# Optimisation of microwave absorption of carbon nanotube composites through use of carboxyl-epoxide functional group linkages

P. Theilmann, K.M. Chu, P.R. Bandaru, P. Asbeck and S.H. Park

Lightweight, flexible and highly efficient microwave absorbing single-walled carbon nanotube (SWNT)/polymer composites were fabricated through chemical functionalisation to ensure uniform dispersion of SWNTs in a polymer matrix. These composites were used to fabricate thin electromagnetic absorption coatings, which achieve a maximum reflection loss (*RL*) magnitude of 24 dB at X-band frequencies. Based on analysis of measured results it is discovered that the frequency of peak absorption is dependent on coating thickness ($d$) and filler wt%. Trade-offs between $d$ and SWNT wt% are discussed with respect to peak $|RL|$.

*Introduction:* Polymer composites containing conducting fillers such as carbon black and fibres that form a conducting network have been extensively investigated for various applications such as electromagnetic interference (EMI) shielding, electronic packaging, radar absorption, and high charge storage capacitors. Specifically, research on microwave absorbing materials for military aircraft, vehicles, consumer electronics and cellular phone systems has been popular. The advent of carbon nanotubes (CNTs) has enabled the achievement of lightweight and high absorbing efficiency materials owing to their unique chemical and physical properties [1]. However, there are still challenges to the utilisation of CNTs such as aggregation and bundling which lead to non-uniform dispersion. For large-scale processing and uniformity, it is desirable to ensure effective mixing and dispersion of the CNTs within the polymer. In addition, although previous reports have shown the microwave absorption properties of CNT based composites [2], there are few studies that cover the design considerations of such composites. In this Letter, enhanced nanotube–polymer interactions are obtained, through chemical functionalisation, which result in uniform dispersion conditions and consistent reproducibility. Furthermore, the process of frequency optimisation of the microwave absorption properties of CNT composite systems through the tuning of filler content and thickness is reported in the X-band (8.2–12.4 GHz) frequency range.

*Fabrication:* In this work, a composite of CNTs and an RET (Reactive Ethylene Terpolymer, density 0.94 $g \cdot cm^{-3}$) consisting of 1. polyethylene; 2. a polar methyl methacrylate group; and 3. epoxide functional groups was used. The epoxy group has high reactivity and is amenable for effective anchoring of the ring bonds with functional groups (e.g. $-OH$, COOH, $-NH_2$ etc.) on the CNTs. The underlying rationale is that the epoxide ring rupture [3] on the RET would be facilitated by the $-COOH$ groups on the functionalised nanotubes and then contribute to bonding of the COOH on the SWNT with the epoxy group of the RET.

A mixture of sulphuric and nitric acids (in a 3:1 ratio) was used for nanotube surface functionalisation with $-COOH$ groups, and for removing impurities. Subsequently, the CNTs were rinsed with deionised water, and then dried at $\sim$60 °C for 10 h. The single-walled carbon nanotubes (SWNTs) were then dispersed in toluene with sonication for 20 min. The RET was then added to toluene solvent with heating to $\sim$60 °C for 2 h and subsequent stirring. The CNT dispersion was then added to the RET solution and sonicated again for $\sim$50 min. To remove excess solvent, the mixture was stirred, at 60 °C for 3 h, poured into glass dishes, and then evacuated in vacuum ($10^{-3}$ torr) for 12 h. Subsequently, a hot press was used to form the composites to a desired thickness.

*Measurement:* The electromagnetic properties of the CNT-RET nano-composites, as measured through *S*-parameters ($S_{ij}$), were recorded in the microwave frequency range (8.2–12.4GHz, X-band) using a vector network analyser (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 used in the measurement system. The determination of $S_{11}$ and $S_{21}$ enables the calculation of the complex permittivity ($\varepsilon = \varepsilon' - j\varepsilon''$) and permeability ($\mu = \mu' - j\mu''$) [4].

The reflection loss (*RL*) of a single-layered electromagnetic absorber in decibels is defined as [5]

$$RL = 20 \log_{10} \left| \frac{z_{in} - z_0}{z_{in} + z_0} \right| \quad (1)$$

where

$$Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh\left[ \frac{j2\pi}{c} \sqrt{\mu_r \varepsilon_r} f d \right] \quad (2)$$

In (1) and (2), $Z_{in}$ is the input impedance at the interface of free space and the material (which is placed on top of a perfect conductor), $Z_0$ is the characteristic impedance of free space ($Z_0 = 377\ \Omega$), $c$ is the velocity of light, $f$ is the frequency and $d$ is the sample thickness. Using the measured complex permittivity and permeability of samples of specific CNT concentrations, *RL* was calculated for a selected thickness $d$. In this way, changes in *RL* due to the tuning of $d$ can be investigated for different CNT concentrations.

*Results:* A uniform dispersion was observed when using functionalised SWNTs as shown Fig. 1, which displays scanning electron microscopy (SEM) images of the fractured surfaces of two composites. In Fig. 1*a*, functionalised SWNTs were used resulting in even dispersion whereas non-functionalised nanotubes were used in Fig. 1*b* causing visible clumping of the CNTs. Besides uniformity of nanotube dispersion, the strategy of employing mutual chemical reaction between functional groups on the CNT and the polymer through covalent functionalisation of the nanotube surface resulted in reinforcement effects and reproducibility suitable for mass production.

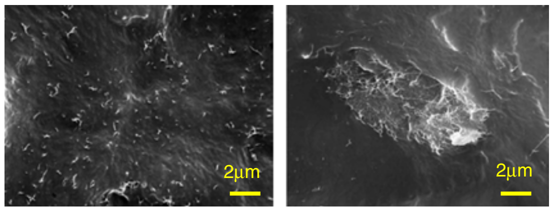


**Fig. 1** *SEM images of fractured surfaces of two composites*

*a* Functionalised SWNTs were used resulting in even dispersion
*b* Non-functionalised nanotubes were used causing visible clumping

The frequency variation in the real and imaginary permittivity of the functionalised SWNT composites as a function of SWNT concentration is depicted in Fig. 2. The increases in $\varepsilon'$ as the CNT volume fraction is increased can be attributed to the formation of distributed capacitance (CNT-polymer dielectric-CNT). The increment of $\varepsilon''$ is due to increased electrical conductivity through the CNT filling fraction. The real and imaginary permeability of SWNT composites was found to be equivalent to pure RET, indicating no magnetic loss in the measured carbon-based nano-composites. The results were consistent across various samples of different thickness, indicating that permittivity is independent of $d$ and performance is reproducible.

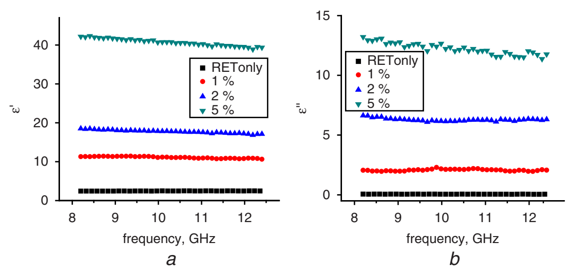


**Fig. 2** *Measured relative permittivity of composite samples*

*a* Real relative permittivity
*b* Imaginary relative permittivity

The *RL* of SWNT composites with different content and thickness is presented in Fig. 3. To maximise microwave absorption, according to (1) and (2), $Z_{in}$ should be close to $Z_0$. This denotes impedance matching through a combination of thickness, permittivity, permeability and frequency. In general, a close match will only occur at a single frequency for a given SWNT wt% and thickness $d$. Furthermore, higher SWNT wt% (larger $\varepsilon'$, $\varepsilon''$) and thicker samples will obtain matches at lower frequencies. For example, when a 2 wt% SWNT composite sample is used, setting $d = 1.75$ mm results in an absorption maximum near the centre of the X-band (see Fig. 3*a*). On the other hand, if a 5 wt% SWNT composite sample is used, maximum absorption near the centre of the X-band can be obtained for a thickness of only 1.15mm (see Fig. 3*b*). This indicates that through the tuning of wt% and *d*, the frequency band of peak absorption of a composite can be selected for a given application. Thus a designer can simply use (1) and (2) to construct a coating of desired thickness to operate at a given frequency.

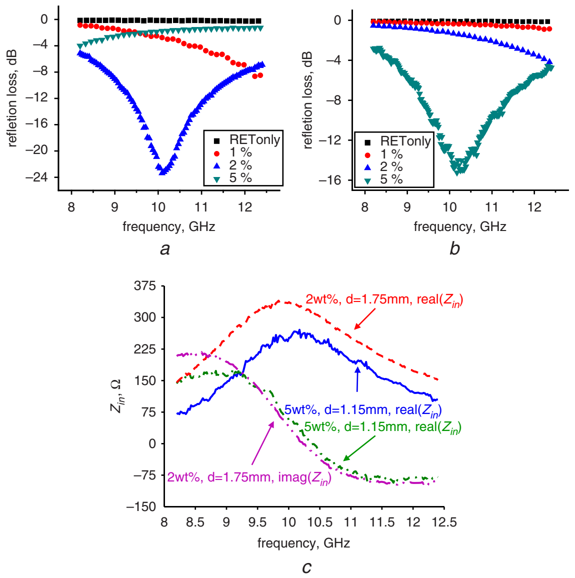


**Fig. 3** *RL and $Z_{in}$ at X-band calculated from measured permittivity and permeability*

*a* Sample thickness 1.75 mm
*b* Sample thickness 1.15mm
*c* Real and imaginary $Z_{in}$

It is important to note that even though higher wt% composites allow for the use of thinner samples, the peak $|RL|$ obtained can differ. This issue is illustrated in Fig. 3: the 2 wt% sample with $d = 1.75$ mm achieves a peak $|RL| \sim 24$ dB while the 5 wt% sample with $d = 1.15$ mm reaches a peak $|RL| \sim 15$dB. The reason for this is somewhat subtle: the peaks in $|RL|$ occur when *f*, *d* and $\varepsilon$ are such that the imaginary part of $Z_{in}$ crosses 0. The magnitude of the peak is then set by how close the real part of $Z_{in}$ is to $Z_0$ when imag($Z_{in}$) crosses 0. In Fig. 3*c*, it is clearly seen that at the imag($Z_{in}$) = 0 point, the 2 wt% sample achieves a real($Z_{in}$) closer to $Z_0 = 377\ \Omega$ than the 5 wt% sample.

*Conclusion:* In this Letter, uniform dispersion through functionalised nanotube-polymer interaction has been shown to be useful in reproducibly fabricating microwave absorbing coating material. Because of the formation of increased distributed capacitance and electrical conductivity, real and imaginary permittivity increased by a factor of up to 40 times that of pure RET polymer. In addition, it was shown that through trade-offs between desired frequency of operation, coating thickness and SWNT wt%, microwave absorbing shields can be designed for specific applications using SWNT/polymer composites.


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One or more of the Figures in this Letter are available in colour online.

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