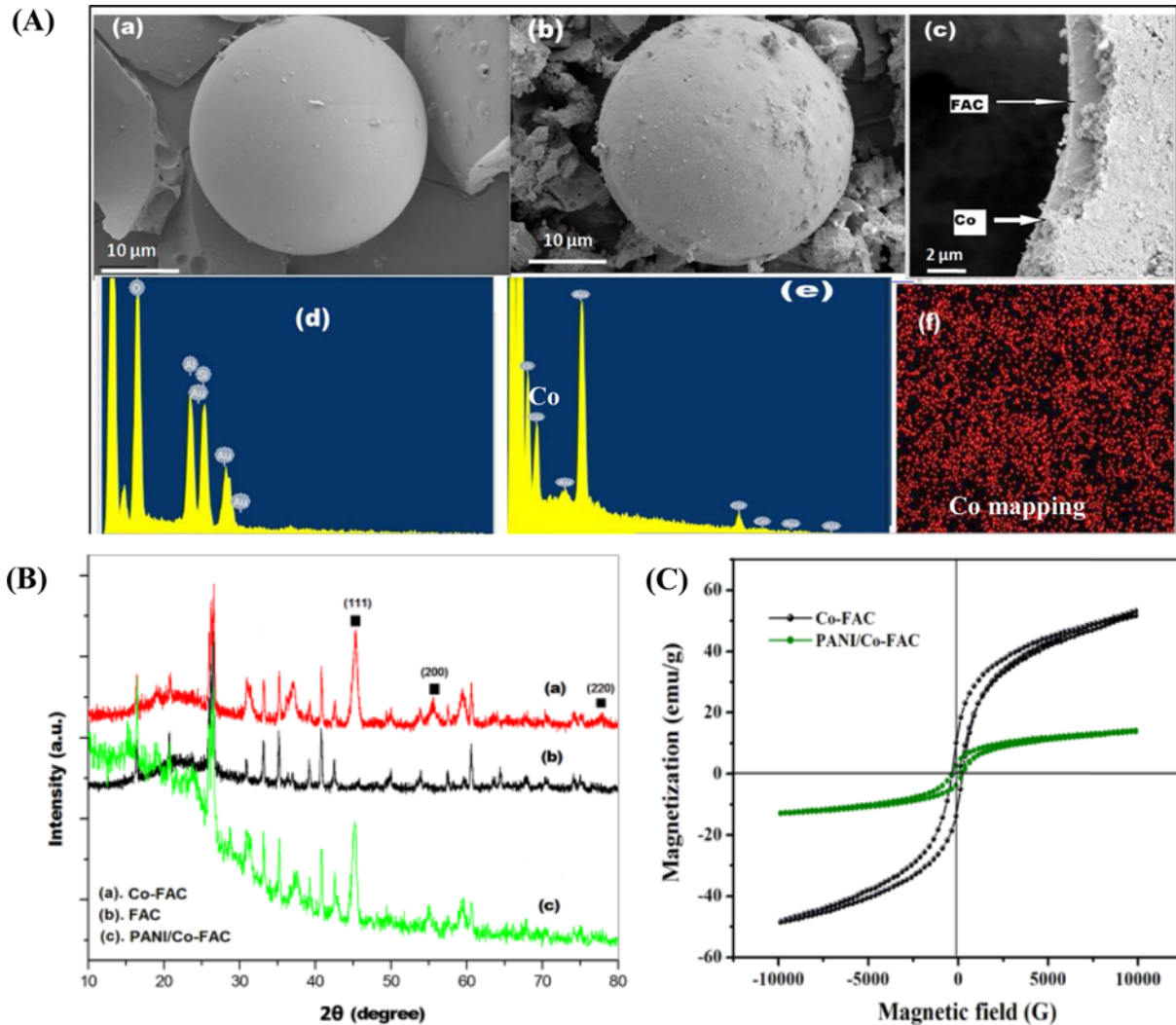
Fig. 1. (A) Surface morphology and EDX of FAC and Co-FAC. (a) cleaned FAC, (b) Co-FAC, (c) cross-sectional view of Co-FAC (d) EDX of pure cleaned FAC, (e) EDX of Co-FAC, (f) Co mapping on FAC, (B) XRD pattern of the composites, (C) Magnetization of synthesized composites.

neglected if EMI *SE* is ~ 10 dB,[28] which especially takes place at lower frequencies (less than 20 KHz) for low absorbing materials.[2] Obtained EMI SE over the frequency range of 12.4-18 GHz (Ku-band) for PC and PCC films are shown in Fig. 3.(A). The EMI SE of PCC film (89 ± 3 μm) was found ~ 30 dB which is much higher than PC film (~ 18 dB). The obtained SE_A and SE_R of PC and PCC films are shown in Fig. 3(B), here it was found that EMI shielding due to absorption is the dominant part. The obtained SE_A of PCC film was ~ 28 dB, on the other hand, for PC film it was found ~ 14 dB. Corresponding SE_R value of PCC and PC film was obtained ~ 2 dB and ~ 4 dB respectively. Thus, it suggests the shielding due to absorption property of PCC film is nearly two times higher than PC film. A comparison of various reported materials under optimal conditions with present material is tabulated in the Table 1. From the Table 1, it can be suggested that the PAN/Co-FAC (film) composite is

much superior to the other reported materials in terms of higher shielding at minimum thickness.

The principle reason behind high EMI SE value of PCC film is the loss of time average power of incident electromagnetic wave,[29] to propagate an electromagnetic wave (energy) around the material. The time average power is needed i.e. $P_{av} = \frac{1}{2} \int (E \times H^*) dS$, where E (electric field) and H (magnetic field) are the field values and the asterisk indicates complex conjugate and it travels by changing phase and exponentially decreasing the magnitude ($E = E_o e^{-1(1+j)Z/\delta}$, $H = H_o e^{-1(1+j)Z/\delta}$). Since the FAC (Co-FAC) is dispersed optimally in the composite films, the incident electromagnetic wave has to pass through scattering and thus loses energy which is absorbed by the composite film (due to heterogeneity of the system) and helping increase of SE (SE_A). PCC film has magneto-dielectric properties (Co coated FAC), hence it increases SE_A. The incident
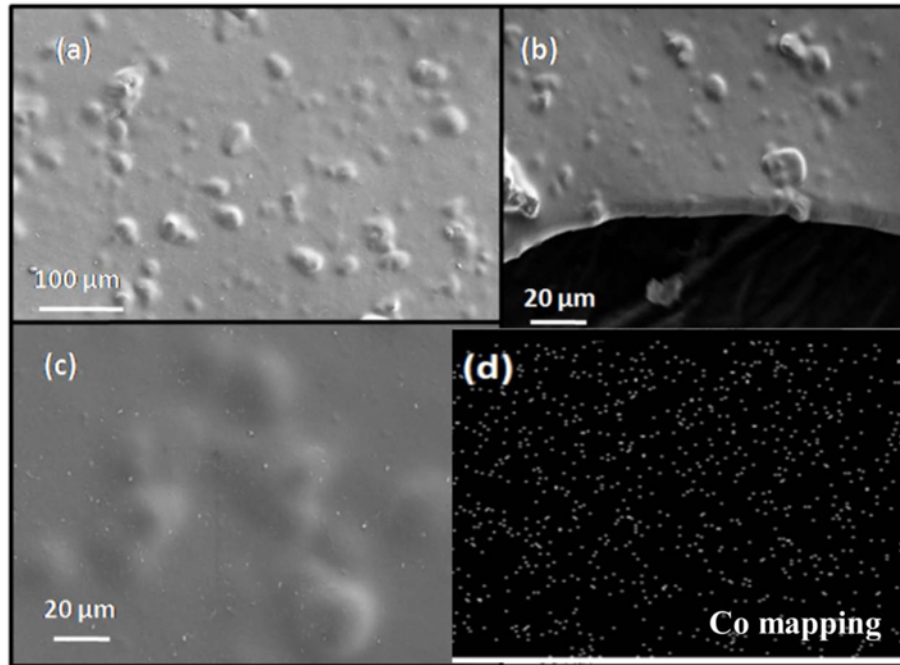
Fig. 2. Surface morphology of (a) PCC film, (b) edge view of PCC film, (c) embedded Co-FAC in PCC film and (d) elemental mapping of Co.
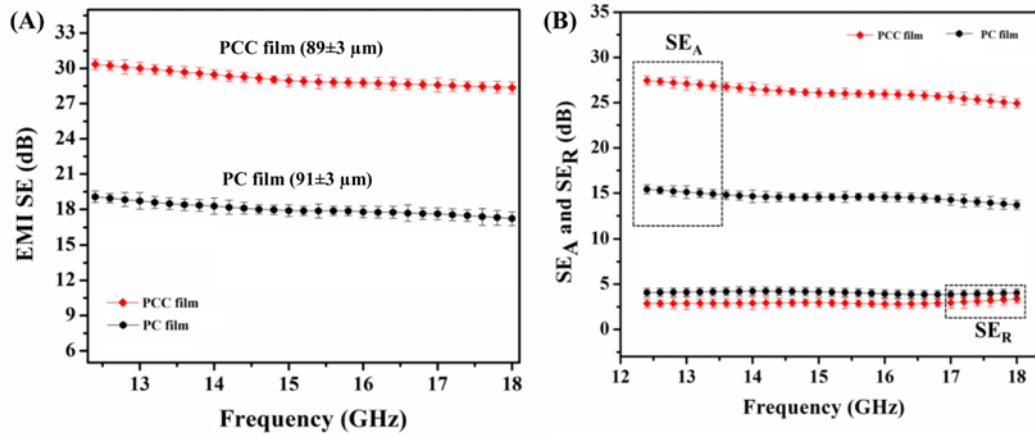

Fig. 3. (A) EMI Shielding effectiveness (B) EMI Shielding effectiveness due to absorption (SE_A) and reflection (SE_R) of PCC and PC film.

Table 1. Comparison of EMI shielding property of the various reported materials under optimal conditions.

Material	Frequency	SE (dB)	SE_A (dB)	SE_R (dB)	Thickness	Reference
Glass microspheres coated with $CoFe_2O_4$	2-18 GHz	-	~ 8	-	1.5 mm	[19]
Barium-ferrite-coated FAC	2-18 GHz	-	~ 15	-	3 mm	[20]
Polyaniline-flyash	12.4-18 GHz	~ 30	~ 20	~ 10	2 mm	[23]
Polyaniline-Y_2O_3	12.4-18 GHz	~ 16	~ 13	~ 3	2.8 mm	[34]
Polypyrrol-Co	2-18 GHz	~	~ 10	~	4 mm	[22]
Polypyrrol-flyash	12.4-18 GHz	~ 21	~ 14	~ 7	2.6 mm	[35]
Polyaniline-antimony oxide	12.4-18 GHz	~ 21			2.8 mm	[36]
Polyaniline-graphene-Fe_2O_4	12.4-18 GHz	11	9	2.5	2 mm	[37]
Polyaniline/Co-FAC (film)	12.4-18 GHz	~ 30	~ 28	~ 2	$89 \pm 3 \ \mu m$	Present work
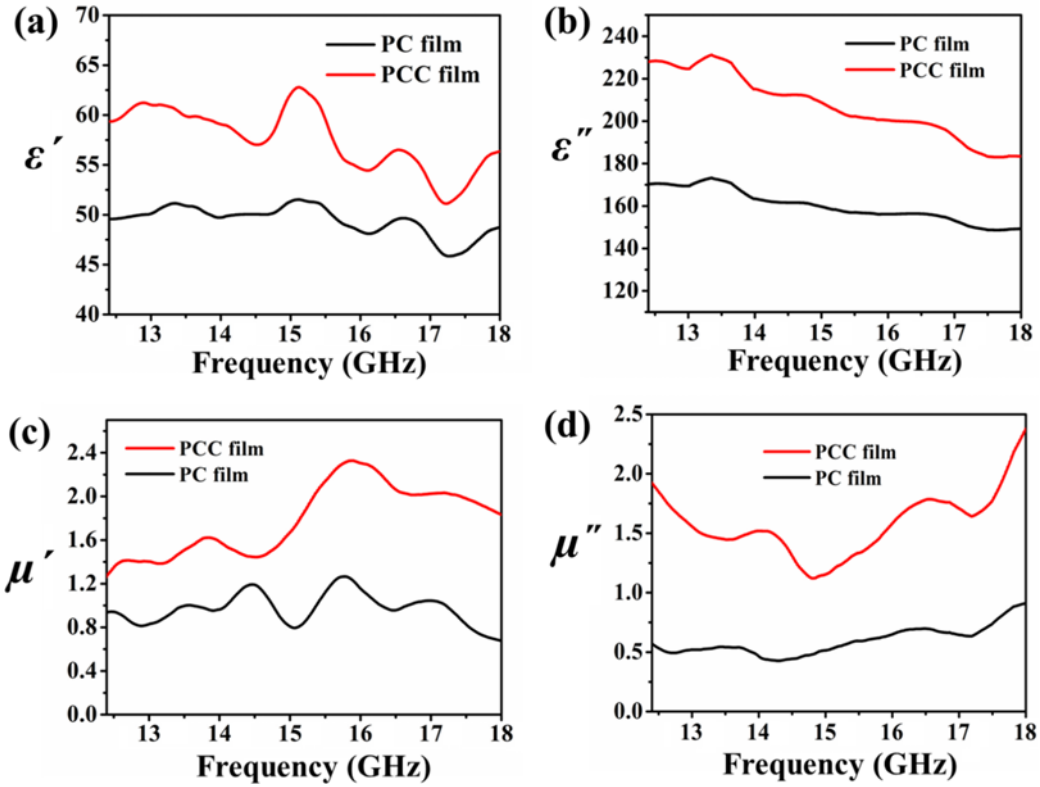
Fig. 4. Frequency dependencies of the (a) real and (b) imaginary parts of the complex permittivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$) and (c) real and (d) imaginary parts of the complex permeability ($\mu^* = \mu' - i\mu''$) of PCC and PC film over the frequency range 12.4-18 GHz (Ku-band).
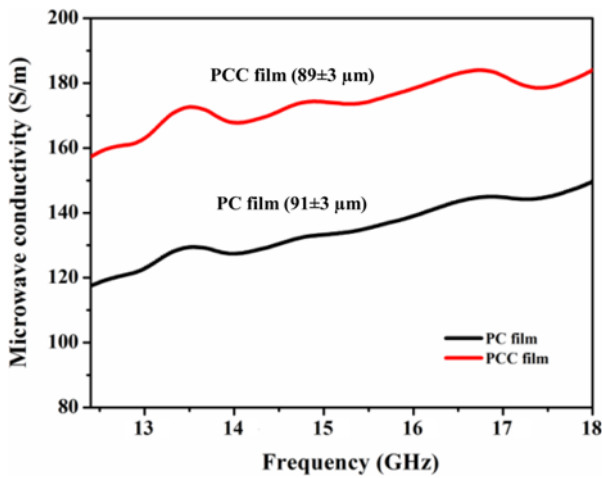
Fig. 5. Variation of microwave conductivity (σ) of PCC and PC film with respect to frequency.

electromagnetic wave generates an electric field over the PANI surface opposite to applied field as the electron cloud near the surface gets distorted. This combined opposite electric fields cause reflection of the electromagnetic wave from the surface rather than the penetration as a result of the impedance mismatch.[29] This is the reason for the high SE_R value of PC film compared to PCC film. In addition,

enhancement of anisotropic energy, eddy current loss effect and the synergetic effect in between PANI and Co-FAC might be conducive to the high EMI SE (SE_A) of PCC film.[7,8,21,30]

In case of conducting materials (metals), EMI shielding mainly depends on conductivity and thickness.[29] The important parameter for EMI shielding due to absorption (SE_A) is skin depth (δ), the distance up to which the intensity of the electromagnetic wave decreases to $1/e$ of its original strength, along with other parameters. Mathematically it is written as,[28] $\delta = \sqrt{2/\mu'\omega\sigma}$, where, μ' is the real part of complex permeability ($\mu^* = \mu' - i\mu''$) ω is the angular frequency, σ is the microwave conductivity and it is written as, $\sigma = \sigma_{ac} + \sigma_{dc} = \omega\varepsilon_o\varepsilon''$, where ε'' is the imaginary part of complex permittivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$). For electrically thick samples (sample thickness (t) > δ),[29]

$$SE_A = -20\frac{t}{\delta}\log e = -8.68t\left(\frac{\sigma\omega\mu'}{2}\right)^{1/2}$$

The complex permittivity and permeability of the PC and PCC films were determined from the measured S-parameters by using Nicholson-Ross-Weir (NRW) method.[31] Obtained results are shown in Fig. 4. The FAC (Co-FAC) in the PANI matrix results in the formation of more interfaces and a
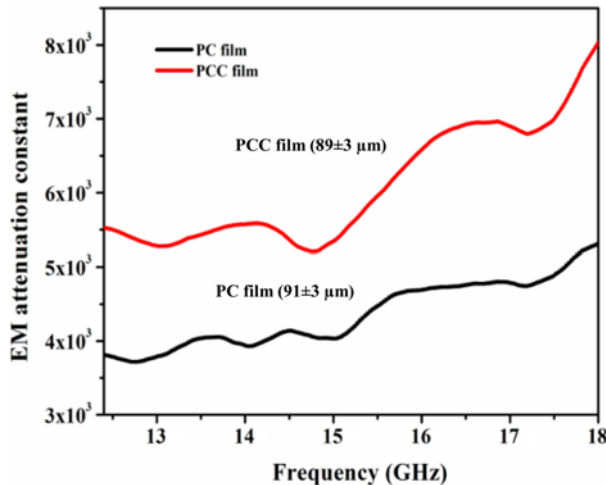
Fig. 6. Variation of EM attenuation constant of PCC and PC film with respect to frequency.

heterogeneous system and creates the interface space charge accumulation sites. Trapping of some polaron / bipolarons on FAC (Co-FAC) surface (due to the dielectric difference) and dielectric loss of SiO_2, Al_2O_3 (main constituents of FAC) could be considered as another reason for the obtained high value of ε'' (loss part).[21] The variation of microwave conductivity (σ) with respect to frequency is shown in Fig. 5. The σ value is increases with frequency, obtained σ value of PC and PCC film was 118-142 Sm^{-1} and 157-184 Sm^{-1} respectively. The effective EMI absorption is dominated by two factors, viz. impedance matching and the EM attenuation in the interior absorber. Ideally impedance matching is important for electrically thin sample. The propagation of the electromagnetic wave inside a material is determined by the propagation constant (γ_s).[32] The equation of propagation constant is $\gamma_s = \sqrt{j\omega\mu_s\sigma_s}$, the real part of γ_s represents EM attenuation constant (α).[32] According to the transmission line theory, the EM attenuation is determined by α and it depends on frequency, permeability and permittivity values. Mathematically EM attenuation constant (α) is expressed as,[33,32]

$$\alpha = \frac{\sqrt{2}\pi f}{c} \times$$
$$[(\mu''\varepsilon'' - \mu'\varepsilon') + \{(\mu''\varepsilon'' - \mu'\varepsilon')^2 + (\mu'\varepsilon'' - \mu''\varepsilon')^2\}^{1/2}]^{1/2}$$

where f is the frequency of the EM wave and c is the velocity of the light. The variation of EM attenuation constant of the PC (3829-5306) and PCC film (5517-8012) in the frequency range 12.4-18 GHz was shown in Fig. 6. It was observed that α value increase with frequency. This anomalous behaviour of as prepared films is due to the increase of electric and magnetic energy loss with frequency. The real part of complex permittivity (ε') and permeability (μ') corresponds to the amount of polarization taking place inside the material

whilst imaginary parts (ε'' and μ'') correspond to the dissipation of electric and magnetic energies respectively.[33] From the dielectric study (Fig. 4), it was found that μ' and μ'' of PC and PCC film increases with frequency and ε'' is much higher than ε'. Therefore, expected electromagnetic loss ($\mu''\varepsilon'$) is high with frequency. Thus it results increase of α value with frequency.

In the recent times, the electromagnetic interference (EMI) problem becomes serious due to the rapidly expanding small communication devices.[38] Hence, the need of coating material is increasingly felt for these devices. The key advantage of this lightweight composite system is that it has both conducting polymer as well as thermally stable magneto dielectric hollow microsphere that is useful for impedance matching and microwave absorption. The present investigation shows that the PCC film exhibits excellent EMI shielding and EMI shielding due to absorption property with outstanding EM attenuation. Therefore, PCC film can be coated over small communication devices as its efficiency decreases due to the common EMI problem. Moreover, this film could be considered as a potential candidate to coat over modern unmanned vehicles as well as for microwave, robotic engineering.

4. CONCLUSIONS

The *in situ* soft magnetic PANI-Co-FAC hollow core shell composite was synthesized. The highly flexible thin films (thickness 89 ± 3 μm) of this composite (PCC) obtained by solution processing shows an EMI SE of ~ 30 dB over frequency range of 12.4-18 GHz. Mechanistically, shielding due to the absorption was found to be dominant. The EMI shielding due to absorption capability of as prepared PCC film is nearly two times higher than PC film. The microwave conductivity and EM attenuation constant of PCC film is also high demonstrating the excellent EMI shielding due to absorption.

ACKNOWLEDGMENTS

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