Enhanced dielectric constants and shielding effectiveness of, uniformly dispersed, functionalized carbon nanotube composites

Sung Hoon Park,[1] Paul Thielemann,[2] Peter Asbeck,[2] and Prabhakar R. Bandaru[1,a)]
[1]*Department of Mechanical Engineering, Materials Science Program, University of California, San Diego, La Jolla, California 92093, USA*
[2]*Department of Electrical Engineering, University of California, San Diego, La Jolla, California 92093, USA*

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It was seen that composites constituted of functionalized single-walled nanotubes (SWNTs) dispersed in a reactive ethylene terpolymer (RET) matrix possess a complex dielectric permittivity an order of magnitude larger than composites composed of pristine SWNTs and two orders of magnitude larger than functionalized multiwalled nanotube-RET composites. We seek to understand such an enhancement, both in terms of uniform nanotube dispersion and through a parallel resistor-capacitor model. We subsequently show that the ac electrical conductivity is a good predictor of the electromagnetic interference shielding effectiveness of nanocomposites. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3156032]

Polymer composites containing conducting fillers[1] have been extensively investigated for various applications such as electromagnetic interference (EMI) shielding,[2] electronic packaging,[3] radar absorption,[4] and high charge storage capacitors.[5] However, currently used composites require high filler to polymer loading ratios, which deteriorates the overall mechanical properties through deterioration of intrinsic matrix morphology. A possible way to ameliorate the above problems, through using low filler volume fractions, incorporates carbon nanotubes (CNTs)[6–9] in composites. A concomitant large aspect ratio and tunable electrical conductivity would enable electrical percolation to be achieved at very small CNT volume fractions,[8] with large shielding efficiencies being obtained, e.g., ~28 dB in CNT films[10] and ~16 dB in polyurethane/CNT composites[11] at 10 GHz. However, economic costs and clustering of the CNTs within the polymer matrix are issues that have to be overcome prior to large scale application. In this paper, we tackle the clustering problem by considering the synthesis of well dispersed functionalized CNT composites. The superior nature of these composites, for EMI applications, is then characterized in the microwave frequency range of 8.2–12.4 GHz (*X*-band), used for civil and military communications with applications as diverse as weather monitoring, vehicular detection, air traffic control, and defense tracking.[12]

Reactive ethylene terpolymer (RET) was chosen as the polymer matrix for its elastomeric properties and corrosion resistance. Additionally, the constituent epoxide functional group is reactive[13] and allows for effective anchoring with functional groups (e.g., –OH, COOH, $–NH_2$ etc.) on the CNTs, as confirmed through Fourier transform Infrared spectroscopy.[14] As the functional groups are associated with defects on the CNTs and are randomly dispersed,[15] isotropic bonding of the nanotubes with the polymer matrix was implied and could yield uniform CNT dispersion.

In the results presented in this paper, both pristine/unfunctionalized single-walled CNTs (SWNTs) (average diameter of 1–2 nm, length of 5–20 μm, 90% purity, and density of 2.1 g cm^{-3}) along with COOH-functionalized SWNTs and multiwalled CNTs (MWNTs) (average diameter of 140 nm, length of 5–9 μm, 90% purity, and density of 1.7 g cm^{-3}) were tested as fillers.[14,16] The MWNTs and SWNTs were then dispersed in toluene with sonication for 20 min. It was typically seen through atomic force microscopy characterization that subsequent to sonication, the average length of the SWNTs was reduced to ~4.3 μm, with a bundle diameter of ~4.8 nm, resulting in an aspect ratio of ~880. On the other hand, the MWNTs have an average length of 5.6 μm, with a bundle diameter of ~190 nm, yielding an aspect ratio of ~30. The RET was also mixed with toluene and heated to ~60 °C for 2 h by stirring. The nanotube dispersion was then added to the RET solution and sonicated again. To remove excess solvent, the mixture was evacuated in vacuum (10^{-3} Torr). Subsequently, a hot press was used to press the CNT-RET composites into a thickness of ~2 mm.

We indeed observed a more uniform dispersion using functionalized SWNTs for both low [Fig. 1(a)] and high [Fig.

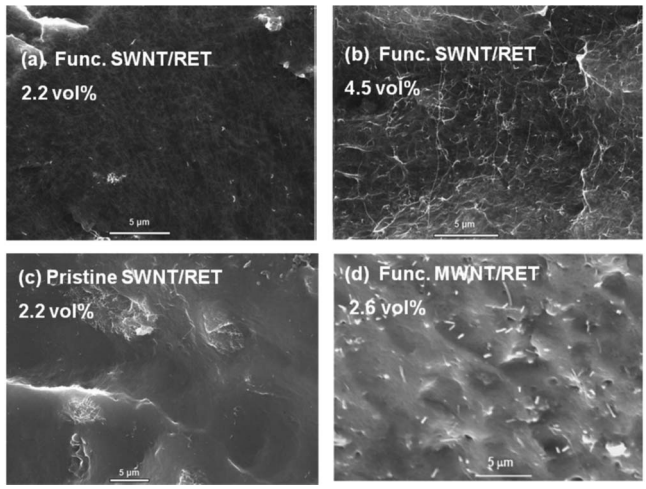

FIG. 1. SEM micrographs of (a) 0.9 vol % and (b) 4.5 vol % *functionalized* SWNT-RET composites, (c) 2.2 vol% of *nonfunctionalized* SWNT-RET composites, (d) 2.6 vol % *functionalized* MWNT-RET compostes.

a)Electronic mail: pbandaru@ucsd.edu.

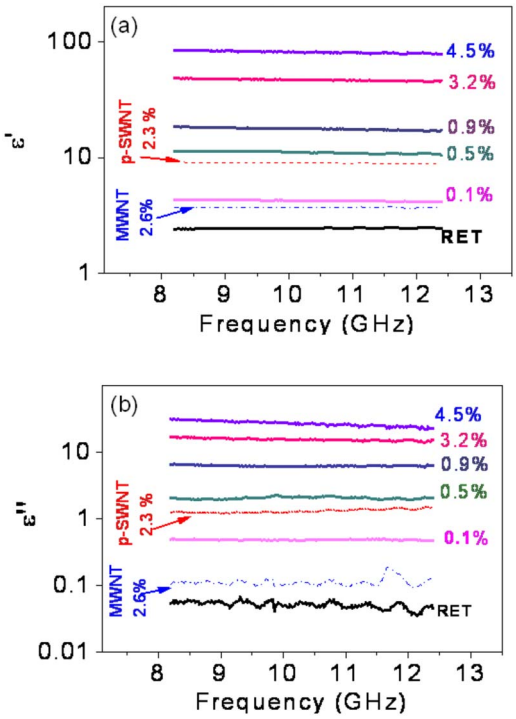

FIG. 2. (Color online) The (a) real—ε', and (b) imaginary—ε'' components of the dielectric constants of functionalized SWNT-RET composites (numbers in % indicate volume fraction of SWNTs), are larger than pristine SWNT (p-SWNT) and functionalized MWNT (f-MWNT)-RET composites.

1(b)] CNT filling fractions, through scanning electron microscopy (SEM) (Phillips XL30) images of the fracture surfaces of the composites, in comparison to the clumping observed [Fig. 1(c)] when unfunctionalized nanotubes were mixed into the polymer. Uniform dispersion was also seen for functionalized MWNTs [Fig. 1(d)].

The electromagnetic properties of the CNT-RET nanocomposites, as measured through the S-parameters[12] (S_{ij}), were recorded in the microwave frequency range (8.2–12.4 GHz, X-band) using a vector network analyzer (Agilent 5242A PNA-X). The composite loaded sample holder was inserted between two 15 cm lengths of WR-90 X-band waveguide to mitigate the near-field effects of the coax to waveguide transitions. The determination of S_{11} and S_{21} enables the calculation of the complex permittivity ($\varepsilon=\varepsilon'+j\varepsilon''$) and permeability ($\mu=\mu'+j\mu''$), where $j=\sqrt{-1}$, through[17]

$$S_{11}=\frac{(1-\Gamma^2)z}{1-\Gamma^2z^2}, \tag{1}$$

$$S_{21}=\frac{(1-z^2)\Gamma}{1-\Gamma^2z^2}. \tag{2}$$

Equations (1) and (2) permit the determination of the reflection coefficient, $\Gamma=\sqrt{\mu_r/\varepsilon_r}-1/\sqrt{\mu_r/\varepsilon_r}+1$ and the transmission coefficient z, $[=e^{-j(\omega/c)\sqrt{\mu_r\varepsilon_r}}]$, from which ε_r and μ_r were ascertained,[18] with an error of at most 7%. The frequency variation in the real (ε') and imaginary (ε'') permittivity of the functionalized SWNT-RET composites, as a function of SWNT concentration (ϕ_{CNT}) is depicted in Figs. 2(a) and 2(b), respectively. It was seen that composites constituted of functionalized SWNTs have ε' ($/\varepsilon''$) $\sim 5(/25)$ times greater than composites composed of (i) pristine SWNTs, presumably due to the better filler dispersion, and $\varepsilon'(/\varepsilon'')\sim 10(/300)$ times larger than (ii) functionalized MWNT-RET composites, attributed to a larger aspect ratio. While an increase in ε' with increased SWNT volume fraction could be due to the formation of an increased number of SWNT-RET dielectric-SWNT capacitors, the increase in ε'' $[=\mathrm{Re}(\sigma/\omega\varepsilon_o)]$ was possibly due to an increased electrical conductivity (σ), at increased SWNT filling fractions. Additionally, enhancement in ε'', through dielectric loss, could be also related to an interphase region at the CNT-RET interface.[19] Preliminary modeling of the dielectric constant of the nanotube composites (ε_c) was done through the law of mixtures,[19] i.e.,

$$\varepsilon_c=\phi_{CNT}\varepsilon_{CNT}+(1-\phi_{CNT})\varepsilon_{RET}, \tag{3}$$

where ε_{CNT}($/\varepsilon_{RET}$) and ϕ_{CNT}($/1-\phi_{CNT}$) are the complex dielectric constants and volume fractions) of the CNT fillers (/RET polymer matrix), respectively. A good agreement ($\pm$ 10%) with the experimental values was obtained for ε_c.

The four-wire resistance method was then used to measure the electrical conductivity (σ) of the CNT-RET composites. For samples with low ϕ_{CNT}, with very large resistance (>1 GΩ), two point measurements using the Agilent B1500A semiconductor device analyzer with triaxial probes were used. For higher ϕ_{CNT}, with smaller resistance, the measurements were made through the Keithley 487 picoammeter and the Keithley 2400 Sourcemeter. In both cases, the composites were treated with oxygen plasma (Oxford Plasmalab 80 RIE) prior to the electrical contacting (using 50 nm of sputtered Au) of the surface. The dc conductivity (σ_{dc}) of the composites measured as a function of the incorporated volume fraction of functionalized SWNTs is shown in Fig. 3(a) and fit to a percolation theory[20] based expression of form

$$\sigma\sim\sigma_0(\phi_{CNT}-\phi_c)^t, \tag{4}$$

where ϕ_{CNT} is the SWNT volume fraction, ϕ_c is the percolation threshold volume fraction and t is a critical exponent. σ_o is a constant. From the fit, the values of ϕ_c ($\sim$0.11%) and t ($\sim$3.4) were obtained. While t seems to be appropriate to a thick film resistor configuration with elongated fibers,[21] the observed ϕ_c is one of the *lowest* reported in literature. We calculated from excluded volume based percolation theory[22] that for the given SWNT aspect ratio ($\sim$880), a theoretical ϕ_c of 0.1 vol % which is in excellent agreement with our results. The low ϕ_c also implies a correlated bond model of percolation,[20] with SWNT interactions. Supporting evidence for such interactions was obtained through the determination of the ac conductivity (σ_{ac}) of the composites (calculated[8] through $\sigma_{ac}=2\pi f\varepsilon_0\varepsilon''$, at a given frequency f with $\varepsilon_0=8.854\times10^{-12}$ C^2/Nm^2) and is shown in Fig. 3(b). The following was noted: (1) σ_{ac} varies *linearly* with ϕ_{CNT}, (2) $\sigma_{ac}>\sigma_{dc}$, even below ϕ_c, and that (3) σ_{dc} approaches σ_{ac} at high (>4 vol %) filling fraction of the SWNTs. These observations indicate a frequency dependent mechanism of electrical conduction, which was sought to be understood through a very simple model of parallel resistors and capacitors formed in the nanocomposite[8]—Fig. 3(b) inset. In this model, the SWNTs contribute to the electrical resistance while the polymer matrix serves as the capacitor dielectric and contributes to the AC conductance. As the SWNT concentration in the matrix increases, equivalent to an increasing

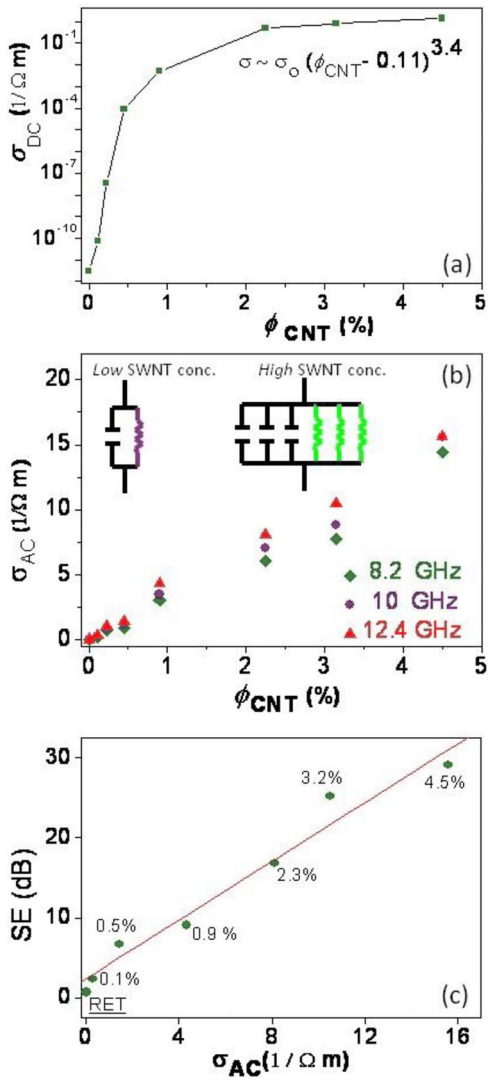

FIG. 3. (Color online) (a) The dc conductivity, σ_{dc}, of functionalized SWNT-RET composites follows a power law characteristic of percolation-like behavior (with a threshold volume fraction, $\phi_c \sim 0.11\%$ and an exponent of ~3.4). (b) The ac conductivity σ_{ac} of the SWNT-RET composite increases linearly with SWNT volume fraction (ϕ_{CNT}), and frequency, at a particular ϕ_{CNT}. The inset shows the parallel resistor-capacitor combination used to model σ_{ac}. (c) The σ_{ac} can be used as a predictor of the SE of the nanocomposites (numbers indicate ϕ_{CNT})-data obtained at 12.4 GHz. The polymer matrix reference is indicated by RET.

number of parallel resistors and capacitors, the net resistance and capacitive impedance ($X_c = |1/2\pi fC|$) decreases due to the availability of several alternative electrical conduction paths. Consequently, both σ_{dc} and σ_{dc} increase, with a diminishing difference at higher f. Such a parallel conduction model was also supported from the linear relationship of the shielding effectiveness (SE), which was independently obtained from the *S*-parameter measurements[12] to σ_{ac} [Fig. 3(c)], through $SE = -10\log(T)$, where T ($\equiv |S_{21}|^2$) is the transmittance. We also observed higher values of SE at a lower loading fraction of SWNTs (i.e., ~30 dB at 4.5 vol % of SWNTs) compared with literature, e.g., <15 dB with 15% SWNTs at 1 GHz,[7] with 11.6% SWNTs at 8 GHz,[11] and ~20 dB with 8.6% SWNTs at 8 GHz,[23] presumably due to the uniformity of dispersion. Additionally, our values are comparable to those obtained in CNT films, of ~28 dB at 10 GHz.[10]

In summary, we have seen that functionalized SWNTs, with a high aspect ratio, favor uniform dispersion into an RET polymer matrix and have a major influence on the electromagnetic properties. The relationship of ε'' to σ_{ac} was used as a metric for the EMI SE and understood in terms of a parallel resistor-capacitor model. Future work would focus on the validity of the model and the utility of uniformly dispersed composites for various applications.

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[1] D. D. L. Chung, Carbon **39**, 279 (2001).
[2] D. M. Bigg and D. E. Stutz, Polym. Compos. **4**, 40 (1983).
[3] E. S. A. Rashid, K. Ariffin, H. M. Akil, and C. C. Kooi, J. Reinf. Plast. Compos. **27**, 1573 (2008).
[4] Z. Liu, G. Bai, Y. Huang, F. Li, Y. Ma, T. Guo, X. He, X. Lin, H. Gao, and Y. Chen, J. Phys. Chem. C **111**, 13696 (2007).
[5] M. Hughes, *Dekker Encyclopedia of Nanoscience and Nanotechnology* (Taylor & Francis, London, 2004), pp. 447–459.
[6] M. Moniruzzaman and K. I. Winey, Macromolecules **39**, 5194 (2006).
[7] N. Li, Y. Huang, F. Du, X. He, X. Lin, H. Gao, Y. Ma, F. Li, Y. Chen, and P. C. Eklund, Nano Lett. **6**, 1141 (2006).
[8] A. Saib, L. Bednarz, R. Daussin, C. Bailly, X. Lou, J. M. Thomassin, C. Pagnoulle, C. Detrembleur, R. Jérôme, and I. Huynen, IEEE Trans. Microwave Theory Tech. **54**, 2745 (2006).
[9] P. Ajayan, L. S. Schadler, C. Giannaris, and A. Rubio, Adv. Mater. (Weinheim, Ger.) **12**, 750 (2000).
[10] H. Xu, S. M. Anlage, L. Hu, and G. Gruner, Appl. Phys. Lett. **90**, 183119 (2007).
[11] Z. Liu, G. Bai, Y. Huang, Y. Ma, F. Du, F. Li, T. Guo, and Y. Chen, Carbon **45**, 821 (2007).
[12] D. M. Pozar, *Microwave Engineering*, 2nd ed. (Wiley, New York, 1998).
[13] S. Antoniotti, S. Antonczak, and J. Golebiowski, Theor. Chem. Acc. **112**, 290 (2004).
[14] S.-H. Park, P. Thielemann, P. Asbeck, and P. R. Bandaru, "Enhanced electromagnetic interference shielding through the use of functionalized carbon nanotube-reactive polymer composites," IEEE Trans. Nanotech. (in press).
[15] J. A. Nichols, H. Saito, C. Deck, and P. R. Bandaru, J. Appl. Phys. **102**, 064306 (2007).
[16] D. Tasis, N. Tagmatarchis, A. Bianco, and M. Prato, Chem. Rev. (Washington, D.C.) **106**, 1105 (2006).
[17] A. M. Nicolson and G. F. Ross, IEEE Trans. Instrum. Meas. **19**, 377 (1970).
[18] W. B. Weir, Proc. IEEE **62**, 33 (1974).
[19] M. G. Todd and F. G. Shi, IEEE Trans. Dielectr. Electr. Insul. **12**, 601 (2005).
[20] S. Kirkpatrick, Rev. Mod. Phys. **45**, 574 (1973).
[21] D. S. McLachlan, M. Blaszkiewicz, and R. E. Newnham, J. Am. Ceram. Soc. **73**, 2187 (1990).
[22] I. Balberg, C. H. Anderson, S. Alexander, and N. Wagner, Phys. Rev. B **30**, 3933 (1984).
[23] N. C. Das and S. Maiti, J. Mater. Sci. **43**, 1920 (2008).