Microwave properties of carbon nanotube/microwire/rubber multiscale hybrid composites

F.X. Qin\textsuperscript{a,b,*}, C. Brosseau\textsuperscript{b}, H.X. Peng\textsuperscript{a}

\textsuperscript{a} Advanced Composite Centre for Innovation and Science, Department of Aerospace Engineering, University of Bristol, University Walk, Bristol BS8 1TR, UK
\textsuperscript{b} Université Européenne de Bretagne, Université de Brest, Lab-STICC, CS 93837, 6 Avenue Le Gorgeu, 29238 Brest Cedex 3, France

Abstract

A novel microwire/carbon nanotube (CNT)/rubber multiscale hybrid composite is reported here. Compared to CNT composites, the hybrid composite shows enhanced conductivity and permittivity and decreased intrinsic impedance, giving rise to significant improvement of absorption yet along with the increase of reflection loss. The hybrid composite also shows a field tunable effect with a featured critical bias, which divided two opposite frequency dispersion trend with the field due to the different biasing mechanism decided by the field magnitude. The counter-influence of wires and CNTs plays an important role in formulating the resulting electromagnetic responses.

1. Introduction

The intriguing high-frequency electromagnetic properties of artificial heterogeneous composites enabled by the micrascale or nanoscale fillers have excited the scientific community and industrial sectors due to their multifunctionalities ensuring a broad application perspective ranging from reconfigurable microwave devices \cite{1} to microwave non-destructive testing \cite{2,3}. The multifunctionalities are actually a collection of peculiar responses to various external stimuli such as magnetic field, stress and temperature. One case in point is microwires enabled multifunctional composite \cite{4–6}. By virtue of the excellent soft magnetic properties and giant magnetoimpedance (GMI)/giant stress-impedance (GSI) effects of microwires \cite{7–9}, their composites exhibit excellent microwave tunable properties in presence of field and/or stress and excellent microwave absorption and electromagnetic interference (EMI) shielding performance of significant practical value \cite{10–12}. Also, thanks to the unique property of a single microwire or wire arrays, a wire-composite can exhibit metamaterial behaviours with negative permittivity owing to the plasma resonance and negative permeability owing to the ferromagnetic antiresonance \cite{13–15}.

In parallel, another example of significant interest is carbon nanotube composites. CNTs have superior elastic modulus (~1TPa) and tensile strength (50–500 GPa) than the conventional fibres \cite{16}. They also possess an aspect ratio up to several thousands and specific surface area up to 1300 m\textsuperscript{2}/g \cite{17}. They have been successfully used to reinforce a variety of thermostet polymers such as epoxy and thermoplastic polymers such as polypropylene and elastomers such as nitrile rubbers \cite{18}. The incorporation of CNTs, in analogy to molecules, also improves the electrical and thermal (thermal–mechanical) properties of the composite \cite{19}. With very large aspect ratio (10\textsuperscript{2} to 10\textsuperscript{3}), only a small concentration of CNT is needed to achieve a conductive network and maximum polarization loss, which is the major contribution to the microwave absorption for CNT composites \cite{20}. Thus, CNT composites are ideal candidates for cost-effective and lightweight absorbers.

However, as an individual filler responds discriminately to the external field, it is necessary to modify its structure in order to release the limitation to its field selectivity. Alternatively, one can mix different types of fillers together to improve the overall performance of the resultant composite. Obviously, the latter is a much more facile approach than the former which often involves complicated chemical processes. In this context, we try mixing CNT and microwires together to create a multiscale hybrid composite to improve, among others, the microwave absorption performance.

2. Experimental

2.1. Materials

Silicone elastomer was purchased from RS Components (UK) and used as received. Multiwall CNTs were purchased from Cheetah. The MWNTs had the diameter ranging between 20 nm and 30 nm, and length varying between 10 µm and 30 µm. The purity of the MWNTs are >95% and the specific surface area equals to 110 m\textsuperscript{2}/g. Glass-coated amorphous microwires Fe\textsubscript{4.84} Co\textsubscript{56.51} B14.16...
Si$_{11.41}$ Cr$_{13.08}$ with a core diameter of 19.8 μm and total diameter of 29.4 μm were provided by MFTI, Moldova.

2.2. Hybrid composite fabrication

(1) CNTs were first dispersed in a fixed amount of rubber contained in a 500 ml beaker through the use of an ultrasonication horn at 40% amplitude for 60 min total sonication time.

(2) Microwires were cut to around 5 mm and blended into the CNT solution. The mixture was then placed in a vacuum oven and degassed for 30 min at room temperature.

(3) The curing agent (resin: curing agent = 9:1) was added into the above mixture. The high viscosity solution was then compounded by high shear mixer for another 20 min. The resulting mixture was then ready for casting use.

(4) The mixture was poured into a designed rubber mould of 70 mm × 10 mm × 1.8 mm and cured in room temperature for 24 h.

2.3. Microwave characterization

Complex effective magnetic permeability and permittivity spectra were measured using a modified microwave frequency-domain spectroscopy with/without a magnetic field applied along the length direction of the tested composite samples at a frequency range of 1–6 GHz as shown in Figure 1a, and then extracted by a built-in utility program. In outline, our experiments consist of measuring the transmission and reflection coefficients of an asymmetric microstrip transmission line containing the sample as shown in Figure 1b. The electromagnetic measurement was carried out with a wave vector of the electromagnetic field perpendicular to the sample length. The quasi-TEM transverse electromagnetic mode was measured with a wave vector of the electromagnetic field perpendicular to the sample length. The quasi-TEM transverse electromagnetic mode, which is the only mode that propagates in the structure, to the sample length. The quasi-TEM transverse electromagnetic mode, which is the only mode that propagates in the structure, of dielectric loss were observed from 2.5 to 6 GHz with the wires amount doubled. Notably, at 4.8 GHz (resonance region), εʹ shows slight increase of εʹ for the case of 1 wt.%; while there appears a significant increase of εʹ for 2 wt.% sample. εʹ remains almost unchanged for all measured concentrations. We extracted the values of εʹ taken at a relatively lower frequency of 2.55 GHz and higher frequency of 5.54 GHz, respectively. They are analysed using Lichtenecker’s model (LIC) and Stölze–Enders–Nimtz (STO) models [23] (Figure 2b and c), respectively. Details of these models are described in Ref. [23].

The volume fraction is estimated as one third of the weight concentration [24]. The impact of wires addition on the 0.2 wt.% CNT composites is illustrated in Figure 3. The addition of wire concentration greatly improves both εʹ and ε″. Marked increases of dielectric loss were observed from 2.5 to 6 GHz with the wires amount doubled. Notably, at 4.8 GHz (resonance region), ε″ increases more than twice. The lossy features (Figure 4) present a remarkable increase of loss tangent with increasing wire concentration. The intrinsic impedance calculated from $\eta = \sqrt{\varepsilon / \mu}$, shows an opposite trend. The fractional change in impedance shows the same evolution trend as reflection does; the effect of wires amount from 50 to 100 mg is blurred. The absorption of our ultimate interest, as expected, shows positive dependence on wires concentration. The magnetic field tunable effect was also examined for a composite containing 0.2 wt.% CNT and 50 mg wires (Figure 5). The field effect is visible but weak. The tunability $(|\varepsilon'|-|\varepsilon'(0)|)/|\varepsilon'(0)|$ reaches maximum at 150 Oe, which is clearly shown at the magnetic field dependence of tunability plotted at 1.97 GHz (inset of Figure 5).

4. Discussion

Due to the existence of percolation threshold, which sees an abrupt increase of conductivity, it can be inferred from the sudden increase of εʹ for 2 wt.% that the percolation threshold occurs for the current CNT composites at 0.33–0.67 vol.%, which is reasonable for the nanotubes with the aspect ratio of around 300. According to $\nu \propto \sqrt{l/d}$[24], where $l/d$ is aspect ratio, the aspect ratio might be close to the lower bound of the above predicted range. Although it is a formidable task to predict the CNT loading dependence of permittivity in considering multiple factors involved such as geometry and dispersion of CNTs, the LIC model fits the experimental data well at for low concentration; the large deviation of the last data point at 2 wt.% indicates that it exceeds the percolation threshold since this model is only valid for the non-percolative case. This is consistent with our discussion on the percolation threshold above. Mcl model is also capable of good prediction at
low concentration but fails either at 2 wt.%. Above percolation, the calculation based on STO model is more close to the experimental data in the current work. It is worth reiterating that, although these models are not robust in calculating the permittivity of CNT composites, they do show certain capability to describe the experimental observations, particularly at relatively low concentration. This clearly suggests that the accuracy of model depends on intimately on the complexity of mesostructure parameterized by the random-ness and connectedness of the particles within the embedding matrix. At low concentration, these terms can be better controlled both experimentally and numerically (via appropriate fitting parameters) so that the real mesostructure features can be simplified to reasonably predict the effective permittivity. To resolve the issue of aggregation and agglomeration of particles at high concentration remains a hurdle to developing robust models. In such instance, one may have to resort to the expensive computational electromagnetics approaches.

Next, let us discuss the significance of advancing such CNT/microwire multiscale hybrid composites. The direct result of the wires addition into the CNT composites is to elevate the conductivity of the composite and hence the complex permittivity due to the higher conductivity of these metallic microwires and additional interfacial polarization induced [25]. This also accounts for the
decreased intrinsic impedance with wires loading. Both wires loading dependence of loss tangent and surface impedance are indicators of the evolution of absorption, however, they cannot exactly predict the effect of wires amount increasing from 50 to 100 mg on the absorption performance; one can clearly see the large discrepancy among the influences of wires amount on these three parameters. This can be explained as follows. The abrupt increase of loss tangent also involves an increase of conduction loss in addition to that of polarization loss; the similar surface impedance which indicates a similar impedance mismatch is irrelevant to the extent of pure polarization loss. An argument can then be arrived at that the addition of wires increases both reflection loss (conduction loss) and absorption (polarization loss). Further, the composites containing more than one kind of fillers possess more freedom to formulate their microwave properties by varying the content or local properties of either kind of fillers, thus rendering such kind of composites configurable to meet a broad range of applications with different requirements [20]. These merits suggest that such a multiscale hybrid composite would be especially useful in shielding or absorption applications, which provides a new recipe to the on-going efforts of modulating CNT composites for shielding or camouflage applications.

The last point deals with the capability of the prepared composites responding to external magnetic field characterized by the field dependence of effective permittivity. It is the microwires that transform the CNT composites from no response (not shown here) to visible responses to external field. It should be noted that, even with the presence of magnetic catalyst impurities, its minor fraction in CNT and the small concentration of CNTs in the studied composites will not produce visible change of response to the external magnetic field for the composites with CNT only. For composites containing hybrid fillers, the criticality of 150 Oe can be accounted for by the different bias effect below and above [26]. Below 150 Oe, the bias effect influences the dielectric response through the GMI effect of microwires. With the increasing bias, the impedance increases, the permittivity spectra tend to relax [1]. After 150 Oe, the high magnetic bias induces ferromagnetic resonance (resonance of circumferential permeability) and the increasing field will elevate the permittivity [27]. The criticality of 150 Oe is actually somehow decided by the local properties of individual wires. We have reported this particular crossover phenomenon in a previous study [28]. Although the physical mixing of wires and CNTs creates no strong interactions between micro-wires and CNTs of different scale, but when the external field is applied, their responses to external field will be influenced by one another, i.e., the microwires on the surface of samples might dominate the EM responses over CNTs and the microwires inside could be shielded by the surrounding CNTs as schematically shown in the inset of Figure 3b. Indeed, the SEM images (Figure 3c and d) reveal that, after the wire was pulled out, the nanotubes are clearly seen on the walls of the resulted cavity. This well explains why only weak field effect on the permittivity spectra is observed.

A note is in order here. Such a multiscale hybrid composite is promising for a variety of engineering applications apart from microwave absorption. First of all, it can be applied to structural health monitoring application, which is a demanding issue in the aeronautical and civil industry, especially with the increasing use of polymer composites in the fuselage and architectures. Capitalizing on the field-tunable properties of microwires at gigahertz frequency range [2,3] for rapid detection and the high piezoresistivity of carbon nanotubes, it is viable to realise a broadband structural health monitoring based on a combination of contact and non-contact methods. Specifically, the non-contact method serves as rapid analyses to detect damaged area and contact method to identify precise damage location. Secondly, both carbon nanotubes/nanofibres and microwires are competitive candidate fillers to make meta-composites [29–31]. Compared to the conventional metamaterials, the meta-composites are subject to mass-scale production with more economically feasible engineering fabrication methods. However, previous work [31] shows that carbon nanotubes can only excite the negative dielectric response. With the involvement of the magnetic wires, it is possible to induce the negative magnetic response too [14]. To realise this, sufficient amount of microwires would be required, which may create some challenges in sample preparation. Nevertheless, this is also a promising direction to work on in view of the intriguing applications of metamaterials such as cloaking. Finally, we have demonstrated that the microwires can benefit the impact resistance performance of composite laminates as the wire breakage becomes an important factor contributing to the composite failure in addition to the delamination [32]. With the involvement of nanotubes, the relevant mechanical properties can be further enhanced. With better control of wire and nanotube orientation, one may even be able to relieve the notorious delamination issue to some extent [33]. Further work will be done in these aspects.

5. Conclusion

A multiscale hybrid CNT/microwire composite has been prepared and studied in terms of its microwave properties. The microwave dielectric behaviour is well explained by the percolation theory and LIC model. The large improvement of absorption with microwire addition promises a new approach to better the application perspective of CNT composites in microwave or shielding applications. The counter-influence of wires and CNTs in terms of responses to external magnetic field provides more possibilities to design the composite mesostructure to modulate the electromagnetic behaviour based on the additional degrees of freedom with the fillers. The proposed composites possess strong application potentials in aerospace, civil and electrical industry ranging from structural health monitoring to mechanical components to cloaking.

References