Ag induced electromagnetic interference shielding of Ag-graphite/PVDF flexible nanocomposites thinfilms

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Ag induced electromagnetic interference shielding of Ag-graphite/PVDF flexible nanocomposites thinfilms

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We report Ag nanoparticle induced Electromagnetic Interference (EMI) shielding in a flexible composite films of Ag nanoparticles incorporated graphite/poly-vinylidene difluoride (PVDF). PVDF nanocomposite thin-films were synthesized by intercalating Ag in Graphite (GIC) followed by dispersing GIC in PVDF. The X-ray diffraction analysis and the high-resolution transmission electron microscope clearly dictate the microstructure of silver nanoparticles in graphite intercalated composite of PVDF matrix. The conductivity values of nanocomposites are increased upto 2.5 times when compared to neat PVDF having a value of 2.70 S/cm at 1 MHz. The presence of Ag broadly enhanced the dielectric constant and lowers the dielectric loss of PVDF matrix proportional to Ag content. The EMI shielding effectiveness of the composites is 29.1 dB at 12.4 GHz for the sample having 5 wt. % Ag and 10 wt. % graphite in PVDF. *© 2015 AIP Publishing LLC*.
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A modern kind of pollution that affects the efficiency and lifetime of commercial and military electronic devices is Electromagnetic Interference (EMI). The electromagnetic radiations emitted from the electrical circuits make severe interrupts to the functioning of the devices and also affect the human organs. In civil and military functions, the shielding materials play significant role in order to control these harmful electromagnetic radiations.[1,2] So, tremendous efforts have been put by the researchers for making different shielding materials to control the EMI pollution. Efforts have been made over past two decades to reduce EMI using a number of strategies and variety of materials such as metals, carbon composite materials, conducting polymers, and dielectric/magnetic materials.[3–5] Among several approaches, applying a conductive polymer layer on devices evidenced to be the most prominent and has been widely studied for EMI shielding purpose because of its light weight, good processability, and adhesion nature to metal surfaces.[6]

Carbon based materials have been widely involved in shaping of polymer based materials for EMI shielding applications due to their properties related to microstructures. Graphite, a beneficial low cost conductor has been well examined for its utilization in polymer composites. Due to its poor dispersion in polymer, the graphite has been functionalized with acids and reinforced with the polymer for better results.[7] A light weight carbon material graphite holds good electrical conductivity, better mechanical properties, high aspect ratio, and large surface area which proves to be a good and attractive filler for many potential applications in electronic devices, light emitting devices, super capacitors, corrosion resistance, and electromagnetic interference shielding effectiveness (SE).[8]

Generally, metal nanoparticles have been engrafted in polymer composites for its potential electrical conductivity. Silver nanoparticle is considered to be a promising material for its novel applications in the field of printing, imaging, optical sensors, catalysis, bioengineering, photonics, and electronics. Silver Nanoparticles (Ag NPs) that exhibit small size, controlled shape, and large volume ratio and possess good thermal and electrical conductivity have been widely used in nanocomposites for their broad applications in integrated circuits and EMI SE.[9,10]

A transparent PVDF polymer due to its strong piezoelectric behaviour, compact size, light weight, excellent flexibility, and good dielectric properties has attracted good attention of the researchers used in modern electronics and electric power systems, especially in EMI SE applications.[11] Wang *et al.*[1] report the reflection loss values as −64.4 dB at 10.59 GHz for graphite reinforced PVDF. The incorporation of Ag NPs into graphite filled PVDF for total EMI SE was not reported so far, and this paper paves the enhancement of EMI SE values by these composites. Further, we anticipate that incorporation of Ag into the polymer composite will enhance the conductivity that relates to a number of mobile charge carriers (electrons or holes) within shielding material that primarily interacts with Electromagnetic (EM) radiations.[12] Moreover, the free electrons present in material are credible for reflection mechanism of EMI shielding which can be enhanced by adding a noble metals such as Ag.

About 1 g of graphite was acid functionalized by 3:1 conc.H_2SO_4 and conc.HNO_3 24 h, and it was filtered and washed until pH reaches 6. The graphite-COOH was mixed with 5.0×10^{-3} mol dm^{-3} $AgNO_3$ and stirred well at Room Temperature (RT). The reducing agent $NaBH_4$ was slowly added to the above suspension, and stirring was continued vigorously for 5 h and then it was washed several times with

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Double Distilled (DD) water and centrifuged. The wet powder was dried for 10 h at 60 °C.

Polymer nanocomposites were prepared from a suspension containing Ag-graphite nanohybrid with PVDF in Dimethylformamide (DMF) solution. The PVDF was added to DMF and stirred well under sonication for 2 h. Then Ag-graphite nanohybrid was added to PVDF solution and stirred at 50 °C for 2 h to obtain a homogeneous solution and the solution was casting to films at 65 °C for 6 h.

X-Ray diffraction (XRD) patterns were taken on Cu kα radiation XRD-RIGAKU MINIFLEX II-C XRD system. Raman spectra were recorded on a confocal micro-Raman microscope (Renishaw inVia Reflex) with Ar^{+} ion laser source of 0.6 mW power and 514.5 nm. High resolution image and the selected-area electron diffraction (SAED) pattern were observed with LA D6 source in TECNAI T-30 High-resolution transmission electron microscope (HRTEM). The dielectric constant, conductivity, and dielectric loss were measured using BDS novocontrol-concept 80 instrument. A N5230A Vector Network Analyzer with an S-parameter set was used to measure frequency dependence EMI SE.

Fig. 1 shows the XRD pattern of pristine PVDF, graphite/PVDF, and Ag/graphite/PVDF nanocomposites. The PVDF and the stacking graphite show diffraction peaks at $2\theta = 20.26°$ (JCPDS File No: 38–1638) and 26.49° (JCPDS File No: 75-2078) which correspond to (110) and (002) planes, respectively. The observed peaks at 38.12°, 44.30°, 64.41°, and 77.41° match well with a cubic phase of Ag (JCPDS File No: 89-3722) which correspond to (111), (200), (220), and (311) peaks of crystallite Ag Nanoparticles present in graphite/PVDF composites.[13,14]

The Raman spectra of PVDF and graphite/PVDF are shown in Fig. 2. The characteristic bands appeared at 837 cm^{-1} and 811 cm^{-1} are due to PVDF matrix. The peaks appeared at 1582 cm^{-1} and 1315 cm^{-1} correspond to graphite layers dispersed in PVDF matrix.[10] The intensities of the band are shifted after the incorporation of Ag NPs in graphite. The D band occurs at 1308 cm^{-1} from 1313 cm^{-1} and G band occurs at 1578 cm^{-1} from 1582 cm^{-1}. The D and G bands get shifted towards lower wave numbers which is attributed to chemical interaction and charge transfer between Ag NPs and graphite.[15]

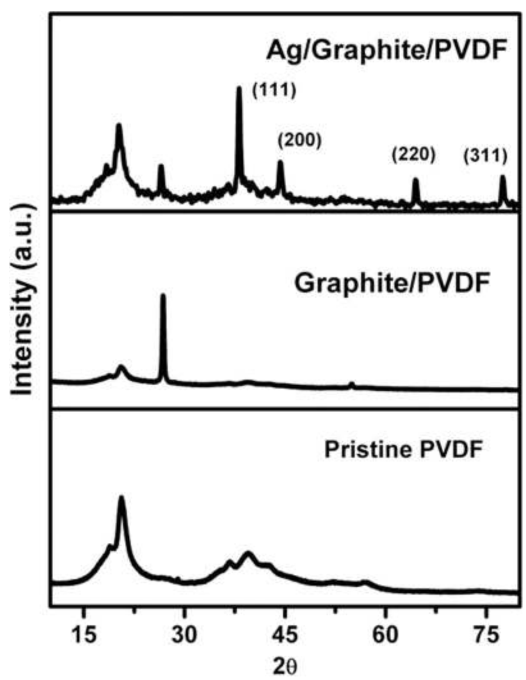

FIG. 1. XRD patterns of pristine PVDF, graphite/PVDF, and Ag/graphite/PVDF.

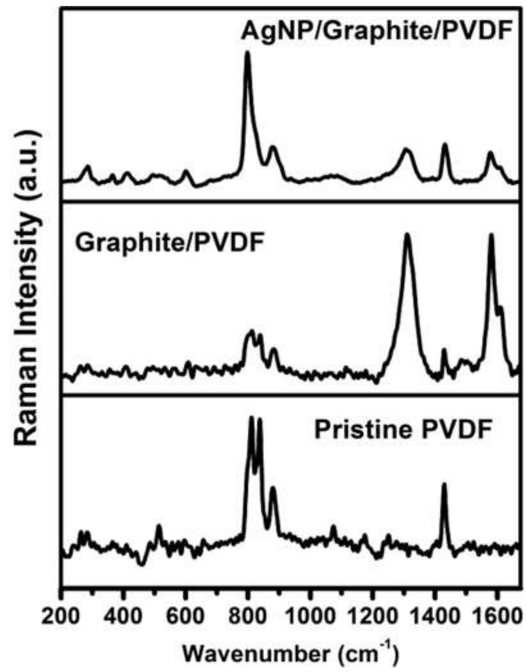

FIG. 2. Raman spectrum of pristine PVDF, graphite/PVDF, and Ag/graphite/PVDF.

Figs. 3(a)–3(c) show the SEM images of pristine PVDF, graphite reinforced PVDF, and Ag nanoparticles incorporated graphite/PVDF, respectively. Fig. 3(a) shows the pristine PVDF image, Fig. 3(b) clearly demonstrates the graphite is finely stacked with PVDF, and Fig. 3(c) evinces incorporation of the Ag nanoparticles on graphite fillers. The good dispersion of Ag nanoparticles and graphite in PVDF matrix is well credent for enhancing effective shielding values. Fig. 4(a) shows the high resolution transmission electron microscope image of Ag nanoparticles incorporated graphite reinforced PVDF nanocomposite. From the HRTEM image, the Ag NPs were observed in the edge of thin sheet like 2D graphite layers which are discerned by dark spots with diameter of 10–20 nm.[16] The SAED pattern (Fig. 4(b)) proves that Ag nanoparticles incorporated graphite reinforced PVDF nanocomposite are crystalline in nature and ordered diffraction spots correspond to (111) and (200) lattice planes of Ag crystals.[17]

Figs. 5(a) and 5(b) show the dielectric constant, dielectric loss tangent, and electrical conductivity of Ag anchored graphite/ PVDF composites. The dielectric constant is found to be decreased as frequency increases at RT. At low frequency, the dispersion in the dielectric plot is due to the Maxwell–Wagner–Sillars interfacial polarization,[18,19] The dielectric constant for PVDF at 1 MHz is 5.5. The values of dielectric constants are increased with filler graphite loading to PVDF, and the value is found to 6.2 at 1 MHz. The graphite reinforced polymer has slightly high value of dielectric constant compared to neat PVDF. The reason is attributed to

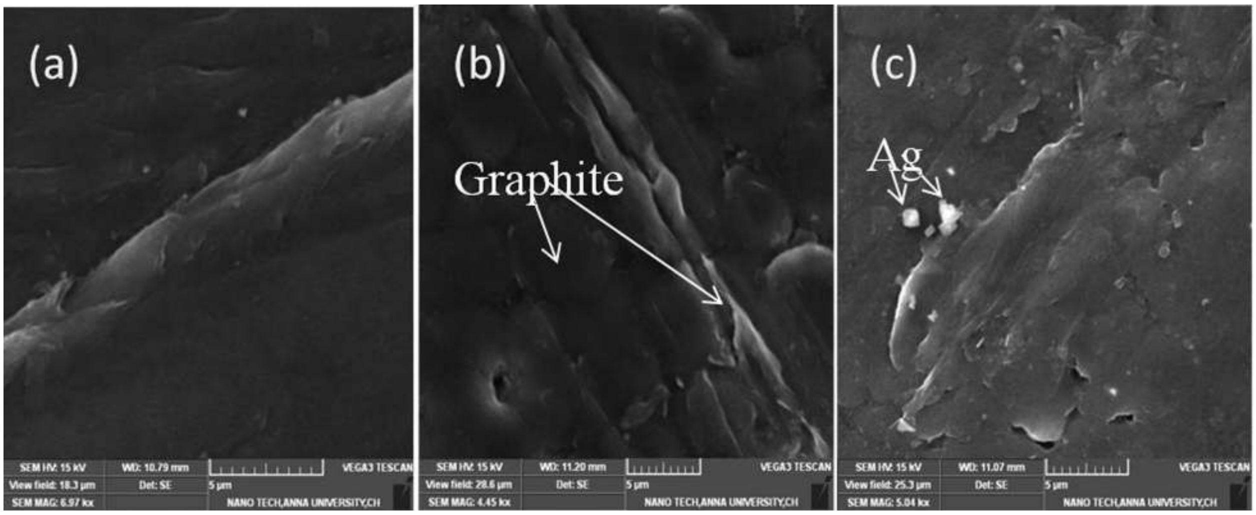

FIG. 3. SEM micrographs of (a) pristine PVDF, (b) graphite/PVDF, and (c) Ag/graphite/PVDF.

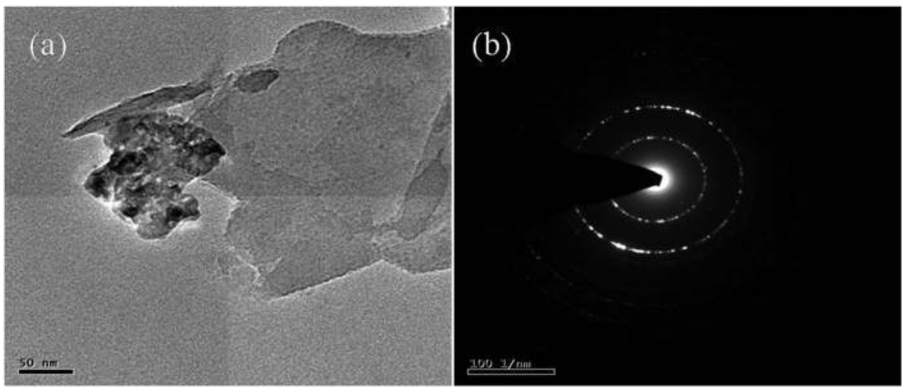

FIG. 4. HRTEM images of (a) Ag/graphite/PVDF and (b) SAED pattern.

the dispersion and network of graphite filler within the polymer. As silver nanoparticles loading increases, the dielectric constant value gets enhanced to 6.9 and 10.01 for 1 and 5 wt. % Ag in graphite, respectively. The availability of free electrons can act as the interface between graphite and PVDF in the polymer composites and enhances the value of dielectric constant.[20] Maxwell–Wagner–Sillars (MWS) fit is given in Figure S1 of supplementary material.[21]

The conductivity value of neat PVDF is 1.08 S/cm at 1 MHz. The conductivity value shows the enhancement when graphite filler is loaded and the value is increased to 1.4 S/cm. The reason is attributed to movement of electrons in graphite layers, and electron transitions between the layers increase the conductivity of graphite/PVDF composites. For 1 and 5 wt. % of Ag NPs in graphite, the conductivity value is increased to 1.65 and 2.70 S/cm at 1 MHz, respectively. The homogeneous dispersion of Ag-graphite in PVDF composites enhances the conductivity. The incorporation of Ag nanoparticles accounts for the formation of charge transfer complex between graphite and PVDF which increases the conductivity.[22,23] The charge transfer complexes are increased by AgNPs loading and the conductivity is enhanced by electrons moves across the barrier and insulator chains in polymer composites.

The dielectric loss of pristine PVDF is 0.07 at 1 MHz. For the graphite/PVDF composite, it is found to be 0.06 which is almost equal to the conductive filler-polymer composites at 1 MHz. The interfacial polarization is the reason for enhancing dielectric loss and the acid functionalization leaves C-O and C = O groups on the surface of graphite layers which may be responsible for the increase of dielectric loss values.[1] The incorporation of AgNPs on graphite layers reaches dielectric loss to 0.05 and increasing AgNPs content on the graphite leads to the minimum dielectric loss of 0.029 at 1 MHz. The conduction loss, migration of molecular dipoles, and interfacial polarization phenomena are the three noteworthy causes for the obtained dielectric loss values.[24,25]

The EMI SE of polymer nanocomposites can be calculated by the equation

$$Effective\ EMI\ SE = SE_R + SE_A, \tag{1}$$

$$\text{where } SE_R\,(dB) = -10\log\left(1 - S11^2\right) \text{ and } SE_A(dB) = -10\log\left(S21^2|1 - S11^2\right). \tag{2}$$

Here, SE_R is reflection shielding effectiveness, SE_A is absorption shielding effectiveness, and S11 and S21 are magnitude of scattering parameters.[26] Fig. 6 demonstrates the total EMI SE of PVDF, graphite/PVDF, and Ag incorporated graphite reinforced PVDF polymer. The EMI shielding effectiveness of pristine PVDF is found to be 1.1 dB at 12 GHz due to its insulating behaviour. The effective shielding value is enhanced by increasing the conducting nature of polymer composite by incorporating the graphite filler. The interweaving of graphite and PVDF can result in blocking

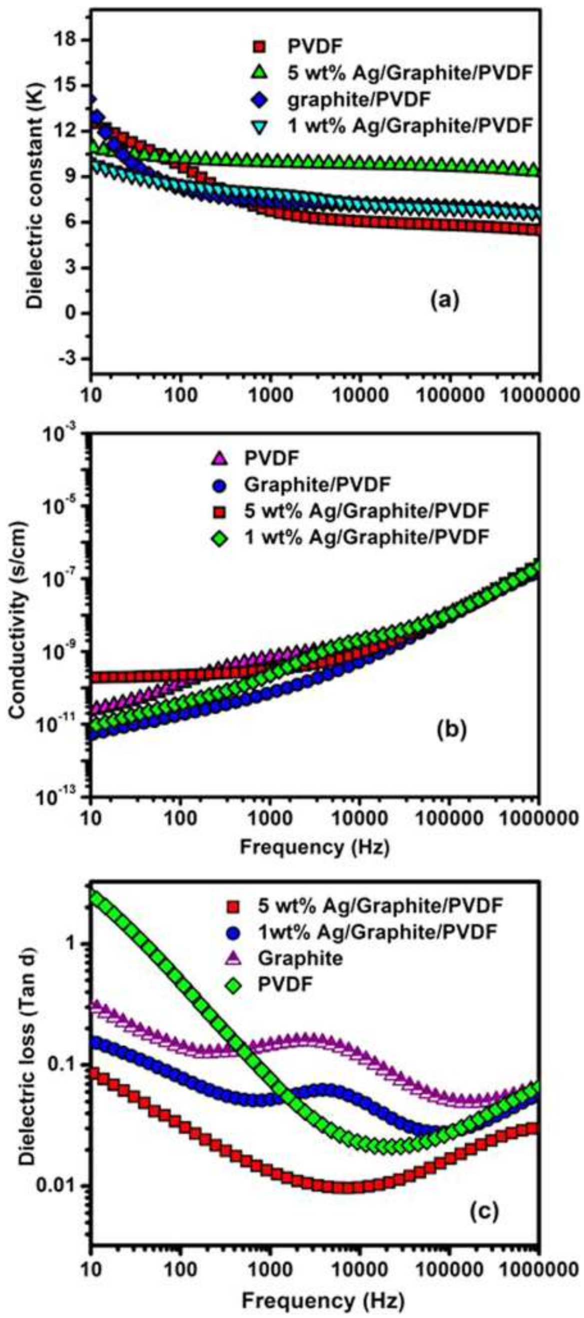

FIG. 5. Dielectric constant (a), conductivity (b), and dielectric loss (c) for pristine PVDF, graphite/PVDF, and Ag/graphite/PVDF.

the EM radiation by the better interaction between the polymer composites and EM radiation. The total EMI on 10 wt. % of graphite is 2.25 dB and 1 wt. % of AgNPs incorporation in graphite is found to be 4.9 dB. The loading of AgNPs increased to 5 wt. % resulted in enhanced EMI SE with a value of 29.1 dB at 12.4 GHz. The conflated effect of filler and AgNPs in PVDF composites is responsible for shielding effectiveness. The good dispersion of AgNPs and the interfacial polarization phenomena in the conductive filler nanocomposites, and the high aspect ratio which in turn credit worthy for enhancing the EMI SE of the composites. Another noteworthy factor for EMI SE application is return loss or reflection loss, which ascertains the transmission of electromagnetic waves into the shielding material. The shielding values decrease with increase in reflection loss

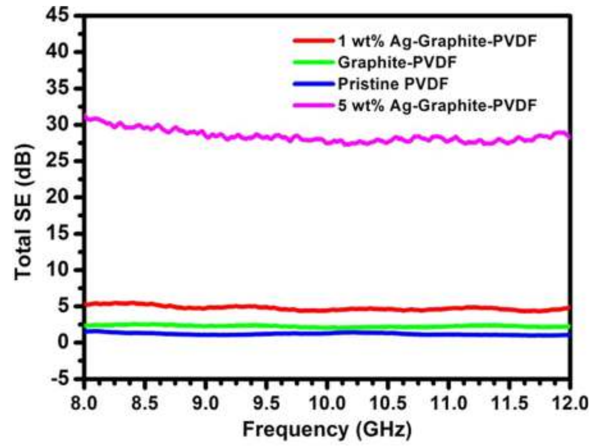

FIG. 6. EMI shielding effectiveness of pristine PVDF, graphite/PVDF, and Ag/graphite/PVDF.

values. The impedance mismatch between free space and conducting filler is responsible for increasing reflection loss of the materials and thus usually, the shielding effectiveness values decrease.[25] In our composites, the reflection loss values decrease due to increase of impedance match between AgNPs and GIC of the composite material and it enhances the total EMI SE values. Zhang *et al.*[27] report that the reflection loss value of rGO/PVDF composite is −25.6 dB at 10.8 GHz and He and Tjong[28] reveal only the surface resistivity of the Ag–RGO/PVDF films which is applicable for EMI shielding and we demonstrate the total EMI SE of Ag nanoparticles incorporated graphite reinforced PVDF composites in x-band region.

Table I presents the return loss values and total shielding values of composites with different weight percentages with respect to PVDF matrix. It obviously proves that the decrease in return loss values enhances the total shielding effectiveness of higher loading of AgNPs in the graphite/PVDF composites. The required values of shielding effectiveness to accomplish the demands in commercial applications are 20 dB,[29] and the prepared composites have achieved 29.1 dB at 12.4 GHz which clearly suggests that it is an efficient material for shielding the electronic devices from interfering electromagnetic radiations.

This work depicts the incorporation of AgNPs and Graphite into poly-vinylidene difluoride matrix. The existence of AgNPs in polymer graphite composite is demonstrated clearly by XRD and HRTEM analysis. The conductivity values of nanocomposites are increased upto 2.5 times when compared with neat PVDF having a value of 2.70 S/cm at 1 MHz. The presence of Ag broadly enhanced the dielectric constant and lowers the dielectric loss of

TABLE I. Return loss and total shielding effectiveness values of the PVDF nanocomposites.

Sample designations (wt. %)	Return loss (dB)	Total SE (dB) at 12 GHz
Pristine PVDF	32	1.11
10 wt. % graphite/PVDF	11.8	2.25
1 wt. % of AgNP-10 wt. % graphite/PVDF	7.75	4.9
5 wt. % of AgNP-10 wt. % graphite/PVDF	2.02	29.1

PVDF matrix proportional to Ag content. The highest EMI shielding effectiveness of the composites is 29.1 dB at 12.4 GHz for the sample having 5 wt. % Ag and 10 wt. % graphite in PVDF. The enhanced EMI shielding values of Ag-graphite/PVDF in x-band region describe that the composite material is applicable for high-tech fields.

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