

Modeling the Relative Dielectric Permittivity and Impedance of Carbon Nanotube Constituted Polymer Composites in the Sub-GHz Regime

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A model-based approach to characterize the electrical impedance of polymer matrices with carbon nanotube fillers, based on dielectric permittivity measurements in the sub-GHz regime, is proposed. In this context, an equivalent-series resistance (ESR) model, constituted of lumped resistances (R) and capacitances (C) is compared with distributed models such as a RC network and constant phase element (CPE) representations. It is shown, through detailed statistical analysis, that the CPE corresponding to a distribution/dispersion of relaxation times may best fit the experimental data. © 2012 The Electrochemical Society. [DOI: 10.1149/2.006301ssl] All rights reserved.

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The determination and modeling of the electromagnetic (EM) characteristics of carbon nanotube (CNT) containing polymer composites is of much interest, with the objectives of obtaining (a) fundamental understanding of the influence of large aspect ratio electrical conductors, as well as for (b) practical applications. A large length to diameter aspect ratio, which could be as much as 10^6 (e.g., for a nanotube of 1 mm length and 1 nm diameter) enables pertinent characteristics, such as electrical percolation, to be obtained at much lower volume fractions, e.g., at <0.01% nanotube filler concentrations.¹ In the context of applications, CNT constituted composites have been advocated for a wide variety of uses, e.g., EM interference shielding,² thermal management,³ energy conversion and electronic packaging applications,⁴ etc., in which characterization of EM properties would be important.

In this paper, we report on the measurement, modeling, and interpretation of the relative dielectric permittivity (ε_r^*) of multi-walled CNT (MWCNT) / polymer composites at frequencies (*f*) less than 0.5 GHz. The real and imaginary parts of the (ε_r^*) were then fit to real and imaginary electrical impedances and compared to lumped and distributed models of the resistance (*R*) and capacitance (*C*) of the nanotube/polymer composite. At the very outset, the composite was modeled to be of three constituents, i.e., (i) an electrically conducting CNT (as is typical of MWCNTs⁵) phase, (ii) a relatively insulating polymer matrix phase, and additionally (iii) an interphase⁶ component. A relevant circuit model would then consist of equivalent electrical *R* and *C*. The inductive response of the measurement instrumentation and the composite sample was negligible (the relative magnetic permeability, μ_r , of the sample was measured⁷ to be ~1), and could be subtracted out through calibration at the considered frequencies.

We incorporated various filler fractions (in the range of 0-10 volume%) of acid-functionalized MWCNTs into reactive ethylene terpolymer (RET) based polymers - see Figure 1a, through procedures that have been previously reported.⁸ Samples of MWC-NTs, with constituent diameters of ~20 nm, and average length of \sim 6.8 µm, yielding a length to diameter aspect ratio of \sim 340, were used. The geometrical parameters were determined by scanning electron microscopy (SEM) and atomic force microscopy (AFM), through subjecting the MWCNTs to similar processing conditions as were used for their dispersion into the polymer. RET (Elvaloy 4170, procured from DuPont Inc.) constituted from (1) polyethylene, (2) a polar methyl-methacrylate, and (3) epoxide functional groups was seen to possess superior mechanical characteristics and corrosion resistance, while the epoxy group has high reactivity⁹ and is amenable for effective anchoring of the epoxide ring bonds with functional groups (e.g., -OH, COOH, -NH2 etc.) on the CNTs, as was verified through

Fourier transform infrared spectroscopy.⁸ The uniformity of the dispersion was gauged by considering SEM micrographs at different length scales, i.e., 1 μ m to 200 μ m and the extensive use of image processing software and algorithms.¹⁰ The permittivity was measured and modeled (over a frequency range of 80 MHz – 0.5 GHz, as used for line-of-sight communications¹¹) using a RF Impedance/Material Analyzer (Agilent E4991A), with the composite sample contacting the upper and lower electrodes in the test fixture (Agilent 16453A). Prior instrumental calibration, using Teflon and silica glass standards, was used to validate the experimental setup. Additionally, the electrode and instrument inductances were compensated through standard instrument testing protocols¹² with connected/open electrodes.

The complex permittivity, ε^* , is related to the real (ε_r') and imaginary (ε_r'') components through $\varepsilon^* = \varepsilon_o \ \varepsilon_r^* = \varepsilon_o \ (\varepsilon_r' - j\varepsilon_r'')$, where ε_o is the permittivity of free space (=8.854 \cdot 10⁻¹² F/m) and $j = \sqrt{-1}$. Representative experimental measurements are indicated in Figures 1b and 1c. The electrical impedance, $Z^* = Z' + j Z''$, constituted of real (Z') and imaginary (Z'') components was then calculated from the complex capacitance $C_S^*(\omega)$ where $\omega \ (= 2\pi \ f)$, is the angular frequency $\varepsilon_r^* (= \frac{C_S^*(\omega)}{C_o} = \frac{1}{j\omega Z * C_o})$, and $C_o = \frac{\varepsilon_o A}{L}$, with A as the electrode area and L the distance between the electrodes. Consequently, $Z' = \frac{\varepsilon_r''}{\omega C_o(\varepsilon_r^2 + \varepsilon_r'^2)}$ and, $Z'' = \frac{-\varepsilon_r'}{\omega C_o(\varepsilon_r^2 + \varepsilon_r'^2)}$. Plots for the frequency dispersion of Z and Z'' were calculated from ε_r' and ε_r'' , and have been indicated in Figure 2.

We compared electrical circuit models (see Figure 3) to characterize the Z^* variation in the nanotube/polymer composite, using (i) an equivalent series resistance (ESR) model, (ii) a two-dimensional random network of resistors and capacitors (2D RC) model,¹³ and a derivative (iii) constant phase element (CPE) model.¹⁴ The idea behind such various representations was to investigate whether the net impedance, in terms of the resistance and capacitance of the composite could be considered in terms of lumped or distributed elements, and estimate the number of minimum needed fitting parameters. In the represented ESR model, of Figure 3a, R_{ESR} (ω) embodies the frequency dependent dielectric polarization losses and R_p accounts for the leakage currents in the capacitor. We could neglect R_p compared to the capacitive impedance $|X_c|$ (=1/ ωC) at volume fractions above the percolation threshold (ϕ_c), which was measured to be ~0.17 vol% for our composites. For example, at a CNT volume concentration of ~2%, the R_p was estimated to be 10^8 times larger than the X_c at 1 GHz. Then, $Z^* = R_{ESR} (\omega) - j/\omega C = (\tan(\delta) - j)/\omega C$, where $\tan(\delta) = -\frac{Z'}{Z''} = \frac{\varepsilon_r''}{\varepsilon'}$ is the loss-tangent defined in terms of the real and imaginary components of the impedance/dielectric permittivity.

The 2D RC model considers the composite with dispersed nanotubes and the intervening polymer to form a *distributed* electrical network of resistors and capacitors (e.g., constituted from the dielectric between the conductors/nanotubes). To describe the electrical

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5

3

2

0.22

0.20

0.18

0.16

0.14

0.12

0.10

Ô

2

4

(b)

100

Figure 1. (a) Typical MWCNT/RET polymer composites. The variation of the real (ε_r') and imaginary (ε_r'') dielectric permittivity with (b) frequency (ω) (with 3 vol% CNT fillers) and (c) CNT filler concentrations (at 100 MHz). In (b) the fit lines to the data (points) followed a power law relation, with $\varepsilon_r'(=a \omega^{-t} + b)$ and $\varepsilon_r'' (=d \omega^{-t})$ varying as $\sim \omega^{-t} (a, b, d, and t are fitting parameters)$. (d) The variation of the power law exponent, *t*, with CNT filler concentration.

3.0

2.5

2.0

1.5

1.0

0.5

0.0

10

conductivity of a composite, σ_c^* , consisting of a complex mixture of dielectric/polymer (with a conductivity: σ_P^*) along with nanotubes (with a conductivity: σ_N^*) we may invoke a mixing rule, with the consideration that the measured resistance would be a combination of the polymer and nanostructure resistances in parallel *or* in series. Assuming equivalent geometries, for the case of parallel addition: $\sigma_c^* = p\sigma_P^* + n\sigma_N^*$, while for series addition: $(\sigma_c^*)^{-1} = p(\sigma_P^*)^{-1} + n(\sigma_N^*)^{-1}$, where *p* and *n* are the relative contributions from the polymer and the nanostructure, respectively. Nominally, the sum of *p* and *n* would be expected to be equal to unity. We may then write that $(\sigma_c^*)^v = p(\sigma_P^*)^v + n(\sigma_N^*)^v$ (adopting the

6

Volume % CNTs

8

30

25

20

15

10

5

0

0

(c)



Figure 2. The variation of the real (*Z'*) and imaginary (*Z''*) parts of the electrical impedance (*Z**) with frequency (with 3 vol% CNT fillers), as obtained from ε_r' and ε_r'' .

Lichtnecker mixing rule¹⁵) with $-1 \le v \le 1$, where the upper and lower bounds relate to the parallel and series combinations discussed above. Consequently, for $v \to 0$ (assuming an equal number of series and parallel connections), it can be derived that ${}^{16} \sigma_c^* = (\sigma_P^*)^p (\sigma_N^*)^n$.

0.6

0.5

0.4

0.3

0.2

0.22

0.20

0.18

0.16

0.14

0.12

0.10

300 400500

(d)

0 200 300 4 Frequency (MHz)

6

Volume % CNTs

8

10



Figure 3. Circuit models for (a) an equivalent series resistance (ESR) model, and (b) a two-dimensional random network of resistors and capacitors (2D RC) model, were used to fit the Z^* variation (from Figure 2) of the nanotube-polymer composites. The 2D RC displays 194 capacitors and 6 resistors, to model the nanotube/polymer composite, corresponding to a $\beta = 0.97$ (=194/200), which was obtained through the Z^* fits.

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From considering the polymer, where σ_p^* (= $j\omega\varepsilon_o\varepsilon_r'$) and assuming that σ_N^* for the nanotube is purely real, we derived the complex conductance of such a network to be $\sigma_{2DRC}^* = \frac{(j\omega\varepsilon)^{\beta}}{R^{1-\beta}}$, where $\beta = \frac{2}{\pi} \cot^{-1}(\tan \delta)$. It has been previously shown that a three dimensional dispersion may adequately be represented through a two-dimensional network model.¹⁷ The complex impedance was then derived to be: $Z^* = \frac{LR^{1-\beta}}{A(j\omega\varepsilon)^{\beta}} = \frac{LR}{A(\omega\kappa\varepsilon)^{\beta}} [\cos(\frac{\beta\pi}{2}) - j\sin(\frac{\beta\pi}{2})]$, and fitted to our experimental data. The 2D RC model is displayed, in Figure 3b, with 194 capacitors and 6 resistors corresponding to a $\beta = 0.97$ (=194/200), which was obtained through the fits.

While the ESR model considered a frequency dependent resistance, the CPE based representation invokes a distribution/dispersion of relaxation times, $\tau(\omega)$. While such representations have been extensively used to parameterize the frequency response of solid electrolytes¹⁸ and solid-solid interfaces,¹⁹ the present work is the first to utilize the CPE construct for the description of the electrical impedance of CNT/ polymer composites. From a physical point of view, the influences of non-uniform potential and current distribution, roughness, composition variations, etc., are some of the parameters¹⁸ that could be described through such a model. The underlying idea of the CPE is to fit the impedance data, say that obtained through the distributed RC type model, over a *defined* frequency range. The constraint of a frequency range then implies that the electrical impedance, $Z^* = \frac{1}{(Q_0)^{\beta}} \left[\cos(\frac{\beta \pi}{2}) - j \sin(\frac{\beta \pi}{2}) \right]$, with Q as the only fitting parameter, and which can be reduced to resistive ($\beta = 0$), inductive (β = -1), or capacitive ($\beta = 1$) behaviors. The CPE aspect is manifested through the $\frac{Z''}{T}$ ratio, from which the magnitude of the phase, $\beta \pi/2$ is independent of frequency.

Concomitant to the data fitting, further detailed statistical analysis indicated that the coefficient of determination²⁰ (i.e., the r^2 value) was larger for the distributed models (2D RC and CPE) compared to the lumped (ESR based) model. Another important metric to describe the goodness of fit between competing models uses the Akaike Information Criterion (AIC).²¹ The underlying idea behind the AIC is that it incorporates a penalty for increasing the number of fitting parameters and consequently, a model with the minimum number of fitting parameters is preferred and given a low AIC number. We have then generally found a lower AIC number for the distributed CPE and the 2D RC models, e.g., for a 1 vol% (and 3 vol%) nanotube filler percentages, the AIC numbers were 239 (58) and 241 (60). The corresponding AIC numbers for the ESR model were 523 and 379 respectively. We thus conclude that distributed models may more accurately determine nanotube-polymer composite properties.

From considering the $\sigma^* (=j\omega\varepsilon_o [\varepsilon_r' - j\varepsilon_r''])$ for the composite and the polymer and assuming that σ_N^* for the nanotube is purely real, we obtained a functional relation for the frequency dispersion of the composite dielectric constants, both for ε_r' as well as ε_r'' to be varying as ω^{p-1} . We have then fitted our experimental data – see Figure 1d, to the forms $\varepsilon_r' = a \, \omega^{-t} + b$, and $\varepsilon_r'' = d \, \omega^{-t}$, where *a*, *b*, *d*, and *t* are fitting parameters. It would then be expected that as the contribution from the polymer decreases (i.e., *p* decreases) due to increasing the nanotube fillers, that *t* should increase. However, an opposite trend was observed as indicated in Figure 1c. We then hypothesize that the original assumption, i.e., that σ_N^* is purely real, may not be correct and a complex conductivity, proportional to ω should be considered. Consequently, the frequency dispersion of the composite for ε_r' as well as ε_r'' would vary as ω^{p+n-1} . If the decrease in *p* is lower than the increase in *n*, the correct trend in *t* could be obtained.

We justify the frequency dispersion of the nanotube fillers on the basis that its constituent electromagnetic properties could change depending on the environment, e.g., the formation of an interphase⁶ region, which could considerably modify the relative contributions of the filler and the polymer matrix. We have seen, for example, a smaller variation of the exponent, *t*, when lower aspect ratio nanotubes were used. It was also noted from Figure 1d, that the *t* tends to |p-1|, as *p* decreases,²² which may indicate increasing contribution from the nanotubes. The *t* values were similar to those reported earlier²³ for multiwall MWCNT/poly-vinylidene fluoride (PVDF) composites. However, unlike this earlier study, we have not observed a drastic increase in the dielectric constants at the electrical conductivity percolation threshold (ϕ_c), due to the higher frequencies.

In summary, we have shown that the electrical characteristics, such as the dielectric permittivity and the complex impedance, of nanotube/RET polymer composites could be best modeled by considering a distributed network of resistances and capacitances, constituting a constant phase element (CPE) based approach.

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