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Electromagnetic interference shielding of carbon nanotube/ethylene vinyl acetate composites

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Abstract Single-walled carbon nanotube (SWCNT) and ethylene vinyl acetate (EVA) composites were synthesized in an internal mixer by melt mixing. The electrical conductivity as well as electromagnetic interference (EMI) shielding effectiveness (SE) over the X-band (8–12 GHz) and microwave (200–2,000 MHz) frequency ranges of these composites were investigated. It was observed that the electrical conductivity of composites increases with increasing SWCNT loading. A percolation threshold of about 3.5 wt.% was obtained and the electrical conductivity of EVA was increased by ten orders of magnitude, from 10^{-14} to $10^{-4}\,\Omega^{-1}\,cm^{-1}$. The effect of sample thickness on SE was investigated. The correlation between SE and conductivity of the composites is discussed. The experimental data showed that the SE of the composites containing higher carbon nanotube loadings (above 10 wt.%) could be used as an EMI shielding material and lower SWCNT loadings could be used for the dissipation of electrostatic charge.

Introduction

Owing to their low cost, light weight, design flexibility, corrosion resistance and ease of mass production, polymer-based conductive composites are finding increasing use in various advanced technological applications such as energy storage, antistatic packaging, electro-optical devices, welding of plastics, and electromagnetic interference (EMI) shielding [1–5]. The EMI remains a technical challenge in the proper functioning of numerous electrical and electronic devices; EMI tends to degrade the interception of signals thus affecting the performance of these equipments adversely. So, it is quite important to shield these electrical and electronic devices from EMI frequency spectrum to ensure their proper working. Conventionally, metal sheeting is used for this purpose, but the seams commonly encountered in metal sheets tend to cause leakage of the radiation and diminish the effectiveness of the shield. Polymer-matrix composites containing conductive fillers are quite attractive as an EMI shielding material because these seams are significantly reduced or are completely eliminated [6, 7]. Besides this fact, polymers carry the usual advantage of ease of processibility and corrosion resistance over the metals. Polymer composites containing conductive polymers such as polyaniline or polypyrole as EMI shields have been reported in the literature [8, 9], but their mechanical strength is often very poor. The use of carbon materials as fillers in polymer composites for EMI shielding has been advocated [10–12], as they can enhance the mechanical properties of these composites considerably.

Carbon nanotubes have received great attention since their discovery by Iijima in 1991 [13]. The intrinsic superconductivity [14], field emission behavior [15], potential as molecular quantum wires [16], ability to store hydrogen [17], unusually high thermal conductivity [18], potential use as sensor for gas detection [19], and the potential for biomolecular recognition [20] along with biocompatibility have been reported for this class of materials. However, it is the combination of exceptional

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conductivity (electrical and thermal), low density, and mechanical properties of carbon nanotubes that have drawn attention toward their use in filled composites [19]. As the filler in polymer matrix materials, single-walled carbon nanotubes (SWCNTs) represent an extraordinary opportunity for the development of new products with many desirable physical properties. Significant property modifications can be obtained with a relatively low addition of SWCNT to the polymers as compared to carbon black or carbon fiber materials. In addition, SWCNTs possess diverse electrical properties, thermal/electrical conductivity comparable with metallic conductors, very high aspect ratio (length to diameter ratio), and better thermal and air stability, which make them an ideal candidate for high strength and low weight EMI shielding, printable circuit wiring, and electrostatic dissipation applications [1, 20–24]. To the best of our knowledge, studies on the effectiveness of EMI shielding in a broad frequency range of SWCNT/polymer composites through melt mixing technique have been quite limited. This method provides composites with higher concentration of carbon nanotube that result in better mechanical properties. In this paper, we report the results of electrical conductivity and EMI shielding effectiveness (SE) of different SWCNT/ethylene vinyl acetate (EVA) composites. The EMI shielding over the microwave range of 200–2,000 MHz and X-band frequency range of 8–12 GHz is discussed. The effect of sample thickness on EMI SE was also investigated.

Experimental details

Ethylene vinyl acetate copolymer (PILENE 2806, 28% vinyl acetate content, melt flow index 6 g/10 min, and density 0.95 g cc^{-1}) was used as a matrix while dicumyl peroxide, obtained from Merck, was used as the curing agent for this study. The purified high-pressure carbon monoxide method (HiPCO) EMI shielding grade SWCNTs with an average diameter (D) of 0.9–2 nm and a length (L) of 350–400 nm (aspect ratio, L/D ratio $\sim$200–400) (Carbon Nanotechnologies Inc.) was used. SWCNT/EVA composites with weight fractions 1–30 wt.% of SWCNT were prepared in Brabander Plasticoder (PLE330) at 100 °C under the identical conditions of processing time (time of mixing = 5 min; rotor speed = 20 rpm and same sequence of mixing) to avoid the effect of processing conditions on electrical conductivity and thereby on the EMI SE. The mixes were cured on an electrically heated press at 160 °C for specific time of 11 min, as obtained from rheographs (Monsanto Rheometer R100S).

The JEOL 8900 scanning electron microscopy (SEM) was employed to study the morphology of dispersion of SWCNT on the facture surface of the SWCNT/EVA composites. The detailed method of electrical conductivity and EMI shielding measurement was reported elsewhere [6, 11]. A programmable DC voltage/current generator (Advantest TR6142), a digital precision voltmeter (Schlunberger UK 7071), and a Hewlett Packard (Model 16008A) resistivity cell coupled with a Hewlett Packard HP 4329A resistance meter were used to measure the electrical conductivity. A scalar network analyzer (HP 8753 C/E, Hewlett Packard) coupled with a sweep oscillator (HP 8350B, Hewlett Packard), a power splitter, and a detector was used to measure the EMI SE. All these instruments were connected to a test chamber. The SE was measured in the two frequency ranges: 100–2,000 MHz frequency range using coaxial cable line and 8–12 GHz frequency range using an X-band waveguide as a sample holder. Samples having thicknesses of 1.5, 2.5, and 3.5 mm were used for measurement purpose. The EMI shielding measurement was carried out for each sample by continuously sweeping the frequency ranges of 100–2,000 and 8–12 GHz. The reported samples represent the mean of five to seven samples whereas the standard deviation relative to the mean is less than 10%.

Results and discussion

The conductivity of HiPCO SWCNT is about 5.1×10^3 s cm^{-1} [25]. Figure 1 shows the relationship between the conductivity and the weight percentage of SWCNTs in the SWCNT/EVA composites. This figure clearly shows that the conductivity property of the composites was improved by increasing SWCNT loading. At a very low level of SWCNT, the conductivity of the composites is

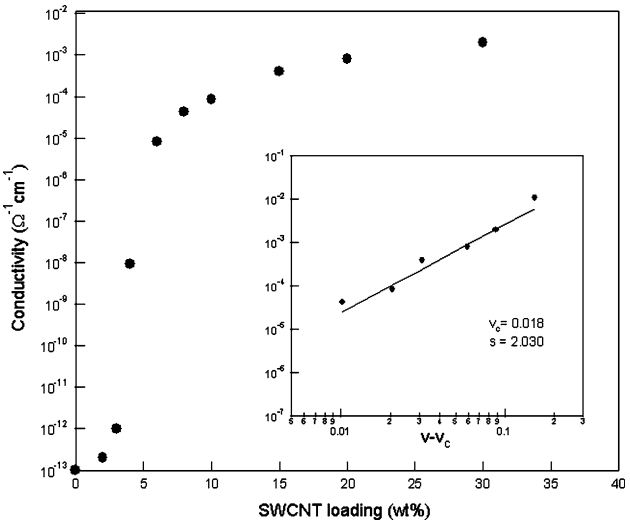

Fig. 1 The conductivity of EVA filled with various SWCNT loadings. Inset shows a log–log plot of the conductivity as a function of $v - v_c$. The best-fit line determining s is also shown

nearly equal to that of the base polymer, about $\sim 10^{-13}$ Ω^{-1} cm^{-1}, whereas with an increase of SWCNT level (>3.5 wt.%), the conductivity gradually increases. However, the composites containing 4 wt.% SWCNTs show a remarkable increase in conductivity: in the order of 10^{-5} Ω^{-1} cm^{-1}. The stepwise change in the conductivity of SWCNT/EVA composites is a result of the formation of an interconnected network of SWCNTs. In other words, at a low level of weight percentage of carbon nanotubes (<2 wt.%), SWCNTs embedded in the polymer matrix are isolated from each other by the insulating polymer surrounding them. Hence, the SWCNTs do not contribute significantly toward the overall conductivity of SWCNT/EVA composites, and resulting conductivity of the composites is almost same as the constituent polymer phase (EVA). But at a certain level of SWCNT, between 3 and 4 wt.%, the measured conductivity clearly demonstrates a conductor–insulator transition as the SWCNTs form a conductive network in the matrix. Existence of this network permits a very high percentage of electrons to flow through the interconnecting conductive path in the matrix. This is a typical percolation threshold as reported in the literature [26–31]. Percolation theory allows one to describe the conductivity of the composites (σ) near the conductor–insulator transition using the laws of power as follows: $\sigma \propto (v - v_c)^s$, where v is the volume fraction of SWCNT, v_c is the percolation threshold, and s is the critical exponent beyond the percolation threshold ($v_c \approx 0.0181$) [25, 32–34]. The best-fit of the conductivity data to the log–log plots of the power laws gives $s = 2.03$ in SWCNT/EVA composites, as shown in the inset of Fig. 1. The conductivity of a binary composite filled with a conducting component is chiefly dominated by the filler characteristics, morphology, and dispersion in the matrix. When conducting carbon black with a particle form is loaded into a polymer matrix, the percolation threshold is usually up to 15–25 wt.% depending on the dimension and dispersion of carbon black [35, 36]. Polymer composites filled with carbon fibers with a rod form show a threshold in the range of 10–15 wt.% [37, 38]. However, when carbon nanotubes were used as the conducting fillers in this study, the percolation threshold is much lower owing to a typically high aspect ratio (length to diameter ratio) and thin diameter of dispersed SWCNTs. This high aspect ratio than aggregates of carbon nanotubes is important for obtaining low percolation thresholds [39, 40]. Network formation through particle chaining can be a key factor in lowering the percolation limit. The composites appear to be uniform over large scales. SEM micrographs of 20 wt.% SWNT/EVA composite are shown in Fig. 2, indicating good SWNT dispersion at submicrometer scales as well as conductive networks formation through the sample. At higher concentration of SWCNT (>4 wt.%), the change in conductivity of the composites with increasing

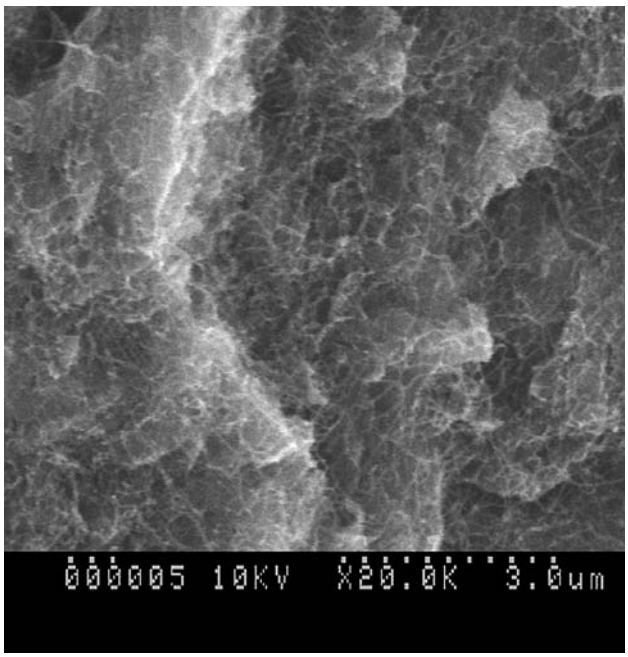

Fig. 2 SEM images the morphology of (**a**) distribution of SWNTs and (**b**) network formation in SWNT/EVA composite containing 20 wt.% SWNT

SWCNT weight percent is marginal as beyond the percolation limit, only the number of conductive paths increases which does not improve the overall conductivity significantly.

The chief purpose of an EMI shielding is to create a barrier comprising of electrical conductive materials that attenuates radiated or conducted electromagnetic energy through reflections and absorption. SE is typically defined as a measurement of an attenuation of the electromagnetic signal after a shield is introduced. The relation between transmittance (T), reflectance (R), and absorbance (A) through shielding materials can be described as $T + R + A = 1$. Total SE (SE_{total}) is expressed as the summation of SEs due to absorption (A), reflection (R), and multiple reflection (B), i.e., $SE_{total} = (SE_A + SE_R + SE_B)$ dB [41, 42]. The transmittance T is measured from the ratio of power P (electric field, E) of incident and transmitted wave, i.e., $T = (P_T/P_I) = (E_T/E_I)^2$. Thus, the SE_{total} for the shielding materials can be written as $SE_{total} = 10 \log(P_T/P_I) = 20 \log(E_T/E_I)$. Figure 3 shows the SE of EVA composites containing different concentrations of SWCNT. The figure indicates a gradual rise in SE with increasing SWCNT concentration in the composites. As expected, pure EVA is transparent to electromagnetic radiations; but an increase in the SWCNT concentration increases the conductivity of the composites and consequently SE increases with increasing SWCNT concentration. Composite containing only 4 wt.% of SWCNTs shows a SE of $\sim$11 dB while a SE of $\sim$37 dB is observed for 30 wt.% of

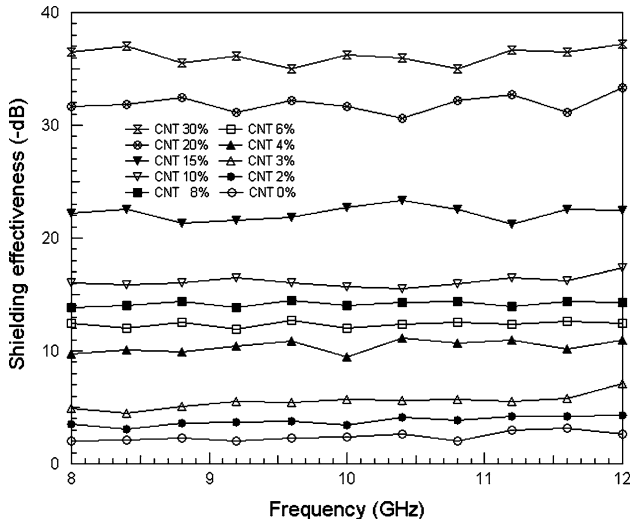

Fig. 3 EMI SE as a function of frequency measured in the 8.0–12.0 GHz range for SWCNT/EVA composites with various SWCNT concentrations

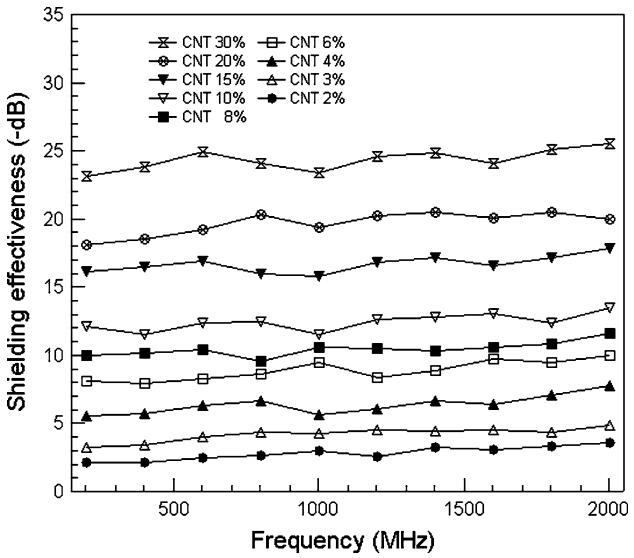

Fig. 4 EMI SE as a function of frequency measured in the 200–2,000 MHz range for SWCNT/EVA composites with various SWCNT concentrations

carbon nanotubes. This can be explained by noting that as the SWCNT concentration increases, the SWCNTs become close enough to one another to allow electron hops across gaps among the SWCNTs or jumps to other SWCNTs. However, the SWCNTs could easily come into contact with one another to form a continuous network when more SWCNTs were dispersed in the matrix resulting in a very high value of SE. Figure 4 shows the SE of the same composite in the frequency range of 100–2,000 MHz. Notice the increase in SE with increasing SWCNT concentration as in the case of 8–12 GHz (Fig. 3). These two results indicate that the SE of all composites exhibits a higher value at a high frequency range. An increase in frequency of the electromagnetic waves is associated with an attendant reduction in the wavelength, and the length scale becomes more comparable to the size of the carbon nanotubes. Thus, higher frequency waves are more likely to encounter the filler materials (carbon nanotube in this case) embedded in the polymer matrix. The carbon nanotubes are more likely to reflect or absorb the wave as compared to the polymer rich areas giving rise to an increase in SE with the increasing frequency range. The similar behavior in EMI SE with frequency was also observed in our previous paper [43]. The electrical conductivity and EMI SE of SWCNT/EVA composites shows much higher value than carbon fiber and carbon black-EVA composites at the same loading due to high aspect ratio and thin diameter of the dispersed SWCNTs. The percolation limit for SWCNTs/EVA composites is about three times and ten times lower than carbon fiber and conductive carbon black composites, respectively. The lower SWCNTs loading and improved properties will be cost effective EMI shielding materials than carbon fiber and carbon black-filled polymer composites in different electronics device applications. The required EMI shielding of the conductive composites for different electronics devices is about 15–20 dB. Therefore, the EMI SE of the composite with 15 wt.% SWCNTs is ~22–23 dB in GHz frequency range, showing promise for its commercial use as an EMI shielding material for different electrics devices [44]. The SWCNT/EVA composites containing 3 wt.% of SWCNTs shows a SE of the order of 7 dB which cannot be used effectively in EMI shielding materials, but it can be used in applications where static charge dissipation is important.

Although high electrical conductivity is not a criterion for EMI shielding, increasing electrical conductivity will result in a higher EMI shielding because of the reflection effect. If multiple reflections are ignored, the EMI SE of electro-conductive composites can be estimated as

$$\mathrm{SE} = 50 + 10\log(\sigma/f) + 1.7t(\sigma f)^{1/2}, \quad (1)$$

where SE is in dB, σ is the conductivity (Ω^{-1} cm^{-1}) at room temperature, t is the thickness of the sample (cm), and f is the measurement frequency (MHz), respectively [45, 46]. This empirical relationship omits the effect of multiple reflections. As can be observed from this equation, SE is a function of sample resistivity, thickness, and measurement frequency. The first two terms estimate the shielding effect by reflection mechanism (R) while the last term represents the part by absorption (A). A reverse trend is observed in return loss (RL) against frequency for the same composites, as shown in Fig. 5. This figure clearly points to the fact that composites with higher SE have a lower RL. The variation of RL with frequency is uneven

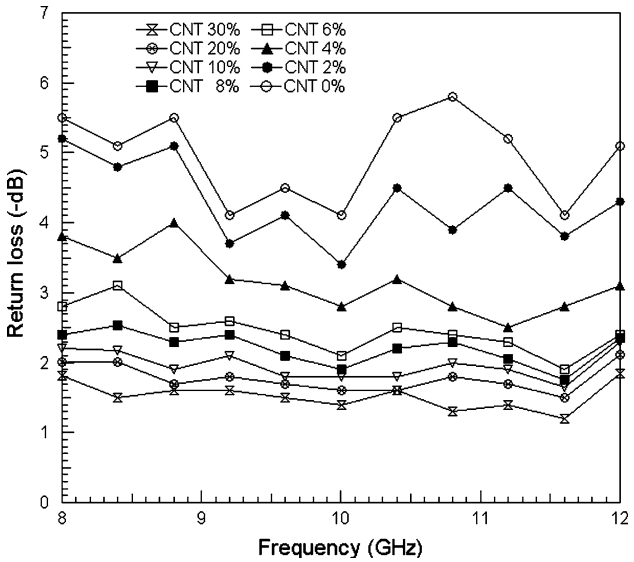

Fig. 5 Return loss as a function of frequency measured in the 8.0–12.0 GHz range for SWCNT/EVA composites with various SWCNT concentrations

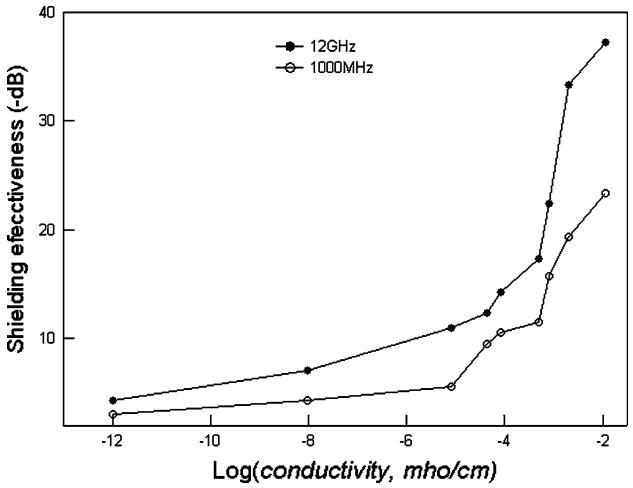

Fig. 6 EMI SE at 200 MHz and 12 GHz as a function of electrical conductivity for SWCNT/EVA composites

because of the random distribution of the SWCNT inside the specimen leading to the formation of voids of different sizes in the conducting mesh. These voids affect return loss because of their effect on the external reflection. Equation 1 indicates that the SE depends not only on the conductivity, but also on the frequency and thickness of the sample. Figure 6 describes the correlation between the SE and the electrical conductivity of SWCNT/EVA composites. It can be observe that a minor increase in SE occurs with the initial variation of logarithmic conductivity from -12 to -5, but at higher conductivities ($\log \sigma > -4$) the SE increases dramatically, and the system becomes more efficient in shielding EMI. This variation in the SE against conductivity can be correlated with the change in conductivity of SWCNT/EVA composites against SWCNT loading. Initially with the addition of carbon nanotube in the EVA matrix the change in conductivity remained marginal up to the critical concentration (percolation threshold). Then the increase in conductivity was abrupt, that is, the insulating EVA matrix became conductive at and above this critical concentration because of the formation of conductive nanotube networks (refer to Fig. 2). Conductivity is a consequence of conductive network formation in the insulating EVA matrix as discussed earlier. This conductive network is distributed uniformly in the polymer matrix, which interacts with the impinging electromagnetic waves and contributes to the EMI SE. It is important to note that there are large differences for SE between the empirical equation and experimental results. For all the composites, the experimental SE is larger than the empirical value calculated from Eq. 1 for the studied frequency range. The discrepancy is about 15–22 dB. Recall that the empirical equation only considers the SE from reflection and absorption. This difference is probably as SE from multiple reflections for these SWNT/EVA composite reflections, which depends on the surface area of SWNT, its orientation, structure, and intrinsic characteristics of the composites that is omitted in Eq. 1. There is no mathematical equation available to express multiple reflections so far, but it has significant contribution to the EMI shielding when the absorption contribution to the SE shielding <15 dB as discussed above [42]. In other way, the contribution of the reflection and absorption to the EMI shielding is also changed each other with the frequency [47].

Figure 7 shows the shielding efficiency of SWCNT/EVA composites containing 15 wt.% SWCNTs as a function of sample thickness. The plot shows that SE increases

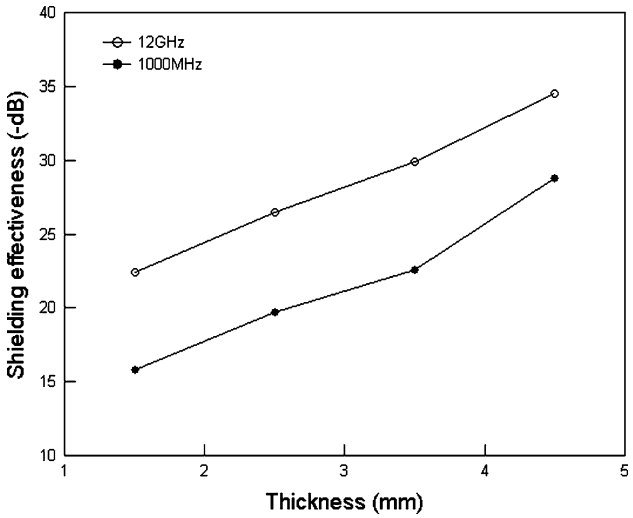

Fig. 7 EMI SE as a function of sample thickness of EVA/SWCNT (15 wt.%) composites

monotonically with increasing thickness. Conductivity is an intrinsic parameter of the SE while the thickness is an extrinsic parameter for the same. As the thickness of the material increases, the conductive networks interacting with the electromagnetic waves also increase in the system, and consequently the absorption of electromagnetic wave increases resulting in a higher SE.

Conclusions

In conclusion, we have synthesized a class of SWCNT/EVA composites with higher concentration of SWCNT for EMI shielding purpose through melt mixing. The conductivity as well as EMI SE of SWCNT/EVA composites have been shown to increase with a higher loading of SWCNT with a percolation threshold of 3.5 wt.%. The composites studied in this article should find use in various electrical applications where EMI shielding is important. The EMI SE of the composite with 15 wt.% SWCNTs is $\sim$22–23 dB in GHz frequency range, its showing promise for its commercial use as an EMI shielding material.

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