Tuning the microwave absorption through engineered nanostructures in co-continuous polymer blends

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Tuning the microwave absorption through engineered nanostructures in co-continuous polymer blends

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Keywords: PVDF, ABS, MWNT, EMI shielding

Abstract
Herein, we report tailor-made properties by dispersing nanostructured materials in a co-continuous polymer blend (PVDF/ABS) that is capable of shielding electromagnetic (EM) radiation. To accomplish this, lossy materials were employed like multi-walled carbon nanotubes (MWNTs), and barium titanate (BT), (which exhibit relaxation losses in the microwave frequency domain) and ferrites (like Fe3O4). To improve the state of dispersion, the MWNTs were non-covalently modified using 3,4,9,10-perylenetetracarboxylic dianhydride (PTCD) via π–π stacking, and for effective shielding the MWNTs were conjugated with either BT or Fe3O4 nanoparticles through suitable modifications. The hybrid nanoparticles were selectively localized in the PVDF phase, governed by its polarity, and exhibited excellent microwave attenuation. In order to gain insight into the dielectric and magnetic attributes, the microwave parameters were assessed systematically. Taken together, our results uncover polymer blend as a promising candidate for designing lightweight, thermally stable microwave absorber materials.

Introduction
The extensive use of electronic equipment in today’s world poses a huge challenge as the electromagnetic (EM) waves from nearby devices can interfere with the functioning of others. The electromagnetic interference (EMI) is responsible for the malfunctioning of electrical and electronic systems, military operations, space research activity and, most importantly, human health. Hence, enormous attention has been paid to designing and fabricating materials that can shield EM waves [1–5]. EM waves are the result of electric and magnetic waves propagating perpendicularly to each other. EMI shielding materials with dielectric and magnetic properties interact with the EM waves and hence EM waves are reflected or/and absorbed in the materials. Metals are excellent candidates for shielding materials. The free electrons in metals can easily interact with the EM, thereby, reducing the intensity of the incident waves. However, metals are of high density, prone to corrosion and difficult to process. In this context, lightweight, flexible and chemically inert polymers are suitable candidates for the fabrication of EMI shielding materials [6–14]. However, polymers are insulating in nature, limiting their application in EMI shielding. Carbonaceous materials like carbon nanotubes, graphene oxide, and carbon nanofibers have revolutionized the design of conducting polymer composite (CPC) and blends. A plethora of studies has been carried out for the development of EMI shielding materials with CPC. Multi-walled carbon nanotubes (MWNTs), possessing excellent mechanical and conducting properties are effectively dispersed in an insulating polymer matrix to design conducting composites. The high aspect ratio of the MWNTs aids in the formation of an interconnected network in the polymer matrix. Numerous researchers have reported carbon nanotube (CNT)-polymer composite for the fabrication of EMI shielding materials. For instance, Li and co-workers have designed single-walled carbon nanotube (SWCNT)-epoxy resin composites which can shield EM waves in the frequency range where mobile phone systems operate [15]. The highest shielding efficiency was shown by the composite with 15 wt% SWCNTs reaching – 49 dB at 10 MHz. The electrical properties of SWCNTs are very different to MWNTs [15]. Similar results were observed by Huang et al, in SWCNT/epoxy
composite in the X-band range (8.2–12.4 GHz). A shielding effectiveness of 20–30 dB was achieved with the SWCNTs [2]. The SWCNTs can be metallic or semiconducting, depending on the chirality integers (n,m) and shorter diameters can be exceptionally metallic and exhibit ballistic transport at lower temperature. But MWNT's show zero gap semiconductor, leading to weak semi-metallic behavior [15]. In the Ku-band (12.4–18 GHz) poly(trimethylene terephthalate) (PTT)/MWNTs have been shown to be effective EMI shielding materials. With 10 wt% MWNTs loading, PTT/MWNT composite shows 36–42 dB shielding effectiveness in the Ku-band [16]. Pande and her co-workers fabricated polycarbonate (PC)/MWNT composites for EMI shielding applications by solvent casting and compression molding. With 20 wt% of MWNTs in PC a very high shielding effectiveness of 43 dB was achieved in the X-band [17]. Sachdev et al [18] adopted a dry-state tumble mixing for the dispersion of MWNTs in a polystyrene (PS) matrix. A shielding effectiveness of ca. 23 dB was reported for PS/MWNT (5 wt%) composite. Conducting polymers along with CNTs are another class of excellent EM absorbers. For instance, Makeiff et al [19] fabricated para-toluene sulfonic acid doped polyaniline (PANI)-coated MWNTs and examined the shielding effectiveness in the X-band (8–12 GHz) frequency [19]. Phang and co-workers achieved a high shielding effectiveness of 21.7 dB with PNAI/TiO2/MWNT composites [20]. It is envisaged that when EM waves impinge upon a shield, the electric and magnetic dipoles interact with the materials. Hence, materials with high dielectric constant like BaTiO3, TiO2, SiO2, ZnO or with high magnetic permeability such as γ-Fe2O3, Fe3O4 are ideal candidates for shielding EM radiation [21]. Saini et al prepared PANI-tetragonal BaTiO3 composite which showed a very high shielding effectiveness of 71.5 dB in the Ku-band (12.4–18 GHz) [21]. However, for enhancing the bulk conductivity, MWNTs can be added along with ferroelectric materials like BaTiO3 [22]. High dielectric and magnetic lossy materials can assist in EM absorption. Bayat et al [23] fabricated a conducting carbon nanofiber matrix with Fe3O4 and achieved a total shielding effectiveness of 67.9 dB in the X-band. Hybrid magnetic/dielectric materials are also efficient EMI shielding materials. Yu-Lan Ren and co-workers developed a quaternary composite with graphene, Fe3O4@Fe core/shell nanoparticles and ZnO nanoparticles. They achieved very high band width (7.3 GHz) and 20 dB of shielding with 20 wt% of nanoparticles [24]. Ollan and co-workers [25] demonstrated a core–shell poly (3,4-ethylenedioxy thiophene) (PEDOT) nanocomposite with barium ferrite as an efficient EM absorber, which showed microwave absorption of 22.5 dB. Xia et al [26] synthesized uniform BaTiO3 nano-torus and embedded it in epoxy resin, which showed a maximum reflection loss of 28.38 dB. The hollow space in BaTiO3 contributed to the dissipation and scattering effect of EM waves. The coating of conducting polymer can improve the dielectric or magnetic properties of nanoparticles. Saini et al showed the effect of coating polyaniline onto BaTiO3 and Fe3O4 to enhance the EMI shielding performance [27]. Wei et al [28] fabricated ternary-hybrid membranes comprising Fe3O4/polyaniline nanocomposites and a polyzomethine/polyetheretherketone matrix as significant microwave absorbing materials showing a maximum reflection loss of about 18 dB at 14 GHz [28]. Wang et al reported that magnetic γ-Fe2O3, Fe3O4 and Fe incorporated into ordered mesoporous carbon can show a maximum reflection loss of 32 dB [29]. Pawar and co-workers selectively localized hybrid nanoparticle MWNT-g-Fe3O4 in polycarbonate (PC) in PC/SAN [poly(styrene-co-acrylonitrile)] blends. They followed a two-step mixing protocol to selectively localize MWNTs and modified MWNTs in the PC phase and measured the EMI shielding performance in the X- and Kα band. A total shielding effectiveness (SE) of 32.5 dB was observed (at 18 GHz) for MWNTs (3 wt%)-g-Fe3O4 (3 vol%) in PC/SAN blends [30].

Herein, we have adopted a unique strategy to design lightweight, flexible materials with tunable microwave absorption. To accomplish this, a classical immiscible blend (PVDF/ABS, 50/50 wt/wt) was selected as a model system and various engineered nanostructures were designed targeting the key properties like electrical conductivity, relaxation losses at GHz frequency and magnetic hysteresis losses. The MWNTs were melt-blended to achieve the desired conductivity. The selective localization and surface modification of the MWNTs by π–π stacking further enhanced the conductivity in the blend. Although the conductivity is essential for the EMI shielding application, it is observed that highly conductive materials usually shield by reflection. In order to enhance the shielding by absorption, magnetic nanoparticles or highly dielectric particles were added along with the MWNTs and, more importantly, were chemically conjugated with the MWNTs so as to retain the dispersion state of the hybrid nanoparticles and improve the shielding ability. This strategy led to materials with tunable microwave absorption.

Experimental

Materials

PVDF (Kynar-761, with Mw of 440 000 g mol−1) was kindly provided by Arkema. ABS (Absolac 120, with typical composition consisting of acrylonitrile: 24 wt% rubber content: 16.5 wt% and styrene: 59.5 wt%) was procured from Styrolution. 3,4,9,10-perylenetetracarboxylic dianhydride (PTCD), 3-aminopropyltriethoxysilane...
AMINE (-NH₂) FUNCTIONALIZATION OF BT/Fe₃O₄

Amine functionalization was carried out on three nanoparticles (BT/Fe₃O₄). The same protocol was followed for all three nanoparticles. In the first step, the hydroxyl group (-OH) was introduced on the particles by H₂O₂ treatment. The nanoparticles were taken in the required volume of H₂O₂ and dispersed with the aid of sonication. The mixture was then refluxed at 104 °C for 6 h. After completion, the nanoparticles were washed with distilled water and the powder was dried at 80 °C. These –OH functionalized nanoparticles were then treated with APTS using toluene as a solvent. After the completion of 24 h the mixture was washed with toluene and dried under vacuum. Thus, amine-functionalized nanoparticles were made. The schematic of this step is shown in scheme 1 (a).

NON-COVALENT FUNCTIONALIZATION OF MWNTs

PTCD was wrapped onto the MWNTs by non-covalent interaction (scheme 1(b)). The required amount of PTCD was taken in DMF and sonicated for 30 min. Separately, the MWNTs were also taken in DMF and sonication was performed. Then, PTCD and the MWNTs were mixed and stirred for 12 h for non-covalent functionalization of the MWNTs. PTCD was absorbed and non-covalently interacted with the MWNTs. The red-colored PTCD-MWNT conjugate was filtered and dried under vacuum.

SYNTHESIS OF BT/Fe₃O₄–PTCD-MWNTs

Amine-terminated nanoparticles were reacted with the PTCD-MWNTs by refluxing the mixture of the PTCD-MWNTs and the nanoparticles in the common solvent toluene (scheme 1(c)). The mixture was filtered and dried under vacuum.

BLEND PREPARATION

A 50/50 (wt/wt) composition of PVDF/ABS blend with different nanoparticles (BT/Fe₃O₄–PTCD-MWNTs) and PTCD-MWNTs was prepared by melt blending using a MiniLab II HAAKE extruder CTW5 (7 cc) at 230 °C with a rotational speed of 60 rpm for 20 min. The high-temperature melt blending was carried out under N₂ atmosphere to avoid polymer degradation. The extruded sample was hot pressed to make a toroidal sample for EMI shielding efficiency measurement. The effective weight of BT and Fe₃O₄ was 5 wt% and that of the PTCD-MWNTs was 2 wt%.
Morphological analyses for various blends were visualized using an ULTRA 55 scanning electron microscope (SEM) using an energy-dispersive (EDS) detector. The magnetic response was measured on a vibrating sample magnetometer (VSM). An x-ray diffraction (XRD) pattern was obtained using PANalytical X’pert Pro (Cu Kα, λ = 0.154 nm). Conductivity was measured on an Alpha-N analyzer (Novontral) in a broad frequency range of 10⁶–10⁸ Hz. Flow characteristics of the blend were measured on a discovery hybrid rheometer (DHR-3) from TA-instruments under N₂ atmosphere. A 25 mm parallel plate geometry was used. The extruded samples were vacuum dried at 80 °C to minimize the effect of moisture. All the measurements were carried out within the linear viscoelastic region determined a priori. The EMI shielding efficiency was measured on the toroidal sample using an Amritsu MS4642A Vector network Analyzer (VNA) connected to a coax (Damaskos M07T) setup. Toroidal samples were made by hot pressing the melt-extruded samples and S(S₁₁, S₂₁, S₁₂, S₂₂) parameters were measured in the frequency range 2–18 GHz. The 3D structure of the polymer blend was visualized by Xradia versa XRM 500. 50/50 PVDF/ABS with the PTCD-MWNTs etched by CHCl₃ for 3 d for the dissolution of the ABS phase. The dried ABS-etched strand was subjected to x-ray, and the 3D images were reconstructed to form 2D images.

Results and discussion

Synthesis and characterization of hybrid nanoparticles

Inorganic nanoparticles (BT/Fe₃O₄) are highly hydrophilic and, hence, often agglomerate in the host polymeric matrix. To enhance the interaction with the host, amine-functional moieties were harnessed onto these nanoparticles. This is achieved in a two-step process as shown in scheme 1(a). In the first step, the nanoparticles were treated with H₂O₂ to impart hydroxyl groups (-OH). In the second step, the –OH groups were reacted with APTS to synthesize the amine-functionalized BT or Fe₃O₄ nanoparticles. The dispersion of the MWNTs in a given polymeric host is limited by the strong van der Waals’ interaction between the nanotubes. In this context, non-covalent functionalization of the MWNTs is an effective strategy to overcome this van der Waals’ interaction and disperse them efficiently. In this context, the strong affinity of perylene moieties with MWNTs via π–π interaction has been well established in our earlier work [31]. The functionalization of MWNTs with PTCD is described in scheme 1(b) and the details of the synthesis protocol are explained in the experimental section. This mild non-covalent functionalization preserves the integrity of the MWNTs and, hence, retains its effective charge transport. The conjugation of PTCD with the MWNTs is confirmed by the UV–vis spectroscopy as shown in figure 1. Strong absorption peaks at 485 and 520 nm are observed, indicating physically absorbed perylene moieties on the MWNTs. PTCD shows three absorption peaks in the range of 450–500 nm and a shoulder at 520 nm, which are attributed to the 0-0, 0-1, 0-2 and 0-3 electronic transitions. The π–π interaction between the PTCD and MWNTs slightly red-shifted the above-mentioned peaks. The amine functionalization of the nanoparticles and conjugation to PTCD-MWNTs can be assessed by Fourier transform infrared spectroscopy (FTIR) (figure 2(a)). As for example, in the case of BT nanoparticles, the peaks centered at
The peaks at 1636 cm$^{-1}$ and a shoulder at 1566 cm$^{-1}$ are attributed to amide I and II vibrations, respectively. The anhydride and amine groups can react resulting in the conjugation of PTCD-modified MWNTs and NH$_2$-BT or NH$_2$-Fe$_3$O$_4$ as illustrated in scheme 1(c). The functionalized nanoparticles were further characterized by XRD (figures 2(b) and (c)). For BT, the peaks at 2$\theta$ 22.48°, 31.85°, 39.2°, 45.29°, 51.034°, 56.308°, 66.2°, 70.66° corresponding to (100), (101), (111), (002), (201), (112), (202), (212), respectively, are observed and the dominant peaks at 2$\theta$ 30.09°, 35.54°, 43.15°, 53.43°, 57.01°, and 62.16° corresponding to (220), (311), (400), (422), (511), and (440), respectively, are evident for Fe$_3$O$_4$. The diffraction pattern of the modified nanoparticles suggests that the crystal structures are not altered in the final conjugated molecular entity. The magnetic properties of Fe$_3$O$_4$ were studied by VSM at room temperature and the magnetic hysteresis loop is shown in figure 3. The saturation magnetization ($M_s$), remnant magnetization ($M_r$) and coercivity ($H_c$) of the nanoparticles are listed in table 1. The variation of the dielectric constant of the BT nanoparticles is shown in figure 4(a). The BT nanoparticles adopt cubic structure (para-electric) at higher temperature and a tetragonal perovskite type of structure at room temperature. The reversible phase transition is characterized by Curie temperature as depicted in figure 4(b).

Melt rheology

The flow characteristics of the blend were studied by melt rheology. Figures 5(a) and (b) show the viscoelastic properties of different PVDF/ABS blends filled with various nanoparticles. The complex viscosity of PVDF is higher than ABS and the viscoelastic properties of the blends are in between the components. As, shown in figure 5(a), the complex viscosity of the MWNT-filled 50/50 PVDF/ABS is much higher than the neat blend, particularly at lower frequency, suggesting the formation of a pseudo-solid-like structure facilitated by the MWNT network. In the presence of PTCD, the viscosity increases significantly, suggesting more exfoliation of the MWNT network, resulting in a finer mesh-like structure. Similar behavior was observed in our earlier work in the presence of pyrenebutyric acid (PBA) and was attributed to the similar $\pi-\pi$ type of interaction between the ligand and MWNTs [32]. The pseudo-solid-like behavior is also manifested from the secondary plateau.
observed in the blends (figure 5(b)). This behavior is more pronounced in the case of the blend filled with inorganic nanoparticles like BT, Fe$_3$O$_4$. While designing the materials with high EMI shielding performance it is important to assess the mechanical response of the blend. As at higher loading, the poor dispersion of the nanoparticles often results in poor interfacial adhesion, resulting in mechanical failure. Figure 5(b) shows the dynamic storage modulus for different blends at 230 °C. It is evident that the storage modulus is enhanced with the addition of MWNTs and further enhanced due to exfoliated MWNTs aided by PTCD. Moreover, the addition of BT/Fe$_3$O$_4$ also manifests in the increment in storage modulus which can be attributed to the network-like structure of the MWNTs. The other information that can be gathered from these two measurements is that the addition of inorganic nanoparticles does not impede the interconnected network of the MWNTs, which results in a higher storage modulus in the melt.

**Morphology**

The final morphology of immiscible polymer blends plays a key role in deciding the properties, particularly the electrical properties, where high conductivity is desired for designing EMI shielding materials. Depending upon
the polarity, and the viscosity ratio of individual polymers, different kinds of morphology are observed. 50/50 PVDF/ABS displays co-continuous morphology as shown in figure 6(a). With the addition of MWNTs and other nanoparticles the continuity of the filled phase is retained, which is shown in figures 6(b)–(d). While the SEM provides a 2D image, it is often difficult to comment on the overall continuity of the phases in 3D and, in addition, can often result in misleading morphologies, particularly in the co-continuous type. Hence, the 50/50 blends with PTCD-MWNTs were studied in more detail by x-ray micro-computed tomography. The ABS phase was removed by CHCl₃. The x-rays are attenuated by the sample and collected at the detector. The 2D image, as shown in figure 7(a), has been derived from a larger number of 2D slices and was also used to reconstruct a 3D image. Figure 7(c) shows the interconnected 3D network for 50/50 PVDF/ABS images filled with PTCD-
MWNTs. This kind of structure is excellent for the development of a conducting network by MWNTs and is discussed in a subsequent section.

The preferential localization of MWNTs can be predicted, a priori, from classical thermodynamics. From the knowledge of surface free energy, the wetting coefficient can be evaluated using Young’s equation, as given by

$$\omega_{AB} = \frac{\gamma_{p-B} - \gamma_{p-A}}{\gamma_{AB}}$$

where, p, A and B indicate MWNTs, PVDF and ABS, respectively. $\gamma_{AB}$, $\gamma_{p-A}$ and $\gamma_{p-B}$ are the interfacial tensions between PVDF/ABS, MWNTs/PVDF and MWNTs/ABS, respectively. For $\omega_{AB} > 1$, the MWNTs will preferentially localize in A (i.e. PVDF phase) and for $\omega_{AB} < -1$, the MWNTs will prefer the B phase. However, for $-1 < \omega_{AB} < 1$, the MWNTs will localize at the interface. For the determination of the wetting coefficient, the interfacial tension of the individual entities can be calculated using Owens—Wendt—Rebel—Kaelble (OWRK) and Wu’s equation. For the PVDF, ABS system, OWRK can be expressed as

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d} - 2\sqrt{\gamma_1^p \gamma_2^p}$$

where, $\gamma^d$ and $\gamma^p$ are the dispersive and polar components of the total surface free energy. The surface free energy of PVDF, ABS and the MWNTs is given in table 2 [32, 33]. From the equation above, the wetting coefficient $\omega_{AB}$ is estimated to be 3.55, which suggests that PVDF is the preferred phase for the MWNTs [34]. This thermodynamic prediction is also supported by the SEM image as shown in figure 8(a), as MWNTs are found to be selectively localized in the PVDF phase.

Figure 7. X-ray micro-computed tomography of 50/50 PVDF/ABS blend with 2 wt% PTCD-MWNTs. (a) 2D images, (b) orthogonal slices and (c) 3D reconstituted image.
MWNTs along with the inorganic nanoparticles (BT, Fe₃O₄) are also localized in the PVDF phase. This is reflected from the EDS spectra as shown in figures 8(b) and (c). SEM morphology and EDS spectra were collected on the CHCl₃ etched porous structure. Since, CHCl₃ is a good solvent for ABS, it is etched out and PVDF is retained. From the selective dissolution experiments, as shown in figure 8(d), we can conclude the preferential localization of nanoparticles in the PVDF phase. The uneven distribution and preferential localization of the nanoparticles in PVDF are also supported by the melting and crystallization behavior of PVDF in the respective blends. Figures 8(e) and (f) show the DSC thermograms indicating the change in crystallization behavior of PVDF in the blends. The uneven distribution and preferential localization of the nanoparticles in PVDF are also supported by the melting and crystallization behavior of PVDF in the respective blends. Figures 8(e) and (f) show the DSC thermograms indicating the change in crystallization behavior of PVDF in the respective blends.
and melting temperature. The crystallization temperature of neat PVDF is 137 °C. This has risen to 141 °C for the nanoparticle-filled PVDF/ABS blend. This clearly suggests the presence of nanoparticles acting as nucleating agents in the PVDF phase.

Thermal stability for the EMI shielding materials is another important criterion for high-end applications such as in building aircraft materials. Hence, TGA was carried out for the blends. Figure 8(g) shows that the PVDF/ABS blend is thermally stable till 400 °C and the inclusion of different nanoparticles retains the thermal stability.

Electrical conductivity and EMI shielding

An interconnected network is the primary requirement for the transport of mobile charges \([35-39]\). The 50/50 PVDF/ABS blend shows interconnected co-continuous structure that can facilitate charge transport through the network-like structure of MWNTs localized in the continuous PVDF phase. Non-covalent modification of MWNTs usually reduces the percolation threshold as it retains the integrity of the MWNTs and facilitates superior charge transport. PTCD is known to wrap MWNTs via \(\pi-\pi\) interactions and, hence, facilitates the exfoliation of the MWNTs in the blend \([40]\). This is reflected in the enhanced conductivity in the blends with PTCD-MWNTs (see figure 9). However, with the inclusion of inorganic nanoparticles (BT/Fe\(_3\)O\(_4\)) there is a drastic decrease in the conductivity, as the insulating nanoparticles perturb the interconnected network of MWNTs and also act as capacitors. The mismatch in conductivity and dielectric properties among the different components is desired for designing EMI shielding materials \([21, 41]\). To gain insight into the mechanism of

![Figure 8. (Continued.)](image)
charge transport, the power-law equation \[ \sigma_{\text{ac}}(\omega) = \sigma_{\text{dc}} + A\omega^n \] can be used, which is given as

where, \( \sigma_{\text{ac}} \) and \( \sigma_{\text{dc}} \) are AC and DC electrical conductivity and \( \omega \) is angular frequency. ‘\( n \)’ is the exponent, with a value range from 0–1 and is a function of temperature and frequency. From the power-law fit, the value of ‘\( n \)’ for 50/50 PVDF/ABS with PTCD-MWNTs emerges as \(~0.80\), indicating the charge transport mechanism by
hopping. For blends filled with inorganic nanoparticles, the ‘n’ becomes ~0.9, suggesting the charge transport mechanism is dominated by hopping.

EMI shielding properties

EM waves interact with the conducting/magnetic phases and get shielded by three different mechanisms \([6, 31, 43, 44]\). EM waves either get reflected back from the shield \((SE_R)\) if the skin is highly conducting and/or get absorbed \((SE_A)\) by interacting with the electrical/magnetic dipoles and/or get reflected inside the shield through multiple reflection \((SE_{MR})\), thereby reducing the power of the incident waves. This can be expressed mathematically as

\[
SE_T = SE_R + SE_A + SE_{MR}
\]

However, \(SE_{MR}\) can be neglected if the \(SE_T\) is more than 15 dB. Hence, the equation (1) can be rewritten as

\[
SE_T = SE_R + SE_A
\]

The shielding components are directly measured from the scattering parameter \((S_{11} \text{ and } S_{12})\) produced by the vector network analyzer (VNA).

\[
SE_R = 10 \log_{10} \frac{1}{1 - |S_{11}|^2}
\]

\[
SE_A = 10 \log_{10} \frac{1 - |S_{11}|^2}{|S_{12}|^2}
\]

and

\[
SE_T = SE_R + SE_A = 10 \log_{10} \frac{1}{|S_{12}|^2}
\]
where, $S_{12}$ is the reverse transmission coefficient and $S_{21}$ is the forward transmission coefficient, and $S_{11}$ is the forward reflection coefficient. Figures 10(a) and (b) show the total shielding effectiveness of different blends and the SE values are listed in table 3. The introduction of only Fe$_3$O$_4$ and BT enhances the shielding effectiveness; however significant enhancement is achieved by conjugating Fe$_3$O$_4$ and BT nanoparticles with PTCD-MWNTs (see figure 10(b)). Our results have been compared with the available literature on BT and ferrites and are listed in table 4. An important shielding parameter is skin depth. This is the measure of the depth penetrated by the EM wave when the electric field drops to the 1/e, which corresponds to the reduction in the energy by 33% from the incident wave. Skin depth ($\delta$) can be expressed as

$$\delta = \frac{1}{\sqrt{\pi f \mu \sigma}}$$  \hspace{1cm} (6)
Table 4. Comparing EMI shielding efficiency of various literature involving carbonaceous nanoparticles, ferrites and barium titanate particles.

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>Matrix</th>
<th>Fraction</th>
<th>$SE_T$ (dB)</th>
<th>RL (dB)</th>
<th>Frequency range studied (GHz)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$/Al$_2$O$_3$/CNCs</td>
<td>paraffin</td>
<td>25 wt%</td>
<td>—</td>
<td>−49.3</td>
<td>2–18</td>
<td>[52]</td>
</tr>
<tr>
<td>SiO$_2$ nanopowders</td>
<td>short carbon fiber</td>
<td>80 wt%</td>
<td>−12.4</td>
<td>—</td>
<td>8.2–12.8</td>
<td>[53]</td>
</tr>
<tr>
<td>MWNTs and carbonyl iron (CI)</td>
<td>epoxy-silicone</td>
<td>0.5 vol% MWNT and 50 vol% CI particles</td>
<td>—</td>
<td>−16.9</td>
<td>2–18</td>
<td>[54]</td>
</tr>
<tr>
<td>Graphene</td>
<td>Fe$_3$O$_4$</td>
<td>—</td>
<td>—</td>
<td>−30.1</td>
<td>2–18</td>
<td>[55]</td>
</tr>
<tr>
<td>MWNTs, BT-GO</td>
<td>PVDF</td>
<td>3 wt%</td>
<td>−25</td>
<td>—</td>
<td>2–18</td>
<td>[56]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$/carbon core/shell nanorods</td>
<td>wax</td>
<td>—</td>
<td>—</td>
<td>−27.9</td>
<td>2–18</td>
<td>[57]</td>
</tr>
<tr>
<td>graphene@Fe$_3$O$_4$</td>
<td>polyetherimide</td>
<td>10 wt%</td>
<td>—</td>
<td>−18.2</td>
<td>—</td>
<td>8–12</td>
</tr>
<tr>
<td>Ag to PVDF-20 vol% BT composite</td>
<td>PVDF</td>
<td>10 vol% of Ag to PVDF-20 vol% BT composite</td>
<td>−26</td>
<td>—</td>
<td>8–12</td>
<td>[59]</td>
</tr>
<tr>
<td>Fe/Fe$_3$O$_4$</td>
<td>Polyurethane</td>
<td>71 wt%</td>
<td>—</td>
<td>−20</td>
<td>2–18</td>
<td>[60]</td>
</tr>
<tr>
<td>BT, Fe$_3$O$_4$</td>
<td>Polyaniline</td>
<td>—</td>
<td>−16.8, −19.4</td>
<td>—</td>
<td>12.4–18.0</td>
<td>[27]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$-PTCD-MWNTs</td>
<td>PVDF/ABS</td>
<td>Fe$_3$O$_4$(5 wt%)-PTCD-MWNTs (2 wt%)</td>
<td>−26.5</td>
<td>—</td>
<td>2–18</td>
<td>This work</td>
</tr>
<tr>
<td>BT-PTCD-MWNTs</td>
<td>PVDF/ABS</td>
<td>BT(5 wt%)-PTCD-MWNTs (2 wt%)</td>
<td>−27.5</td>
<td>—</td>
<td>2–18</td>
<td>This work</td>
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</tbody>
</table>
where \( f \) is the frequency in Hz, \( \mu \) is the permeability and \( \sigma \) is the conductivity of the blend. The absorption part of the total shielding effectiveness can also be related to the skin depth as

\[
SE_A = -8.68 \left( \frac{t}{\delta} \right)
\]

where \( t \) is the thickness of the sample placed in the VNA. For the attenuation of the EM wave, the primary requirement is that the materials should be conducting. While the conductivity can be achieved by the MWNTs, the van der Waals’ forces between the MWNTs result in agglomeration and, hence, reduces the effective aspect ratio. Hence, in this study, the non-covalent interaction between PTCD and MWNTs is exploited for better dispersion and connectivity between the MWNTs. As can be seen in figure 9, we observe a significant increase in conductivity with PTCD-assisted dispersion of the MWNTs. As reported by Biswas et al., the SE\( _T \) increases with increasing the fraction of MWNTs in the co-continuous blends and reflects is the dominant mechanism [45]. However, heterogeneous particles with dielectric or magnetic properties shield through the absorption mechanism (figures 10(c) and (d)). When the EM wave propagates through the blend, the dielectric and magnetic dipole interact with the nanoparticles causing local field variation, which contributes to energy absorption [46–48]. From EMI shielding theory, the absorption and reflection components can be expressed as,

\[
SE_A = 8.68 \left( \frac{t}{\delta} \right) \mu \] and \( SE_R = 39.5 + 10 \log(\sigma/2\pi f \mu) \),

where \( \mu = \mu_0 \mu_i \) and \( \sigma = 2\pi f \sigma_0 \epsilon'' \). Hence, the higher absorption will be contributed by the nanoparticles with high \( \mu_i \) and \( \epsilon'' \) where \( \mu_i = \mu'' - j\mu' \) and \( \epsilon'' = \epsilon'' - j\epsilon' \) [49, 50]. From figures 10(e) and (f), it is clear that after the addition of nanoparticles an enhancement is observed in \( \mu_i \) and \( \epsilon'' \) values for the Fe\(_3\)O\(_4\)-PTCD-MWNTs and BT-PTCD-MWNTs, respectively, which controls the shielding mechanism.

In order to study shielding mechanism, shield thickness is another essential parameter [51]. We have evaluated the total shielding effectiveness of various blends with different thickness to analyze the effect of shield thickness. It is clear from figure 10(g) that the shielding effectiveness scales with shield thickness, which is consistent in all the blend structures designed here, irrespective of the type of nanoparticles. However, the BT-containing blend represented the highest shielding effectiveness at any given thickness even for 1 mm thickness. This observation clearly suggests the key role of BT for shielding EM waves.

**Conclusions**

In this work, we have clearly demonstrated that by the ordered arrangement of nanoparticles possessing different characteristics (electrical/magnetic dipoles), excellent microwave absorbers can be designed using co-continuous blends. PTCD-modified MWNTs improved the dispersion and connectivity between the MWNTs via \( \pi-\pi \) stacking and which further resulted in enhanced electrical conductivity through preferential localization in the blend structure. While MWNTs can shield EM radiation only by reflection; by conjugating them with a dielectric (like BT) or magnetic nanoparticles (like ferrites), the microwave absorption can be tailored. Interestingly, this strategy significantly enhanced the shielding effectiveness in the blends and shielded the incoming radiation, mostly by absorption. Such materials can thus be explored further for EMI shielding applications.

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**References**

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