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Multilayered absorber over K-and Ka-band based on graded concentration of carbon nanofillers: Modeling, Fabrication, and Experimental validation

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Abstract

In this paper, a thin wideband microwave absorber is modeled and validated experimentally between 18and40GHz. The absorber is built by stacking conductive nanocomposite slabs having graded concentrations of conductive carbon nanofillers in order to achieve a reflectivity below-10dB.These conductive composites are fabricated through blend compounding method using carbon nanotube (CNT) and graphene nanoplatelets (GNP)nanofillers loaded in a polycarbonate matrix. A systematic loading of nanofillers yields a hierarchical effect on nanocomposite permittivity and electrical conductivity, which are successfully modeled using Maxwell-Garnett formulation. It is shown that 1D and 2D geometry of nanofillers are individually and together influencing the real and imaginary parts of the permittivity and associated conductivity. This plays an important role to fabricate substrates having dedicated electromagnetic properties required for the design of efficient wideband absorbers, as demonstrated in this paper.

1. Introduction

Today's rapid growth in electronic industries demands not only high performance compact electromagnetic absorbers but also multi-functionality properties such as flexibility, thermal stability, corrosion resistance, ease of processing *etc.* In order to achieve a thin, light-weight, low-cost and wideband microwave absorber, electronically conductive polymer nanocomposites (PNC) loaded with various types of carbon nanofillers, *i.e.*carbon nanotubes (CNT), graphene nanoplatelets (GNP), carbon black (CB), carbon nanofibers (CNF) are gaining much attention to develop compact microwave absorbing structure (MAS), compared to classical solutions [1]. PNC provides multiple degrees of freedom to achieve the desired electromagnetic (EM) parameters $(\varepsilon, \sigma, \mu)$that can be tuned depending on the nanofillers properties, volume fraction, their degree of dispersion, processing methods *etc.*[2].In [3], various EM absorbers are studied where PNCs incorporated with different loadings of CB, CNF, CNT in single and multilayer configurations show reflection below -10dB in narrow frequency band. PNCs having one-type of inclusion such as graphite flake, single or multiwall CNT or CNF, were stacked together in multilayer configuration using optimization algorithm [4]. They show good wideband EMI shielding at various incident angle but for large absorber thickness. Going one step further, in multiphase filler systems, two or more nanofillers like multiwall CNTs, Nickel-CNFs, GNPs were mixed together to fabricate thin nanocomposites, but the reflection band below -10dB is narrow [5]. A three-phase composite absorber (CB, CNF, CNT mixed together) was demonstrated in Salisbury-screen dielectric configuration for aerospace application at 15GHz having below -20dB reflection [6]. Various nanofiller loading strategies have been used to increase the absorption performance at reduced MAS thicknesses [7-8].Nevertheless, limited studies are reported in the literature on the hierarchical combination of CNTs and GNPs into multiphase composite in order to tailor its electromagnetic parameters (ε', σ) at high frequencies[9].Based on such combination, a multilayer stacking having gradient nanofiller concentration can be used for developing thin absorbers[10].

In polymer nanocomposites, 1D tubular geometry of CNT has the ability to form interconnected percolation networks at nano-scale, which facilitates electron transport throughout the polymer matrix, affecting mainly the electrical conductivity. By opposition, 2D surface of GNPs forms capacitor-like structures and other polarization effects(such as interfacial and space charge),are also determining the dielectric constant of the nanocomposite [11].

In this paper, nanocomposites made of polycarbonate matrix loaded with both GNPs (2D) and CNTs (1D),as individual nanofillers and in a mixed configuration, are developed for various predefined *weight%* ratios, then measured for their EM properties (ε', σ).This gives a clear understanding on the contribution of GNPs (2D) and CNTs (1D) to dielectric constant ε', and conductivity σ in a more systematic manner. Then selected measured permittivities are modeled through a Maxwell-Garnett formulation for multiscale system. Secondly, fabricated nanocomposites having different values of permittivity are used to design a thin and wideband multilayer absorber in 18-40GHzfrequency band. Multilayer is organized in concentration-gradient stacking to mimic the step-wise transition of impedance and allow the progressive dissipation of the wave inside the lossy medium to achieve reflectivity below -10dB, resulting in wideband absorption.

2. Materials and Characterization

Carbon nanotubes (NC7000 from Nanocyl), graphene nanoplatelets (TIMREX) and Polycarbonate (PC) Makrolon™ OD2015 resin pellets were used. Polymer nanocomposites were fabricated by blend compounding method. CNTs and GNPs are taken in weight as CNTs (0.5, 1, 2, 3*wt%*), GNPs (1, 2.5, 5, 10 *wt%*), and GNPs + CNT [(0.5, 1, 2 *wt%*)+ (1, 2.5, 5, 10 *wt%*)] in polycarbonate (PC) matrix. For blending, compositions were melt-mixed in a DSM15 twin-screw micro-compounder preheated at 260°C with 150 rpm screw rotation. Then extrudates were hot pressed at 260°C under10MPa pressure using hydraulic press into approximately 400µm flat sheets and annealed for further characterization [2,13].

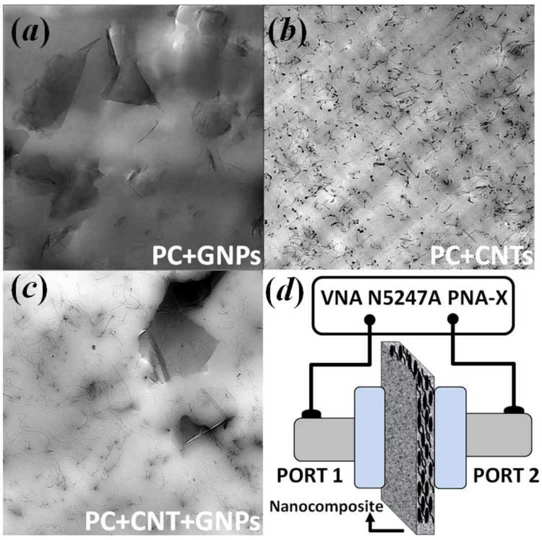

Figure 1. TEM images of fabricated nanocomposites loaded with nanofillers:*a*) GNP (5*wt%*), *b*) CNT(0.5*wt%*) and mixed *c*) GNP+CNT(5*wt%*+0.5*wt%*), *d*) Schematic of waveguide measurement setup.

Fig.1 shows that carbon nanotubes have uniform entangled distribution and graphene nanoplatelets show good spatial distribution but lack to form connected network. Polycarbonate (PC) possesses high polarity and surface energy that significantly helps in uniform dispersion of CNT and GNP nanofillers without much agglomeration. In case of higher loading of CNT and GNPs in polymer matrix it would make it very difficult for processing, and drastically affect the mechanical properties of the nanocomposite. In mixed configuration i.e. nanocomposite containing both CNT and GNPs, both are distributed homogeneously and form a nicely interconnected network even at low loading rate owing to their shape and aspect ratio [9,11].

Figs.2 and 3show the measured dielectric constants and conductivity of polycarbonate matrix containing various CNT and GNP loading rates. The measuring scheme is illustrated in Fig. 2(d) and explained in [15].In Fig. 2, pure CNT loaded composite (green curve) shows excellent increasing trend in conductivity between 1-29S/m for concentration increase from 0.5*wt%* to 3*wt%*. However, the dielectric constant shown in Fig.3 begins to saturate around 15 at 3*wt%* starting from host pure polycarbonate permittivity at ~2.9 (Fig. 3, green curve).

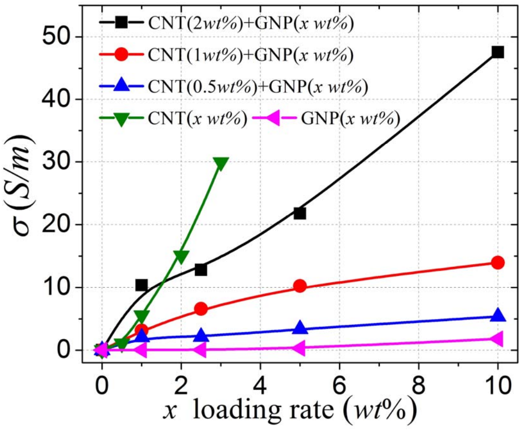

Figure 2. Measured conductivity of polycarbonate nanocomposite with various CNT, GNP loading rate.

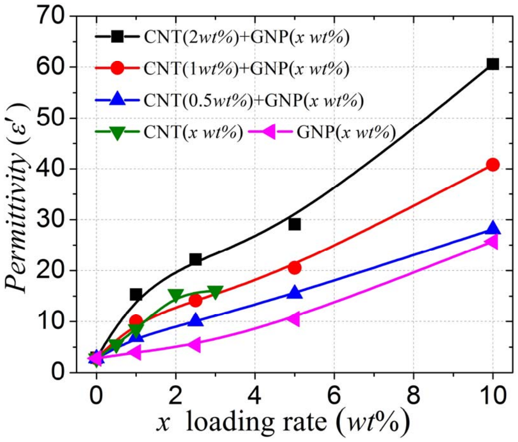

Figure 3. Measured permittivity of polycarbonate nanocomposite with various CNT, GNP loading rate.

On the contrary, GNPs based composites show good linear increment in dielectric constant upto 23 for concentrations from 1*wt%*to 10*wt%*(Fig.3, pink curve) but its conductivity shows very low increment rate due to poor nanofiller connectivity (Fig.2, pink curve). When observing mixed case of CNT fixed at 2*wt%* and increasing GNPs concentration from 1*wt%* to 10*wt%* (black curves), it shows excellent linear increase in both ε, σ simultaneously which is slightly different from other mixed composites. It is due to the fact that, at CNT 2*wt%*, the CNT-CNT gap is reduced drastically and each time GNPs is added (increasing *wt%*), it continues to form bridges inbetween CNT-CNT and significantly improves the co-supportive conductive pathways. Thus, it is clearly understood from Fig.2, Fig.3 and from TEM micrographs of Fig.1that CNT and GNP nanofillers, when dispersed in polycarbonate matrix, have the ability to impact individually the conductivity and dielectric constant of the resulting nanocomposite respectively due to their 1D-cylindrical and 2D-planar geometries, but give improved performance synergistically when mixed together.

3. Numerical modeling of permittivity

Maria Sarto *et al.*[12] have proposed a modified Maxwell-Garnett (M-G) formulation allowing to calculate the effective permittivity for a multiscale nanocomposite system consisting of inclusions having two different geometries (1D & 2D)of composite.

In our case, CNT and GNP are 1Dand 2D nanoscaled structures respectively, interacting at different levels with polymer medium to form the composite. Thus M-G equation is applied in recursive manner to compute the effective permittivity[14]. Therefore, at first, permittivity ε_{2D} of polymer mixture containing 2D-flake GNPs is computed according to eq. (1).Then it is applied recursively for filled 1D-cylindrical CNT nanofillers to calculate the overall effective permittivity ε_{eff} of the composite(eq. 1).Thus $\varepsilon_{2D}$of composite can be expressed as follows[12,14]:

$$\varepsilon_{2D}=\varepsilon_m+\frac{\frac{1}{3}v_{fGNP}\left(\varepsilon_{GNP}-\varepsilon_m\right)\sum_{k=1}^{3}\frac{\varepsilon_m}{\varepsilon_m+N_{GNPk}\left(\varepsilon_{GNP}-\varepsilon_m\right)}}{1-\frac{1}{3}v_{fGNP}\left(\varepsilon_{GNP}-\varepsilon_m\right)\sum_{k=1}^{3}\frac{N_{GNPsk}}{\varepsilon_m+N_{GNPk}\left(\varepsilon_{GNP}-\varepsilon_m\right)}} \qquad (1)$$

Then, applying eq.(1) in recursive manner to include the contribution of CNT nanofilleryieldsε_{eff} permittivityof the multiscale system as:

$$\varepsilon_{eff}=\varepsilon_{2D}+\frac{\frac{1}{3}v_{fCNT}\left(\varepsilon_{CNT}-\varepsilon_{2D}\right)\sum_{k=1}^{3}\frac{\varepsilon_{2D}}{\varepsilon_{2D}+N_{CNTk}\left(\varepsilon_{CNTs}-\varepsilon_{2D}\right)}}{1-\frac{1}{3}v_{fCNT}\left(\varepsilon_{CNT}-\varepsilon_{2D}\right)\sum_{k=1}^{3}\frac{N_{GNPsk}}{\varepsilon_{2D}+N_{CNTk}\left(\varepsilon_{CNTs}-\varepsilon_{2D}\right)}} \qquad (2)$$

where $\varepsilon_{GNP(CNT)}=1-j\sigma_{GNP(CNT)}/\omega\varepsilon_o$, and $\sigma_{GNP(CNT)}$, $N_{GNP(CNT)}$, $v_f$are conductivity, depolarization factors and volume fraction of GNP and CNT nanofillers, respectively.
Values from material data sheets from manufacturers are used as input to equations (1-2)to model the effective permittivity and are not detailed here for sake of brevity. The obtained results shown in Fig.4 show good agreement between measured and computed values for real and imaginary parts of the permittivity as function of frequency. The fitting of the numerical curves is achieved by MATLAB *fminsearch* function including few fitting parameters that may be attributed to experimental factors, material crystallinity and grade, dispersion and filler orientations *etc*. Establishing its physical relevance is out of scope of this paper [12-14].

4. EM absorption and Measurement

Microwave absorption in thin lossy composites mainly depends on wave dissipation due to ohmic/dielectric losses inside the material and destructive interference due to impedance matching condition. Reflection coefficient S_{11}at input is minimized, and absorption through composite is maximized, when composite input impedance Z_{in} matches to free space impedance Z_o, which is expressed according to transmission line theory as follows[3-4]:

$$|S_{11}|=\sqrt{\frac{\{Re(Z_{in})-Z_0\}^2+\{Im(Z_{in})\}^2}{\{Re(Z_{in})+Z_0\}^2+\{Im(Z_{in})\}^2}} \qquad (3)$$

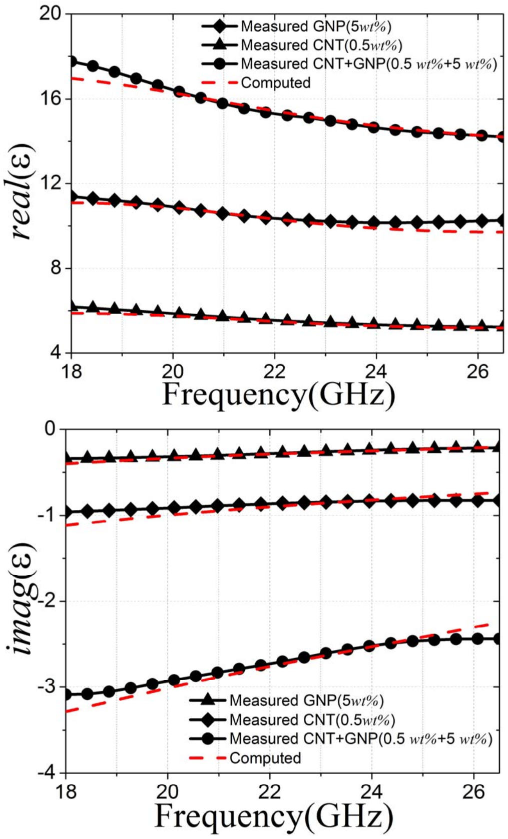

Figure 4. Examples of measured and calculated (from eq. (2)) permittivity (real, imaginary)for some polycarbonate matrixes loaded with CNT (0.5*wt%*), GNP (5*wt%*), mixed CNT+GNP (0.5*wt%*+5*wt%*).

To achieve an excellent absorption level it is important to cancel the reflection coefficient from eq. (3) in order to maximize the power entering the composite and being dissipated. In other words, the imaginary part of input impedance should be equal to zero and the real part of it should match the free-space impedance [3-4] i.e. :

$$Re(Z_{in})\approx Z_0,\quad Im(Z_{in})\approx 0 \qquad (4)$$

$$Z_{in,x}=\eta_x\frac{Z_L cos(\beta_x d_x)+j\eta_x sin(\beta_x d_x)}{\eta_x cos(\beta_x d_x)+jZ_L sin(\beta_x d_x)}, \qquad (5)$$

$$d=(2\mathrm{n}-1).\lambda/4,\ (\mathrm{n}=1,2,3..)$$

$$\lambda=\lambda_0/\sqrt{\varepsilon_{\mathrm{r}}},\ \eta_x=\mathrm{Z}_0\sqrt{\mu_r/\varepsilon_r},\ \beta=\omega\sqrt{\varepsilon_{\mathrm{r}}}$$

Where Z_L is the impedance backing the layer. In general, a single layer absorber provides wave attenuation in a narrowband and in order to increase the bandwidth, its thickness needs to be increased to a few centimeters, which is often prohibitive. In order to achieve thin wideband absorbers, Huynen*et.al.*[1] reported a multilayered arrangement of nanocomposites having a gradient concentration of nanofillers, which provides excellent absorption performance Graded-medium allows the EM wave to penetrate progressively in lossy medium and attenuate through wave cancellation or dissipation inside medium, resulting in absorption.

Following this approach, a3-layer absorber structure is modeled in MATLAB using eq.(3-5). Table1 describes properties of each nanocomposite layer of the MAS, acting as a wideband absorber in K and Ka band.

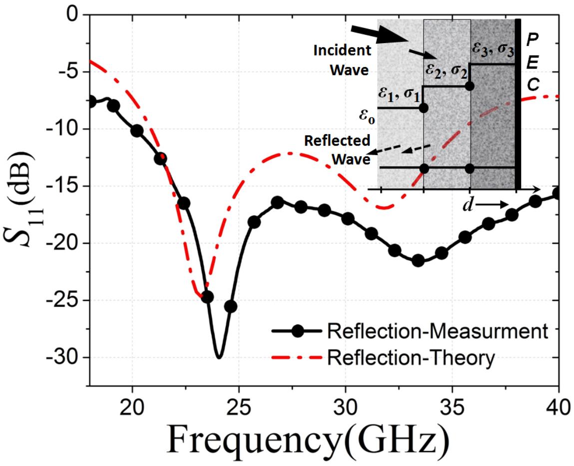

Figure 5. Reflection coefficient (S_{11})for 3-layer absorber of thickness 3.2 mm. Inset: absorber schematic.

Fig.5 illustrates the excellent agreement between measured and modeled reflection coefficient for 3-layer absorber constructed using a stack of fabricated nanocomposites from Figs.2 and 3, backed by a perfect conductor, see Table 1. The reflectivity below -10dB is achieved from 20 to 40 GHz for a 3.2mm thickness and arrangement of nanocomposites in a concentration-gradient stacking (such as $\varepsilon_1 < \varepsilon_2 < \varepsilon_3$) allowing to attenuate/dissipate the propagating wave in lossy medium.

Table 1. EM Properties and thickness of 3-layer absorber

Layers	Multilayer Configuration	d (mm)	ε'	Tan δ	σ
1.	GNP (1 $wt\%$)	1.2	3.971	0.01573	0.0677
2.	CNT (0.5 $wt\%$) + GNP (5 $wt\%$)	1.2	15.47	0.17582	3.374
3.	CNT (2 $wt\%$) + GNP (2.5 $wt\%$)	0.8	22.13	0.4694	12.83
PEC	PEC	-	-	-	-

6. Conclusion

Polycarbonate matrix loaded with CNT and GNP nanofillers shows a strong and cooperative effect on the measured permittivity of a nanocomposite, which is successfully modeled depending on the concentration. Nanocomposites stacked in a graded-concentration hierarchical arrangement achieve -10dB reflectivity in20-40GHz band for only 3.2mm thickness. This opens new door to flexible, thin, low-cost and easy to fabricate wide-band absorbers.

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