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AIP ADVANCES **2**, 022151 (2012)

Designing of epoxy composites reinforced with carbon nanotubes grown carbon fiber fabric for improved electromagnetic interference shielding

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In this letter, we report preparation of strongly anchored multiwall carbon nanotubes (MWCNTs) carbon fiber (CF) fabric preforms. These preforms were reinforced in epoxy resin to make multi scale composites for microwave absorption in the X-band (8.2-12.4GHz). The incorporation of MWCNTs on the carbon fabric produced a significant enhancement in the electromagnetic interference shielding effectiveness (EMI-SE) from −29.4 dB for CF/epoxy-composite to −51.1 dB for CF-MWCNT/epoxy multiscale composites of 2 mm thickness. In addition to enhanced EMI-SE, interlaminar shear strength improved from 23 MPa for CF/epoxy-composites to 50 MPa for multiscale composites indicating their usefulness for making structurally strong microwave shields. *Copyright 2012 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License*. [http://dx.doi.org/10.1063/1.4730043]

Electromagnetic interference (EMI) is becoming a serious problem now a days due to the rapid growth in electronics and instrumentation. It can disturb normal functioning of equipment or may lead to its complete breakdown. Therefore, some shielding mechanism must be developed to prevent the appliances from the harmful effect of these electromagnetic (EM) noise. Carbon nanotubes (CNT)-polymer composites have gained popularity recently over the metal because of their light weight, resistance to corrosion, flexibility and processing advantages. For a high value of EMI shielding, high loading of CNTs are used in past.[1,2] Another way to get high EMI SE even at low loading is to prepare the sample of high thickness.[3] However, such high thickness is not practically possible in commercial applications. It is quite evident from the earlier reports that the reinforcement effect of CNT can be realized only for low loading level ($<1\%$) and afterward it starts to decrease dramatically due to several issues e.g. dispersion, alignment and interface.[4,5] Furthermore, the use of CNT alone as reinforcement often failed to achieve the superior mechanical properties in the composites. Therefore, different routes have been adopted, notably a combination of CNT and carbon fibre (CF)[6–8] that involves dispersion of CNT into epoxy matrix followed by impregnation in carbon fabric. However, the above compositions had the limitation of reinforcing $<1\%$ CNT beyond which the viscosity of the CNT-epoxy mix was raised so much that it became impossible to impregnate the fabric completely. Using the present technique of CNT grown CF, 3% CNT by vol. was incorporated as one of the reinforcements in the epoxy composites. We show for the first time that these multiscale composites can serve as an efficient EMI shielding material with added advantage of light weight, high mechanical strength and good electrical conductivity.

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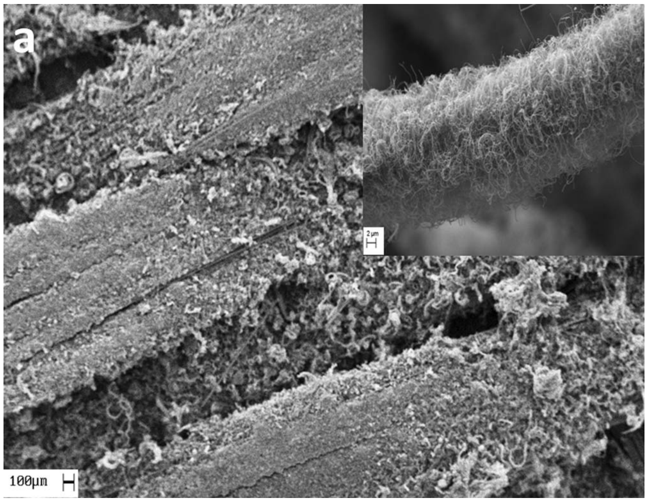

FIG. 1. SEM image showing uniform growth of CNTs over the surface of the CF fabric preform. The inset shows masking of CF monofilament with CNTs.

Different amount of CNTs were grown on a plane weave CF fabric using the set up and the experimental conditions described earlier.[9] The SEM images of the multiscale preform show a uniform growth of CNTs throughout the surface of the fabric (Fig. 1). The inset (Fig. 1) shows a copious growth of CNTs on the carbon monofilament virtually covering its entire surface. The preform thus forms a nice combination of micro and nano reinforcement. The CNT-CF preforms were impregnated with epoxy matrix (Huntsman LY-556 resin and HT 972 hardener) to keep the reinforcement (CF+CNT) to the matrix ratio always as 30:70 by volume. These prepregs were stacked together to form a laminated assembly of the CNT-CF multiscale fabric. The laminates were then compression molded in a mold at 80°C followed by a curing cycle, i.e. 1hr. at 150°C to obtain composite bars of size 60mm × 20mm × 2.5mm. The multiscale composites batches prepared with CNT: CF: epoxy ratios as 0.5:29.5:70; 1.1:28.9:70; 1.25:28.75:70; 3:27:70 and designated as msc-1, msc-2, msc-3 and msc-4 respectively in the following text. In a separate experiment the laminates of as received CF fabric were also compression molded under similar condition to prepare CF/epoxy composites designated as cfc.

Interlaminar shear strength (ILSS) and flexural strength (FS) of these composites were measured on INSTRON universal testing machine (model 4411). The samples of size 15mm × 5mm × 2.5mm with span to depth ratio 4 and crosshead speed of 1mm/min were used for measuring ILSS while composite bars of size 60mm × 20mm × 2.5mm were used for flexural strength. Fig. 2 shows a gradual increase in the ILSS values w.r.t. MWCNT loading and increased to 50 MPa for sample msc-4 from 23 MPa for base composite (cfc). An overall improvement of 117% is the highest improvement reported so far in such type of composites. Similarly the FS of the composite msc-4 increased to 560 MPa from 300 MPa for ‘cfc’. The improvement in the ILSS as well as in FS can be correlated to the scaffolding effect of the CNT between the carbon filaments and therefore arresting the propagation of cracks in the matrix as shown in the inset b of Fig. 2.

The d.c. electrical conductivity (σ_{dc}) of the composites was measured by the four probe technique described elsewhere.[10] As shown in Fig. 2, σ_{dc} increases with the concentration of MWCNT. This can be attributed to the increase in the number of conducting links within electrically insulting epoxy matrix. Such links are missing for cfc as shown in inset a of Fig. 2. Such a high conductivity suggests the suitability of these composites for making efficient microwave shields. Further it should be emphasized here that the MWCNT produced inside the CVD reactor contains entrapped iron catalyst as impurity (∼10% by weight) imparting ferromagnetic character to the tubes. This is revealed by the VSM plot of MWCNT scrapped out of the CF fabric and shown in the inset of Fig. 3. The saturation magnetization (Ms), remnant magnetization (Mr) and coercivity (Hc) of these MWCNTs were found to be 7.0 emu/g, 2.23 emu/g and 580.0 G respectively. These results are of

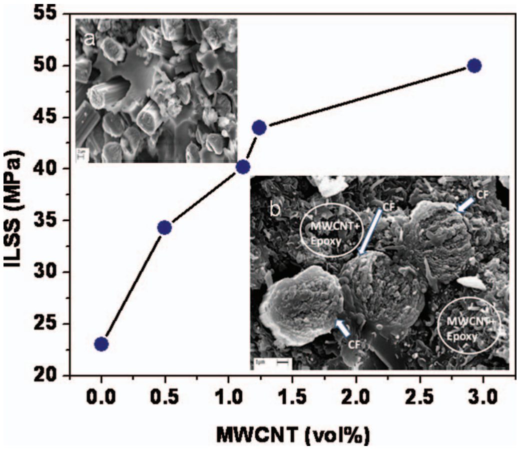

FIG. 2. Variation of ILSS of multiscale composite with MWCNT loading. The inset figure a & b shows the SEM images of fracture surface of cfc and msc-4 respectively.

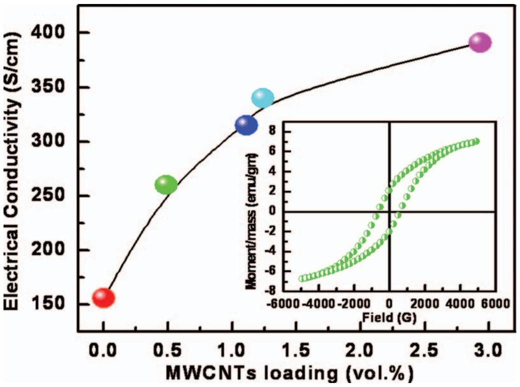

FIG. 3. Variation in the electrical conductivities of the CF-MWCNT/epoxy composites with increasing MWCNT contents in the preforms. The inset figure shows the VSM of the scraped MWCNTs from the CF fabric.

particular interest as good magnetic (e.g. high magnetization) and electrical properties (enhanced conductivity) expected to improve the EM energy absorption and dissipation capability resulting in enhancement of microwave shielding effectiveness.[11] EMI shielding measurements were taken on rectangular strips of composites inside the home made sample holder. The holder matches the internal dimensions of X-band (8.2-12.4 GHz) waveguide placed between the two ports of vector network analyzer.

The EMI shielding is a direct consequence of reflection, absorption and multiple internal reflection losses at the existing interfaces, suffered by the incident EM waves. EMI shielding effectiveness can be expressed as[12,13]

$$SE_T(dB) = 10\log\left[\frac{P_T}{P_I}\right] = 20\log\left[\frac{E_T}{E_I}\right] = 20\log\left[\frac{H_T}{H_I}\right]$$

Where P_I $(E_I \text{ or } H_I)$ and P_{T} $(E_T \text{ or } H_I)$ are the incident and transmitted EM powers (electric or magnetic field) respectively. It is convenient to express the losses due to reflection ($\mathrm{SE_R}$) and absorption ($\mathrm{SE_A}$) in the form of reflectance ($\mathrm{R} = |S_{11}|^2$) and transmittance ($\mathrm{T} = |S_{21}|^2$) as:

$$SE_R = 10\log(1-R) \text{ and } SE_A = 10\log[T/(1-R)]$$

The term skin depth (δ) is the penetration at which the intensity of incident wave is reduced to 1/e of its original strength. The δ dependent upon various parameters like angular frequency (ω), real relative permeability ($\mu\prime$), total conductivity (σ_T) and it can be expressed as $\delta = (2/\omega\mu'\sigma_T)^{1/2}$. Therefore, at

TABLE I. Data on the EMI-SE of carbon based polymer composites in X-band reported by different authors.

S.No.	Type of Filler /% Filler/Thickness	Polymer	Frequency	Shielding Effectiveness (dB)	Reference
1	CF/30phr/3.5mm	EVA	12 GHz	34.1	15
2	CB/50phr/5mm	75%NBR+25%EVA	8-12 GHz	55-62	16
3	Vapor grown carbon fiber/20 wt.-%/1 mm	polystyrene	10GHz	19.5	17
4	MWCNT /40wt-%/0.165mm	poly(methyl methacrylate)	50 MHz-13.5 GHz	27	11
5	MWCNT/10 vol.-%/.3mm-2.1mm	poly(methyl methacrylate)	12.4 GHz	18-40	18, 19
6	MWCNT/4.76 vol%/2 mm	Poly(trimethylene terephthalate)	8.2 GHz	22.0	20
7	MWCNT/4.76wt.-% /10 layers of 0.1 mm thick film	poly(methyl methacrylate)	12.4 GHz	∼42	21
8	MWCNT/7.5 vol. %/lmm	polypropylene	12.4 GHz	36.4	22
9	MWCNT/5wt.-%/1.85mm	polycarbonate	8.2-12.4 GHz	26	23
10	MnO_2 Nanotubes & f-MWCNTs/5wt.-% MnO_2 & lwt.- % f-MWCNT/lmm thick	polyvinylidene fluoride	8.2-12.4 GHz	18-22	24
11	MWCNT/20wt.-%/l .5mm	styrene acrylic emulsion	8.2 GHz	28	25
12	SWCNT/15wt.-%/2mm	epoxy	8.2-12.4 GHz	20-30	26
13	SWCNT/20wt.-%/2mm	polyurethane	8.2 GHz	17	27
14	SWCNT/15wt.-%/1.5mm	ethylene vinyl acetate	8.2-12.4 GHz	22-23	28
15	f-SWCNT/4.5vol.-%/2mm	reactive ethylene terepolymer	12.4 GHz	30	29
16	CF fabric/30 vol.-%. 2mm	epoxy	12.4 GHz	29.4	Present work
17	CF fabric (27 vol.-%)+MWCNT (3 vol.-%)/2mm	epoxy	12.4 GHz	51.1	Present work

any given frequency, skin depth decreases with the increase in both magnetic permeability as well as electrical conductivity. Further, the theoretical SE_R and SE_A can be expressed as:[14]

$$SE_R = -10\log\left(\frac{\sigma_T}{16\omega\varepsilon_o\mu'}\right) \qquad SE_A = -8.68t\left(\frac{\sigma_T\omega\mu'}{2}\right)^{\frac{1}{2}}$$

The shallow skin depths and high conductivity (σ_T) values in the microwave region often results in contribution of SE_A becoming much more compared to SE_R. The variation of total shielding effectiveness (SE_T) of different composites is shown in Fig. 4(a). It has been observed that the SE_T value for CF-epoxy composite (without any CNT) was ∼−29.4 dB. However, as we add and increase the filler in polymer matrix the SE_T value increases from −41.2 dB (msc-1) to −51.1 dB (msc-4) at 12.4 GHz. This value is found superior compared to other work by several authors (Table I) except the work carried out by Rahman *et al.*[16] who reported EMI-SE of ∼60 dB at 50 phr (part per hundred part of resin) of carbon black (CB) in a blend of ethylene vinyl acetate (EVA) and acrylonitrile-butadiene copolymer (NBR) for 5 mm thick sample. However, there are several reports[30,31] indicate that high loading of CB degrades the mechanical properties of polymer. In addition to degradation of mechanical properties, such a high thickness (5mm) of the material is not commercially viable for some applications where 2-3 mm thickness is preferred. However, in our case we obtained the SE of ∼51 dB at a thickness of only 2 mm with the improved mechanical properties due to the multiscale reinforcement (CNT grown CF fabric). In addition to above study, we have also investigated shielding mechanism by dividing SE_T into two components i.e. SE_R

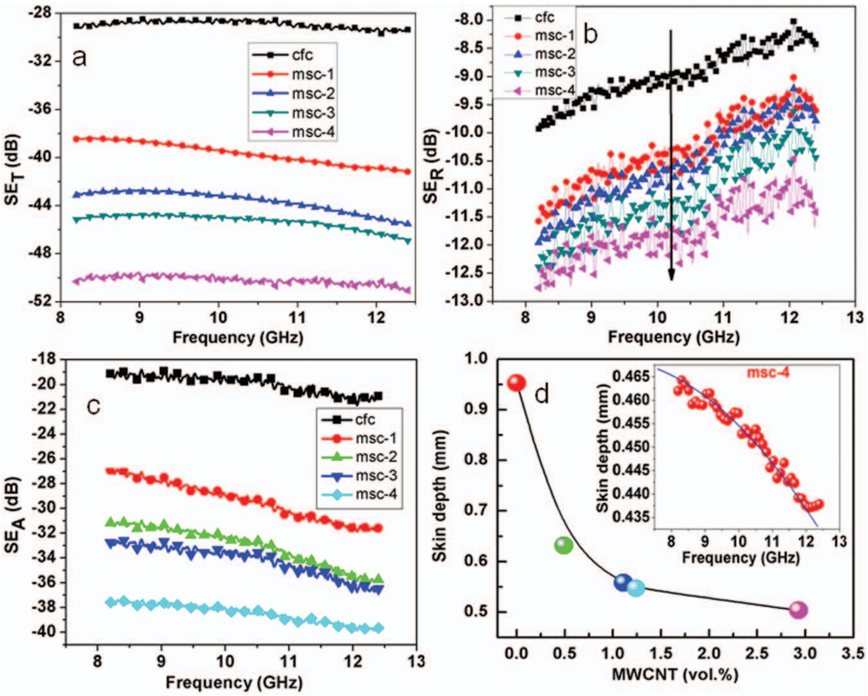

FIG. 4. (a) Total EMI shielding effectiveness (b) Reflection loss (c) Absorption loss of different composites as a function of frequency measured in the 8.2–12.4 GHz range (d) Variation in skin depth with the growth of MWCNTs on CF fabric and inset figure showing the variation of skin depth of msc-4 sample with the frequency.

(due to reflection) and SE_A (due to absorption). These results revealed that SE_R (Fig. 4(b)) increases slightly from −9.6 dB (msc-1) to −11.4 dB (msc-4) whereas SE_A (Fig. 4(c)) shows rapid enhancement from −31.6 dB (msc-1) to −39.7 dB (msc-4). The enhanced absorption can be explained in terms of reduction of skin depth with the increase in both permeability (due to presence of iron) as well as electrical conductivity (due to MWCNTs). The above equations predict that shallow skin depths make possible the achievement of same level of attenuation with thinner shield of the same material. In other words, at same thickness, the material with shallowest skin depth is expected to give the maximum absorption loss. The variation of skin depth of different materials has been shown in Fig. 4(d) whereas the inset shows the frequency dependence of skin depth of msc-4. The results show that skin depth increases in moving from msc-1 to msc-4 resulting in enhancement of absorption loss. This can be attributed to enhancement of both electrical as well magnetic properties with loading of more CNTs. The result also clarifies that skin depth decreases with increase in frequency which is responsible for observed rise of absorption loss with frequency. Thus, for a given thickness, absorption loss increases with decrease in skin depth i.e. in moving from msc-1 to msc-4.

In summary, CNT grown CF fabric multiscale substrate proved to be an effective reinforcement for producing high strength light weight composites for efficient EMI shielding material. The EMI shielding effectiveness was found to be enhanced from −29.4 (cfc) to −51.1dB (msc-4). The high value of shielding effectiveness demonstrates the potential of these materials as futuristic microwave shielding materials.

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