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Short communication

Electrical conductivity and microwave absorption of shortened multi-walled carbon nanotube/alumina ceramic composites

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Abstract

Multi-walled carbon nanotubes (MWCNTs) snipped by the acidification process were fabricated into alumina (Al_2O_3) matrices via hydrothermal crystallization and hot-pressing techniques for achieving MWCNT/Al_2O_3 composites. The electrical conductivity and complex permittivity of the as-fabricated composites were investigated in the range of 8.2–12.4 GHz, and the corresponding microwave reflection loss was evaluated. Compared to the pristine MWCNT/Al_2O_3 composites, the percolation threshold of electrical conductivity was observed to increase from the range of 0.094–2.5 wt% to 3.89 wt%, mainly owing to the decrease of MWCNT aggregations based on the shortened tubes. The resulting shortened MWCNTs/Al_2O_3 were found to demonstrate strong microwave absorption in the investigated region.

Keywords: Shortened carbon nanotube; Ceramic composite; Percolation threshold; Microwave absorption

1. Introduction

Since discovered by Iijima [1], carbon nanotube (CNT) has been considered as one of the most promising nano-sized materials for various potential applications [2]. In particular, the light-weight composites embedded with CNTs for their unique electrical properties have been found to show excellent electromagnetic interference (EMI) shielding and microwave absorption performance [3,4]. However, weak oxidation resistance of CNTs limits their applications at high temperatures (> 500 °C). Among various improvement strategies, incorporation of CNTs into ceramic matrices has been observed to be an effective approach to enhance the oxidation resistance of CNTs and simultaneously improve the mechanical properties of ceramic matrices [5–7]. Therefore, the CNT/ceramic composites are considered as potential candidates with wide applications in high-temperature microwave absorption.

Generally, dielectric loss associated with electrical properties can be used to evaluate microwave attenuation [4,8–10]. In order to obtain excellent microwave absorption performance, remarkable variety of approaches, such as introduction of metals or semiconductors to adjust the electrical conductivity of insulating matrices, have been well documented [11–14]. CNT/alumina (Al_2O_3) composites are considered as typical conductor-insulating composites with good electrical properties when the CNT loading (the aspect ratio around 100–1000) is higher than their percolation threshold (in the range of 0.094–2.5 wt% for MWCNTs) [15–21]. However, the materials with high electrical conductivity, resulting in interface impedance mismatch, could increase the interface reflectivity and decrease the microwave absorption [22]. On the other hand, the decrease of electrical conductivity for the composites by changing CNT loadings may inhibit the microwave absorption performance due to the decrease of conductive fillers. This contradiction based on filler loadings and responding electrical properties is highly

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significant in the development of high-performance composites for microwave absorption applications. In this present study, MWCNTs were shortened to low aspect ratio (~10) by a controllable acid treatment, making the percolation threshold of MWCNTs in Al_2O_3 matrices increase from the range of 0.094–2.5 wt% to 3.89 wt%. The composites embedded with the shortened MWCNTs at the filler loading close to the percolation threshold were observed to demonstrate excellent microwave absorption performance.

2. Experimental

The MWCNT/Al_2O_3 composites were fabricated using hydrothermal crystallization method and hot-pressing according to our previous report [6,23]. The pre-treatment for the pristine MWCNTs (20–40 nm in diameter, 5–20 μm in length, and 1.8 g/cm^3 in density) was modified. In a typical experiment, the MWCNTs were soaked into a mixed acid (98% sulfuric and 68% nitric acids, 3:1) for about 72 h after ultrasonic stirring at 50 °C for 2 h. The resultants were embedded into Al_2O_3 nanoparticles by hydrothermal crystallization method using aluminum isopropoxide (AlIP) as an inorganic source. The weight loadings of MWCNTs in the mixed powders were 1.0, 2.0, 3.0, 3.5, 3.8, 4.0, 5.0, and 7.0 wt% by the molar ratio of Al and C in the starting materials. Subsequently, the mixed powders were hot-pressed at 1500 °C in vacuum (4.0×10^{-3} Pa) under a pressure of 40 MPa in a cylindrical graphite mold (50 mm inner diameter). The relative density of the sintered samples was measured by Archimedes's method, showing higher than 96%. Cubic samples with dimensions of 22.86 mm × 10.16 mm × 2.5 mm were prepared for measuring the electrical conductivity and complex permittivity. The electrical conductivity was applied on a high-sensitivity digital micro-ohmmeter (Keithley 580) using the two-point method on silver electrode specimens. The relative complex permittivity was determined on an Agilent E8362B vector network analyzer (VNA) by the waveguide method in the range of 8.2–12.4 GHz (*X*-band). Similarly, the composites with pristine MWCNTs (0.5, 1.0, 2.0, and 3.0 wt%) were achieved by the same fabrication process and applied to similar techniques for comparison.

3. Results and discussion

The transmission electron microscopy (TEM) images on the MWCNTs show that the as-treated MWCNTs are much shortened with length of several hundred nanometers, compared to pristine MWCNTs (Fig. 1). Fig. 2 shows the electrical conductivity of the MWCNT/Al_2O_3 composites. The electrical conductivity of the three types ceramic composites were all increased with growing MWCNT loading, exhibiting a typical insulator–conductor transition. According to the previous literature [15–21], the percolation threshold of the MWCNT-based composites is generally in the range of 0.094–2.5 wt%. Thus, the electrical conductivity of the pristine MWCNT/Al_2O_3 composites in this work is consistent with the previous

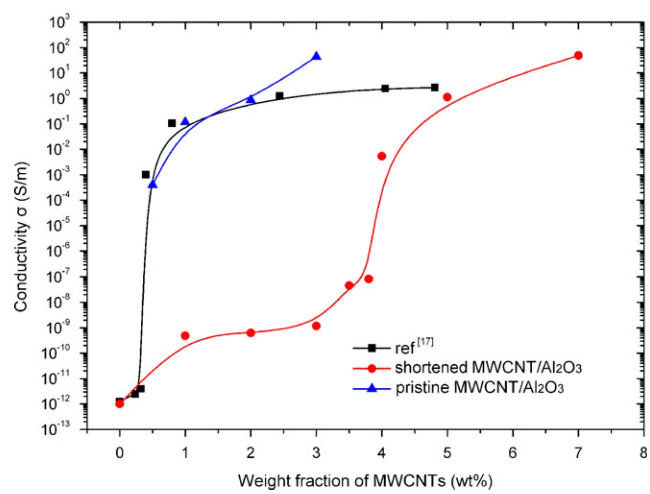

Fig. 2. Curve of dc conductivity of MWCNT/Al_2O_3 composites as a function of the MWCNT loading.

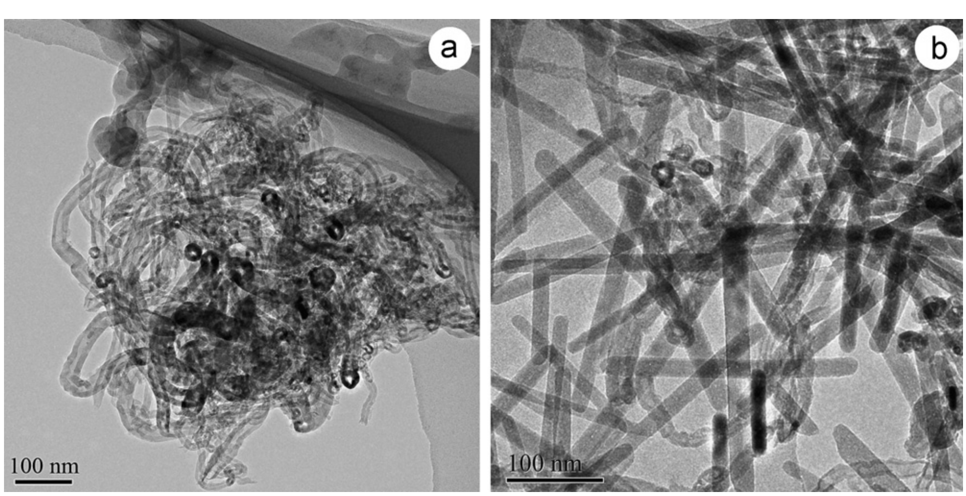

Fig. 1. SEM images of MWCNTs. (a) Pristine MWCNTs; (b) the MWCNTs after acidification.

results. On the other hand, the percolation threshold of the shortened MWCNT/Al_2O_3 composites increases to 3.89 wt%. This observation confirms that the percolation threshold is inversely proportional to aspect ratio, which follows the excluded volume theory [24] and Dalmas' numerical simulation [25].

The pristine MWCNTs were cut down to shortened straight nanotubes by the acid treatment. Fig. 3 exhibits the distribution of MWCNTs in the matrices before and after acid treatment, demonstrating that shortened MWCNTs are relatively easier for achieving homogeneous dispersion in the matrices due to the decrease of aggregation, consistent with our previous report [6]. The schematic illustrations of the distribution for these two MWCNTs in matrices are shown in Fig. 3(c). Accordingly, the matrices with pristine MWCNTs are easier to establish conductive network based on the MWCNT aggregations [26], leading to the much lower percolation threshold in the electrical conductivity.

The relationship between complex conductivity (σ^*) and complex permittivity (ε^*) for composites can be described by the following formula [27]:

$$\sigma^* = i\omega\varepsilon_0, \quad \varepsilon^* = i\omega\varepsilon_0(\varepsilon' - i\varepsilon'') \tag{1}$$

where ω is the angular frequency, ε_0 the dielectric constant in vacuum, ε' and ε'' the real part and imaginary part of the ε^*, respectively. The complex permittivity of both the composites embedded with pristine and shortened MWCNTs was found to increase with increasing MWCNT loadings separately, as shown in Fig. 4(a, b, d, and e), demonstrating conductivity-dependent dielectric properties due to the long tubular structures and conductive properties of the MWCNTs. The results are consistent with the previous report [28,29]. Furthermore, very high complex permittivity was observed in both of the composites when the electrical conductivity was largely increased (~60 S/m for 7 wt% shortened MWCNT/Al_2O_3 composites, for 3 wt% pristine MWCNT/Al_2O_3 composites). In Fig. 4(c, and f), the tangent loss factor exhibits the resonant behaviors and an enhancing trend with increasing MWCNTs added in the composites. However, the increasing of conductance and complex permittivity should change the impedance match of the free space and the composites and enhance the reflection coefficient [29]. Therefore, the increasing of the tangent loss factor could not be the one and only reason for excellent microwave absorption performance.

In order to evaluate the microwave absorption performance of the as-prepared composites, reflection loss (R) was calculated according to the following equation [30]:

$$R = 20\lg\left|\left(\sqrt{\mu^*/\varepsilon^*}\tanh\left(j\cdot 2\pi\cdot f\cdot d\cdot\sqrt{\mu^*\cdot\varepsilon^*}/c\right)-1\right)\Big/\left(\sqrt{\mu^*/\varepsilon^*}\tanh\left(j\cdot 2\pi\cdot f\cdot d\cdot\sqrt{\mu^*\cdot\varepsilon^*}/c\right)+1\right)\right| \tag{2}$$

where $\varepsilon^*$and μ^* are the relative permeability and permittivity of the composites, respectively, c the velocity of

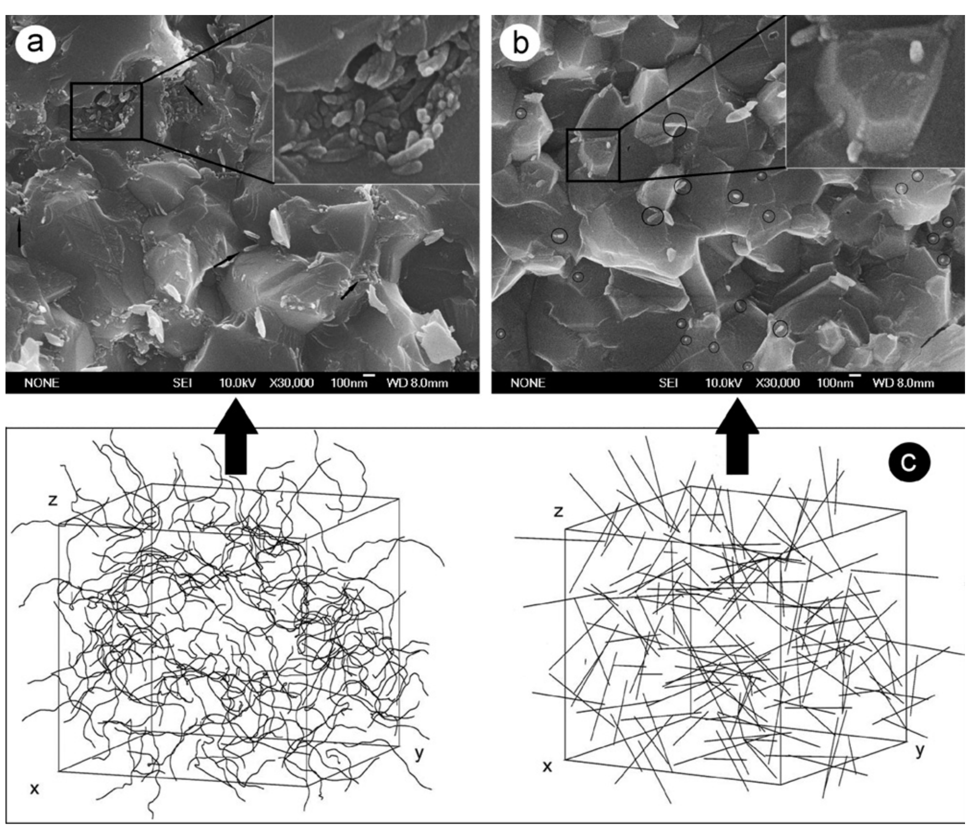

Fig. 3. (a) SEM fractured surface images of pristine MWCNT/Al_2O_3 composite with MWCNT loading of 2 wt%; (b) SEM fractured surface images of shortened MWCNT/Al_2O_3 composite with MWCNT loading of 2 wt% and (c) sketch maps of the distribution of MWCNTs in Al_2O_3 matrices.

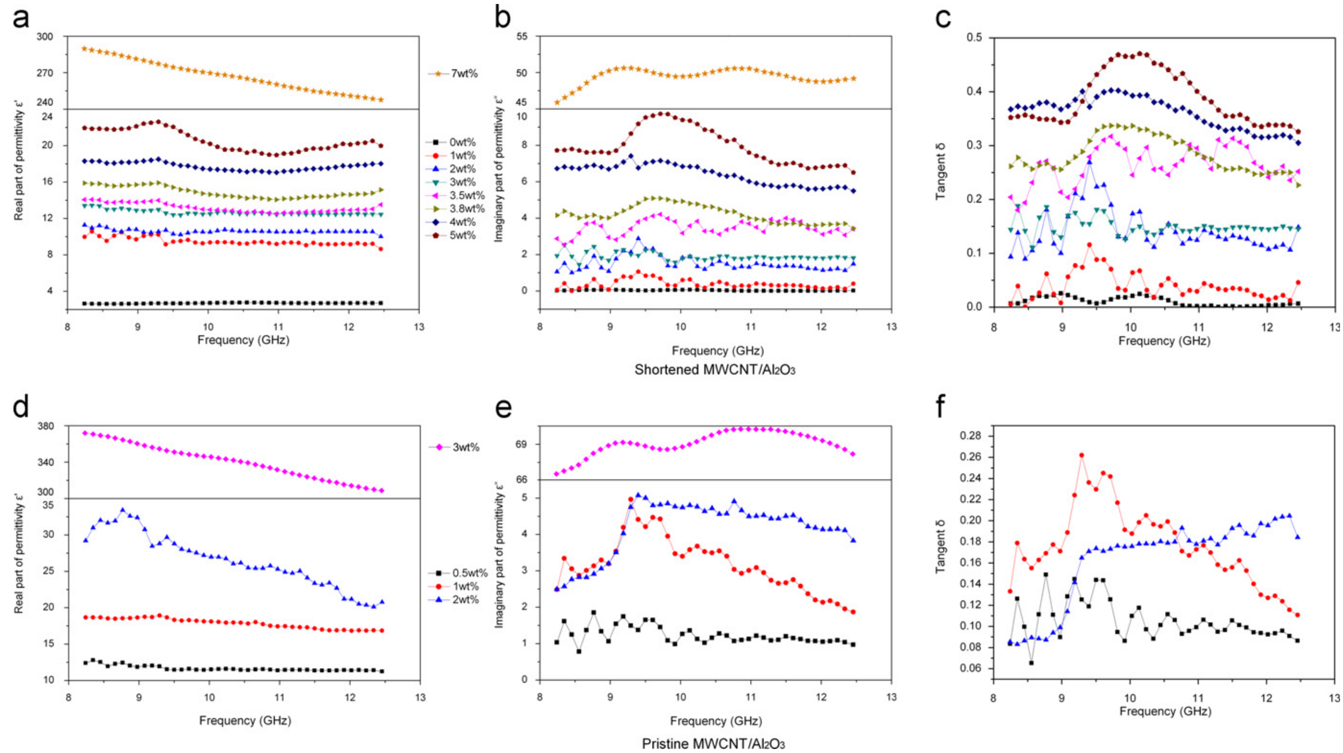

Fig. 4. Complex permittivity and tangent loss factor of MWCNT/Al_2O_3 composites as a function of frequency of *X*-band. (a) ε′ and (b) ε″ of the shortened MWCNT/Al_2O_3 composites; (d) ε′ and (e) ε″ of the pristine MWCNT/Al_2O_3 composites; tangent loss factor of (c) shortened and (f) pristine MWCNT/Al_2O_3 composites.

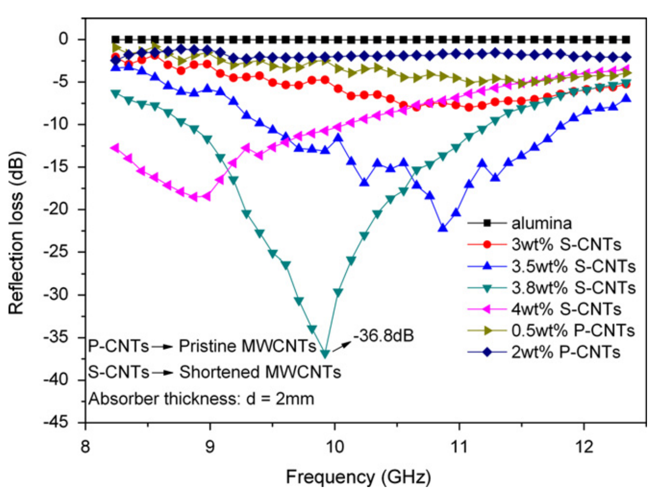

Fig. 5. Calculated results of the reflection loss versus frequency for the composite ceramic in X-band.

microwave in free space, *f* the frequency of microwave, and *d* the thickness of the as-prepared composites. In this work, Al_2O_3 and most of carbon materials, such MWCNTs and carbon fibers, exhibit weak magnetic properties, thus μ^* considered to be one [22,28]. Fig. 5 shows the calculated results of the reflection loss versus frequency for the composite in *X*-band. The shortened MWCNT/Al_2O_3 with a MWCNT loading at 3.8 wt% shows the best absorption performance with a maximum peak (~ -37 dB) and a broad effective absorption band (< -10 dB, 8.7–11.2 GHz), much more sufficient than pristine MWCNT/Al_2O_3 composites with any tested filler loading (Fig. 5). It is also highly interesting to observe that the filler loading for such best absorption performance is around the percolation threshold. The results suggest the shortened MWCNTs with better dispersion may offer much enhanced microwave absorption performance in the alumina-based composites, which indicates great potentials for fabricating high performance microwave absorption composites.

4. Conclusions

In conclusion, acid treatment was applied to achieve shortened MWCNTs, and related MWCNT/Al_2O_3 composites were prepared by hydrothermal crystallization and hot-pressing. The percolation threshold of the composites increases to 3.89 wt%, inversely proportional to aspect ratios of the MWCNTs. The complex permittivity of the composites demonstrates conductivity-dependent characteristic in the investigated region. Compared to the pristine MWCNTs, the shortened MWCNTs were observed to show much enhanced microwave absorption performance in the as-fabricated composites with the MWCNT loading around percolation threshold.

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