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Enhanced microwave absorption of multi-walled carbon nanotubes/epoxy composites incorporated with ceramic particles

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Microwave absorbing composites composed of both multi-walled carbon nanotubes (MWCNTs) and various ceramic particles as absorbers were prepared, and their mechanical properties, electrical conductivity, complex permittivity, and microwave absorbing properties were investigated. Thin thickness, broadband absorption composites with homogeneously dispersed MWCNTs and ceramic particles were obtained. The influences of temperature and ceramic particles on the complex permittivity and microwave absorbing properties of the composites were investigated in the frequency range of 12.4–18 GHz. The incorporation of ceramic particles demonstrated enhanced electrical conductivities, as well as altered the values and complex permittivity frequency dependencies of the MWCNTs/epoxy composite. These changes led to significantly improved microwave absorptions.

1. Introduction

The demand for high performance microwave absorbing materials (MAMs) has increased dramatically, and it is well known that the effectiveness of a MAM is mainly depended on its electromagnetic (EM) characteristics (such as complex permittivity and permeability) [1–3]. Although many studies have focused on improving microwave absorption properties, until now, none has produced a single absorbing material that fulfills demand for a large absorption, wide working frequency bandwidth and thin thickness [4–6]. For example, MAMs filled with carbon nanotubes (CNTs) in the GHz frequency range have been of great interest because of their high dielectric losses, excellent electrical properties, and unique mechanical properties [7–10]. Although CNT-filled composites commonly show higher complex permittivity, the reflection effectiveness of such composites have not been considered and their absorptions cannot be improved effectively by changing the diameters or lengths of the CNTs, the CNT contents of the composites, or the properties of the matrix [8–10]. In response to the obtained thin-layer broadband MAMs based on CNTs, the control of the EM properties of the CNT-filled composites is the key point.

Recently, the attentions of researchers have been directed toward adding magnetic materials to CNT-filled composites to enhance their complex permeability. Therefore, CNTs/magnetic particles-filled composite MAMs, such as iron nanowires encased in CNTs, $CoFe_2O_4$/CNTs, and Fe/CNTs, have been intensively investigated to improve the microwave absorption abilities of CNT-filled composites [11–15]. Experimental results show that the enhanced microwave absorptions of CNT/magnetic particle-filled composites are mainly due to the increased magnetic losses that occur as a result of the presence of the magnetic particles. On the other hand, controlling the complex permittivity of CNT-filled composites is also important to fabricate thin absorbers with broadband microwave absorptions, especially when both the real (ε') and imaginary (ε'') parts of the complex permittivity meet the impedance match.

More recently, the addition of secondary particles (such as, Al_2O_3 or $BaTiO_3$ particles) has been used to improve CNT dispersion and increase electrical conductivity without harming mechanical performance of the CNT filled composites [16,17]. It is well known that the complex permittivity of filled composites depend mostly on the contents, dispersions, intrinsic conductivities, and dielectric constants of the fillers. Such results indicate that the values and/or frequency dependencies of complex permittivity of CNT-filled composites can be adjusted by adding ceramic particles with different properties, making them good filler candidates for obtaining more suitable complex permittivity and, thereby, increasing the microwave absorptions of such composites. Therefore, dielectric particles with different dielectric constants and electrical properties can be used as fillers in the CNT-filled polymer composites. Al_2O_3 and $BaTiO_3$ particles have commonly and widely been used as secondary particles in order to improve the dielectric properties of CNT-filled composites. On the other hand, because of their high

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melting points, good thermal conductivities, high electrical conductivities, and considerable chemical stabilities, TiB_2 and $MoSi_2$ particles are materials that could be employed in MAMs [18–20]. Therefore, the excellent properties of TiB_2 and $MoSi_2$ particles mentioned above, especially their high electronic conductivities ($\sim 2 \times 10^5\ \Omega^{-1}\ cm^{-1}$ at room temperature), make them well suited for use as secondary particles in CNT-filled composites. Such particles have dual purposes, acting as both absorbers and to improve CNT dispersion and, thus, enhancing the microwave absorptions of such composites.

Most of the prior investigations into MAMs have been concerned with high reflection losses (RL) at specific single frequencies. In fact, the thicknesses and ranges of microwave frequencies of the MAMs have been shown to be key factors in determining the suitability of materials for engineering applications. These properties have also been shown to be quite challenging to control. Therefore, the aim of this work was to develop a simple way to design thin MAMs with broadband microwave absorptions in the 12.4–18 GHz frequency range simply by adding different ceramic particles to multi-walled carbon nanotubes (MWCNTs)-filled composites. This paper explores the influences of ceramic particle properties (such as complex permittivity and electrical conductivity) and temperature on the complex permittivity and RL of MWCNTs/ceramic particle/epoxy composites made from non-functionalized MWCNTs. Additionally, the microwave absorbing coatings developed herein can act as a potential effective solution for broadband absorption and thin thickness microwave absorber by optimizing the absorber content and EM properties, which also is simple and possible for industrial scale application.

2. Experimental procedure

The epoxy resin, used as the matrix material, and the polyamide resin, used as the curing agent, was supplied by XI'AN Leeo Technological Co. Ltd., Shaanxi province, China. The MWCNTs were supplied by Shenzhen Nanotech port Co. Ltd., China. The MWCNTs had lengths of 2–5 μm, diameter of 60–100 nm, were 95% pure, and had a volume resistivity of approximately $1.21 \times 10^{-4}\ \Omega$ cm. The starting ceramic particles, Al_2O_3 particles ($d_{50} \approx 4$ μm, volume resistivity $\approx 1.11 \times 10^{14}\ \Omega$ cm), $BaTiO_3$ particles ($d_{50} \approx 3$ μm, volume resistivity $\approx 8.25 \times 10^{7}\ \Omega$ cm), TiB_2 particles ($d_{50} \approx 2$ μm, volume resistivity $\approx 1.44 \times 10^{-5}\ \Omega$ cm), and $MoSi_2$ particles ($d_{50} \approx 2$ μm, volume resistivity $\approx 2.15 \times 10^{-5}\ \Omega$ cm), used to prepare the composites were provided by Nantong Ao Xin Electronic Technology Co. Ltd., JiangSu province, China.

In order to explore the characteristics of composites made from the various ceramic particles, samples containing different volume contents of MWCNTs and the various ceramic particles were fabricated and tested. Sample IDs specify the ceramic particle and MWCNT contents of the samples, as shown in Table 1. In this experiment, the resin matrix was prepared using a mixture of epoxy and polyamide resins mixed in a weight ratio of 4:1. In order to fully achieve the reinforced potential of MWCNTs and ceramic particles, such as mechanical and electrical properties, a highly homogenized dispersion of the fillers is required. First, the MWCNTs were dispersed in ethanol using an ultrasonic bath, at room temperature, for 2 h. After adding the ceramic particles to the ethanol dispersion, the mixtures were stirred at 2000 rpm for 10 min and then sonicated at room temperature for 1 h. Subsequently, the mixtures were placed in an oven heated to 80 °C and left there until the ethanol had evaporated completely. Then the epoxy resin and polyamide resin mixture was added, followed by stirring at 2000 rpm for 30 min. The samples were cured at 120 °C for 4 h to obtain well-shaped hard disks.

The morphologies of the samples were observed using scanning electron microscopy (SEM, Model VEGA3 SBH, TESCAN, Brno, Czech Republic). Electrical resistivities were measured using a two-wire method, using a current source (6220 DC Keithley, Ohio, USA). The flexural properties of five specimens of each sample were measured using an Instron 8516, according to ASTM D-790. The complex permittivity of the composites was measured using the T/R waveguide method, in the frequency range of 12.4–18 GHz, using a network analyzer (Agilent Technologies E8362B: 10 MHz–20 GHz). The RLs of the samples were measured using a network analyzer (Agilent Technologies E8362B) by comparing the signals transmitted by the samples to those reflected from their inputs. Samples used for RL measurements were 180 mm long × 180 mm wide, and had various thicknesses. There were adhered to 2 mm thick aluminum substrates. Complex permittivity and RL were measured in the Ku-band at various temperatures, ranging from 25 to 200 °C. Details are described in our pervious papers [16,6].

3. Results and discussion

Highly homogenized dispersions of MWCNTs and ceramic particles are required for the fully reinforced potential of the absorbers. One common approach to improving CNT dispersions is to introduce surfactants into aqueous or organic solutions. Improvements are attributed to high electrostatic repulsive forces attributed to the adsorbed surfactant [14]. Another commonly adopted approach is to expose the CNTs to ultrasound in ethanol and then stirring the mixture intensely. This approach can lead to a dramatic improvement in CNTs dispersion throughout the matrix [16]. A third method is to add three-phase particles to the CNT-filled composite. The addition of three-phase particles is thought to lower interfacial excess energy and hinder CNT aggregation during ultrasonication, giving a uniform dispersion of CNTs and three-phase particles in the final composite [21,22]. In this study, the three

Table 1
The compositions and properties of the MWCNTs, ceramic particles, and MWCNT/ceramic particle-filled epoxy composites studied in this work.

Sample	MWCNT content (vol%)	Ceramic particle and content	Volume resistivity (Ω cm)	Flexural strength (MPa)
CNT	0.2	–	2.25×10^{10}	35.7 ± 4.1
AL	–	Al_2O_3 (40 vol%)	7.13×10^{12}	29.2 ± 3.3
BA	–	$BaTiO_3$ (40 vol%)	4.28×10^{10}	30.5 ± 3.4
TI	–	TiB_2 (40 vol%)	6.34×10^{8}	28.4 ± 2.9
MO	–	$MoSi_2$ (40 vol%)	1.78×10^{8}	27.9 ± 2.5
C1-AL4	0.1	Al_2O_3 (40 vol%)	7.13×10^{8}	42.2 ± 4.5
C2-AL4	0.2	Al_2O_3 (40 vol%)	8.32×10^{7}	69.8 ± 6.2
C3-AL4	0.3	Al_2O_3 (40 vol%)	9.51×10^{5}	76.3 ± 6.9
C4-AL4	0.4	Al_2O_3 (40 vol%)	1.75×10^{4}	83.1 ± 7.3
C2-BA4	0.2	$BaTiO_3$ (40 vol%)	2.66×10^{6}	69.1 ± 6.1
C2-TI4	0.2	TiB_2 (40 vol%)	4.83×10^{4}	67.7 ± 5.9
C2-MO4	0.2	$MoSi_2$ (40 vol%)	2.58×10^{3}	70.3 ± 6.5