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Electromagnetic interference (EMI) shielding performance of lightweight metal decorated carbon nanostructures dispersed polyvinylidene fluoride flexible films

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Abstract

The electromagnetic interference shielding of metals decorated MWCNT/rGO in polyvinylidene fluoride (PVDF) flexible films have been studied and reported. X-ray diffraction patterns show the presence of metallic nanoparticles bound with carbon reinforcement of the composites. The morphological studies confirm the homogeneous decoration of metallic nanoparticles in MWCNT and reduced graphene oxide (rGO) nanohybrid fillers of the composites. The enhanced value of electrical conductivity of the prepared composite films to 4.52 x 10^{-6} S/cm at 1MHz attributes to the facilitation of space charge distribution by the conducting networks on the incorporation of metallic nanoparticles. The effective EMI shielding of the polymer nanocomposites, 28.5 dB at 12 GHz with the incorporation of metallic nanoparticles in MWCNT-rGO/PVDF composites, clearly ascertains the formation of interconnected networks that reflect as well as absorb the incident electromagnetic radiations.

Keywords: PVDF, metallic nanoparticles, polymer nanocomposites, MWCNT, reduced graphene oxide (rGO), electromagnetic interference shielding.

Introduction

Recent researches on controlling electromagnetic radiations that interfere with electronic and communication equipments, have gained importance. Electromagnetic interference (EMI) is a radiation pollution emitted from external sources that affects the functionality, life-time and the efficiency of the electronic gadgets. With increase in the number of electronic devices in automation, civil, military and communication systems, the harmful effects of electronics ambience also increase. To control EMI pollution, electromagnetic compatibility (EMC) has

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standardized two regulations for the devices. One is the design of electronic circuits to overcome EM pollutions and the other one is the fabrication of efficient electromagnetic interference shielding materials to avoid the interference from dangerous EM radiations. [1-4] Most of the communication systems use microwave frequency spectrum and therefore, shielding of unwanted microwave radiation is necessary to safeguard the electronic, civil and military equipments.[5-7] Development of new or improved promising shielding materials plays a crucial role in EMI shielding.

In general, EMI shielding is achieved by reflection or absorption (or both) of the electromagnetic radiations. The mobile charge carriers in metals, which interacts with electromagnetic radiations, lead to electrically conducting phenomena that attributes to the reflection mechanism of shielding. The absorption mechanism requires the magnetic or electric dipoles in the shielding materials that interact the electromagnetic fields in the radiation. Ferrites based nanomaterials and $BaTiO_3$ provides magnetic dipoles and electric dipoles respectively which enable the absorption mechanism in the shielding materials. Besides reflection and absorption, multiple internal reflections are also important. The multiple reflections may be provided by porous and foam materials with large surface area or interface area in the composite materials. Depending on the nature of the application, it is possible to develop materials with dominant nature of shielding. In the case of prevention of external radiation pollution, it is better to use material with reflection behaviour, while to avoid internal radiation pollution (generated within the equipment), it is better to use absorption property.

Carbon based nanomaterials such as multiwalled carbon nanotubes (MWCNT) and reduced graphene oxide (rGO) play a significant role in shielding the incoming electromagnetic radiations due to an enhanced electrical conductivity, improved mechanical properties, high surface area, light weight, high aspect ratio, flexibility and skin depth.[8,9] Also, the different architects of thinnest carbon nanomaterials such as carbon nanotubes, carbon nanocoils, carbon nanoribbons, carbon nanofibers and carbon nanosheets exhibits higher carrier mobilities to facilitate in enhancing the high loss tangent and effective EMI shielding in the composites. The reason attributes the thermally activated carrier hopping with defects in the carbon structures and the substitutions such as epoxy, carboxyl and hydroxyl groups.[10-12]

In order to make the composite material with light weight and flexible shielding nature, it is essential to select a suitable polymeric material as a base matrix to obtain the nanomaterial loaded polymer-nanocomposites. In this method, the interfacial interactions occurred between the MWCNTs and the polymer can be increased by covalent functionalization of

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MWCNTs. The strong van der Waal's forces that account for the aggregation of MWCNTs in polymer, create challenges in preparing the efficient polymer nanocomposites. To avoid this problem, organic functionalized (-COOH) MWCNTs can be prepared to increase the degree of dispersion of nanotubes in the polymer. The enhancement in the intermolecular interactions in the polymer matrix is well credent for preparing high performance polymer nanocomposites. Reduced graphene oxide (rGO), a 2D single layered nanostructures with sp^2 hybridised carbon atoms in honeycomb crystal lattice, possesses an extremely high mobile charge carriers (mobility values close to 10^5 $cm^2V^{-1}s^{-1}$), electron wave propagation and broad absorption bandwidth. These properties make it attractive for designing devices and fabrication techniques.[10,11] The second reinforcing filler, rGO coupled with MWCNTs, creates the synergetic effect in the composite which greatly enhances the conductivity and EMI shielding performance of the material. Metal nanoparticles with smaller in size and larger surface area, high charge carrier density, high electrical conductivity and oxidation stability have been utilized as a good candidate in the field of optical sensors, bioengineering electronic devices and EMI shielding.[12,13]

A thermoplastic polymer, polyvinylidene fluoride (PVDF) and its copolymer with good flexibility, light weight, compact size and ease of processing together with excellent piezoelectric behaviour has created a great attention among the researchers for utilizing in modern electronic appliances.[14,15] The high dielectric behaviour, high volume resistivity and low shrinkage rates make PVDF a potential material for preparing conducting polymer nanocomposites. Anil kumar et al.[16] reported the observed EMI shielding for heat treated polyaromatic-hydrocarbon (PAC) based carbon metallic composites 58 dB at 2 mm thickness by electroless techniques. Al-Ghamdi reports[17] the EMI shielding for PVC/graphite-Cu (20 wt %) composites is 22-70 dB in 1-20 GHz.

In the present investigation, a multi-phase composites with low percentage of metallic nanoparticles decorated MWCNT/rGO reinforcing fillers in PVDF have been prepared by a simple solvent cast method and characterized for structural and physical properties. It was observed that the lower weight percentage incorporation of metal nanoparticles in highly conducting MWCNTs and rGO binary reinforcing fillers in the composites significantly enhanced the electrical conductivity which attributes to attenuate the incoming electromagnetic radiations.

Experiment

The materials that have been utilized for the preparation of composites are as follows: Polyvinylidene fluoride (PVDF) (99%, Sigma-Aldrich), multi walled carbon nanotubes(98%,

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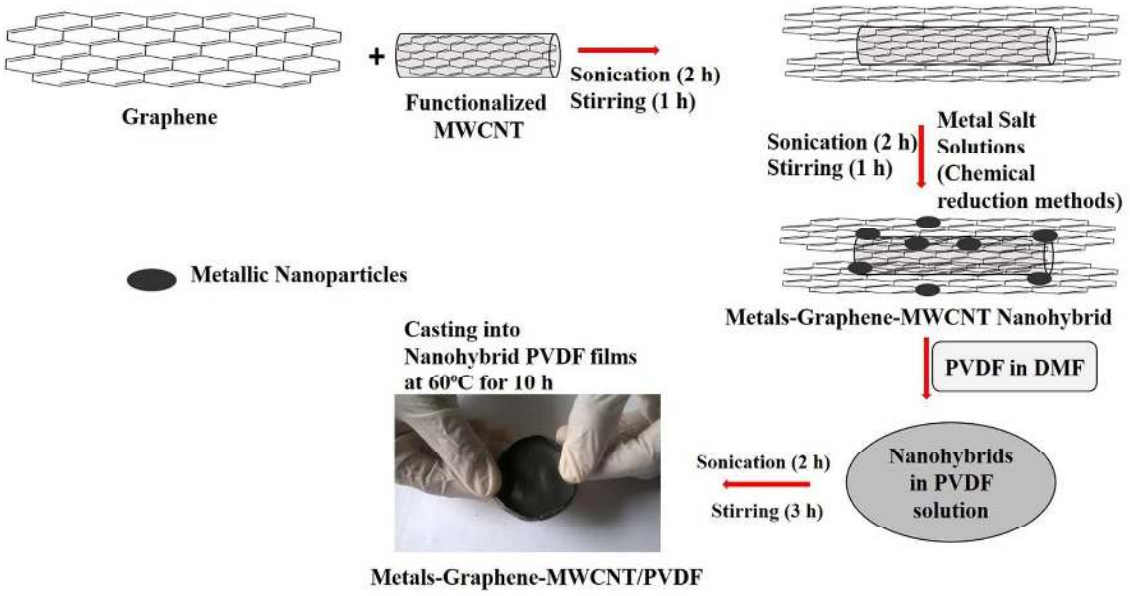
Sigma-Aldrich), silver nitrate, gold chloride and copper sulphate (99%,Sigma-Aldrich), graphite fine powder, sulphuric acid, hydrogen peroxide and $KMnO_4$. About 1g of MWCNT (MWCNT−TMC 100−20) was treated with 3:1 conc. H_2SO_4 and conc. HNO_3 for 24 h for acid functionalization by oxidation.[18] Reduced graphene oxide (rGO) was synthesized using modified Hummers method.[19] A metallic nanoparticles was prepared by chemical reduction method.[20] To 1.0 x 10^{-3} mol dm^{-3} of corresponding metal solution ($AgNO_3$, $HAuCl_4$ and $CuSO_4.5H_2O$), 0.01g of MWCNT and 0.01g of rGO were added to obtain the corresponding metal nanoparticles of MWCNT-rGO nanohybrid composites.

Preparation of polymer nanocomposites

Metals-carbon nano-hybrid materials were dispersed well in dimethyl formamide (DMF) through sonication for 3 h. The dispersed nanohybrids were mixed well in 1g PVDF in DMF solution and stirred well for 6 h at 50°C. The nanocomposites were prepared with 1% metal nanoparticles in carbon fillers and the same nanohybrids were dispersed in PVDF/DMF solution. The dispersed solution was casting into films for 10 h at 60°C and the thickness of the prepared composites was 0.5 mm. The schematic representation of preparation of polymer nanocomposites is shown in Scheme 1.



Scheme 1. Schematic representation of preparation of polymer composites

Characterization

X-Ray diffraction (XRD) patterns were taken on Cu ka radiation XRD-RIGAKU MINIFLEX II-C XRD system. TEM images and the selected-area electron diffraction (SAED) pattern were observed with LA D6 source in TECNAI T-30 Transmission electron microscope (TEM). XPS analyses were carried out in a Thermofisher Spectrometer with Al Kα surface

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analyzer. 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 dependent EMI shielding efficiency (SE). The thicknesses of the prepared samples are 0.5 mm for the measurements of EMI shielding.

Results and discussions

XRD

Fig 1 describes the XRD patterns for pristine PVDF, MWCNT/rGO reinforced PVDF and metallic nanoparticles incorporated MWCNT/rGO reinforced PVDF. The presence of β phase of PVDF is confirmed by the presence of peak corresponding to (110) plane at 2θ=20.18° (JCPDS File:38-1638).[21] The reinforcement of MWCNT/rGO in PVDF polymer results in a peak at 2θ=20.49°. This peak, corresponding to (002) plane, indicates the reinforcements of carbon fillers (MWCNT/rGO) in PVDF polymer.[22] The cubic phases of Ag (JCPDS File No: 89-3722), Au (JCPDS File No: 04-0784) and Cu (JCPDS File:04-0836) at 2θ = 38.1°, 44.18°, 50.56° and 78.79° corresponds to (111), (200), (220) and (311) planes respectively.[23] The presence of all metallic (Ag, Au and Cu) nanoparticles is further confirmed by x-ray photoelectron spectroscopy analysis.

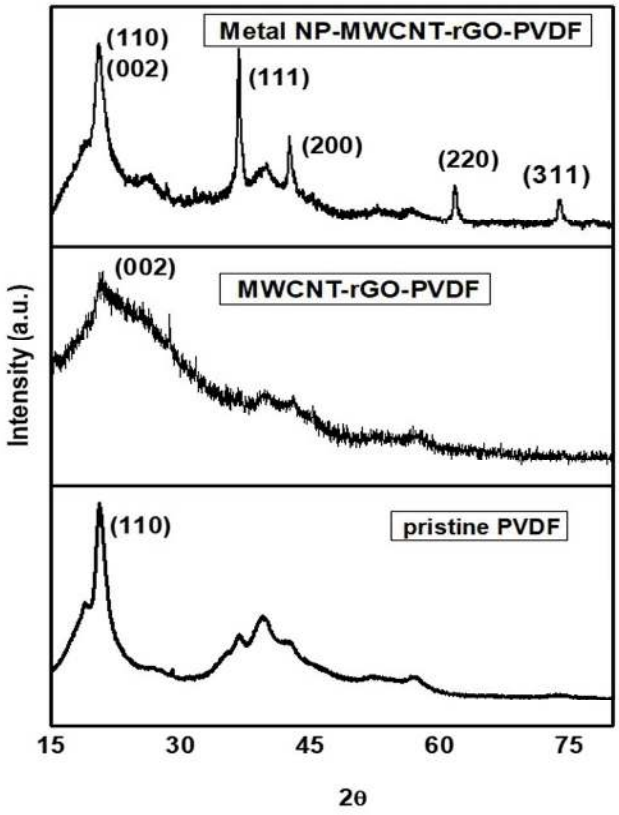

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Fig 1. X-ray Diffraction patterns of pristine PVDF, MWCNT-rGO-PVDF and metal nanoparticles-MWCNT-rGO-PVDF composites

Scanning Electron Microscope (SEM) Analysis

The SEM images for pristine PVDF, MWCNT-PVDF, rGO-MWCNT-PVDF and metallic nanoparticles (Cu and Ag-Au) decorated rGO-MWCNT-PVDF composites are shown in Figure 2. While pristine PVDF is seen in Fig. 2a, Fig. 2b indicates the presence of MWCNTs in PVDF in the form of ribbon shaped nanotubes. A weak interfacial adhesion exists between the MWCNTs and PVDF polymer resulting in the heterogeneous dispersion of MWCNTs in the composites. On high sonication, the rGO is well stacked in MWCNT/PVDF which is well evident as planar network in Fig. 2c and the incorporation of metallic nanoparticles (Cu) and (Ag, Au) in the MWCNT/rGO nanohybrid is manifested well in Fig. 2d and Fig. 2e respectively.

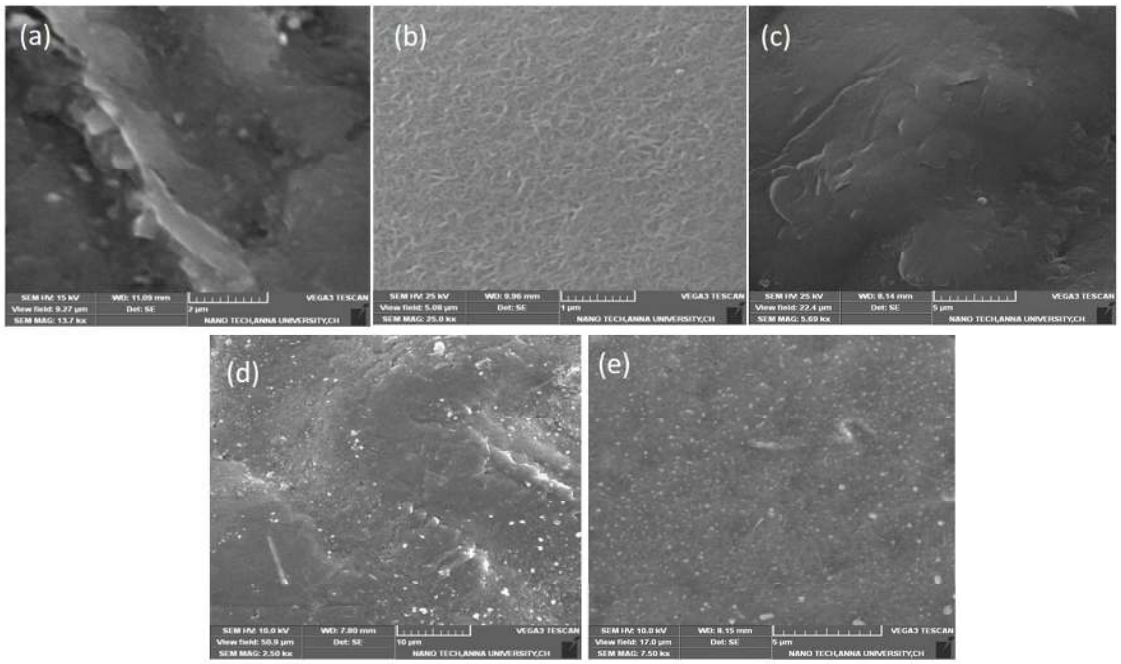

Fig 2. SEM Micrographs for Pristine PVDF (a), MWCNT-PVDF (b), rGO-MWCNTPVDF (c), Cu decorated rGO-MWCNT-PVDF (d) and Ag-Au decorated rGO-MWCNT-PVDF (e) Composites

High Resolution Transmission Electron Microscope (HRTEM) Analysis

The HRTEM image of rGO/MWCNT in the composite (Fig. 3a) shows that the rGO/MWCNT is well dispersed in polymer matrix and the bundle of MWCNT is

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homogeneously dispersed in polymer. The lower amount of incorporation of metallic nanoparticles (Cu) and (Ag, Au) around with 50 nm in rGO/MWCNT filler is well featured in Fig. 3b and Fig. 3c respectively. The SAED patterns show the crystalline nature of the prepared composites.

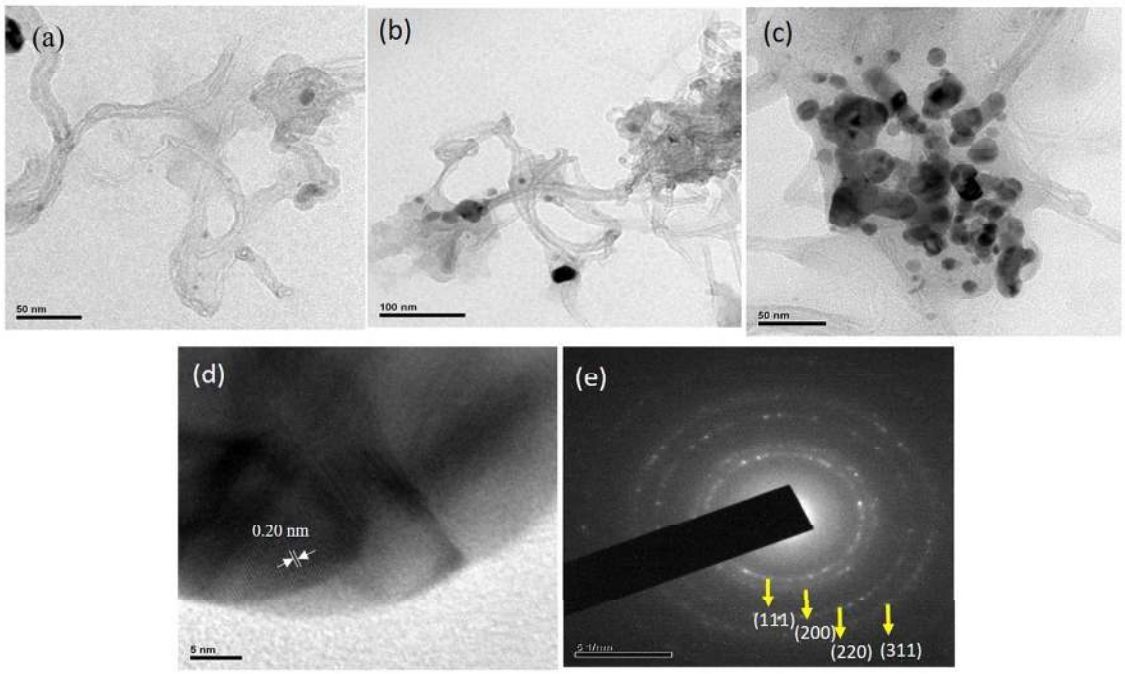

Fig 3. HRTEM image of rGO-MWCNT (a), Cu decorated rGO-MWCNT (b), Ag-Au decorated rGO-MWCNT (c), high resolution image (d) and its SAED patterns (e X-ray Photoelectron Spectra (XPS) Analysis

Fig. 4 shows the XPS results for metallic nanoparticles in the composites. The elemental constitution and the bonding nature of the nanocomposites have been clearly depicted in the survey spectra (supplementary information, S1). The wide scan of the spectra detects C, O and F signals in the nanocomposites. The peaks, observed at 288.6 eV and 531.8 eV, represent the C 1s and O 1s respectively. The reinforcement of carbon with PVDF is indicated by a peak at 292.5 eV as $–CF_2$-. The observed peaks at 288.6 eV and 531.8 eV of carbon/PVDF clearly attributed to sp^2 and sp^3 carbons respectively. In addition, a new peak, formed at 293.2 eV, represents the $–CF_3$- group. The two satellite peaks formed at 368.2 eV and 374.5 eV ascertain the presence of Ag $3d_{5/2}$ and $3d_{3/2}$ respectively, which further confirm the existence of Ag in Ag^0 state.[24,25] The peak at 88.2 eV proves the existence of Au nanoparticles at Au $4f_{5/2}$ in Au^0 state. The formation of Cu nanoparticles, in Cu^0, is confirmed by the peaks at 933.4 eV and 952.8 eV.[26]

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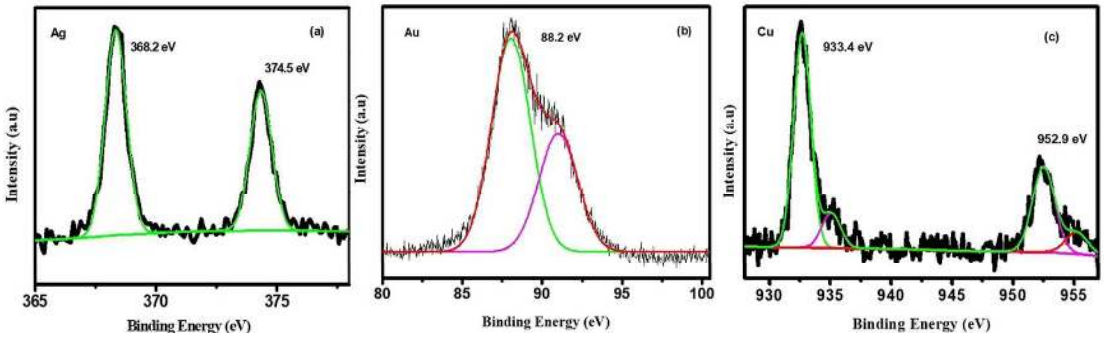

Fig 4. XPS Spectra of Ag, Au and Cu Nanoparticles decorated in composites

Dielectric constant

The electrical behaviour of the composites is shown in Figure 5. The dielectric constant obtained for pristine PVDF is around 2.25 at 1 MHz. After engrafting MWCNTs in PVDF matrix, the enhancement in the dielectric constant is observed which attributes to the charge trapping and dipole orientation between acid functionalization of MWCNT and PVDF polymer in the composites.[27] After the reinforcement of rGO in the composites, the value of dielectric constant is enhanced creditably due to Maxwell-Wagner-Siller interfacial polarization for the conductive layers and PVDF polymer.[28] On decorating with the metallic nanoparticles in the composites, the free electrons availability is increased between the fillers and PVDF which in turn accounts for further enhancement in the value of dielectric constant. The dielectric constant fairly remains constant throughout the measurement frequency region.

Electrical Conductivity

The electrical conductivity for pristine PVDF is 5.01×10^{-8} S/cm at 1 MHz. The enhancement in the conductivity was noticed with the addition of MWCNT to PVDF due to the formation of conductive clusters and high aspect ratio in the composites. With the reinforcement of rGO in the composites, the formation of double percolation concept enhances the electrical conductivity further.[29] The minimum reinforcement of carbon fillers (MWCNT/rGO) in the polymer contributes the enhancements of electrical conductivities through sonication which attributes the mobility of electrons through the percolation of conduction paths in the polymer composites. The incorporation of metallic nanoparticles in MWCNT/rGO contributes the space charge distribution at the interlayer between carbon fillers and PVDF enhances the electrical conductivities of the composites.[30]

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Dielectric loss

Loss tangent (tanδ) is the resultant of the combined effect of conductivity and dipole relaxation (dielectric loss).[31] In general, one can use the effective loss tangent when both dielectric loss and conductivity are involved in the lossy nature. As expected, the dielectric loss tangent (tan δ) for pristine PVDF is close to 0.037 at 1 MHz. By incorporating rGO/MWCNT, the loss tangent increases since it depends on the nature of transport of electrons in the composites. With the incorporation of metallic nanoparticles in the composites, enhanced mobility of electrons and the formation of interfacial polarization between the carbon fillers and PVDF, dielectric loss further enhances.[32,33]

Formula for dielectric constant of sample:

$k' = 1 / Co \{C_1 + [C4(C_2-C_1)(Cs-C_1) / C_4(C_2-C_1) C_2(C_4-C_3)] \}$ at lower frequencies

Formula for loss tangent of sample:

$D = D_4 + [(k'C_0-C_4)(D_4-D_3) / (C_4-C_3)]$ at lower frequencies

C1, C2,C3,C4 are the capacitance measurements at lower frequencies

K' – dielectric constant, Co – cell vacuum capacitance, D – loss tangent

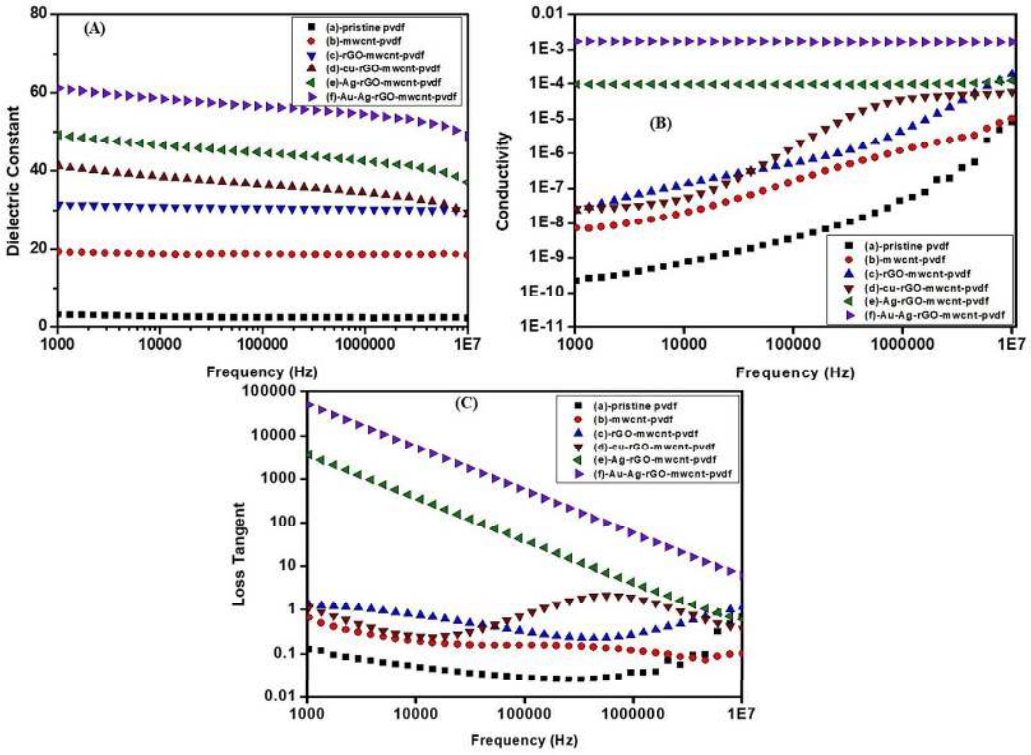

Fig 5A. Dielectric Constant (a), Electrical Conductivities(b), Dielectric Loss(c) of Pristine PVDF(A), MWCNT-PVDF(B), rGO-MWCNT-PVDF(C), Cu-rGO-MWCNT-PVDF(D) composites

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Electromagnetic Shielding Effectiveness (EMI SE)

The EMI shielding effectiveness of the composites is illustrated in Figure 6. It may be noted that the shielding is due to both reflection and absorption. The shielding due to reflection alone, SE_R, can be obtained by (expressed in dB),

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

While the shielding due to absorption, SE_A, is given by (expressed in dB)

$SE_A = -10 \log [S_{21}^2/ (1-S_{11}^2)]$.

The total shielding of electromagnetic radiation, expressed in dB, is given by

EMI Shielding = $SE_A + SE_R = -10 (\log S_{21}^2)$.

Here, S_{11} is the magnitude of the reflection coefficient and S_{21} is the magnitude of the transmission coefficient[34,35]

The EMI shielding for pristine PVDF is around 2.13 dB at 12 GHz. On reinforcing COOH-MWCNT in PVDF, the composite shows an enhancement in EMI shielding. The composites exhibit better conductivities with high aspect ratio of conductive nanofillers through the compact networks and in turn contributes to the enhancements in microwave reflection and absorption. The charge build-ups could be occurred in the composites at the interface of the conducting nature of fillers-polymer matrix (interfacial polarization phenomena) and is credit worth for higher heat loss which may be attributed to dielectric and ionic conduction losses in the material.[36] The acid functionalized MWCNT, which possesses an excellent dispersion in PVDF, clearly attributes that the material absorbs microwave radiations due to π-π electrons mounted at the interface between MWCNT and PVDF.

Addition of rGO in the composites further enhances the EMI shielding that may be due to the existence of covalent bonds between MWCNT and rGO in the composites. Usually, defects play a crucial role in suppressing the shielding of EM radiations. But, MWCNT provides free radical in the composites which in turn acts as a remarkable factor for reducing the defects in the composites. The surface area of rGO is large providing high interfacial energy at the surface between the fillers and PVDF in the composites.[37] The $\pi - \pi$ interaction of the carbon reinforcing fillers and PVDF along with the dipolar interactions between the functional groups in carbon fillers and $-CF_2$ groups in PVDF are responsible to enhance the EMI shielding effectiveness of the composites.[38]

The incorporation of metallic nanoparticles is expected to improve the EMI shielding due to the mobile charge carriers present in the composites by interacting with incident radiations. The good dispersion of metallic nanoparticles in the carbon fillers contributes to an

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interconnecting networks with better conductivities which in turn enhances the effective EMI shielding in the composites. One of the significant concepts in EMI shielding is skin depth, which defines the penetration of electromagnetic radiations to the near surface region of the conducting materials. Hence, the EM radiations are expected to decay within a small distance in the materials.

In the present work, the improvement in the electric field on increasing the conducting fillers accounts the enhancement in EMI shielding in the composites. Arranz-Andrés et al[39] reported that the EMI shielding of 25 vol% Cu nanoparticles blended PVDF by twin-screw extruder method showed an EMI SE value of 110 dB at 12 GHz. It may be noted that the thickness of the sample used in this work is only 500 μm and even with this low thickness, the shielding efficiency is around 28.5 dB for metallic nanoparticles in binary carbon fillers (MWCNT-rGO) in PVDF. This clearly shows that the conducting networks with tunnelling of electrons at the interface between the fillers and polymer matrix enhances the EMI shielding. It may be noted that incorporation of small amount of metallic nanoparticles, having unique properties of noble metals, increases the shielding efficiency supported by the second conducting fillers (rGO) with minimum defects.

The functional groups and clustered defects present in the materials arises through the preparation of composites by chemical methods which attributes the dipoles in the composites.

The unevenly distributed dipoles in the carbon materials and indexed to orientation polarization and relaxation loss. Moreover, the increasing weight ratio of carbon nanomaterials results in capacitor like junctions and it may attributed to polarization in electromagnetic fields. The formation of capacitor like junctions may leads to enhancement in relaxation. The conductive networks in the composites arises from the carbon nanomaterials in the matrix when the weight ratios of carbon materials is over the threshold and it can leads to enhancing the dielectric loss of the materials. Furthermore, the impedance matching can be responsible for tunable microwave absorption of the materials which may be controlled by different weight ratios and thickness of carbon nanomaterials in the polymer composites and it can also contributes the changes in electrical properties of the materials.[40-44]

The decoration of metallic nanoparticles in binary component carbon fillers (1 wt% rGO -1 wt% MWCNT) in PVDF matrix by solvent cast technique clearly infers the improvement of shielding efficiency of the prepared composites at minimum weight percentage of loading in the polymer matrix when compared with previous reports.

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One of the captivating phenomena in EMI shielding is the return loss which describes the transmission of electromagnetic radiations through the material rather than reflection, absorption and multiple internal reflections. The EMI shielding value increases on decreasing return loss of the materials. The conducting networks formed between the components of the composites attributes to the low return loss indicating the dominance of reflection in enhancing the EMI shielding of the composites. The prepared composite metals-MWCNT-rGO/PVDF achieved EMI shielding around 28 dB in X-band frequency region which satisfies the commercial need of 20 dB[45]. The mechanism of electromagnetic interference shielding effectiveness (EMI SE) is presented in Scheme 2. The following table compares the previous works of EMI Shielding with the present investigation.

Table

Composites	**Filler content (%)**	**Thickness (Mm)**	**EMI SE (dB)**	**Ref**
Graphene/PMMA	1.8 %	4 mm	20 dB	46
Graphene	10 wt%	8.4 μm	22 dB	47
$BiFeO_3$	-	2 mm	11 dB	48
Microcellular polyetherimide/Graphene	10 wt%	2.3 mm	22 dB	49
rGO/PVA	-	0.3 mm	15 dB	50
Graphene Foam	-	1 mm	23 dB	51
MWCNT-QMCA/PDMS	2 wt%	2 mm	22 dB	52
Bimetals(1wt%)-bifillers(1wt%)/PVDF	**1wt%**	**0.5 mm**	**28 dB**	**This work**

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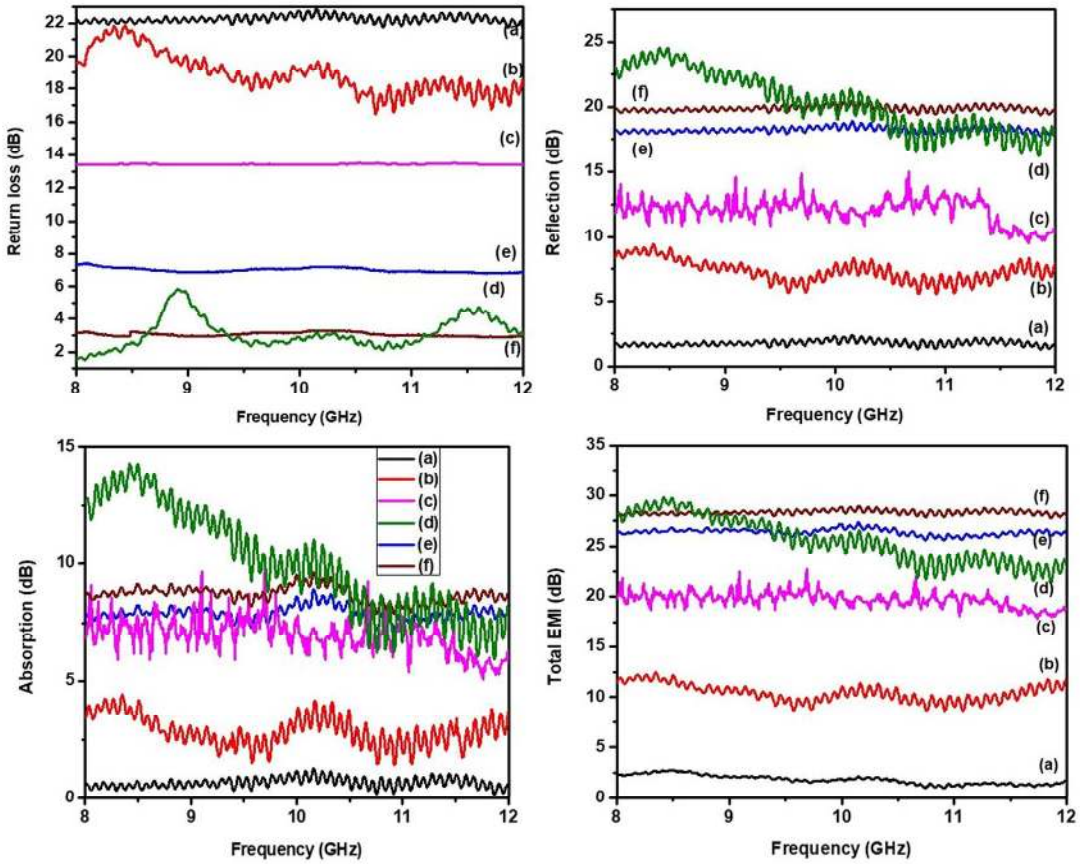
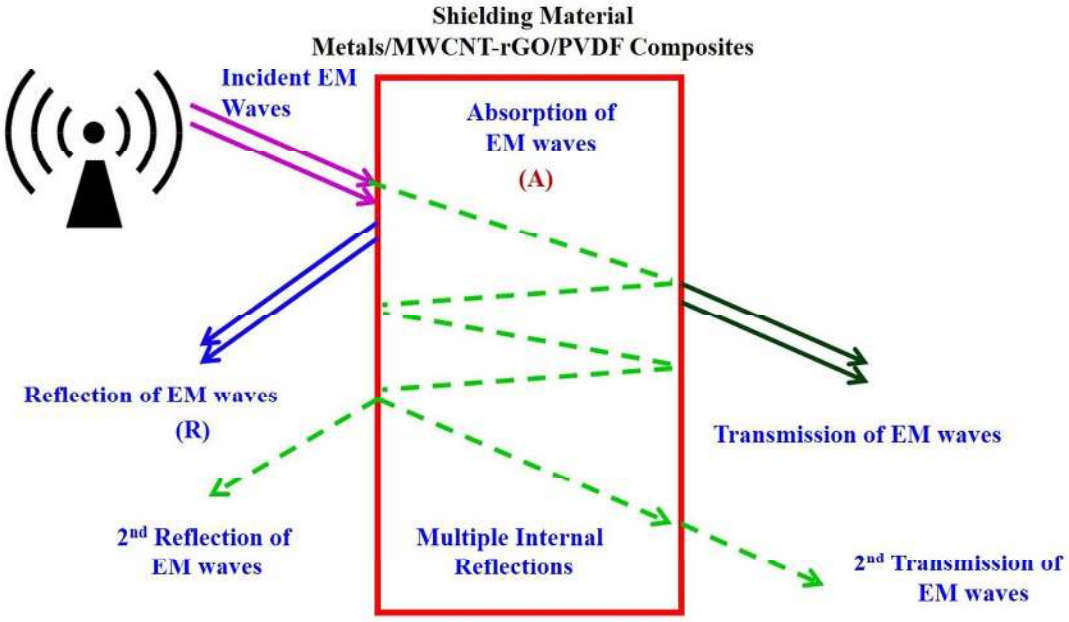


Fig 6A. Return loss, Reflection, Absorption and Effective EMI SE(d) at 12 GHz respectively for (a) Pristine PVDF, (b) MWCNT-PVDF, (c) rGO-MWCNT-PVDF,(d)Cu-rGO-MWCNT-PVDF composites



Scheme 2. Schematic representation of EMI Shielding Material

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Conclusion

In the present work, metallic nanoparticles adorned carbon fillers (MWCNT/rGO) in polyvinylidene fluoride matrix by simple solvent cast method was prepared. The morphology and the distribution of metallic nanoparticles in carbon reinforcing fillers were ascertained from x-ray diffraction patterns. The SEM and HRTEM morphologies showed the decoration of metals on MWCNT/rGO nanofillers. The prepared conducting flexible composites possessed a significant enhancement in the values of dielectric constant and electrical conductivity which were obtained from the polarization and synergic effect occurred in the composites. The EMI shielding of the composite enhanced to around 28.5 dB, for a thickness of 500 μm, in the X-band microwave region (8 to 12 GHz) due to the increase in electrical conductivity through the charge build ups and the interfacial polarization phenomena. The prepared flexible polymer composite materials, with enhanced conductivities and shielding values, clearly show that these materials have promising applications in high tech fields such as satellite broadcasting, military, civil and gigahertz electronics.

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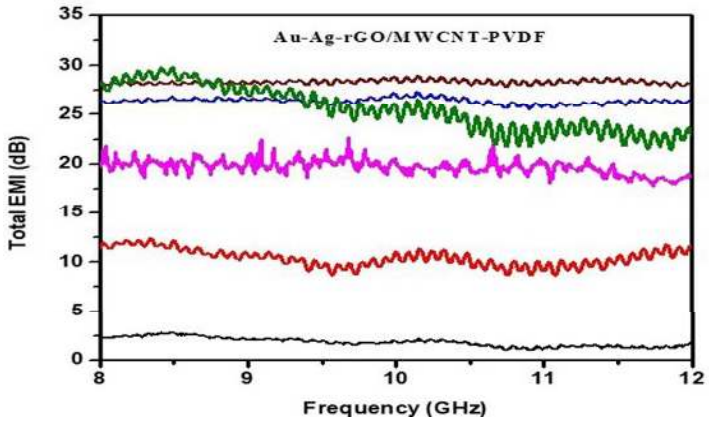
Graphical image



The work demonstrates the enhanced EMI Shielding of lower incorporation of metals/carbon nanomaterials in PVDF matrix with better electrical properties.