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Ni filled flexible multi-walled carbon nanotube–polystyrene composite films as efficient microwave absorbers

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In this letter, we report flexible, non corrosive, and light weight nickel nanoparticle@multi-walled carbon nanotube–polystyrene (Ni@MWCNT/PS) composite films as microwave absorbing material in the frequency range of S band (2-4 GHz). Dielectric permittivity and magnetic permeability of composites having 0.5 and 1.5 wt. % filler amount were measured using the cavity perturbation technique. Reflection loss maxima of −33 dB (at 2.7 GHz) and −24 dB (at 2.7 GHz) were achieved for 0.5 and 1.5 wt. % Ni@MWCNT/PS composite films of 6 and 4 mm thickness, respectively, suggesting that low concentrations of filler provide significant electromagnetic interference shielding. © *2011 American Institute of Physics*. [doi:10.1063/1.3638462]

Since electromagnetic shielding is useful to protect humans and electronics from radiation emitted by computers, electronic equipments, cellular phones, etc., there is an increasing demand for the development of novel and effective electromagnetic (EM) absorbing materials, especially in the S band (2-4 GHz), the boundary between the ultra high frequency (UHF) and super high frequency (SHF) ranges, where nowadays communication and Direct to Home satellites, mobile satellite services, and weather radars operate. Metals are widely applied for effective EM shielding; however, their use is limited by heavy weight, rigidity, and tendency for corrosion. As alternatives, carbon based materials such as carbon black, single and multiwalled carbon nanotubes (SWNTs and MWNTs), as well as carbon fibers have been suggested[1–3] although their shielding properties are not excellent derived from the diamagnetic nature of carbon. An effective microwave absorbing material need to satisfy the impedance matching condition, $\mu_r/\varepsilon_r \sim 1$, where μ_r and ε_r represents complex magnetic permeability and dielectric permittivity, respectively, with high dielectric and magnetic values.[4,5] Recently nickel/carbon hybrid nanostructures, nickel ferrite nanocomposites, and partially/completely filled multi-walled carbon nanotube (MWCNTs) by 3d metallic elements—iron (Fe), nickel (Ni), and cobalt (Co)—were reported with highly enhanced microwave absorption.[6–9] The flexibility and moldability of the polymer matrix used in the composites allows various ways of applications of the nanomaterial fillers. Among the different polymers used as matrices, polystyrene (PS) is a very important one due to its easy processibility, low density, low price, good optical transparency, and acceptable thermal insulation and damping properties. Electromagnetic percolation theory[10] states that the filler materials in the polymer should possess high conductivity and high aspect ratio to form a conductive network easily and reach percolation threshold at low concentration of the conductive filler.[11]

Here, we report low concentration nickel filled multi-walled carbon nanotube-polystyrene (Ni@MWCNT/PS) composite as an efficient microwave absorber. MWCNTs have been synthesized by using template-assisted chemical vapor deposition method on a commercially available alumina template (anodized aluminum oxide (AAO) template, 99.9% pure, Whatman, pore size ∼150 nm, thickness ∼60 μm) using acetylene and argon as carbon source and carrier gas, respectively, at 650 °C. The open caps of the nanotubes[12] grown by this method allow the incorporation of metal nanoparticles inside the core of MWCNTs.[13] After removal of the amorphous carbon from the nanotubes by oxygen plasma treatment, electrochemical deposition was employed to incorporate Ni into the open-ended MWCNTs in a three-electrode potentiostate system (Princeton EG &G 273A) from an aqueous solution of 0.2 M $NiSO_4 \cdot 6H_2O$ in 0.1 M boric acid H_3BO_3. For the synthesis of Ni@MWCNTs/PS composite the AAO template was dissolved using 3M NaOH as dissolving media. The required amount of Ni@MWCNTs was mixed with PS ($M = 1 \times 10^5$) solution in toluene, and the resulting mixture was sonicated for 30 min to obtain homogeneity. The mixture was cured at room temperature for 12 h to form a flexible composite film. Composites with 0.5, 1.0, and 1.5 wt. % Ni@MWCNT in PS were prepared.

Ni nanoparticles (d less than 40 nm) homogeneously incorporated into the MWCNTs are shown by a scanning electron microscopy (SEM) image in Fig. 1(a), the distribution of nanoparticles along the nanotube is visualized in Figs. 1(b) and 1(c) via SEM and atomic and magnetic force microscopy (AFM/MFM) imaging. The morphology of the composite material showed good wetting properties, and therefore strong interaction between the filler and the matrix is expected as shown in Fig. 1(d). Fig. 1(e) demonstrates the macroscopic integrity and flexibility of the Ni@MWCNT/PS composite film. Measurement of the real and imaginary part of the dielectric permittivity and the magnetic permeability of various samples have been carried out using a vector network analyzer (Rohde & Schwarz ZVB4) to characterize microwave absorption in the S band. The cavity perturbation

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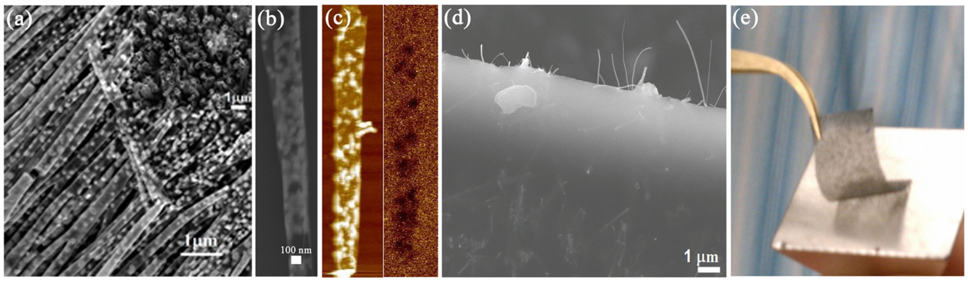

FIG. 1. (Color online) (a)-(c) FESEM, SEM, and AFM/MFM images of Ni nanoparticle filled MWCNTs show uniform distribution of Ni particles. (d) SEM image of the composite film shows good dispersion of Ni@MWCNTs in the PS matrix. (e) Optical image of the flexible composite film.

technique[14] was employed to calculate complex permittivity and permeability of different wt. % composite in the frequency range of 2.4-3.8 GHz. Fig. 2(a) represents complex dielectric permittivity (ε_1 & ε_2) of pure PS, 0.5 wt. % and 1.5 wt. % of Ni@MWCNT/PS composites. The result shows that both the real and the imaginary parts of the permittivity are significantly enhanced with addition of small amounts of Ni@MWCNTs into the PS matrix. The value of real part of the permittivity, ε_1, increased from 2.8 to 10.8 for 1.5 wt. % Ni@MWCNT/PS composite at 2.5 GHz frequency, whereas the imaginary part of the permittivity ε_2 value increased from 0.8 to 6.5 for 1.5 wt. % Ni@MWCNTs/PS at the same frequency. It is clear from the graph that both ε_1 & ε_2 values decreased as frequency increases. At 3.6 GHz frequency, the value of ε_1 decreases to 7 for 1.5 wt. % Ni@MWCNT/PS composite from 10.8 (at 2.5 GHz) value and ε_2 becomes 1.8 from 6.5 (at 2.5 GHz). Fig. 2(b) displays the magnetic permeability values (μ_1 and μ_2) of the 0.5 and 1.5 wt. % Ni@MWCNT/PS composites. The value of real part of the permeability (μ_1) is 14 for 0.5 wt. % Ni@MWCNT/PS composite and 25 for 1.5 wt. % Ni@MWCNT/PS composite at 2.5 GHz frequency, whereas the value of the imaginary part of the permeability (μ_2) is 8 and 13 for 0.5 and 1.5 wt. % Ni@MWCNT/PS composites, respectively, at 2.5 GHz frequency. The value of the permeability also decreased when frequency increased from 2.4 to 3.6 GHz. Therefore, we can see that by increasing the filler concentration in PS matrix, the percolation threshold is approached which in-turn increases the conductivity of the composite. So, by analyzing the permittivity and permeability of 0.5 and 1.5 wt. % Ni@MWCNT/PS composite, we can conclude that nickel particles play a key role for improving the permittivity and permeability value for MWCNTs, which enable better utilization in EMI application.

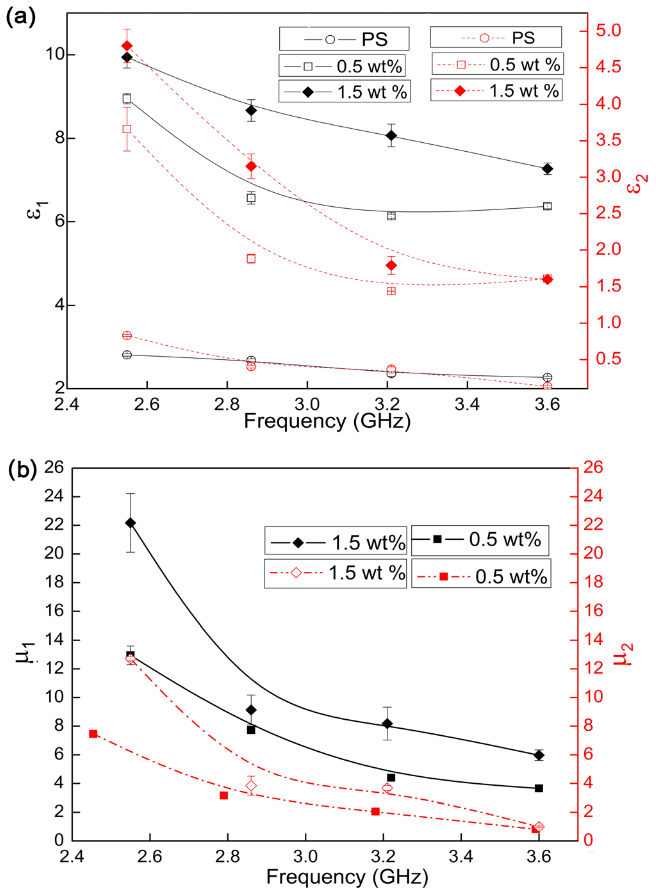

FIG. 2. (Color online) Real and imaginary parts of permittivity (a) and relative permeability (b) values measured for differently loaded composites.

The reflection loss (RL) of different thickness of 0.5 and 1.5 wt. % Ni@MWCNTs/PS magnetic composite films have been analyzed by using a single layer metal backed absorber model.[15] The reflection loss for different absorber layer thickness are calculated by using the following equation:[16]

$$Reflection\,loss\,(dB) = 20\log\frac{Z_{in}-1}{Z_{in}+1},$$

where

$$Z_{in} = \sqrt{\frac{\mu_r}{\varepsilon_r}}tanh\left(j2\pi fd/c\sqrt{\frac{\mu_r}{\varepsilon_r}}\right),$$

where ε_r and μ_r are the complex permittivity and permeability, respectively, of the composite medium, f is the frequency, d is the thickness of the absorber, and c is the velocity of light in free space. Figs. 3(a) and 3(b) display the results of the calculation of reflection loss for 0.5 and 1.5 wt. % Ni@MWCNT/PS composite, respectively, at varying film thickness. It is apparent from these results that the maximum reflection loss for 0.5 wt. % sample is −33 dB for 6 mm thickness, whereas for 1.5 wt. % sample is −25 dB for 4 mm thickness. These values of reflection loss are one of the highest reported values for these low loadings. The significant increase of reflection loss with decreasing thickness of the composite indicates its high conductivity and magnetic response (magnetic loss) contributing to the enhanced microwave absorption. Since PS has negligible microwave absorption, this indicates that defects in MWCNTs and amount of loading play a key role in deciding the net microwave

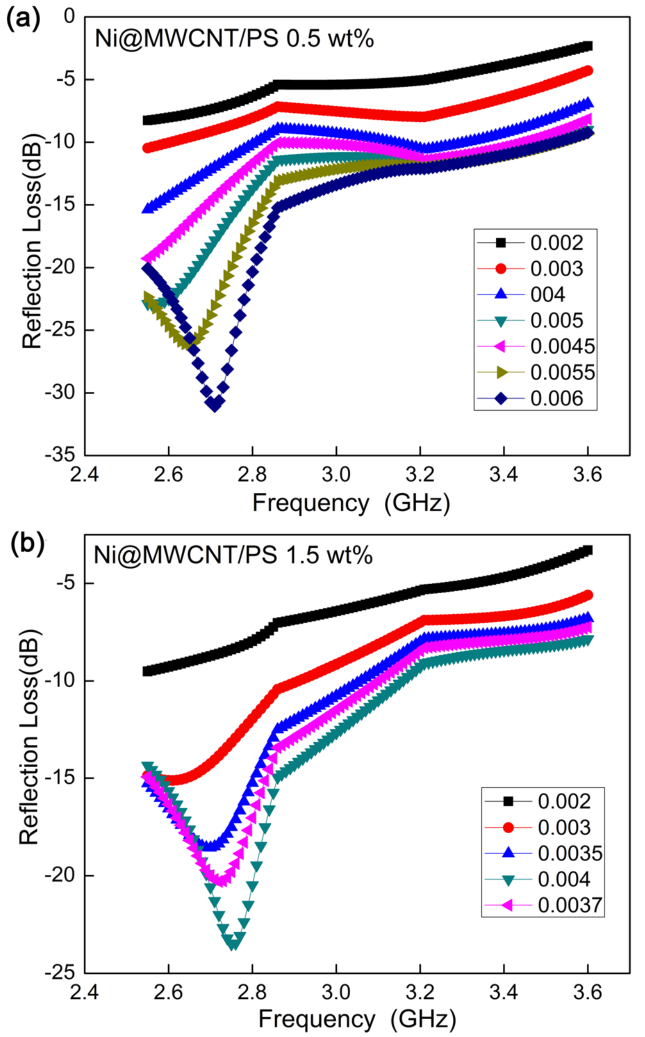

FIG. 3. (Color online) Calculation of optimum thickness and reflection loss for 0.5 wt. % (a) and 1.5 wt. % (b) Ni@MWCNT/PS composites. This calculation depicts the reflection loss, i.e., absorbtion, for different wt. % composite films of different thickness as function of frequency.

absorption of Ni@MWCNT/PS composite matrix. Recent reports on the biocompatibility of PS propound to the fact that this Ni@MWCNT/PS can find applications in microwave assisted medical therapy also.

In conclusion, Ni nanoparticles have been incorporated inside MWCNTs by electrodeposition method, and the resulted in hybrid material was used as a filler material to fabricate a flexible, non corrosive, and light weight Ni@MWCNT/PS composite. This composites prepared with different load were found to be efficient microwave absorbers in S band. Complex dielectric permittivity and magnetic permeability have been used to calculate reflection loss in S band by varying different thickness of PS, 0.5 and 1.5 wt. % Ni@MWCNT/PS composite. Reflection losses −33 dB (2.7 GHz) and −24 dB (2.7 GHz) for 0.5 and 1.5 wt. % Ni@MWCNT/PS composite films have been observed for 6 and 4 mm thickness, respectively, and therefore Ni@MWCNT/PS composites are prominent applications in EM absorption.

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