NaCl leached sustainable porous flexible Fe₃O₄ decorated RGO-polyaniline/PVDF composite for durable application against electromagnetic pollution

R. Bera, S. Paria, S. K. Karan, A. K. Das, A. Maitra, B. B. Khatua*

Materials Science Centre, Indian Institute of Technology, 721302 Kharagpur, India

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Abstract. To avoid the interference of electromagnetic radiation from other devices, an electronic device needs to be fabricated with flexible and light weight electromagnetic interference (EMI) shielding materials with high efficiency. According, highly flexible porous poly(vinylidene fluoride) (PVDF)/PFR (Fe₃O₄ decorated polyaniline/RGO composite) composite was prepared through solution blending of PVDF with pre-synthesized PFR conductive composite that involves *in-situ* oxidative polymerization of aniline in the presence of reduced graphene oxide (RGO) using FeCl₃ as oxidant. The porous morphology of the composite was created by leaching out of mixed NaCl from the composite. Polyaniline and RGO were mutually decorated by chemically *in-situ* synthesized ferrosferric oxide (Fe₃O₄) using the Fe source of FeCl₃. A homogeneous dispersion of PFR in insulated PVDF matrix resulted in a highly electrical conductive composite (PVDF-PFR) material through formation of three dimensional continuous conductive networks of polyaniline-RGO in the matrix phase. The composite shows an outstanding EMI shielding effectiveness (EMI SE) property due to the porous structure and the presence of conductive network and ferromagnetic Fe₃O₄ nanoparticles. The PVDF-PFR composite (0.5 mm thickness) depicts a great permittivity and permeability value and achieve high EMI SE value (≈ 28.18 dB) and conductivity value of $\approx 1.10 \cdot 10^{-1} \text{ S} \cdot \text{cm}^{-1}$ at very low loading (5 wt%) of RGO.

Keywords: polymer composites, conductivity, microwave absorption, *in-situ* Fe₃O₄, porous flexible composite

1. Introduction

Nowadays, in both civil and military fields electronic technology is rapidly developing with its mounting popularity [1]. The electromagnetic (EM) waves emitted from ubiquitous sources of electronic gadgets or equipment and interacts with each other, creating serious Electromagnetic Interference (EMI) problems or EMI pollution that has negative influence on the human health, environmental pollution, and normal performance of electronic equipment [2]. In July 1967 it was claimed that 134 lives and electronics equipment (cost \$72 million) were damaged due to undesirable interference from EM waves at the USS Forrestal off the coast of Vietnam [3]. Thus, material

scientist have been highly focused to develop the EMI shielding materials which can be applicable in the area of aerospace, aircraft, automobiles, and fast-growing next-generation portable electronics. The conductive nanofiller based polymer composite (low cost, light weight, strong corrosion resistance, broad absorption bandwidth properties and has excellent processibility) shows efficient properties for the said area as EMI shielding materials in compare to traditional metal based materials [4]. The EMI shielding property of the polymer composites depends on its conductivity, permeability, permittivity and morphological properties. The conductive polymer composites for efficient EMI shielding materials are usually

*Corresponding author, e-mail: khatuabb@matssc.iitkgp.ernet.in
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prepared by incorporation of conductive fillers like CNT [5], graphene [6], carbon nanohorn [7], inherently conductive polymer [8], etc. in the polymer matrix through *in-situ* polymerization of monomers, melt or solution mixing processes.

The rationale behind choosing reduced graphene oxide (RGO) in this work as a conductive filler is its' remarkable properties such as excellent electric and thermal conductivity, mechanical strength, flexibility, and barrier properties and also it contains functional groups and residual defects that create impedance mismatch, defect polarization relaxation and electronic dipole relaxation which altogether help to enhance EMI SE, especially, microwave absorption [9]. Many researchers reported that graphene based materials are very efficient for EMI shielding application [10, 11]. The conductive polyaniline also used in this work as a microwave absorbing material due to its low cost, good environmental stability, ease of synthesis, and high electrical conductivity. Also, polyaniline can increase the dielectric loss of the composites materials which facilitate the microwave absorption capability of the materials [12–14]. The presence of magnetic materials, such as, Fe_3O_4 magnetic material (having large magnetic anisotropy, high permeability, good biocompatibility and low toxicity property) in the composites highly influences the permeability (by their large saturation magnetization) of the composites which is strongly related to the microwave absorption property of the composites. In this study, Fe_3O_4 magnetic material was synthesized during *in-situ* polymerization of polyaniline to enhance the absorption property of the composites which also has insulating characteristic for eddy currents (due to a drop in the complex permeability (μ'') in the gigahertz range). Many researchers [15, 16] have already reported high microwave absorption property of Fe_3O_4 containing polymer composites.

Foaming and creating of porosity in composite are undoubtedly an effective way to make the shielding materials lightweight with great microwave absorption ability for various scientific and industrial applications [17]. Kuang *et al.* [18] shows light weight poly(L-Lactic acid)(PLLA)-MWCNT foam achieve ~23 dB SE value with 2.5 mm thickness at 10 wt% MWCNT loading. Eswaraiyah *et al.* [19] reported that PVDF/graphene foam shows EMI SE ~28 dB at 7 wt% functionalized graphene loading. The formation of foam at high filler loading is extremely difficult by traditional foaming methods (e.g., decomposition

of chemical foaming agent) [10]. Thus, the porous structure creates by using templates gets more important than foaming process. Shen *et al.* [20] reported that poly urethane/graphene composite foam shows EMI SE ~39.4 dB at 10 wt% graphene loading with 60 mm thickness. Porous polydimethylsiloxane (PDMS)/graphene foam depicts 20 dB EMI SE at 0.8 wt% graphene loading with 1 mm thickness, reported by Chen *et al.* [21] In this work particulate leaching technique was followed where NaCl was mixed and leached out to create porous structure in the composite.

The properties ((easy processing, flexibility, high dielectric strength ($\sim 13 \text{ kV} \cdot \text{mm}^{-1}$), high thermal stability, good chemical resistance, low density ($1.76 \text{ g} \cdot \text{cm}^{-3}$), excellent mechanical properties, in addition its well-known ferroelectric, piezoelectric and pyroelectric properties)) [22, 23] of poly(vinylidene fluoride) (PVDF) makes it very applicable for the said purpose [24, 25]. In this manuscript, we have discussed the EMI SE properties of a relatively new hybrid porous composite (PVDF-PFR), consisting of PVDF, polyaniline, Fe_3O_4 and RGO, where RGO and polyaniline act as conductive filler in PVDF matrix. *In-situ* formation of Fe_3O_4 during the polymerization of aniline using FeCl_3 as oxidant also acts as the Fe source of the oxide in presence of RGO. Although, following different procedure few works [26, 27] have already been reported on the preparation of polyaniline/RGO/ Fe_3O_4 ternary composites EMI SE material mostly in powder form that limits its application because of its brittle nature and difficulties associated with moldability. However in the present study, we focus on the preparation of a highly flexible porous polyaniline/RGO/ Fe_3O_4 based composites through conventional facile solution blending technique with great EM microwave absorption ability.

2. Experimental

2.1. Materials details

Aniline (ANI) monomer (synthetic grade, $M = 93.13 \text{ g/mol}$, $d = 1.02 \text{ kg/L}$, purity > 99%) was obtained from Merck, Germany. Hydrogen peroxide 30% (H_2O_2 , Nonvolatile substance < 0.1%) and potassium permanganate (KMnO_4) were procured from Merck, India. Graphite fine powder, potassium iodide GR (KI), and ferric chloride anhydrous (FeCl_3) were purchased from Loba Chemie Pvt. Ltd., India. PVDF was obtained from Alfa Aesar, USA. Sodium chloride (NaCl , 99%) purchased from Merck, India. GO and

RGO were synthesized from graphite in our laboratory.

2.2. Preparation of PFR and porous

PVDF-PFR composite

Modified Hummer's method was followed to synthesize GO [28]. Graphite powder (3 g) was oxidized by concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (360:40 mL) acid mixture and KMnO_4 (18 g). The solid mixture of graphite powder and KMnO_4 slowly added into the concentrated acid mixture ($\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$) in stirring condition. The reaction mixture was stirred for 12 h at room temperature and then poured into cold water (0°C , 500 mL). Subsequently, H_2O_2 was slowly added in to the aqueous-reaction mixture in stirring condition until the color of the mixture changed to light yellow. After 1 h stirring, the mixture was left for 2 days without any disturbance. Then the supernatant part of the mixture was decanted away and the brown color precipitate part was washed for several times (until it becomes neutral) with water, dilute HCl (5%) and ethanol. Finally, 4.6 g of product was obtained after drying the washed precipitate.

The prepared brown colored GO was reduced by KI in acid medium (HCL) [29]. The GO (1.5 g) was dispersed in distilled water by ultrasonication (OSCAR Model: PR-250 probe tip diameter 6 mm, frequency 25 kHz and ultrasonic power 250 watt) for 1 h at room temperature. After that 500 mL of HCl (6 M) was added into the dispersed GO solution and solid

KI (10 g) was slowly added in to the reaction mixture under stirring condition. Gradually a yellow color with black particle mixture was developed in the reaction mixture. The reaction mixture was stirred for 8 h and left for overnight without any disturbance. The precipitated black particles (RGO) were filtered. The precipitate part (RGO) was collected after washing by water and ethanol, followed by drying in air oven at 40°C .

The PFR composites were synthesized by *in-situ* polymerization of aniline in the presence of RGO. At the beginning, RGO (0.66 g) was dispersed through ultrasonication in water. ANI (4 mL) was added in the 200 mL of (1 M) HCl solution in a beaker. The acidic suspension was stirred for 30 min in an ice bath. After that, dispersed RGO and measured weight (1.4 g) of anhydrous FeCl_3 (oxidant) were added respectively into the acidic suspension at the same condition. H_2O_2 (30%, 1.0 mL) was slowly added in to the reaction mixture after 30 min. The reaction mixture was allowed to react under ice bath in stirring condition for 7 h. A deep greenish color solution of polyaniline with RGO was developed. After that, NH_4OH solution was added into the greenish solution and maintained the $\text{pH} \approx 10$. The reaction mixture was allowed to stir for 10 h at room temperature to synthesize Fe_3O_4 in the reaction mixture [30]. After 10 h of stirring, the resulting black colored precipitate (Fe_3O_4 synthesized) was filtered and washed with dilute HCl ($\text{pH} \approx 6$) to acidify the precipitant. The precipitant was

Figure 1. (a) Schematically shown the preparation of PFR and porous PVDF-PFR composites. Digital photograph (b), (c), and (d) of the PVDF-PFR porous composite demonstrates the flexibility

collected after drying it under vacuum at 30 °C for 36 h. Following the same procedure we also prepared *in-situ* synthesis Fe₃O₄ decorated polyaniline (PF) composite without RGO.

The porous PVDF-PFR composites were prepared by simple solution blending technique. PVDF powder (2 g) was taken and dissolved in dimethylformamide (DMF, 20 mL). Separately, PFR (0.11 mg) was dispersed in DMF (20 mL) by ultrasonication for 2 h. After that, the dispersed PFR solution was added into the PVDF solution under stirring condition. The solution was ultrasonicated for 2 h. Next, NaCl (0.5 g) was added to mix in the dense homogeneously dispersed PVDF-PFR mixture and followed by casting onto a Petri dish and left it for 72 h at room temperature without any disturbance. Final drying was done in a vacuum oven at 35 °C for 48 h. After drying, NaCl was leached out from the composite by stirring it in water to create pore in the prepared composite. The resulting composites (PVDF-PFR5) having thickness 0.5 mm with 5 wt% PFR loading was used for further characterizations. PVDF-PFR composites with various amount of PFR loadings, such as, 10, 15, and 25 wt%, were also prepared following the same method and were denoted as PVDF-PFR10, PVDF-PFR15 and PVDF-PFR25, respectively. The RGO loading for PVDF-PFR5, PVDF-PFR10, PVDF-PFR15 and PVDF-PFR25 are 1, 2, 3, and 5 wt%, respectively. The flexibility of the prepared composites is shown in the Figure 1 by digital photograph.

3. Characterization

Field emission scanning electron microscope (FESEM) (Carl Zeiss-SUPRA 40, Germany, operated at an accelerating voltage of 5 kV), and transmission electron microscope (TEM), JEM-2100, JEOL, Japan, operated at an accelerating voltage of 200 kV) were used to study the morphology and the elemental distribution of GO, PF, PFR and PVDF-PFR composites. Porous morphology of the prepared composite also observed by FESEM. The protonation of PFR was studied by using UV-visible absorption spectroscopy (PerkinElmer, Lambda 750, USA). X-ray diffraction (XRD) analysis was done for GO, RGO, PF, PFR, PVDF-PFR and PVDF by an X'Pert PRO diffractometer (PANalytical, Netherlands) with nickel-filtered Cu K α ($\lambda = 0.15404$ nm) at a scanning rate of 0.25°·min⁻¹. FT-IR (Fourier Transform Infrared Spectroscopy, Jasco FT-IR 300E, USA, ATR mode) was used to study the characteristic vibrational modes

of GO, RGO, PF, PFR and PVDF-PFR. Raman spectroscopic analysis of GO, RGO and PFR was carried out by a Raman triple spectrometer (T-64000, HORIBA Jobin Yvon, Japan, fitted with a synapse detector). The DC conductivity of the composites was measured by electrometer (Keithley 4200, USA).

EMI shielding effectiveness (SE) measurement was carried out for PVDF-PFR composites using an E5071C ENA series network analyzer (Agilent Technologies, USA). The rectangular samples with 0.5 mm thickness were placed between the two ports of the waveguide to perform the measurement in the 8.2–12.4 GHz frequency range. During this study, the S parameters (S_{11} , S_{12} , S_{21} , S_{22}) were recorded to calculate the total SE, shielding by absorption and shielding by reflection of the PVDF-PFR composites.

The following Equation (1) (logarithm of incident power (P_{in}) and transmitted power (P_{out}) ratio) was applied to measure total EMI SE (SE_T):

$$SE_T [\text{dB}] = 10 \log \frac{P_{in}}{P_{out}} \quad (1)$$

The incident power gets absorbed (P_{abs}), reflected (P_{ref}) and transmitted (P_{out}) after hitting the material, stated by the Equation (2):

$$P_{abs} = P_{in} - P_{ref} - P_{out} \quad (2)$$

The ratio of the power, i.e., the power coefficients: reflectivity ($R = P_{ref}/P_{in}$), absorptivity ($A = P_{abs}/P_{in}$) and transmittivity ($T = P_{out}/P_{in}$) are related with each other through Equation (3):

$$A + T + R = 1 \quad (3)$$

Shielding efficiency by reflection, absorption and multiple internal reflections of radiation (SE_R , SE_A and SE_M) together jointly presents the total EMI SE (SE_T) value of the materials, expressed as Equation (4):

$$SE_T = SE_A + SE_R + SE_M \quad (4)$$

SE_M becomes negligible for total EMI SE when $SE_T \geq 15$ dB then Equation (4) can be expressed as Equation (5) [31]:

$$SE_T \approx SE_A + SE_R \quad (5)$$

The power coefficients were measured from the scattering parameters: $R = |S_{11}|^2$ and $T = |S_{21}|^2$ [32]. S_{11} is equal to S_{22} , and S_{21} is equal to S_{12} for the materials which are homogeneous in nature. Thus, the power coefficients are expressed by Equation (6) and (7):

$$T = |S_{21}|^2 = |S_{12}|^2 \quad (6)$$

$$R = |S_{11}|^2 = |S_{22}|^2 \quad (7)$$

In terms of power coefficient and scattering parameter, the shielding efficiency of materials by reflection and absorption can be conveniently expressed by Equation (8), (9) and (10) [33]:

$$SE_R = -10 \log R \quad (8)$$

$$SE_R = -10 \log(1 - R) = -10 \log(1 - |S_{11}|^2) \quad (9)$$

$$SE_A = 10 \log \left| 1 - \frac{|S_{11}|^2}{|S_{12}|^2} \right| \quad (10)$$

The total EMI SE can be expressed in terms of power coefficient and scattering parameter as Equation (11):

$$SE_{total} = -10 \log T = -10 \log |S_{21}|^2 \quad (11)$$

The complex permeability and permittivity were estimated from the recorded S parameter of the sample using a MATLAB code based on Nicolson-Ross-Weir method [34]. The obtained complex permittivity value was used to calculate the frequency dependent AC conductivity of the composites.

4. Results and discussion

Figure 2a and 2b present the FESEM images of the PVDF-PFR composites. The porous morphology was created due to leaching out of NaCl from the composite as shown in Figure 2a. Figure 2b, the higher magnification FESEM image of PVDF-PFR composites shows that the *in-situ* synthesized Fe_3O_4 particles decorated polyaniline and RGO formed a continuous conducting interconnected network path throughout the composite by the homogeneous dispersion of the filler. The red circles in Figure 2b denoting the presence of Fe_3O_4 . The FESEM-EDX spectrum analysis of the PVDF-PFR composites also supports the presence of polyaniline, Fe_3O_4 and RGO in the PVDF matrix by showing the peak of Fe, O, N, F and C, presented in inset of Figure 2b. Figure 3a, the FESEM image of PFR depicts the decoration of Fe_3O_4 on RGO and polyaniline. The X-ray mapping (Figure 3b) of the PFR composites shows the existence of C, N, O and Fe elements in the composite materials which come from polyaniline, Fe_3O_4 and RGO. The TEM image of PVDF-PFR composites is shown in Figure 2c which also supports the

FESEM images of the composites i.e. the presence of polyaniline, Fe_3O_4 and RGO in the composites. The TEM image indicates the existence of continuous conductive network formed by Fe_3O_4 decorated polyaniline and RGO in the PVDF matrix. From this image we assume that there could be some interaction between polyaniline and Fe_3O_4 . The selected area electron diffraction (SAED) pattern of PF has been studied, as shown in inset of Figure 2c which supports the crystalline nature of Fe_3O_4 .

Figure 2d depicts the UV-visible spectra of polyaniline (P) without treatment of ammonium hydroxide and PFR composite after washed with dilute acid (pH ~6). The characteristic peaks of polyaniline (emeraldine salt) are observed at 340–430 and ~750–800 nm for both P and PFR. The peaks of PFR composite shifted compare to P due to possible interaction between polyaniline, RGO and Fe_3O_4 [35].

The XRD analysis of GO, RGO, PF, PFR, PVDF-PFR composites and PVDF powder are shown in Figure 4. The XRD pattern ($2\theta = 10.49^\circ$) of the GO supports the oxidation of graphite powder (i.e. the presence of carboxylic and epoxide groups in the graphite powder) by the improved Hummers' method [28].

The XRD pattern of RGO confirmed the reduction of GO in presence of KI and HCl where the peak corresponding to (002) plane of GO was disappeared and two different peaks (at ~ 25.42 and 43.20°) were observed for the (022) and (100) planes, respectively [29]. Main peaks for polyaniline ($\sim 24^\circ$) and Fe_3O_4 ($30.6, 36, 43.5, 53.8$ and 57.6° corresponding to 220, 311, 400, 422, 511, and 440 plane reflections, respectively) were observed in the XRD pattern of PF [36]. The diffraction pattern of the PFR also confirms the presence of Fe_3O_4 and polyaniline in it. Disappearance of the diffraction pattern of RGO in PFR could be due to possible interaction of RGO with polyaniline and Fe_3O_4 . In the XRD pattern, the peak at 20.54° corresponds to γ/β -phase of PVDF was observed for the PVDF-PFR composites [37]. The peaks of PVDF in PVDF-PFR composite shifted compare to pure PVDF due to possible interaction of RGO, polyaniline and Fe_3O_4 with the polymer. All the observed peaks of Fe_3O_4 in the PVDF-PFR composites have been matched with the standard XRD pattern (JCPDS no. 01-075-0449).

Figure 5a shows the structural changes of GO, RGO, and PFR composites through the Raman spectral analysis. D peak at $\sim 1350 \text{ cm}^{-1}$ and G peak at $\sim 1590 \text{ cm}^{-1}$ of GO indicate that the lattice distortions

Figure 2. FESEM images of (a) PVDF-PFR porous composites, (b) in higher magnification showing the presence of polyaniline and RGO and the red circles are indicating the presence of Fe_3O_4 [The inset figure is the EDX spectrum of PVDF-PFR composite under FESEM study indicating the presence of C, O, N, F, Cl and Fe atoms in the composite] in the PVDF matrix. (c) TEM image of and PVDF-PFR composite [The inset figure is the SAED image of PF]. (d) The UV-visible spectra of polyaniline (P) without treatment of ammonium hydroxide and PFR composite after washed with dilute acid.

Figure 3. (a) The FESEM image of PFR and (b) its' X-ray mapping for all elements

Figure 4. The X-Ray Diffraction pattern of GO, RGO, PF, PFR, PVDF-PFR composites and pure PVDF

of graphite occur through oxidation which was confirmed by XRD and FTIR analysis. This spectral analysis of RGO shows the G band peak at $\sim 1577\text{ cm}^{-1}$ which indicates the E_{2g} symmetry of carbon atoms and the D band peak for the breathing mode of A_{1g} symmetry at $\sim 1350\text{ cm}^{-1}$. The reduction process of GO changed the structure of GO, which is confirmed from the increase in I_D/I_G (intensity ratio of D and G band) value (0.95 for GO to 1.12 for RGO) [38]. The Fe_3O_4 decorated polyaniline/RGO composites (PFR) shows peak for C–H bending of quinoid ring at 1165 cm^{-1} , C–H bending of benzenoid ring at 1263 cm^{-1} , C–C stretching of quinoid ring at 1396 cm^{-1} , C=C stretching of quinoid ring at 1488 cm^{-1} , C–N⁺ stretching at 1330 cm^{-1} and C=C stretching of benzenoid ring at 1555 cm^{-1} in the spectral analysis. The shifting of peaks in PFR composites, compared to that in pure polyaniline was due to the charge transfer or probable interaction among

polyaniline, Fe_3O_4 and RGO [12, 26]. The Raman spectral analysis (Figure 5a) of PFR composites shows alteration of peak position in D band but blue shifting in G band occurs for RGO (~ 1577 to 1587 cm^{-1}) due to π - π interaction along with charge transfer from RGO to polyaniline.

The FTIR spectral analysis of PF and PFR were depicted in Figure 5b. The spectral analysis of PF shows characteristic peaks at 1580 and 1490 cm^{-1} for the C=C stretching of the quinoid and benzenoid rings, respectively. The peaks at 1301 and 1245 cm^{-1} are respectively assigned to N–H bending and the symmetry component of the C–C (or C–N) stretching modes of the polyaniline salt. The C–H in-plane and out-of-plane bending modes shows the peak at 1153 cm^{-1} . These peaks are shifted from the peak of pure polyaniline which indicates probable interaction between Fe_3O_4 and polyaniline backbone [26, 30]. Spectral analysis of PFR shows a further shifting of the PF peaks in presence of RGO, suggesting the interaction among polyaniline, Fe_3O_4 and RGO. The band of Fe–O stretching is shifted to 598 cm^{-1} due to interaction of Fe_3O_4 with polyaniline and RGO.

The electrical conductivity property of the prepared composites mostly depends on polyaniline and RGO. PF shows a relatively low ($3.6 \times 10^{-1}\text{ S}\cdot\text{cm}^{-1}$) conductivity (σ_{DC}) compared to that of pure polyaniline. The presence of magnetic particle (Fe_3O_4) decreases the conductivity of polyaniline. This decrease in conductivity is mainly due to the semiconducting nature of Fe_3O_4 and partial blockage of the conductive path by Fe_3O_4 particle [39]. Again, the conductivity of PFR composites ($55.20\text{ S}\cdot\text{cm}^{-1}$) increases due to the presence of highly conductive RGO. In the presence of

Figure 5. (a) The Raman spectra of GO, RGO and PFR. (b) The FTIR spectral analysis of PF and PFR composite.

Figure 6. The DC conductivity of the PVDF-PFR composites with various PFR loadings (p) and the inset figure presents the linear variation of $\log(\sigma_{DC})$ with $p^{-1/3}$ for PVDF-PFR composites

RGO, conducting polyaniline forms polyaniline-RGO conductive network throughout the composites. The insulating PVDF polymer becomes conductive after blending with PFR composites. The PVDF-PFR composites showed a DC conductivity of $\approx 5.41 \times 10^{-4} S \cdot cm^{-1}$ with 5 wt% PFR loading. The components (polyaniline and RGO) of PFR composites form a three dimensional conductive networks throughout the PVDF matrix after blending. For the PVDF-PFR composites, the conductivity increases with the increase in PFR loading (Figure 6) and shows a σ_{DC} value of $\approx 1.10 \times 10^{-1} S \cdot cm^{-1}$ at 25 wt% PFR loading. The extent of interconnected conductive network of polyaniline-RGO throughout the PVDF matrix increases with the increase in PFR loading which enhances the electrical conductivity of the composites.

The electrical conductivity of the composites not only depends on the charge transmitted through the physical contact between the conductive fillers but also as a result of tunneling and hopping through the insulating gaps between the conductive fillers. These insulating gaps are created by the thin insulated polymer layer among conductive fillers. The tunneling and hopping of electron occur from one filler to another through this insulating gap, as reported between CNT-CNT in polymer/CNT composites [40]. The properties of the matrix phase and the method of composites formation control the energy barrier of tunneling. The tunneling mechanism for conductivity in the polymer/CB composites was theoretically developed by Ryvkina *et al.* [41]. They developed the Equation (12)

to explain the tunneling mechanism in terms of electrical conductivity:

$$\sigma_{DC} \propto \exp(-Ad) \quad (12)$$

where A and d stand for tunnel parameter and tunnel distance. Moniruzzaman and Winey[42] reported that the average distance between the conducting filler (tunnel distance d) of the composites where the conductive fillers are homogeneously dispersed throughout the insulating matrix polymer varies with the loading of filler (p) as Equation (13):

$$d \propto p^{-1/3} \quad (13)$$

Thus, the relation between logarithmic value of DC conductivity and filler loading is established as Equation (14):

$$\log(\sigma_{DC}) \propto p^{-1/3} \quad (14)$$

The linear variation of $\log(\sigma_{DC})$ with $p^{-1/3}$ for PVDF-PFR composites confirms the existence of tunneling mechanism in our prepared composites, as shown in the inset of Figure 6 [43]. Due to the presence of high energy insulating polymer layer between fillers the transport of electron from one electrode to another gets restricted. However, the tunneling of electrons occurs or electron can cross the energy barrier effectively when voltage is applied between the two electrodes.

Fe_3O_4 decorated RGO and polyaniline based flexible porous PVDF composites show excellent shielding efficiency for various electromagnetic sources due to their multifunctional electrical, magnetic properties and presence of porous structure. The non-magnetic RGO contributes to microwave absorption mostly through its dielectric loss property. It is well known that the conducting polymer, polyaniline enhances the EMI shielding efficiency of materials by absorption phenomena due to the presence of localized charges (polarons and bipolarons) leading to strong divergence and relaxation effect [44] and the higher magnetic losses property of Fe_3O_4 also contributes to the higher SE. The porous structure of the composite creates in-homogeneity (impedance mismatch) within the materials which is the cause of multiple reflections of radiation leads the microwave absorption property. This is typically ignored for single phase materials [45]. Thus, the prepared composites PVDF-PFR exhibits both enhanced dielectric losses and magnetic losses in a wide frequency range in presence

Figure 7. (a) Frequency dependent EMI SE of various loading PVDF-PFR composites. (b) and (c) are the variation of SE_A and SE_R respectively with frequency for different loading of PFR in PVDF-PFR composites.

of polyaniline, RGO, *in-situ* synthesized Fe_3O_4 nanoparticle and porous structure. Figure 7a depicts the variation of the shielding effectiveness with frequency for various PVDF-PFR composites. The SE value increases with the increase of PFR loadings in the composites, similar to that of electrical conductivity and achieves ~ -28.18 dB SE at 25 wt% PFR loading where RGO loading is 5 wt%. The EMI SE of the composite varies from ~ -7.7 to ~ -28.18 dB as the PFR loading increases from 5–25 wt%. The conductive network of polyaniline-RGO increases in the PVDF polymer matrix with the increase of PFR loading. The higher numbers of conductive network can easily disperse the EM waves throughout the composites. The loading of ferromagnetic Fe_3O_4 particles also increases with the increase of PFR loading in the composites which enhances the magnetic loss property in the composites. Thus, EMI SE increases with the increase of PFR loading.

The shielding efficiency of the composites by its absorption and reflection were respectively depicted in Figure 7b and 7c. It is noteworthy, the SE_A value was predominantly higher than the SE_R value and both the SE_A and SE_R values were increase with the increase of PFR loading. The shielding by absorption increase from ~ -6.06 to ~ -22.60 dB when the PFR loading increases from 5–25 wt%. The higher microwave absorption ability of the composites is mainly governed by the porous structure, RGO and polyaniline.

The incident electromagnetic microwaves internally multiple times reflect and scatter with in the cell wall due to the impedance mismatch between cell wall and air; thereby it is difficult for the microwave to

escape from the sample before conductive dissipation during EMI shielding. The conductive 3D network of RGO and polyaniline at the cell wall and throughout the composite could convert the entered electromagnetic energy into heat by both conductive dissipation and multiple reflections and scattering as much as possible as shown in Figure 8 [20]. The conductive dissipation of the electromagnetic energy enhanced with the increase of conductive network thus with the increase of polyaniline and RGO loading along with PFR loading in PVDF matrix the SE_A value increases. According to free electron theory ($\epsilon'' = \sigma/\omega\epsilon_0$) highly conductive RGO with its high surface area may degrade its EMI absorption ability [46, 9].

Moreover, irradiation of an EM wave on the highly conductive surface of RGO results the occurrence of a significant skin effect. By the incorporation of RGO and Fe_3O_4 and polyaniline in the PVDF matrix, the skin effect due to the high conductivity was considerably reduced. However, the electron polarization process owing to its carrier mobility is strongly related with the very high dielectric loss of graphene and polyaniline [47]. Thus, it can be assumed that the coating of PVDF over polyaniline, RGO and Fe_3O_4 helps in the impedance match characteristics to befit the absorption and causing the decrease of surface reflection [12]. The absorption property of the composites is also benefited by the nanosize Fe_3O_4 . The nanosize Fe_3O_4 has dipole polarization property which contributes to dielectric loss of the materials [48]. The nanosize Fe_3O_4 also affects the electromagnetic absorption property by their electronic polarization and ion polarization during the electron transfer

Figure 8. Schematic representation for the effect of porous structure and Fe_3O_4 decorated polyaniline-RGO conductive network about attenuating the incident electromagnetic microwaves by reflecting and scattering within the composites

process between iron ions. Additionally, the absorption property is enhanced by an additional dielectric loss generated from polarized center of interface defects for the quaternary composites [49].

The complex permittivity (ϵ^*) and permeability were evaluated from the Nicholson-Ross-Weir [34] method using the S parameters (S_{11} and S_{12}) to better understand the EMI SE characteristic of the composites. The Equations (15) and (16), respectively explain the complex permittivity and permeability in terms

of real (ϵ' and μ' respectively) and imaginary (ϵ'' and μ'' respectively) parts:

$$\epsilon^* = \epsilon' - i\epsilon'' \quad (15)$$

$$\mu^* = \mu' - i\mu'' \quad (16)$$

The real part of the permittivity is mainly related with the created polarization characteristic in the materials and the imaginary part of the permittivity is associated with the electric loss or dissipation of energy in the

Figure 9. (a) Real permittivity, (b) imaginary permittivity and (c) AC conductivity versus frequency for the different PFR loading in the PVDF-PFR composites

materials. The electronic, orientational (created for bound charges) ionic, and space charge polarization (for the heterogeneity in the system) of the composite are strongly affected the permittivity of the materials. According to Maxwell–Wagner polarization [50] theory in a heterogeneous system, interfacial polarization leads to the accumulation of virtual charges at the interface of different media having different conductivity and permittivity. Figure 9a and 9b respectively depicts the variation of real and imaginary permittivity with frequency for the various PVDF-PFR composites. In this work, Fe_3O_4 decorated conductive polymer polyaniline and RGO, having different conductivities and permittivity, were incorporated in the PVDF matrix and thus shows interfacial polarization in the applied frequency range. Due to the presence of insulated thin polymer layer and insulating Fe_3O_4 in the polyaniline-RGO conductive network, space charge accumulates at the interface of PVDF-PFR composites that facilitates in the higher microwave absorption property.

On the other hand, Guan *et al.* [51] reported, a theoretical simulations about electromagnetic loss properties due to the coupling between Fe_3O_4 nanoparticles and graphene for a hybrid assembly system. Two types of charged species are present for conjugated polymers (polyaniline). The first charged species consists of polarons (radical cations) and bipolarons (bi-radical cations) can freely move along the chain. The dipoles or bound charges (second charged species), account for strong polarization in the system, delimited the charge mobility. Thus, it is expected that the orientation or dipolar polarization of polyaniline has

contributed to the dielectric permittivity. Fe_3O_4 decorated polyaniline and RGO contribute the conducting regions in the system, leading to an increase in space charge polarization (dipolar and interfacial). The space charge polarizations are very much dependent on the frequency of the applied field. We assume that with the increase of frequency, the space charge polarization decreases which in turns decreases the ϵ' and ϵ'' values [52].

Figure 9c shows the variation of AC conductivity with frequency for PVDF-PFR composites with various PFR loadings. The AC conductivity (σ_{AC}) of the composites was calculated from the imaginary part of permittivity (ϵ''), frequency (f) and permittivity of free space (ϵ_0), as given below (Equation (17)) [53]:

$$\sigma_{AC} [\text{S} \cdot \text{cm}^{-1}] = 2\pi\epsilon_0\epsilon'' \quad (17)$$

The σ_{AC} value of the PVDF-PFR composites also increases with the increase of PFR loading in the PVDF matrix, similar to that of the σ_{DC} value. The extent of polyaniline-RGO conductive network throughout the polymer matrix increases with increasing PFR loading that causes higher σ_{AC} value for PVDF-PFR25, compared to the PVDF-PFR15. At particular PFR loading, the σ_{AC} of the composites shows remarkably higher value compared to the σ_{DC} and remains almost constant in the X band frequency region. This relation between σ_{DC} and σ_{AC} indicates the existence of tunneling and hopping phenomenon in the composites at this frequency range.

Figure 10 shows the variation in complex permeability (real and imaginary) with frequency for the composites. The energy storage capacity of the materials

Figure 10. (a) Imaginary permeability and (b) real permeability versus frequency for the different PFR loading in the PVDF-PFR composites

strongly related to the real parts of complex permeability, whereas, imaginary parts related to the loss of electromagnetic wave in the materials [54].

As can be seen, the energy storage capacity (μ') and magnetic loss property (μ'') were decreased with the increase in frequency (Figure 10). The μ'' value increases with increasing the loading of PFR in the composites, as it effectively increases the specific weight of the magnetic Fe_3O_4 in the composites. The positive value of the imaginary permeability indicates that the absorption of incident electromagnetic energy occurs by the absorber and the negative value is the resultant of radiated out magnetic energy. According to the Maxwell equations the magnetic energy is radiated due to the motion charge which produces an alternating electric field in electromagnetic field and induces a magnetic field [55, 56].

5. Conclusions

In this work flexible porous conductive PVDF-PFR composites were prepared through dispersion of conductive PFR in the PVDF matrix following conventional facile solution blending method followed by leaching out of mixed NaCl from the composite. In PFR, polyaniline and RGO were well decorated by *in-situ* synthesized Fe_3O_4 nanoparticles during the polymerization of aniline using anhydrous FeCl_3 as an oxidant as well as Fe source to synthesize Fe_3O_4 in PFR composite. The PFR composite was blended with PVDF polymer to improve the flexibility and shaping of this composite material through common fabrication techniques. The high dielectric strength of PVDF enhances the dielectric property of the PVDF-PFR composite. A considerably high value of EMI SE (≈ 28.18 dB) and DC conductivity ($\sigma_{\text{DC}} \approx 1.10 \times 10^{-1} \text{ S} \cdot \text{cm}^{-1}$) were achieved in the PVDF-PFR composites with 25.0 wt% PFR loading (RGO loading is 5 wt%). The porous structure and the conductive network developed by polyaniline and RGO at the cell wall and throughout the PVDF-PFR composites are responsible for such a high conductivity and EMI SE value. The porous structure attenuates microwave by internal multiple reflection with in the cell wall and the conductive network at the cell wall convert the entered electromagnetic energy into heat by conductive dissipation and plays an effective role in absorption of microwave. The presence of air in the composite creates impedance mismatch which cause of more internal multiple reflection. The presence of nanosize Fe_3O_4 also plays as an important role to in-

crease the permittivity and permeability of the composites which facilitated the microwave absorption ability of the composites. Fe_3O_4 decorated conductive polyaniline and RGO, having different conductivities and permittivity, shows interfacial polarization in the PVDF matrix in the applied frequency range. The fabrication of a relatively new hybrid porous composite (PVDF-PFR) unlocks the prospect for the use of conducting composite (powder, non-moldable/brittle) as a flexible and shapeable high efficient EMI shielding materials in areas such as aerospace and next-generation flexible and portable electronics.

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