The influence of coiled nanostructure on the enhancement of dielectric constants and electromagnetic shielding efficiency in polymer composites

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We report through a comparison of the electromagnetic properties of polymer composites constituted of linear and nonlinear (helically coiled) carbon nanotubes (CNTs) that the electromagnetic interference (EMI) shielding efficiency could be much increased in the latter. A higher ac conductivity and relative dielectric permittivity (both ε' and ε'') was recorded when coiled structures were used, and was ascribed to enhanced capacitive and electric field depolarization effects. The EMI shielding was related to the extended length/diameter aspect ratio of the CNTs. Our study has implications in the design of materials for EMI shielding, where nanostructure geometry could play a major role. © *2010 American Institute of Physics*. [doi:10.1063/1.3292214]

A change in structure and morphology, at the nanoscale, could have a profound influence on macroscopic characteristics, through the paradigm of "function follows shape."[1] For example, in the case of carbon based nanostructures, nonlinear and coiled carbon nanotubes (CCNTs)[2]/nanowires (CNWs) have been proposed for a variety of applications such as electrical inductors,[3] springlike mechanical elements for energy dissipation,[4,5] novel electronic devices incorporating alternating metallic and semiconductor junctions,[6] etc. In this letter, we suggest yet another application, based on experimental evidence, that the incorporation of coiled structures could be used to enhance the intrinsic electromagnetic properties, e.g., the dielectric constants and the electromagnetic interference (EMI) shielding, of polymer matrices.

We have previously shown that In and Sn based catalysts could be used to promote CCNT/CNW growth in chemical vapor deposition (CVD) based processes[2] as depicted in Fig. 1(a). It was also found that there was a temperature induced gradation in the coiling characteristics in the CVD reactor, where a higher temperature promotes enhanced nonlinearity. For example, a mixture of linear and coiled CNTs, as seen in Fig. 1(b), could be found in the colder parts of the reactor. A tentative model, incorporating thermodynamic and kinetic factors underlying their growth mechanism was also proposed.[7] Motivated by earlier studies[8–10] where uniform dispersion of linear CNTs was shown to improve the EMI shielding of polymer composites, we investigate the corresponding effects on the electromagnetic properties due to coiled nanostructures in polymers. We have obtained interesting results which exemplify the predominant influence of intrinsic nanostructure geometry, e.g., aspect ratio and capacitive coupling, on electromagnetic characteristics.

In this letter, we report on the effects due to uniformly dispersed CCNTs incorporated into a reactive ethylene terpolymer (RET: Elvaloy 4170) polymer matrix. The RET structure is constituted from[8] (1) polyethylene, (2) a polar methyl-methacrylate group, and (3) epoxide functional groups. While (1) and (2) contribute to the mechanical characteristics (elastomeric properties) and corrosion resistance underlying the utility of RET as a hot-melt adhesive and coating, the epoxy group has high reactivity[11] and facilitates effective anchoring of the ring bonds with functional groups (e.g., –OH, COOH, $-NH_2$, etc.) on the CNTs. For comparison, we also embedded linear CNTs, i.e., both single walled (SWCNTs) and multiwalled (MWCNTs) and a mixture of linear and coiled CNT varieties. While a range of volume fractions were tested, we report here on the results of a particular volume fraction,[12] i.e., ~0.9%. Such a volume fraction is intermediate within the range of percolation thresholds, estimated from excluded volume percolation theory[13,14] of 0.1 to 2 vol %—depending on whether the extended or the coiled length of the helical nanostructure was considered.

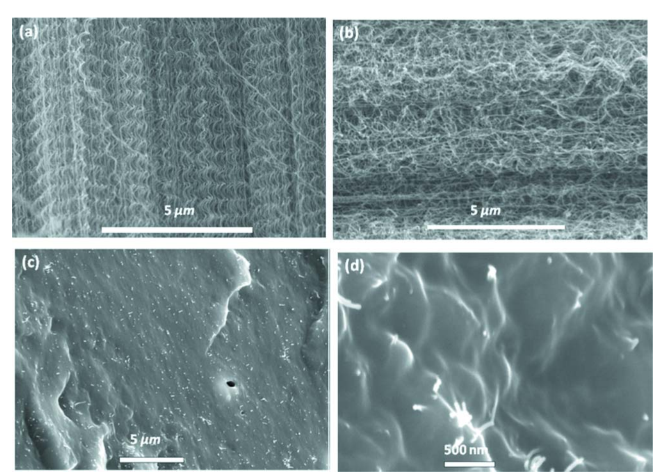

FIG. 1. (Color online) Scanning electron microscope (SEM) micrographs of (a) aligned coiled carbon nanotubes (CNTs) with nearly identical diameter and pitch. (b) A mixture of linear and coiled CNTs, (c) uniform dispersion of the CNTs obtained through mutual chemical reaction between CNT and RET functional groups, (d) a high resolution image of the coiled CNT-RET nanocomposite.

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TABLE I. The geometrical parameters of the fillers (SWCNTs: single-walled CNTs, MWCNTs: multiwalled CNTs, and CCNTs: coiled CNTs) used for the composites. The intrinsic CNT diameter (d_{CNT}), coil diameter (d_{coil}), and the projected (L_{proj}) and extended length, (L_{ext}) are indicated along with the A.R.s relevant for describing the electromagnetic properties.

	SWCNTs	MWCNTs	CCNTs
d_{CNT}(nm)	~4.8	~25	~22
d_{coil}(nm)	...	...	~450
L_{proj}(μm)	~4.3	~10	~15
L_{ext}(μm)	~4.3	~10	~47
$\frac{L_{proj}}{d_{coil}}$	...	...	~33
$\frac{L_{ext}}{d_{CNT}}$	~895	~400	~2140

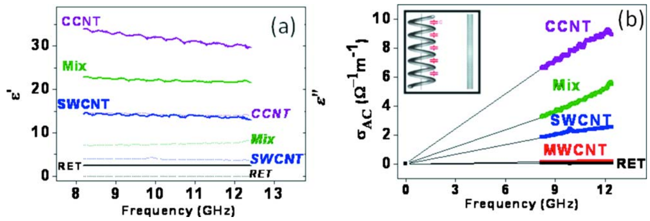

FIG. 2. (Color online) (a) The X-band frequency variation in the real (ε') —*left axis* and imaginary (ε'') —*right axis* permittivity of composites, with CCNT (coiled CNTs), mix (a mixture of coiled and single-walled CNTs), and SWCNT (single-walled CNTs) fillers compared with RET polymer (with a nominal value of permittivity ~2.4+j0.054) (b) the frequency variation in σ_{ac} of the CNT composites, with CCNTs, mix, SWCNTs, and multiwalled CNT (MWCNT) fillers compared with RET polymer [σ_{ac}(0 Hz) $=\sigma_{dc}$]. The *inset* shows capacitive coupling between alternate windings of the CCNT, which is absent in a SWCNT.

The detailed experimental procedures for the CNT composite synthesis has been reported elsewhere.[8] Briefly, uniform dispersion (surmised through considering micrographs at different length scales, i.e., 1–50 μm) without nanotube agglomeration was facilitated through localized chemical reactions between the –COOH functional groups on CNTs with epoxy groups on the RET. The CNTs were then dispersed in toluene with sonication for 20 min. It was typically seen, through atomic force microscopy, that sonication reduces the average length of the CNTs. Table I then illustrates the length, diameter and other geometrical parameters of the CNT varieties as observed through scanning electron microscopy (SEM) subsequent to sonication. The CNT dispersion was added to the RET (also mixed with toluene) and then the mixture was stirred, poured into glass dishes and evacuated in vacuum. A hot press was used to fabricate composites of desired thickness (~2 mm, in the present study). SEM micrographs of the composite fracture surfaces do indicate a uniform dispersion of the CNTs, e.g., as seen in Figs. 1(c) and 1(d), due to such a procedure. Figure 1(c) is a low resolution image indicating uniform dispersion of the coiled CNTs over a ~400 μm^2 area, while Fig. 1(d) is a higher resolution micrograph (~7 μm^2 area) of how individual coiled CNTs are positioned in the polymer matrix.

The EMI shielding efficiency (SE) of the CNT-RET composites was then determined, in the microwave frequency (f) range (8.2–12.4 GHz: X-band) through the use of a vector network analyzer (VNA: Agilent 5242A PNA-X). For this purpose, the composite loaded sample holder was inserted between two 15 cm lengths of WR-90 X-band waveguide to mitigate the effects of the coax to waveguide transitions. The R (reflection), A (absorption), and the T (transmission) components were then obtained through the measurement of the S-parameters[15] (S_{ij}) using the VNA, where T=$|S_{21}|^2$, R=$|S_{11}|^2$, and A=1-$|S_{11}|^2$-$|S_{21}|^2$. The total effective shielding effectiveness, SE(Tot), of the composite was considered as: SE (Tot)=SE(R)+SE(A), where SE(R) $=-10\log(1-\mathrm{R})$ and SE(A)$=-10\log[\mathrm{T}/1-\mathrm{R}]$. The SE (Tot) of the composites was then determined to be equal to $10\log(P_i/P_t)$, where P_i and P_t are the magnitudes of the incident and transmitted power densities.

The determination of S_{11} and S_{21} also enables the calculation of the relative complex permittivity ($\varepsilon=\varepsilon'+j\varepsilon''$) and permeability ($\mu=\mu'+j\mu''$), where $j=\sqrt{-1}$, along with the reflection and transmission coefficients. More details of such conversions and analysis have been reported in literature.[8,16] Concomitantly, the dc conductivity (σ_{dc}) was measured on the composite samples through four-point electrical measurements (using the Keithley 487 picoammeter and the Keithley 2400 sourcemeter) using sputtered Au contacts. It was noted that the σ_{dc} was similar at $\sim 10^{-3}$ Ω^{-1} m^{-1} for the composites constituted from CCNTs, SWCNTs, and the mixture while $\sim 10^{-5}$ Ω^{-1} m^{-1} for the MWCNT based composites.

It was observed that the relative dielectric permittivity (both ε' and ε'') of the CCNTs is larger, by approximately a factor of 2, compared to SWCNTs, Fig. 2(a). In the figure is also shown the corresponding variation for a mixture of linear and coiled CNTs (with an approximately 1:1 distribution)—as in Fig. 1(b), which is seen to be intermediate to the CCNTs and SWCNTs. The increased ε' in the coiled CNTs over linear CNTs (SWCNTs/MWCNTs) is explained on the basis of enhanced capacitive coupling between alternate windings/segments of the coil in the former—see Fig. 2(b) inset, which effectively increases ε'. The relatively weak f dependence of ε'' could be indicative of the composition used in the present study. A greater variation was found, for example, in higher volume percent CNTs.[17] The values of both ε' and ε'' for the mixture (Mix, in Figs. 2 and 3), composed of both coiled and linear CNTs seem to be intermediate to the individual values.[17,18]

The linear dispersion of the ac conductivity, σ_{ac} (computed through $\sigma_{ac}=\omega\varepsilon_o\varepsilon''$, where $\omega=2\pi f$ and ε_0 $=8.854\cdot 10^{-12}$ C^2/Nm^2) with frequency is plotted next in Fig. 2(b). As could be expected from Fig. 2(a), the CCNT based materials have a higher σ_{ac} compared to the linear CNT based composites. Concomitantly, we explain the enhanced σ_{ac} on a simple model based on the formation of parallel resistors and capacitors in the composite. In this

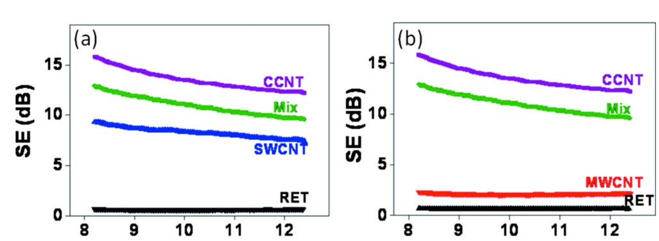

FIG. 3. (Color online) The frequency variation in the shielding efficiency (SE) of the composites with fillers of (a) the same σ_{dc}, and (b) similar diameter.

model, the CNTs contribute to the electrical resistance while the polymer matrix serves as the capacitor dielectric and contributes to the ac conductance. The increased number of parallel resistors and capacitors in the CCNTs due to the coiled structure, compared to linear CNTs, decreases the overall resistance and capacitive impedance $[X_c = |(1/2\pi f C)|]$ of the composite due to the availability of several alternative electrical conduction paths.

Using a simple parallel plate capacitor model–as in the inset to Fig. 2(b), we calculate a capacitance/unit area of ~ 0.1 mF/m^2 with a pitch of ~ 1 μm—from Fig. 1(a). We estimate from the nanotube geometry (Table I) and sample volume (with $\sim 10^{12}$ nanocoils) a substantial capacitance which leads to a low X_c and large σ_{ac}. Such effects may be less significant in composites constituted from linear CNTs. As the CNTs are much smaller than the effective EM wavelengths used it is unlikely that the chirality would affect the electromagnetic properties.[19] Consequently, the μ of the coiled samples was comparable to that obtained from the use of the linear CNTs and close to unity, i.e., $\mu' \sim 1$ and $\mu'' \sim 0$.

However, the length/diameter aspect ratio (A.R.) of the nanostructures does seem to make a difference, and will be discussed next. Generally, the depolarization electric field is enhanced[20] with a smaller A.R. and modifies the effective permittivity. This implies, for a given electric displacement, a higher ε for the CCNTs when the projected/coiled length (L_{proj}) and coil diameter (d_{coil}) is considered, yielding an A.R. ($=L_{proj}/d_{coil}$) of ~ 33 (see Table I). On the other hand, the SWCNTs have a correspondingly much larger A.R., i.e., ~ 895, which is now considered with respect to the ratio of the extended length, L_{ext} to the CNT diameter (d_{CNT}) and a smaller ε It is to be noted that for SWCNTs, L_{ext} is taken to be identical to L_{proj}.

Additionally, a higher EMI SE was observed for the CCNT composite, Fig. 3(a), which shows a comparison of the frequency variation of the SE values of composites with similar σ_{dc}. Figure 3(b) illustrates the variation for the case of CNTs with similar diameters and length. It was indicated[21] that the reflection mediated EMI shielding decreases with frequency (f) as $\sim \log_{10}(\frac{\sigma}{f})$ while absorption dominated shielding increases with f and is thickness (t) dependent, varying as $t\sqrt{f\sigma}$. Since we observe that the SE *decreases* with frequency, Figs. 3(a) and 3(b), the shielding mechanism seems to be reflection dominated at 0.9 vol %. We could also explain the higher SE by invoking the A.R. of the constituent nanostructures (from Table I), by considering the total/extended length and intrinsic CNT diameter. For example, in the case of CCNTs the L_{ext} to d_{CNT} ratio (~ 2140) was on the average much larger than in the case of SWCNTs (~ 895) or MWCNTs (~ 400). It was previously determined[8] that composites constituted of the former indeed have a higher SE. While SWCNT and MWCNT constituted composites cannot strictly be compared (due to significantly different σ_{dc} and diameters) it can be surmised that a greater constituent nanostructure A.R. ($=L_{ext}/d_{CNT}$) would yield enhanced EMI shielding. A good agreement ($\pm$ 10%) of the SE for the composite composed of both linear and coiled CNTs, SE$_c$, was obtained through $SE_c = \Sigma_i SE_i \phi_i$, where SE$_i$ refers to the SE of the ith constituent, i.e., i=coiled CNT, linear CNT, etc.

Our observations are interesting as it was seen that the CNT filler morphology and geometry can substantially influence the electromagnetic properties of polymer composites. It was noted that while the projected length and diameter could influence the dielectric permittivity due to depolarization effects, the total extended length and diameter could determine EMI shielding. Future work would focus on putting our proposed models on a firm quantitative basis.

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