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Ultrathin structures derived from interfacially modified polymeric nanocomposites to curb electromagnetic pollution†

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The use of electronic devices and wireless networks is increasing rapidly, and electromagnetic (EM) pollution remediation remains a challenge. We employed a unique approach to fabricate two ultrathin (approx. 53 μm) multilayered assemblies to address this. By sequentially stacking thin films of polyvinylidene difluoride (PVDF) and polycarbonate (PC) nanocomposites and interfacially locking them with a mutually miscible polymer (PMMA, polymethyl methacrylate), materials with enhanced structural properties and electromagnetic interference (EMI) shielding performance can be designed. Utilizing reduced graphene oxide (rGO) and molybdenum disulfide (MoS₂) as a template, ferrite was grown on the surface to design two different nanohybrid structures (rGO-Fe₃O₄ and MoS₂-Fe₃O₄). PVDF was composited with either rGO-Fe₃O₄ or MoS₂-Fe₃O₄, and multiwall carbon nanotubes (CNTs) were dispersed in the PC component. As PC and PVDF are immiscible, their poor interface would result in inferior structural properties, which can be challenging in designing EMI shielding materials due to cyclic thermal fatigue. Hence, PMMA is sandwiched to interfacially stitch the components (PC and PVDF) and improve interfacial adhesion. This was confirmed using SEM/EDS and Raman mapping/imaging. The mechanical stability of the multilayered assemblies was characterized using a dynamic mechanical analyzer (DMA), and the storage modulus was found to be as high as 2767 MPa at 40 °C (@constant frequency and strain amplitude), for the multilayered film with rGO-Fe_{$\frac{1}{2}$}O₄ in PVDF, PMMA as a sandwich layer and CNTs in PC. A typical assembly of 9 multilayers (\sim 480 μ m) with rGO-Fe₃O₄ in PVDF, and CNTs in PC, and interfacially stitched with PMMA gave rise to a high EMI shield effectiveness (SE_{T}) of -26.3 dB @ 26.5 GHz. This unique arrangement of a multilayered assembly suppressed EMI primarily by absorption.

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1. Introduction

With the increasing development of high-speed electronic devices, electromagnetic interference (EMI) has become a significant concern. To protect sensitive electronic circuits from unwanted electromagnetic (EM) radiation, EMI shielding materials need to be developed. EMI shielding refers to minimizing the transmission of incoming EM radiations by introducing a shielding material that can obstruct the waves by reflection and/or adsorption. Research in the last couple of decades has focused on metals and polymer nanocomposites as

a solution to EM pollution. 1-3 Polymer nanocomposites have an

Herein, two functional hybrid structures were synthesized using reduced graphene oxide (rGO) and molybdenum disulfide (MoS₂) as templates; rGO-Fe₃O₄ and MoS₂-Fe₃O₄. Several studies have been performed on rGO, MoS₂, and Fe₃O₄ based materials for EMI shielding applications.^{10,11} For a polymer to act as an EMI shield, conducting and magnetically/dielectrically lossy nanoparticles have to be incorporated. In our work, we have used multiwalled carbon nanotubes (CNTs) as

added advantage over metals due to their ease of processing, corrosion resistivity, and low density.^{3,4} Both intrinsically conducting and insulating polymers have been extensively explored for EMI shielding applications.^{2,3,5–8} The polymer acts as a matrix for incorporating nanoparticles that interact with the EM waves and attenuate them *via* reflection, absorption, or multiple reflections. The most common and useful fillers for EMI shielding applications include carbon-based nanofillers such as carbon nanotubes (CNTs), reduced graphene oxide (rGO), graphene platelets, carbon black, *etc.*^{5–7} Magnetically lossy or dielectrically lossy fillers also interact and suppress the incoming EM radiation *via* absorption.⁹

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a conducting filler,12 given their ability to form a percolated

network at a relatively lower concentration on account of their high aspect ratio, and incorporated rGO-Fe₃O₄ and MoS₂-Fe₃O₄ as the lossy counterpart. Fe₃O₄ is a ferrimagnetic semiconducting material.13 In the case of rGO, the extent of reduction of GO decides the properties of rGO in terms of conductivity as well as defects, which play a significant role in EMI shielding. MoS₂ is semiconducting and known to be dielectrically lossy.14-17

The dispersion of nanoparticles in a polymer matrix and the interaction between the polymer and nanoparticles play a crucial role in EMI shielding performance. In addition to this, several studies have focused on optimizing nanoparticle design for better EMI shielding properties. This includes synthesizing heterostructured nanoparticles such as core-shell structures and studying their effect on EMI shielding performance by varying the interfaces/interfacial properties. 18-20 Another important aspect is the polymer blends/nanocomposite architecture, which includes selective localization of nanoparticles, the multilayer architecture with nanofillers, etc. 4,21-23

Multilayered architecture is an exciting research domain known to enhance the shielding effectiveness (SE_T) at lower thicknesses primarily due to multiple scattering and interfacial polarization, thus giving an advantage over conventional shields. Zhang et al.23 reported a multilayered assembly of regenerated cellulose as the supporting substrate and polyethylene oxide (PEO)/CNT as the EMI shielding layer. PEO enhanced the interfacial adhesion between the CNTs and the cellulose layers due to its favorable compatibility with cellulose chains. Compression molding was used to sandwich the PEO/ CNT (1:4) layer between the cellulose layer, and EMI shielding measurements were performed in the X-band. For a film thickness of 150 μ m, the layered structure showed a SE_T value of -35 dB compared to −20 dB demonstrated by the plain structured composite, which was prepared by direct mixing of CNTs into cellulose solutions. Xu et al.22 reported a highly conductive sandwich structure of a nylon/nickel film prepared by the electroless deposition method. For a film thickness of 100 μm, SE_T was reported to be -77 dB in the X-band. Wang et al.²⁴ fabricated nitrogen-doped graphene multilayer films by thermal annealing of stacked graphene oxide/copper phthalocyanine (GO/CuPc) multilayer films. The maximum SE_T value of -55.2 dB was obtained for a shield thickness of 0.47 mm in the Xband. Biswas et al.21 stacked individual functional nanocomposites consisting of PC/PVDF blends with CNTs, functionalized CNTs, and CNTs conjugated with flower-like Fe₃O₄ nanoclusters for effective EMI shielding performance. This compression-molded stack showed a shielding efficiency of -64 dB at 18 GHz frequency for a shield thickness of 0.9 mm. In another work by Biswas et al., 4 a multilayered assembly with PC/ PVDF + 3 wt% CNT sandwiched between PVDF + 3 wt% CNT-MnO₂ + rGO/Fe was constructed. For a shield thickness of 0.9 mm, the EMI shielding effectiveness was approximately -57 dBin the frequency range of 8-18 GHz.

The literature also suggests that it is not only the type of nanofiller but also the type of polymer and sequential stacking of these layers that become important in designing a robust

multilayered assembly for EMI shielding applications. The choice of polymers in our work is based on the existing PVDF/ PMMA and PMMA/PC blend systems in the literature. It is reported that PMMA decreases the interfacial tension and enhances the interfacial adhesion between PC and PVDF.25-28 It is miscible with both PC and PVDF and is known to act as a common solvent in the melt state.29-33 Also, few articles report that PVDF/PMMA is miscible in the solution state (forms homogeneous solution under certain conditions) due to the interaction between the H-atom of PVDF and the O-atom in the carbonyl group of PMMA, but they phase separate after solvent evaporation. 30,34 Besides, Sharma et al. 35 reported that the strong intermolecular interaction in the melt state of the PVDF/PMMA blend system not only arises from hydrogen bonding between carbonyl groups in PMMA and the -CH₂ groups of PVDF but also the dipole-dipole interactions between -CH2 of PMMA and CF₂ in PVDF. Similarly, there are reports where PMMA/PC results in a homogeneous solution under certain conditions.36,37 Blend miscibility (above 200 °C) between PMMA and PC can be explained using various chemical reactions such as unzipping of PMMA, the attack of PMMA macroradicals on PC chains, trans-esterification of the PMMA ester pendant group with PC, and termoxidative branching leading to graft copolymer inducing re-homogenization at high temperature.29 Few other articles on PMMA/PC blend systems confirm that the specific interactions between the ester group of PMMA and the phenyl ring of PC under certain conditions play a significant role in miscibility.37,38

This work's uniqueness lies in polymer selection and the processing technique used for the construction of the multilayered EMI shielding stack. Herein a doctor blade setup has been used to stack the PVDF, PMMA, and PC layers sequentially. Thus, PMMA was chosen to stitch PC and PVDF layers interfacially. We carried out a templated growth of Fe₃O₄ on rGO and MoS₂ for uniform dispersion. By rationally stitching materials with different characteristics as 'interfacially locking, PMMA' between a conducting layer (PC with CNTs) and lossy layer (PVDF with either rGO-Fe₃O₄ or MoS₂-Fe₃O₄), the incoming EM radiations can be blocked.

Experimental section

2.1 Materials

Polycarbonate (PC) (Lexan 143 R, MFI-11 g/10 min, $M_w = 37 492$, $M_{\rm n}=20\,642,~{\rm PDI}=1.8)$ was procured from Sabic. Polymethylmethacrylate (PMMA) with a molecular weight (M_w) of 123 000 g mol⁻¹, Mn of 56 981 g mol⁻¹, and a polydispersity of 2.1 was bought from Gujpol. Polyvinylidene fluoride (PVDF) was purchased from Arkema (Kynar 761 grade) with a Mw of 440 000 g mol⁻¹. A pristine multiwalled carbon nanotube (CNT) material, NC7000 (length 1.5 μm and diameter 9.5 nm), was supplied by Nanocyl SA (Belgium). Graphene oxide (GO) powder (BTGOX) was procured from BT Corp. Ferric chloride hexahydrate (FeCl₃·6H₂O) LR 98% was obtained from Thomas Baker. Hydrazine hydrate $(H_4N_2 \cdot H2O)$ (99%), ethylene glycol $(C_2H_6O_2)$, and urea (NH2CONH2) were procured from SDFCL. Sodium molybdate dihydrate $(Na_2MoO_4 \cdot 2H_2O)$ thiourea

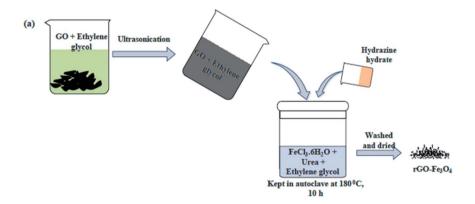
(NH₂CSNH₂) were procured from MERCK. Chloroform and dimethylformamide (DMF) were procured from SDFCL. Analytical grade absolute ethanol was procured from Changshu Hongsheng Fine Chemical Co., Ltd.

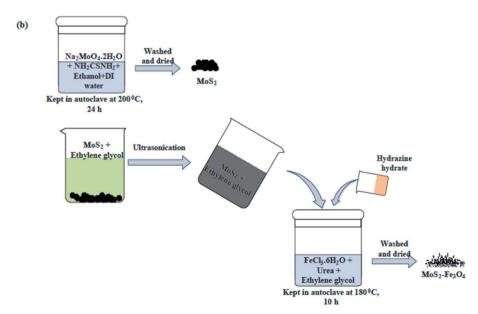
2.2 Synthesis of nanoparticles

2.2.1 Synthesis of rGO–Fe_3O_4. A solvothermal approach was used for the synthesis of rGO–Fe $_3$ O $_4$ nanoparticles 39 (Scheme 1a). As per the typical synthesis procedure, 200 mg of GO was dispersed in 60 mL of ethylene glycol and probe sonicated for 20 min to eliminate the primary agglomeration. Further, the reaction mixture was bath-sonicated for 45 min to eliminate the secondary agglomeration. The GO dispersion was then added to the solution of FeCl $_3$ ·6H $_2$ O, prepared by adding 500 mg of FeCl $_3$ ·6H $_2$ O and 1 g of urea in 20 mL of ethylene glycol. The reaction mixture was stirred well and transferred into a 100 mL Teflon-lined stainless-steel autoclave. Hydrazine hydrate (3 mL) was immediately added, and the autoclave was sealed manually. The reaction was performed in a preheated oven at 180 °C for 10 h. The autoclave was then allowed to cool

down to room temperature, and the black powder of $rGO-Fe_3O_4$ was separated using centrifugation. Lastly, it underwent several washing cycles with DI water and ethanol before drying and storing for further usage.

2.2.2 Synthesis of MoS₂-Fe₃O₄. A two-step solvothermal method was used to synthesize MoS₂-Fe₃O₄ nanoparticles (Scheme 1b). Firstly, MoS₂ nanoparticles were synthesized by dissolving 2.5 g of Na₂MoO₄·2H₂O and 1.55 g of NH₂CSNH₂ (molar ratio of 1:2) in an ethanol: DI water mixture (volume ratio of 1:1). The reaction mixture was prepared in a 50 mL autoclave, and the reaction was carried out for 24 h at 200 °C. The obtained powder was washed with DI water and ethanol before it was dried and stored. Using a similar procedure to previously described (used for the synthesis of rGO-Fe₃O₄), the synthesis of MoS₂-Fe₃O₄ was carried out by dispersing MoS₂ in place of rGO. Unlike rGO, the probe sonication of MoS₂ flowers wasn't performed to avoid the breakage of MoS₂ flowers. But bath sonication of MoS2-ethylene glycol was carried out for good dispersion. The rest of the procedure was the same.





Scheme 1 Synthesis protocol of (a) rGO-Fe₃O₄ and (b) MoS₂-Fe₃O₄.

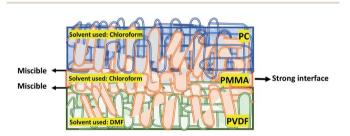
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2.3 Preparation of the multilayered structure of PVDF/ PMMA/PC with nanofillers

2.3.1 The conceptual basis for the choice of polymers and solvents. As PMMA decreases the interfacial tension and enhances the PC/PVDF system's interfacial adhesion, a multilayered assembly of PVDF/PMMA/PC was chosen. This technique's concept is well explained in Scheme 2 and further supported by the digital images in Fig. S1.† The polymersolvent pair was decided after a couple of optimization experiments based on the theoretical calculations in Table S1† and the visual inspection of the obtained film. In addition, the essential characterization of the commercial polymers (PVDF, PMMA and PC) is shown in Fig. S2.†

2.3.2 Experimental procedure for the fabrication of the multilayered assembly with fillers. PVDF-hybrid nanoparticle (rGO-Fe₃O₄ or MoS₂-Fe₃O₄) dispersions (10 wt% nanoparticles), PMMA solution, and PC-CNT dispersion (3 wt% CNT) were prepared by dissolving each of them in dimethylformamide (DMF), chloroform, chloroform, respectively.

Preparation of PVDF-hybrid nanoparticle (rGO-Fe₃O₄ or MoS₂-Fe₃O₄) solution: 1.8 g PVDF was dissolved in 7 mL DMF,



Scheme 2 Schematic showing the conceptual basis for the fabrication of the multilayered assembly of PVDF/PMMA/PC based on the miscibility of individual polymers.

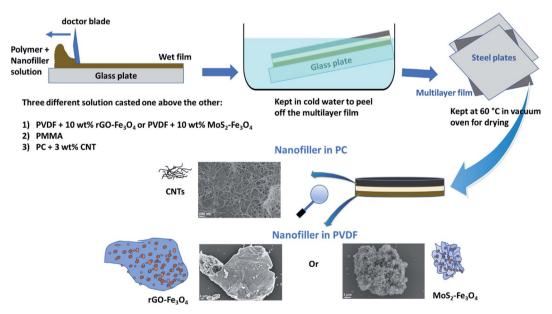
and 200 mg of nanoparticles were dispersed in 3 mL DMF via bath sonication for 30 min. Shear mixing and magnetic stirring were avoided as Fe₃O₄ is magnetic. PVDF solution was then added dropwise to the nanoparticle dispersion, and the final dispersion was bath sonicated again for 20 min to obtain as homogeneous dispersion as possible.

Preparation of PMMA solution: PMMA solution was prepared by dissolving 3 g PMMA in 10 mL solvent.

Preparation of PC-CNT solution: 2.425 g PC was dissolved in 7 mL solvent. 75 mg CNTs were then added into 3 mL chloroform in a separate vial and bath sonicated. Since the viscosity was too high for casting, 10 mL chloroform was further added to the CNT dispersion, and bath sonication was carried out for 30 min. The PC solution was then added dropwise to the CNT dispersion and shear mixed at 9000 rpm for 45 min to obtain a homogeneous PC-CNT dispersion.

After preparing the three solutions/dispersions described in Section 2.3, the PVDF-hybrid nanoparticle dispersion was cast using a doctor blade setup (100 µm slit) and dried partially for 45 min at room temperature. Subsequently, the PMMA solution was cast using the doctor blade (200 µm slit) above the previous film and dried for 15 min at room temperature. Next, PC-CNT dispersion was cast using a doctor blade (300 µm slit) and dried for 15 min. The multilayered film was immersed in cold water for a few minutes and peeled off. It was then placed between two steel plates and dried in a vacuum oven at 60 °C. It is to be noted that this technique of sequential casting using increasing slit height (100 μm, 200 μm, 300 μm) was performed to obtain a 100 μm thick layer, each of PVDF-hybrid nanoparticles, PMMA and PC-CNT. However, after solvent evaporation, the actual thickness obtained is less than the total expected thickness of 300 μm, as is later seen in the scanning electron micrographs.

The final multilayered stack is shown in Scheme 3. PVDF with hybrid nanoparticles (rGO-Fe₃O₄ or MoS₂-Fe₃O₄) and PC-



Scheme 3 Schematic showing the preparation of the multilavered film.

CNT composites are sandwiched using PMMA as an interfacial layer, and this multilayer is denoted as PVDF(nanofiller name)/ M/PC. The multilayered assembly with rGO–Fe $_3O_4$ is represented as PVDF(rGO–Fe $_3O_4$)/M/PC, and MoS $_2$ –Fe $_3O_4$ is represented as PVDF(MoS $_2$ –Fe $_3O_4$)/M/PC hereon. It is to be noted that the multilayered assembly always has CNTs as a nanofiller in the PC layer, but for simplicity of nomenclature, we haven't explicitly mentioned it.

Control samples of PC–CNT were prepared by casting the dispersion of PC + 3 wt% CNT using a 300 μm slit, and the

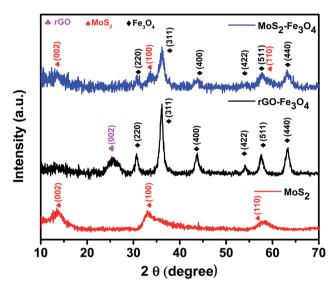


Fig. 1 XRD pattern of MoS₂, rGO-Fe₃O₄, and MoS₂-Fe₃O₄.

subsequent procedure was the same as shown in Scheme 3. The control samples of PVDF + rGO–Fe $_3$ O $_4$ (10 wt% nanoparticles) and PVDF + MoS $_2$ –Fe $_3$ O $_4$ (10 wt% nanoparticles) were also prepared by casting the respective dispersions individually using a 300 μ m slit, but the film obtained was very brittle due to the high loading of nanoparticles, as shown in Fig. S5.† The control samples of single-layered PC + 3 wt% CNT, PVDF + 10 wt% rGO–Fe $_3$ O $_4$, and PVDF + 10 wt% MoS $_2$ –Fe $_3$ O $_4$ using the doctor blade approach will be henceforth represented as PC(CNT), PVDF(rGO–rGO–Fe $_3$ O $_4$), and PVDF(MoS $_2$ –Fe $_3$ O $_4$) respectively.

Characterization

X-ray diffraction (XRD) analysis of the synthesized powder was carried out using an XPERT Pro from PANalytical. A Cu-K α radiation source ($\lambda = 1.5406$ Å, 40 kV, and 30 mA) was used for analysis.

Transmission electron microscopy (TEM) images and the selected area diffraction (SAED) pattern of various nanoparticles were obtained using a Libra 120 TEM instrument. The morphology was analyzed by Raman microscopy using a RAMAN Imaging System WITEC alpha300R (using a 532 nm laser with a power of 5 mW and a $20\times$ objective with a measuring point distance of 500 nm) and scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy analysis (EDS) using a Carl Zeiss Ultra 55 or Carl Zeiss Ultra FE-SEM. Raman microscopy and SEM analysis of the cross-section of the multilayered assembly were performed after embedding it in epoxy and sectioning it using a microtome with a steel knife

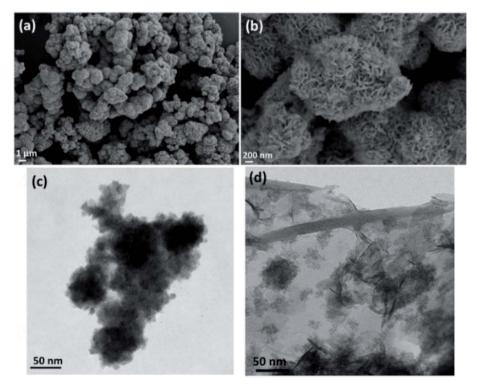


Fig. 2 (a and b) SEM micrograph of MoS₂, (c) TEM micrographs of MoS₂-Fe₃O₄, and (d) TEM micrograph of rGO-Fe₃O₄.

(for Raman microscopy, 20 µm thin sections) and ultramicrotome with a diamond knife (for SEM, block-face cuts). The SEM samples were coated with \sim 10 nm of C to prevent charging in the electron beam. However, the SEM and EDS of nanoparticles were carried out with a few nm of gold coating over it. The differential scanning calorimetry (DSC) of polymers was performed in a copper pan using TA analysis (DSC Q2000) under a N₂ atmosphere. Fourier transform infrared (FTIR) spectroscopy was performed using an FTIR instrument bought from PerkinElmer. % transmittance was obtained in the wavenumber range of 4000-650 cm⁻¹ using universal attenuated total reflectance mode (ATR).

Magnetic measurements of the nanoparticles were performed using a physical property measurement system (9T) from Quantum Design. Room temperature AC conductivity studies were performed using an Alpha-A Analyser (Novocontrol, Germany) in a broad frequency range from 10⁻¹ to 10⁷ Hz. Compression-molded discs (10 mm diameter and 1 mm thickness) were used as specimens for electrical conductivity measurements. Broadband (8.2-26.5 GHz) microwave shielding studies were performed using a keysight fieldfox microwave analyzer N9918A. S-parameters $(S_{11}, S_{12}, S_{21}, \text{ and } S_{22})$ obtained from a vector network analyzer (VNA) were used to determine the total shielding effectiveness and shielding effectiveness due to reflection and absorption. Melt rheological analysis was performed using a Rheometer (model ARES G2) from TA Instruments, USA. The measurements were carried out under a constant strain of 1% in a nitrogen atmosphere. Two sweeps, between 0.1 and 100 rad s⁻¹, forward and backward, were performed with the same filling, whereby the second one was used for interpretation. The following strain sweep was used to confirm that the selected strain was within the linear-

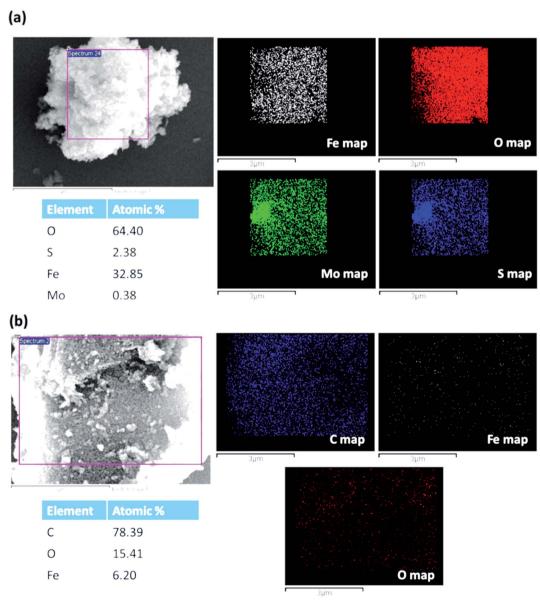


Fig. 3 EDS map of (a) $MoS_2-Fe_3O_4$ and (b) $rGO-Fe_3O_4$.

viscoelastic range. Dynamic mechanical analysis (DMA) of the samples was performed using a DMA Q800. DMA samples were prepared by cutting a piece of size 2.2 cm \times 0.63 cm from the multilayered thin film and were analyzed in tension mode as a function of temperature at a constant frequency of 1 Hz, constant oscillation amplitude of 3 μ m, and strain% of 0.02, which lies in the viscoelastic region.

4. Results and discussion

4.1 Characterization of hybrid nanostructures

The X-ray powder diffraction (XRD) patterns of as-prepared MoS₂, rGO-Fe₃O₄, and MoS₂-Fe₃O₄ are shown in Fig. 1. The

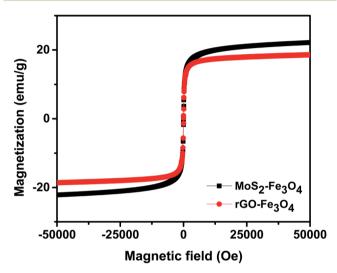


Fig. 4 VSM plot of the synthesized nanoparticles.

Fig. 2 shows the SEM micrograph of MoS₂ (Fig. 2a and b), and TEM micrograph of MoS₂-Fe₃O₄ (Fig. 2c), and rGO-Fe₃O₄ (Fig. 2d), respectively. Fig. S3a and b† show the SEM micrograph of MoS₂-Fe₃O₄, and Fig. S3c and d† show the SEM micrograph of rGO-Fe₃O₄. Fig. 2a and b illustrate a flower-like MoS₂ structure of 0.3-5 µm dimensions. The MoS₂ nanosheets selfassemble to form a thermodynamically and kinetically stable flower-like MoS2 structure during 24 h of a hydrothermal reaction. Fig. 2c, S3a, and b† show the morphology of MoS₂-Fe₃O₄. We observe that the Fe₃O₄ nanoparticles have nucleated and grown on the MoS2 surface covering the entire petal-like structure. The size variation of the agglomerated chunks corresponds to 0.1-8 µm. The smaller sizes are more prominent in the TEM micrographs (Fig. S4a†). Fig. 2d, S3c, and d† show the rGO-Fe₃O₄ structure where spherical Fe₃O₄ nanoparticles decorate the rGO sheets well. Since both probe and bath sonication is used while synthesizing rGO-Fe₃O₄, the sheet obtained is of varying sizes from 0.7-20 µm, as evident from the low

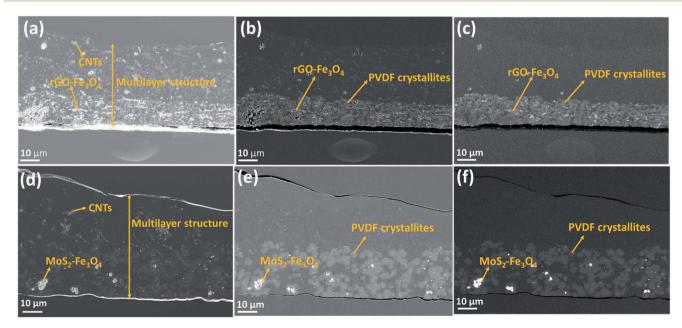


Fig. 5 SEM micrographs of the multilayered film's cross-section (embedded in epoxy and cut using an ultramicrotome). (a–c) PVDF(rGO– Fe_3O_4)/M/PC (d–f): PVDF(MoS₂– Fe_3O_4)/M/PC. Each row depicts the same area with different detectors: in-lens, SE2, and back-scattered electrons detectors, respectively.

magnification TEM micrographs (Fig. S4b†). Additionally, Fig. S4c and d† show the SAED pattern of MoS₂-Fe₃O₄ and rGO-Fe₃O₄ nanoparticles.

Fig. 3a shows the EDS map of MoS₂-Fe₃O₄, and Fig. 3b shows the EDS mapping of rGO-Fe₃O₄. The map of MoS₂-Fe₃O₄ and rGO-Fe₃O₄ shows the presence of individual elements. Though the weight ratios of GO/FeCl₃·6H₂O and MoS₂/FeCl₃·6H₂O were both kept as 0.4 at the time of synthesis, we observe that the Fe atomic wt% is 32.8% in MoS2-Fe3O4 as compared to 6.2% in rGO-Fe₃O₄. However, it is to be noted that EDS is more of a qualitative technique than a quantitative one.

Fig. 4 shows the room temperature magnetization plot of the synthesized nanoparticles. rGO-Fe₃O₄ shows a slightly lower saturation magnetization of 18.6 emu g⁻¹ than MoS₂-Fe₃O₄, which shows a saturation magnetization of 22.2 emu g⁻¹. This is in accordance with the EDS result, where Fe atomic weight%

was found to be higher in MoS2-Fe3O4 as compared to rGO-Fe₃O₄.

Morphological analysis of the multilayered assembly

Such a complex multilayer system could only be characterized by two complementary methods, SEM and Raman microscopy, using the strengths of each of the methods to clarify various aspects of the assembly. SEM imaged the CNTs (with the in-lens detector, Fig. 5a and d) and Fe₃O₄ nanoparticles (with a backscattered electrons detector, Fig. 5c and f). PVDF gives sufficient contrast in back-scattered electrons with respect to PMMA and PC, but PMMA cannot be distinguished from PC. EDS (Fig. 6) was further used to confirm the location of MoS₂, Fe₃O₄ and PVDF. Unfortunately, EDS cannot distinguish PMMA from PC either. On the other hand, PMMA can be distinguished easily from PC with Raman microscopy (Fig. 7). However, due to the

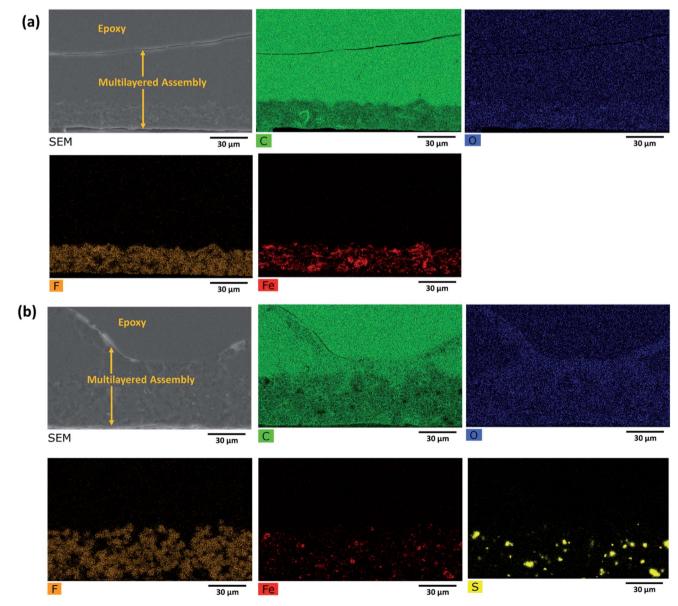


Fig. 6 EDS map of the cross section of the multilayered film: (a) PVDF(rGO-Fe₃O₄)/M/PC; (b) PVDF(MoS₂-Fe₃O₄)/M/PC.

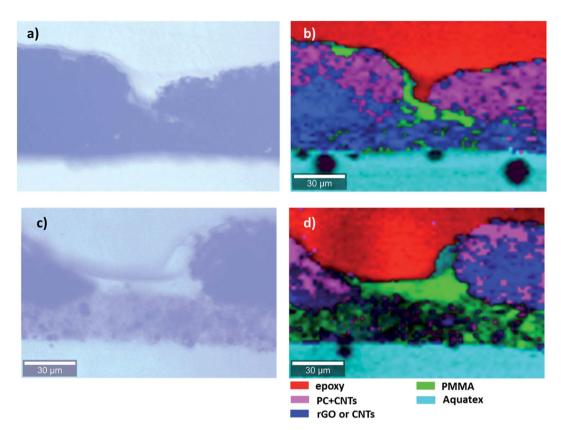


Fig. 7 Light microscopy images (a and c) and Raman map (b and d) of the cross section of the multilayered film: (a and b) PVDF(rGO $-Fe_3O_4$)/M/PC; (c and d) PVDF(MoS $_2-Fe_3O_4$)/M/PC.

spatial resolution of 300 nm, Raman microscopy cannot detect MoS₂ and Fe₃O₄ nanoparticles.

Fig. 5a–c show the SEM micrographs of the multilayered film's cross-section containing rGO–Fe₃O₄, while Fig. 5d–f show the SEM micrographs of the cross-section of the multilayered assembly containing MoS₂–Fe₃O₄. In-lens, SE2 (type II secondary electron), and back-scattered electron detectors are three different SEM detectors used to obtain the images for the same location. The micrographs in Fig. 5a and d are obtained by the in-lens detector (generally surface sensitive and used for high-resolution micrographs; in this case, gives the best possible contrast of CNTs), Fig. 5b and e show the results obtained by the SE2 detector (generally for imaging the topography; in this case for imaging both topography and material contrast) and Fig. 5c and f show the results obtained by the back-scattered electron detector (for enhanced material contrast or atomic number contrast).

At first sight, the assembly consists of two layers: a uniform lower layer and an upper layer with varying thickness. CNTs are visible as white dots, mostly in the upper layer of PC; however, there seems to be a slight diffusion across the layers, as evident from Fig. 5a and d. PVDF is present in the lower layer – the light grey areas in Fig. 5b, c, e and f. In the nanocomposite with rGO–Fe₃O₄, PVDF makes most of the lower layer. In the nanocomposite with MoS₂–Fe₃O₄, PVDF forms spheres uniformly distributed in another polymer. The PVDF is unanimously identified by the presence of fluorine, as can be seen in EDS mapping (F map) in Fig. 6 and S6.† The SEM micrographs show that the hybrid nanoparticles (rGO–Fe₃O₄ or MoS₂–Fe₃O₄) are

mostly restricted to the PVDF layer. Additionally, EDS confirms the location of Fe_3O_4 (Fe map) and MoS_2 (S map), which were attributed to the white dot areas in Fig. 5c and f. Fe and S mapping also confirm that the PVDF portion's layer incorporates maximum Fe_3O_4 and MoS_2 – Fe_3O_4 as expected. Carbon and oxygen EDS mappings cannot be used to distinguish epoxy, PMMA, and PC. Also, it should be noted that the SEM micrographs show no sharp distinguishable interface between the three polymers, suggesting the diffusion of polymers across the interface with no slippage of individual layers (no gaps or cracks between the three different polymeric layers).

Raman microscopy reveals the location of epoxy (red), PMMA (green), and PC (pink) in Fig. 7. PMMA is present with PVDF and PC, suggesting the diffusion of PMMA in both directions as an interfacial agent, sticking the layers of two incompatible polymers (PVDF and PC). This might be due to a combination of factors such as the partial miscibility of PVDF/PMMA and PMMA/PC in the solution state, solvent selection, and the drying time allotted for each layer of the stack processing. PC is not present as a pure component; it always contains CNTs (black areas in light microscopy). In these particular measurements, CNTs were not distinguishable from rGO, and the blue color represents either of the components in Fig. 7. However, CNTs and rGO are well distinguishable in the SEM micrographs. The cyan color marks the presence of an Aquatex embedding substance for light microscopy.

From Fig. 5, we can also observe the variation in thickness along the cross-section of the multilayered film. PVDF, along

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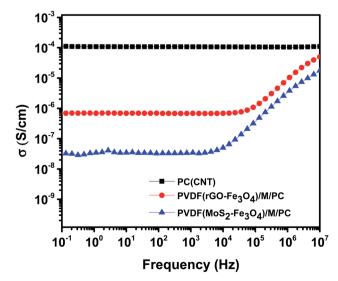
with hybrid nanoparticles, was cast first, and it faced the glass surface. Hence the PVDF side is comparatively flatter than the PC side, which was exposed to air. This might be because of the difference in the solvent's evaporation rates or the not-so-well dispersed CNTs forming agglomerates, which manifested as bumps in the upper layer. The average thickness of the multilayered assembly is observed to be 53 μ m. Also, we observe that this technique has the added advantage of achieving continuous layers of polymeric films with no sharp interface, thus avoiding any slippage between individual layers. Thus, PMMA interfacially locks the PC and PVDF layers.

4.3 Electrical conductivity in the multilayered assembly

Fig. 8 shows the AC electrical conductivity measurements of multilayered assemblies of PVDF(rGO-Fe₃O₄)/M/PC and PVDF(MoS2-Fe3O4)/M/PC with respect to the control film of single layer PC (CNT). The ac electrical conductivity was measured as a function of frequency at room temperature. PC, PMMA, and PVDF are insulating polymers. Multiwalled carbon nanotubes are known to be intrinsically conductive in nature, with an electrical conductivity value of 10⁶ to 10⁷ S m⁻¹. Hence the conductivity of PC (CNT) is the highest as compared to the multilayered assemblies. The conductivity of rGO is controlled by reducing the functional groups, and it is observed to be lower than that of CNTs.41 Fe₃O₄ and MoS₂ are known to be semiconducting. Fe₃O₄ has a bandgap of 2.51-3.01 eV,¹³ while MoS₂ has a bandgap of 1.23 eV.14 Considering the multilayered assembly, the ac electrical conductivity showed a frequencyindependent plateau at a lower frequency following the universal power-law fitting as per eqn (1).39,42

$$\sigma'(\omega) = \sigma(0) + \sigma_{AC}(\omega) = \sigma_{DC} + A\omega^s$$
 (1)

Here, the exponent "s" ranges from 0 to 1 and depends on the temperature and frequency. It indicates the extent of charge transfer that occurs through tunneling/hopping. It denotes the



AC electrical conductivity as a function of frequency.

degree of connectedness of long-range charge hopping pathways or the extent of tortuosity for mobile charges. 43

Here, it is to be noted that the CNTs were concentrated in the insulating PC layer, and thus this layer is expected to be highly conducting in nature. PMMA and PVDF are insulating polymers, and rGO-Fe₃O₄ and MoS₂-Fe₃O₄ are semiconducting fillers. Hence the mid-layer and bottom layer should have ideally made the entire multilayered assembly insulating in nature. But this was not the case, as shown in Fig. 8. This implies that some CNTs have diffused through the layers, as observed in the SEM micrographs, where no sharp and distinct interface at the layer boundary was found.

PVDF(MoS₂-Fe₃O₄)/M/PC shows a lower dc electrical conductivity of 3.6 \times 10⁻⁸ S cm⁻¹ compared to PVDF(rGO- Fe_3O_4 /M/PC, which shows a dc plateau at 6.8×10^{-7} S cm⁻¹ at 10⁻¹ Hz. This can be attributed to MoS₂, which has a bandgap of 1.23 eV. MoS₂ might be comparatively more semiconducting (higher bandgap) than rGO, thus reflecting the difference in the dc plateau value. Also, there might be a possibility that the sheet-like larger structure of rGO makes the percolation threshold lower as compared to that of flower-like MoS2. By fitting the power law, "s" is observed to be 0.99 for PVDF(MoS₂-Fe₃O₄)/M/PC and 0.89 for PVDF(rGO-Fe₃O₄)/M/PC indicating that charge transfer occurs via tunneling/hopping. This nature of the curve is typical to resistor-capacitor (R-C) networks, representing a microstructure that contains both dielectric (the capacitor) and conductive regions (the resistor).44 The fitting suggests that as one moves from MoS₂-Fe₃O₄ to rGO-Fe₃O₄ as a filler, the capacitor content is found to decrease from 99% to 89%.

However, the single-layered PC(CNT) exhibits frequencyindependent dc conductivity in the entire measured range. This indicates that the PC(CNT) film consists of well-connected CNT pathways. The resistor aspect of the network is far more dominant than the capacitance aspect, which is considered negligible. And the dominant mechanism of charge transfer is via tunneling. Additionally, the real permittivity plot of PC(CNT), PVDF(rGO-Fe₃O₄)/M/PC, and PVDF(MoS₂-Fe₃O₄)/M/ PC is shown in Fig. S7.†

4.4 Melt rheological response of the individual composite layers and mechanical characterization of the multilayered assembly

Rheology aims at studying the deformation and flow behavior of materials. Rheological measurements give an idea about the filler-filler network, filler-polymer interaction, and the state of dispersion. Polymers and polymer composites show a viscoelastic response to the applied shear.

To understand the individual layers' rheological properties, PC + 3 wt% CNT, PVDF + 10 wt% rGO-Fe₃O₄, and PVDF + 10 wt% MoS₂-Fe₃O₄ solution mixed samples were prepared and compression-molded at 260 °C, 220 °C and 220 °C, respectively, to form individual disks of 25 mm diameter and 1 mm thickness. PC + 3 wt% CNT, PVDF + 10 wt% rGO-Fe₃O₄ and PVDF + 10 wt% MoS₂-Fe₃O₄ solution mixed-compression molded disc samples are represented as (PC + 3 wt% CNT)/S, (PVDF + 10 wt% rGO–Fe $_3$ O $_4$)/S, and (PVDF + 10 wt% MoS $_2$ –Fe $_3$ O $_4$)/S respectively. The melt rheological measurements of PC-based composites were carried out at 260 °C, and PVDF-based composites were tested at 220 °C using a parallel plate setup. The second sweep results in the frequency range of 100 rad s $^{-1}$ to 0.1 rad s $^{-1}$ are compiled in Fig. 9.

Frequency sweep describes the time-dependent response of the sample in a non-destructive deformation range. High frequencies represent fast motion on short timescales, whereas low frequencies simulate slow motion on long timescales or rest. The amplitude is kept constant, while the oscillation frequency is decreased step-wise from one measuring point to the next. With an increase in the angular frequency, G' and G'' increase, while complex viscosity decreases, as shown in Fig. 9. As observed in Fig. 9c, (PC + 3 wt% CNT)/S is orders of magnitude more viscous than neat PC, and this behavior is more

pronounced at low frequencies. The reduction in $|\eta^*|$ with angular frequency in (PC + 3 wt% CNT)/S is a typical behavior exhibited by shear-thinning materials. It is also to be noted that neat PC shows negligible frequency dependence, and the complex viscosity increases with the CNT content, which is in accordance with the existing literature.45 The increase in complex viscosity with the addition of CNTs is primarily due to the increase in storage modulus G', as is seen in Fig. 9a. As compared to G', the increase in the values of G'' is lower. It is observed that the slope of the storage modulus in the terminal region decreases with the addition of CNTs, which conforms to the literature.46 The higher modulus and solid-like plateau behavior at low frequencies can be attributed to the active interactions between CNTs. It indicates that the percolated CNTs led to developing a solid-like network between PC and CNTs.⁴⁷ In (PC + 3 wt% CNT)/S, G' is observed to be higher than

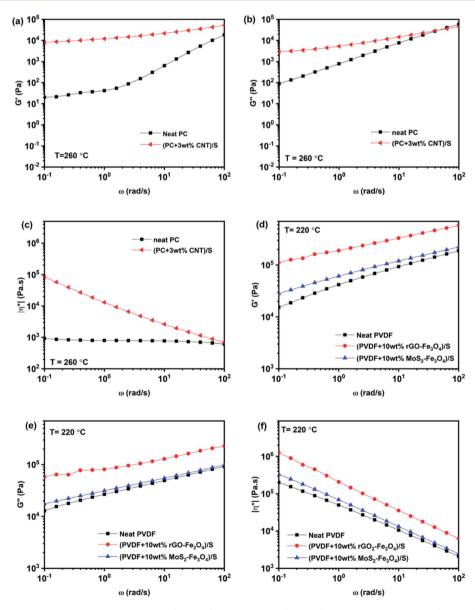


Fig. 9 Melt rheological measurements: storage modulus (a and d), loss modulus (b and e), and complex viscosity (c and f) vs. angular frequency plots of PC and PVDF based composites.

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G'', indicating that the system exhibits a gel-like response with

percolation being prominent in the nanocomposite.46

Similarly, neat PVDF, (PVDF + 10 wt% rGO–Fe₃O₄)/S, and (PVDF + 10 wt% MoS_2 –Fe₃O₄)/S also show shear thinning behavior. However, the enhancement in the rheological parameters (G', G'' and $|\eta^*|$) by filler addition is small in the case of (PVDF + 10 wt% MoS_2 –Fe₃O₄)/S, while it is more prominent in the case of (PVDF + 10 wt% rGO–Fe₃O₄)/S. This can be attributed to the better interaction due to the large sheet-like structure of rGO compared to the structure of MoS_2 , which is also confirmed from the SEM images shown in Fig. 5. A sheet-like structure of rGO holds the ability to lower the percolation threshold and enhance the polymer–filler interaction due to the large interfacial area. It is to be noted that the complex viscosity in neat PVDF exhibits a frequency dependent response, unlike neat PC, which is in accordance with the existing literature.⁴⁸

As explained by rheology, polymers/polymer composites are viscoelastic entities; hence they exhibit an in-phase and out-ofphase response to the applied input strain. To study the viscoelastic response of the multilayered assembly, DMA was performed in tension mode. Thus, the multilayered assembly's mechanical behavior was investigated by applying a sinusoidal tensile deformation to a sample of known geometry and measuring the response. Fig. 10 shows the storage modulus, E' of PVDF(rGO-Fe₃O₄)/M/PC, and PVDF(MoS₂-Fe₃O₄)/M/PC as a function of measuring temperature. At a constant frequency and strain amplitude, the storage modulus at 40 °C for PVDF(rGO-Fe₃O₄)/M/PC and PVDF(MoS₂-Fe₃O₄)/M/PC was found to be 2767 MPa and 2287 MPa, respectively. The storage modulus is larger in PVDF(rGO-Fe₃O₄)/M/PC than PVDF(MoS₂-Fe₃O₄)/M/PC, which can be attributed to the better connectivity and compatibility of the multilayered assembly with rGO due to its large surface area, as compared to MoS₂. This is also in accordance with the rheology analysis, where (PVDF + 10 wt% rGO-Fe₃O₄)/S proved to have a higher storage modulus than (PVDF + 10 wt% MoS₂-Fe₃O₄)/S. Thin films of PVDF(rGO-Fe₃O₄) and PVDF(MoS2-Fe3O4) fabricated using the doctor blade

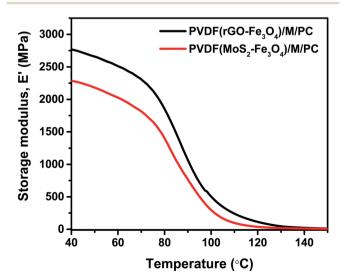


Fig. 10 DMA plot of the storage modulus as a function of temperature.

method had cracks and wear and hence not suitable for mechanical analysis (shown in Fig. S5†).

On the other hand, the PC(CNT) film did not show any visible wear, but it was structurally inferior for DMA analysis. It is to be noted that PC is a brittle polymer, but due to the flexibility and high aspect ratio of CNTs, the incorporation of CNTs in PC is possible. However, the low thickness of the PC(CNT) film is probably the reason for its structural inferiority. It is worth noting that incorporating nanofillers such as rGO-Fe₃O₄ and MoS2-Fe3O4 in PC film casting, especially at such low thicknesses, may not be feasible (extreme brittleness). This is the reason why CNTs were incorporated in PC, and the dielectrically lossy nanofiller (rGO-Fe₃O₄ or MoS₂-Fe₃O₄) was incorporated in PVDF with an interfacial lock using PMMA. Fig. S5† also suggests that a single layer of the PVDF composite film or PC composite film with abundant nanofillers resulted in inferior film quality compared to multilayered films at a similar film thickness. We can conclude that our approach to shifting from single-layered composites to multilayered films is worthful, seeing the mechanical property enhancement in the multilayered assembly compared to the single-layered composite film.

As a control, one can consider comparing the multilayered composite film's storage modulus with the neat commercial polymers'. The storage modulus of the compression-molded samples of commercial PC (same grade) and PVDF (same grade) is reported to be 2440 MPa and ~500 MPa, respectively, at 40 °C. 49,50

4.5 Microwave shielding ability of the multilayered stack

The total shielding effectiveness, SE_{T_i} is defined in terms of the logarithm of the ratio of the incident power (P_I) to the transmitted power (P_T) through the shield material.³⁹

$$SE_{T} = 10 \log \frac{P_{I}}{P_{T}}$$
 (2)

 SE_T is the shield's ability to attenuate EM radiation, and it is expressed in units of dB. Shielding occurs *via* three mechanisms, namely shielding *via* reflection (SE_R), shielding *via* absorption (SE_A), and shielding *via* multiple reflections (SE_{MR}).

$$SE_{T} = SE_{A} + SE_{R} + SE_{MR}$$
 (3)

when SE_T >15 dB or when the shield thickness is greater than the skin depth, SE_{MR} is ignored, and thus SE_T can then be expressed as

$$SE_{T} = SE_{A} + SE_{R} \tag{4}$$

 $SE_A,\,SE_R$ and SE_{MR} are theoretically expressed according to the following equations:

$$SE_{A} = -8.68t \sqrt{\frac{\omega \sigma \mu_{r}}{2}}, SE_{R} = -10 \log \frac{\sigma}{16\omega \varepsilon_{0} \mu_{r}} \text{ and } SE_{MR}$$
$$= 20 \log \left(1 - 10^{\frac{-SE_{A}}{10}}\right)$$
(5)

where σ is the total conductivity, ω is the angular frequency ($\omega=2\pi f$), $\mu_{\rm r}$ corresponds to the relative permeability of the shield material, t is the thickness of the shield, and ε_0 represents the dielectric constant in free space.

A two-port VNA is used to measure the shielding effectiveness experimentally. Since it is difficult to measure the current and voltage at such a high frequency precisely, the instrument measures the scattering parameters (S_{11} , S_{12} , S_{21} , and S_{22}), which in turn is used to calculate SE_T , SE_A and SE_R using the following equations:

$$SE_{T} = 10 \log_{10} \frac{1}{|S_{12}|^{2}} = 10 \log_{10} \frac{1}{|S_{21}|^{2}}$$
 (6)

$$SE_{R} = 10 \log_{10} \frac{1}{\left(1 - |S_{11}|^{2}\right)}$$
 (7)

$$SE_A = 10 \log_{10} \frac{\left(1 - |S_{11}|^2\right)}{|S_{21}|^2} = SE_T - SE_R$$
 (8)

where S_{11} , and S_{22} represent the reflection coefficient and S_{12} , and S_{21} represent the absorption coefficient.

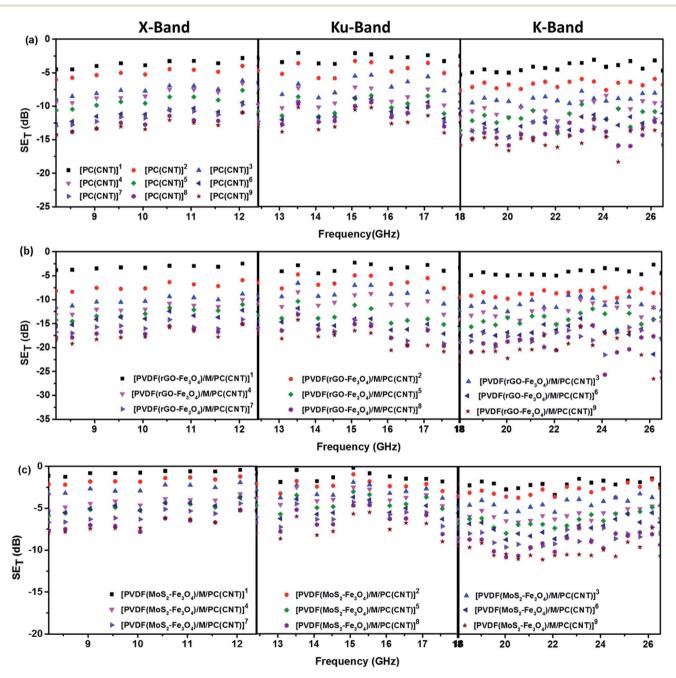
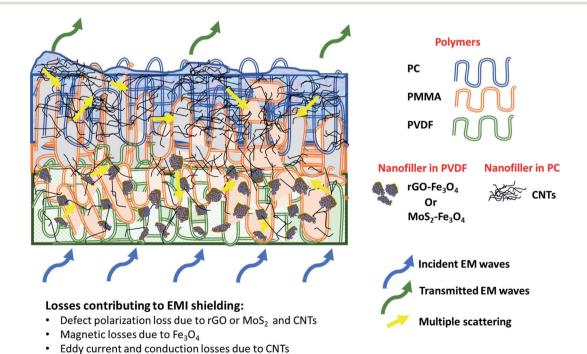


Fig. 11 SE_T vs. frequency for (a) PC(CNT)- set of 9 stacks in an ascending order, (b) PVDF(rGO-Fe₃O₄)/M/PC – set of 9 stacks in an ascending order and (c) PVDF(MoS₂-Fe₃O₄)/M/PC – set of 9 stacks in an ascending order. Note that the legend is common for the plots in one row, *i.e.*, for one type of sample across different frequency bands.

Fig. 11 shows SE_T as a function of frequency in the X (8.2-12.4 GHz), Ku (12.4-18 GHz), and K (18-26.5 GHz) bands. The SE_T values of three different samples, namely PC(CNT), PVDF(rGO-Fe₃O₄)/M/PC, and PVDF(MoS₂-Fe₃O₄)/M/PC, are compiled and presented. The films were sequentially stacked one above the other using an acrylic-based adhesive, and the number of stacked layers is denoted by 'z'. For example, [PVDF(nanofiller name)/M/PC]¹ denotes a multilayered film in which shielding is measured by stacking one multilayered film, [PVDF(nanofiller name)/M/PC]² denotes a multilayered film where shielding is measured by stacking two multilayered films; [PC(CNT)]⁹ denotes single-layered PC(CNT) film where shielding is measured by stacking nine such films, and so on. It is observed that [PVDF(rGO-Fe₃O₄)/M/PC]⁹ shows a SE_T of -26.3 dB, [PVDF(MoS₂-Fe₃O₄)/M/PC]⁹ shows a SE_T of -10.6 dB and $[PC(CNT)]^9$ shows a SE_T of -15.7 dB at 26.5 GHz frequency. Thus, rGO-Fe₃O₄ proved to be a better filler than MoS₂-Fe₃O₄ to maximize the SE_T value. The losses in PVDF(rGO-Fe₃O₄)/M/PC can be attributed to the multilayered assembly's adequate conductivity, the dielectric and magnetic losses due to rGO-Fe₃O₄, and the multiple scattering phenomena. Multiple scattering arises due to the multiple interfaces created by the nanofiller-polymer and nanofiller (type 1)-nanofiller (type 2), as shown in Scheme 4. The shielding in PC(CNT) is mainly due to the high conductivity of the layer owing to the presence of interconnected CNTs, as is obvious from Fig. 8. However, PVDF(MoS₂-Fe₃O₄)/M/PC showed the least SE_T, probably because of the film's low conductivity, which arose from the semiconducting MoS2 obstructing the pathway for charge transfer. Also, rGO is a sheet-like larger structure, compared to

flower-like MoS2. This can be another possible cause of PVDF(rGO-Fe₃O₄)/M/PC exhibiting a higher conductivity (lower percolation threshold) as compared to PVDF(MoS2-Fe3O4)/M/ PC. It is to be noted that conducting fillers (such as CNTs and to some extent rGO) give rise to conduction losses and eddy current losses, which adds to shielding performance. Also, it is observed that the saturation magnetization of MoS2-Fe3O4 is higher. Still, it did not prove to be a superior filler in the desired frequency range, thus confirming that magnetic properties may not have a significant impact on shielding in the chosen frequency range, which is as expected from Snoek's law. Besides, the flower-like morphology of MoS2 creates additional interfaces, which could have added to the shielding performance through interfacial polarization and multiple scattering. However, the poor shielding performance of PVDF(MoS₂-Fe₃O₄)/M/PC only suggests that shielding efficiency is a trade-off between multiple factors. The dielectric losses expected from MoS₂, the interfacial losses, and multiple scattering arising from the flower-like morphology of MoS2 as well as other interfaces are not enough to make PVDF(MoS2-Fe3O4)/M/PC suitable for commercial shielding applications (\sim -20 dB). This also suggests that the choice of fillers and distribution of fillers significantly affect the shielding performance. It is to be noted that the average thickness of the multilayered assembly (for 1 layer) is found to be 53 µm as obtained from the SEM micrograph (shown in Fig. 5). The shielding effectiveness results are also compiled for PVDF(rGO-Fe3O4) and PVDF(MoS₂-Fe₃O₄), and they were found to be -0.85 dB and -0.01 dB at 26.5 GHz, respectively. This confirms that semiconducting/magnetic fillers can generally not show high



Interfacial polarization loss and multiple scattering due to various interfaces (polymer-

Scheme 4 Loss mechanism involved in the multilayered assembly.

nanofiller, nanofiller-nanofiller)

SE_T only by themselves (Fig. S8†). It is to be noted that the thickness of the EMI shielding specimens is similar and hence comparable. As a control experiment, 1 mm disc of PC + 3 wt% CNT + 10 wt% rGO-Fe₃O₄ was prepared by melt mixing, followed by the compression molding technique, and SE_T was found to be approximately -20 dB at 26.5 GHz frequency, which is significantly lower than that of the multilayered stack of 9 layers (SE_T = -26.3 dB @ 480 μ m). The melt mixingcompression molding approach was chosen as a control experiment because a single layered doctor-blade casting with a high nanofiller content gave a structurally inferior film, as already mentioned in Section 4.4. Even the melt mixing approach, with a high nanofiller content, results in processing difficulty, suggesting that a multilayered doctor-blade casting approach can be considered a competent alternative to incorporate a high nanofiller concentration at low thicknesses. The addition of PMMA on its own might not result in an enhanced shielding performance, but this approach allows the addition of a high content of nanofillers at a low thickness (indirectly contributing to enhanced shielding) while maintaining the mechanical performance.

Fig. 12 illustrates the percentage of absorption/reflection for $[PC(CNT)]^9$, $[PVDF(rGO-Fe_3O_4)/M/PC]^9$, and $[PVDF(MoS_2-Fe_3O_4)/M/PC]^9$ at 8.2 and 26.5 GHz frequency. The absorption/reflection plot for one stack is shown in Fig. S9.† The percentage of absorption for $[PC(CNT)]^9$ is found to be 45.5, for $[PVDF(rGO-Fe_3O_4)/M/PC]^9$ is found to be 82.1, and for $[PVDF(MoS_2-Fe_3O_4)/M/PC]^9$ is found to be 82.1 at 26.5 GHz frequency. For the multilayered assemblies of $PVDF(rGO-Fe_3O_4)/M/PC$ and $PVDF(MoS_2-Fe_3O_4)/M/PC$, absorption is the dominant shielding mechanism, irrespective of the frequency in consideration. This can be attributed to the losses from defect dipole polarization of MoS_2 , defect dipole polarization of rGO, magnetic losses from re_3O_4 , multiple interfacial polarizations from re_3O_4 , and re_3O_4 hybrids, and the re_3O_4

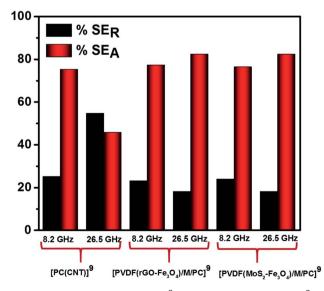


Fig. 12 SE_A and SE_R for $[PC(CNT)]^9$, $[PVDF(rGO-Fe_3O_4)/M/PC]^9$ and $[PVDF(MoS_2-Fe_3O_4)/M/PC]^9$ at 8.2 and 26.5 GHz frequency.

nanoparticle–polymer interface.¹⁵ The loss mechanism is summarized in Scheme 4. In the case of PC(CNT), the reflection percentage fluctuates drastically with thickness as well as frequency, and it is rather difficult to find a correlation based on current data.

Conclusions

A novel approach was developed to fabricate a multilayered assembly of polymeric thin-film composites to enhance EMI shielding properties while maintaining structural stability. rGO–Fe₃O₄ and MoS₂–Fe₃O₄ were synthesized using hydrothermal synthesis, and the doctor blade setup was used to sequentially stack PVDF, PMMA, and PC layers along with fillers (rGO–Fe₃O₄ or MoS₂–Fe₃O₄ (10 wt%) in PVDF and CNTs (3 wt%) in PC). The fabrication approach was chosen such that PMMA acts as a sandwich layer to enhance the interfacial adhesion between the PC/PVDF system. The multilayered assemblies of PVDF–rGO–Fe₃O₄/PMMA/PC–CNT (or PVDF(rGO–Fe₃O₄)/M/PC) and PVDF–MoS₂-Fe₃O₄/PMMA/PC–CNT (or PVDF(MoS₂–Fe₃O₄)/M/PC) were tested for EMI shielding performance in the broadband frequency range (8.2–26.5 GHz), along with mechanical properties.

The SEM micrographs and Raman mapping showed no sharp interface between the layers, proving that PMMA diffused and acted as a stitching layer to lock the PVDF and PC composite layers interfacially. The average thickness of the multilayer film was observed to be $\sim\!53~\mu m$. The mechanical properties of PVDF(rGO–Fe₃O₄)/M/PC and PVDF(MoS₂–Fe₃O₄)/M/PC were measured using DMA. At a constant frequency and strain amplitude, the storage modulus at 40 °C for PVDF(rGO–Fe₃O₄)/M/PC and PVDF(MoS₂–Fe₃O₄)/M/PC was found to 2767 MPa and 2287 MPa, respectively. This value is comparable/higher than the storage modulus of compression-molded samples of neat PC and PVDF, which is reported to be 2440 MPa and $\sim\!500$ MPa respectively at 40 °C^{49,50}

By stacking nine multilayered films (denoted by a superscript in nomenclature) one above the other, reaching an assembly thickness of ca. 480 µm, the total EMI shielding effectiveness (SE_T) at 26.5 GHz frequency was found to be -26.3dB and -10.6 dB for $[PVDF(rGO-Fe_3O_4)/M/PC]^9$ and [PVDF(MoS₂-Fe₃O₄)/M/PC]⁹, respectively. This is significantly higher than the SE_T value of a 1 mm disc of PC + 3 wt% CNT + 10 wt% rGO-Fe₃O₄, obtained from a melt mixing, followed by a compression molding approach (approx. -20 dB for 1 mm thickness). Also, rGO-Fe₃O₄ proved to be a better filler than MoS₂-Fe₃O₄ in enhancing mechanical stability and improving SE_{T} . Shielding *via* absorption is the dominating mechanism for multilayered films, irrespective of the number of stacked layers and the frequency under consideration (8.2-26.5 GHz). The loss mechanism in PVDF(rGO-Fe₃O₄)/M/PC can be attributed to the multilayered assembly's adequate conductivity, the dielectric and magnetic losses due to rGO-Fe₃O₄, and the multiple scattering phenomena. Though $[PC(CNT)]^9$ showed a SE_T of -15.7dB at 26.5 GHz frequency, it was primarily reflection-based shielding, which can be attributed to the high conductivity induced by the presence of the CNT network. However,

PVDF(MoS₂-Fe₃O₄)/M/PC showed the lowest SE_T, probably because of this film's lower conductivity, which arose from the semiconducting nature of MoS2 obstructing the pathway for charge transfer. Despite the dielectric properties of MoS2 and higher saturation magnetization of MoS2-Fe3O4, it showed a lower shielding performance. This suggests that magnetic materials work more effectively in the lower frequency range, as is also proposed by Snoek's limit. Also, large sheet-like rGO in PVDF(rGO-Fe₃O₄)/M/PC made the percolation threshold lower than that of the flower-like MoS2 in PVDF(MoS2-Fe3O4)/M/PC. Our study also deduces that the multilayered strategy can lead to a higher SE_T value as observed when incorporated with the suitable nanofiller.

To the best of our knowledge, this is the first time in the literature that polymer layering has been performed sequentially using the doctor blade setup in EMI shielding applications. Moreover, polymer and polymer-solvent pair selection is unique with respect to their type, and this technique has proven to be efficient in enhancing the SE_T value while maintaining mechanical stability. Besides, this technique may improve the SE_T value, but the generalization is somewhat tricky as the SE_T value is a trade-off between several parameters. But the appropriate choice of fillers and tuning the filler quantity and distribution might help enhance the shielding efficiency while maintaining the structural properties.

Conflicts of interest

There are no conflicts to declare.

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