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High microwave absorption performances for single-walled carbon nanotube–epoxy composites with ultra-low loadings*

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Microwave-absorbing polymeric composites based on single-walled carbon nanotubes (SWNTs) are fabricated via a simple yet versatile method, and these SWNT–epoxy composites exhibit very impressive microwave absorption performances in a range of 2 GHz–18 GHz. For instance, a maximum absorbing value as high as 28 dB can be achieved for each of these SWNT–epoxy composites (1.3-mm thickness) with only 1 wt% loading of SWNTs, and about 4.8 GHz bandwidth, corresponding to a microwave absorption performance higher than 10 dB, is obtained. Furthermore, such low and appropriate loadings of SWNTs also enhance the mechanical strength of the composite. It is suggested that these remarkable results are mainly attributable to the excellent intrinsic properties of SWNTs and their homogeneous dispersion state in the polymer matrix.

Keywords: microwave absorption, single-walled carbon nanotube–epoxy composites, ultra-low loadings

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1. Introduction

Microwave absorbing materials have attracted more and more attention from both scientists and engineers due to their important applications in commercial and military fields, such as wireless antenna systems, electronic devices, computers, and cell phone systems.[1–3] In most instances, magnetic and metal particles or alloys are widely utilized to prepare these microwave absorbing materials. For example, Ni-doped SiC powders have been reported to have microwave absorption properties in a frequency range of 2 GHz–18 GHz.[4] However, some disadvantages, such as high specific gravity, difficult processing, and high cost, have severely restricted their practical applications, so suitable microwave absorbing materials are still urgently needed. Microwave absorbing materials that are relatively lightweight, mechanically strong, low cost, and efficient in absorption with wide band-range are thus still highly desired. Recently, carbon-based nanomaterials have been widely employed in the field of microwave radiation absorption and shielding, owing to their unique chemical, physical, and structural features.[1–3,5–8] In particular, with a low specific gravity, high aspect ratios, and excellent electrical conductivities and mechanical properties, carbon-based nanomaterials, including both single-walled (SWNT) and multi-walled (MWNT) carbon nanotubes (CNTs), have been extensively studied for potential engineering applications,[9–14] including microwave absorption.[1,3,5,7] It has been reported that the addition of CNTs to a lightweight, low cost, and widely used polymer matrix can greatly improve its microwave-absorbing efficiency, mainly owing to the increase of the electrical conductivity of the polymer composite.

Recent progress has been made towards investigating the microwave absorption performances of CNT–polymer composites with different types of CNT and metal filled or loaded CNTs.[1,3,5,7] For example, in our previous work we prepared SWNT–polyurethane composites that achieve a maximum value of 22 dB at 5-wt% loading,[1] and Che *et al.* reported the absorption properties of MWNT–epoxy composites with different shapes and phases of magnetic Fe fillers embedded in CNTs.[5] However, most of these studies may only exhibit good performance in microwave absorption, at the expense of other important properties such as mechanical performance and cost, owing to the excessive loading of CNTs. It is well known that, while most carbon-based absorber materials mainly act as mechanical reinforcement fillers to enhance the mechanical strengths of their polymeric composites at appropriate loadings, they can also bring a negative influence on the mechanical performance of their composites when the proportions are too high because of the aggregation of the fillers.[15] To date, the greatest stumbling block to the commercialization of carbon-based absorber filler–polymer composites may be the dearth of cost-effective approaches to prepare composites which possess high enough microwave absorption properties and improved mechanical strength at low loading of absorbing fillers to meet the demands of practical use. Herein, we pre-

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pare the SWNT–epoxy composites via a facile and effective *in situ* method. Remarkably, with a thickness of 1.3 mm, the maximum microwave absorption performance of our SWNT–epoxy composites can reach as high as 28 dB in a frequency range of 2 GHz–18 GHz with only 1-wt% loading of SWNTs. Besides, this rather low addition of SWNTs also leads to 40% and 25% enhancement of the mechanical performance, with the loads being 0.5 wt% and 1 wt% of SWNTs respectively for the SWNT–epoxy composites. These outstanding results are due to the outstanding intrinsic properties of SWNTs and their homogeneous dispersion in the matrix polymer. To the best of our knowledge, while much work on microwave absorption properties of composites using carbon-based nanomaterials has been done,[1–3,6,8] our SWNT–epoxy composites provide both enhanced mechanical strength and the best radar absorption performance at such a low loading.

2. Experimental details

2.1. Materials

SWNTs were produced by a modified arcing method on a large scale using an Ni–Y catalyst according to our published method.[14] A commercially available bisphenol A-type epoxy resin (618 type), supplied by Tianjin Resin Company, and an amine-type hardener ($[C_{17}H_{31}CONH(C_2H_4NH)_2H]_2$), supplied by Tianjin Ningping Chemical Co. (model A022-2), were used to prepare the epoxy matrix. All materials used here were commercial products.

2.2. Preparation of SWNT–epoxy composites

The SWNT–epoxy composites were prepared according to the following example for a composite with 1 wt% SWNT loading.[14] The bisphenol A-type epoxy resin and an amine-type hardener were used to prepare the polymer matrix with a ratio of 2:1. SWNTs (0.6 g) were first dispersed in acetone (800 mL–1000 mL) in an ultrasonic bath at room temperature for 2 h, followed by the addition of an epoxy resin–acetone solution (39.6 g epoxy in 200 mL acetone). The mixture was then sonicated for another 1.5 h, and the hardener (19.8 g) was added with mechanical stirring. The mixture was again sonicated for 30 min, and then most of the acetone was evaporated under reduced pressure. The mixture was then poured into suitable molds (180 mm $\times$ 180 mm) to allow the remaining acetone to evaporate completely at room temperature in air. After this, the composite was cured further at 60 °C for one day and 80 °C for 6 h respectively. Composites with various loadings of SWNTs (0–15 wt%) were prepared similarly. The thickness values of all the samples are each about 1.3 mm.

2.3. Characterization

Scanning electron microscopy (SEM) was performed on a Hitachi S-3500N scanning electron microscope with an acceleration voltage of 20 kV. Samples were prepared by immersing them in liquid nitrogen for 10 min before fracturing. The fractured surfaces were coated with gold before analysis.

2.4. Electrical conductive measurement

The direct current (DC) conductivity values of the SWNT–epoxy composites were measured utilizing the standard four-point contact method on rectangular sample slabs and the data were collected with a Keithley SCS 4200.

2.5. Mechanical measurement

The mechanical properties of SWNT–epoxy composites were measured by a universal tensile testing machine (KNM 500-10 test metric, UK) at 20 °C with 50% relative humidity. The extension rate was 20 mm min^{-1} with a gauge length of $\sim$ 30 mm. All samples were cut into shapes of about 50 mm $\times$ 7 mm $\times$ 1.3 mm.

2.6. Microwave absorption measurement

The relative complex permittivity $\varepsilon = \varepsilon' - \mathrm{j}\varepsilon''$ and relative complex permeability $\mu = \mu' - \mathrm{j}\mu''$ were determined using the T/R coaxial line method in a range of 2–18 GHz with an O-ring shaped sample (i.d. = 3 mm and o.d. = 7 mm, thickness = 2 mm) using an HP8722ES vector network analyzer. The microwave-absorbing characteristics were evaluated by measuring the reflection loss using an HP8757E scalar quantity network analyzer in the 2 GHz–18 GHz band range, and the sample sheets (180 mm $\times$ 180 mm $\times$ 1.3 mm) were mounted on an aluminum substrate. All the measurements were made at room temperature.

3. Results and discussion

3.1. Electrical conductivity values of SWNT–epoxy composites

The efficacious use of nano-filler in polymeric composites has been extensively investigated to be strongly correlated with the ability to disperse them homogeneously in the matrix.[1–3,5–8,14–16] Hence, the dispersion state of our SWNTs in the epoxy matrix was first detected by SEM, and figure 1 shows a typical SEM image of the cross section for SWNT–epoxy composites with 5-wt% loading of SWNTs. It clearly shows that the SWNTs, which appeared as white spots in Fig. 1(a) or lines in Fig. 1(b), are uniformly dispersed and embedded throughout the epoxy matrix. Moreover, this homogeneous dispersion of SWNTs in the polymer matrix coupled with its extremely high aspect ratio can make the SWNTs form a continuous conductive network in the polymer matrix at very low loadings.[16] Consequently, the combined good dispersion state and unique features of SWNTs facilitate the enhancement of performance of the SWNT–epoxy composites as stated below.

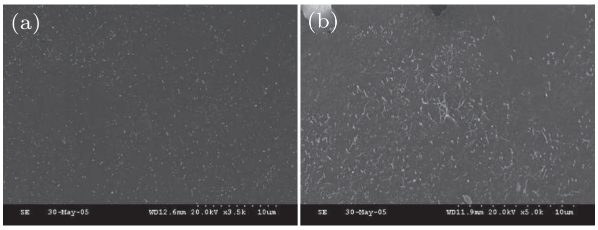

Fig. 1. Representative SEM images of the cross section of the SWNT–epoxy composite with 5-wt% SWNTs. The sample was freeze-fractured in liquid nitrogen and gold coated before measurement.

Figure 2 shows the DC conductivity (σ) of our SWNT–epoxy composites as a function of the SWNT mass fraction (p). A dramatic increase of eight orders of magnitude below 1 wt% was obviously observed in the conductivity of the composites, which indicates the formation of an SWNT percolating network in the polymer matrix. It has been reported that the conductivity of a conductor–insulator composite follows the critical phenomena around the percolation threshold (Eq. (1)):[17]

$$\sigma \propto (\nu - \nu_c)^{\beta}, \tag{1}$$

where σ is the composite conductivity, ν is the SWNT volume fraction, ν_c is the percolation threshold, and β is the critical exponent. Since epoxy and SWNT nanofillers have similar densities, we assume that the mass fraction (p) and the volume faction (ν) of SWNTs in the epoxy matrix are the same. As demonstrated in the inset of Fig. 2 for the $\log(\sigma)$ versus $\log((p-p_c)/p_c)$ plot, a least-squares analysis of the fits using Eq. (1) shows that the threshold value p_c for each set of composites was strongly bounded by the regions between the highest insulating and lowest conducting points, and the conductivity values for SWNT–epoxy composites are highly consistent with the percolation behavior predicted by Eq. (1). As shown in the inset of Fig. 2, the straight line with extremely low percolation threshold $p_c = 0.028$ wt% and $\beta = 1.862$ gives a good fit to the data. This low percolation threshold value, which is comparable to those of other reported SWNT–polymer composites,[18–22] indicates the highly

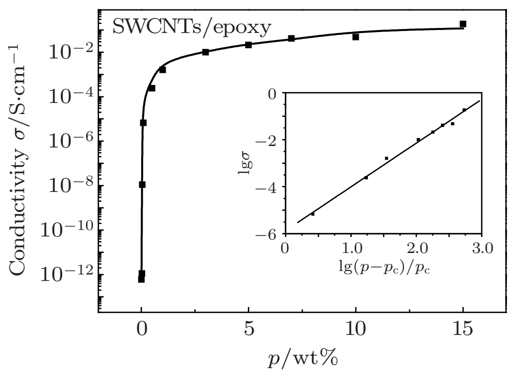

Fig. 2. The $\log_{10}$ DC conductivity (σ) versus mass fraction (p) of SWNT–epoxy composites measured at room temperature. Insets: log–log plots (σ versus $(p-p_c)/p_c$) generated using Eq. (1) and least-squares fit to the data near the threshold.

efficient dispersion of SWNTs into the epoxy matrix at low concentration.

3.2. Microwave absorption performances of SWNT–epoxy composites

The relationship between microwave frequency and reflection loss (microwave absorption performance) for the SWNT–epoxy composite in a frequency range of 2 GHz–18 GHz was analyzed using a model of a single-layered plane wave absorber backed by a perfect conductor. According to the transmission line theory, the reflection coefficient of electromagnetic radiation, R (dB), under normal wave incidence at the surface of a single-layer material backed by a perfect conductor can be defined as[22]

$$R = 20\log\left|\frac{Z_m - Z_0}{Z_{in} + Z_0}\right|, \tag{2}$$

where Z_0 is the characteristic impedance of free space, and

$$Z_0 = \sqrt{\frac{\mu_0}{\varepsilon_0}}, \tag{3}$$

Z_{in} is the input impedance at the free-space–material interface,

$$Z_{in} = \sqrt{\frac{\mu_0\mu}{\varepsilon_0\varepsilon}}\tanh(j2\pi f\sqrt{\mu_0\mu\varepsilon_0\varepsilon}d), \tag{4}$$

with f and d being the frequency of the electromagnetic wave and the thickness of the material, respectively, μ and ε being the relative permeability and relative permittivity respectively. According to Eqs. (2)–(4), the intensity of reflection loss and the frequency position with minimum reflection loss (that is, the maximum microwave absorption) depend on the thickness, magnetic permeability, and dielectric permittivity of microwave absorption material.

Considering that the thickness value of the SWNT–epoxy composite is a fixed value (1.3 mm), the microwave absorption performance is thus mainly determined by the complex permeability and permittivity value of the composite. Accordingly, figure 3 displays the complex permittivity and permeability of SWNT–epoxy composites measured at 2 GHz–18 GHz utilizing the T/R coaxial line method. It can be obviously seen in Figs. 3(a) and 3(b) that with increasing loading of SWNTs, the values of real (ε') and imaginary (ε'') permittivity for the composite both increase. Furthermore, the relative permittivity is almost independent of frequency in the range of 2 GHz–18 GHz. In contrast, the values of real and imaginary permeability show relatively small changes (μ', 0.9–1.2; μ'', −0.2–0.2) around the values (1 and 0, respectively) for free space. Therefore, while the permeability is approximately constant in the measured range, it indicates that the microwave absorption performance is primarily dependent on the dielectric permittivity of composite.

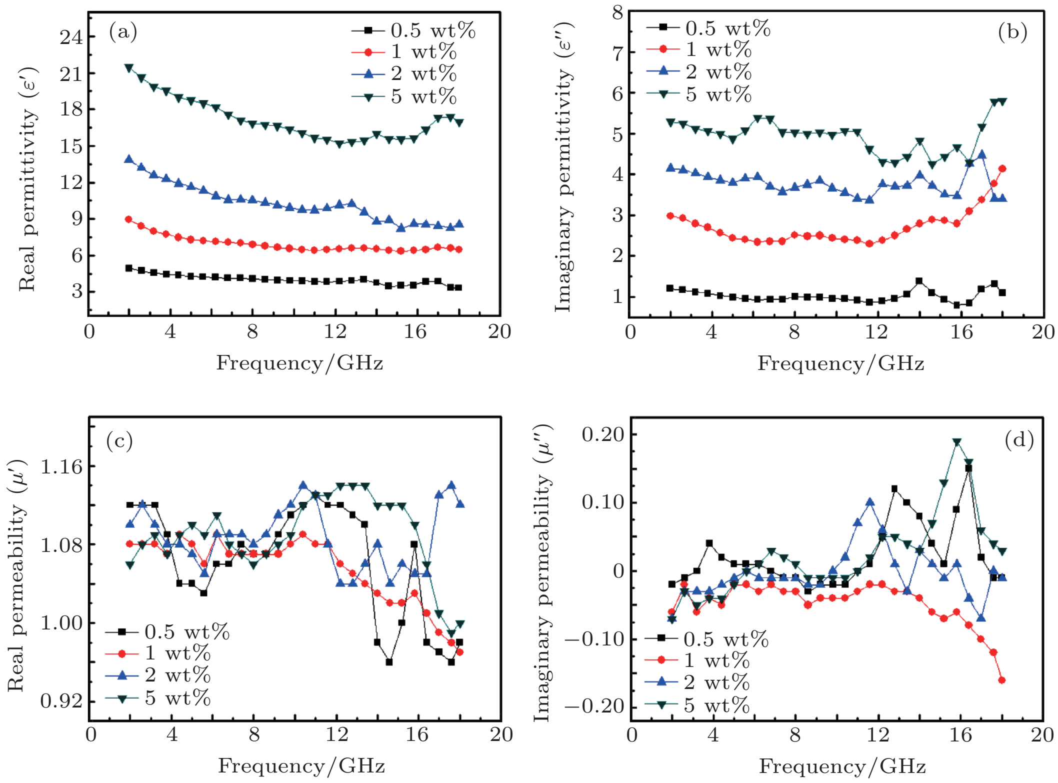

Fig. 3. (color online) The measured room-temperature complex permittivity spectra (a), (b) and permeability spectra (c), (d) for SWNT–epoxy composites with various loadings of SWNTs.

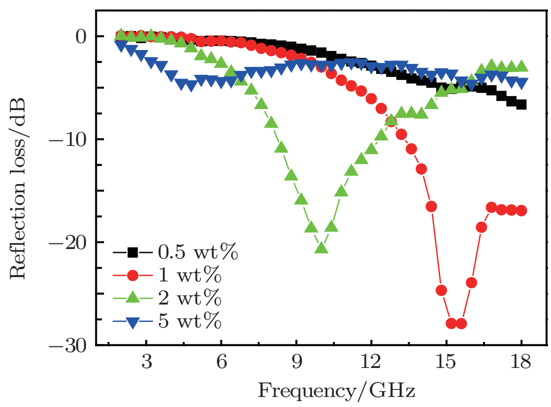

Fig. 4. (color online) The reflection losses versus frequency for SWNT–epoxy composites with different loadings of SWNTs.

Figure 4 demonstrates the reflection losses versus frequency in a range from 2 GHz to 18 GHz for SWNT–epoxy composites with different SWNT loadings. It can be obviously found that, with reducing loadings of SWNT, the position of the reflectivity peak is shifted toward a higher frequency. Similar phenomena of microwave absorption properties have also been found in many other carbon-based nanofiller–polymer composites.[1–3,6] Of great significance is that the maximum microwave absorption of the SWNT–epoxy composite, which reaches as high as 28 dB at 15.6 GHz (or −28 dB for reflection loss), occurs at only 1 wt% of SWNT loading. Additionally, the bandwidth corresponding to microwave absorption higher than 10 dB (i.e. over 90% microwave absorption) is around 4.8 GHz, and the bandwidth corresponding to microwave absorption higher than 5 dB (i.e. over 70% microwave absorption) is approximately 7 GHz. As depicted in Fig. 5, while many excellent studies of microwave absorption properties of composites using carbon-based materials as absorber fillers have been published,[1–3,6,8] to the best of our knowledge, our SWNT–epoxy composites in this study have the best radar absorption performance at such a low loading (1 wt%) of SWNTs with the sample thickness value of only about 1.3 mm.

The highest absorption occurs at the point when the reflection of the microwave power from the material is minimal. The relationship among thickness, relative permeability, and relative permittivity for the minimum reflection loss can be expressed as

$$d = \lambda/4 = \lambda_0/4\varepsilon\mu, \tag{5}$$

where d is the composite thickness; λ_0 is the incident microwave wavelength under vacuum; ε is the relative permittivity; μ is the relative permeability; λ is the microwave wavelength in the composites.[24] Accordingly, at a particular thickness, when the incident and reflected waves in the material are 180° out of phase, the highest absorption is observed due to the maximum cancellation of the reflected and incident waves at the air–material interface. While the values of thickness and relative permeability are both constant in our material, the incident wavelength λ_0 for the highest absorption of the reflected wave that causes maximal interference is dependent on the relative permittivity as shown in Eq. (5).

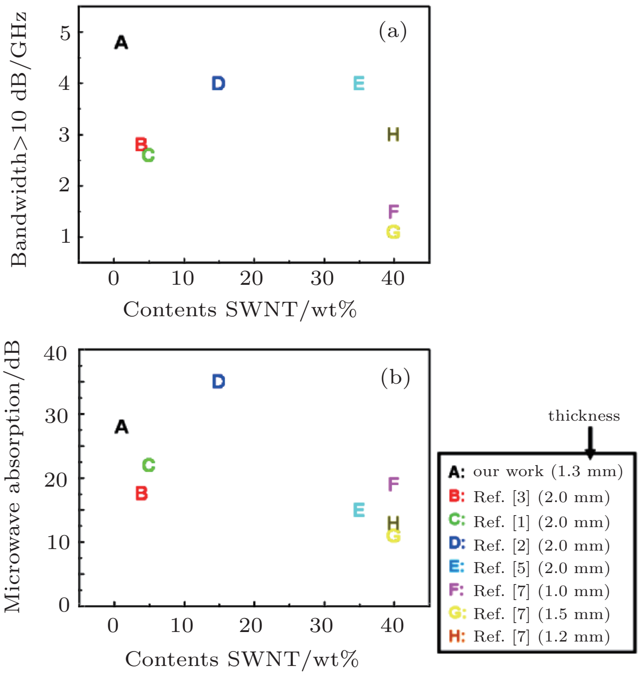

Fig. 5. (color online) (a) The maximum microwave absorption performances for our SWNT–epoxy composite compared with the best available data for similar carbon-based material–polymer composites. (b) The bandwidth corresponding to microwave absorption higher than 10 dB for our SWNT–epoxy composites compared with the best available data for the similar carbon-based material–polymer composites.

According to Eq. (5), for the occurrence of minimum reflection loss, the microwave wavelength λ_0 should increase with the increase of ε. This means that the microwave frequency should decrease with increasing ε. Hence, the ε value of the SWNT–epoxy composite increases and the position of the reflectivity peak moves toward a lower frequency while the SWNT loading increases. According to Eqs. (2)–(4), the minimum reflection loss of an incident plane wave occurs when Z_{in} is closest to Z_0 (i.e., the permeability and permittivity of the SWNT–epoxy composite are the closest, as indicated by Eq. (4). Since the complex permittivity of the SWCNT–epoxy composite increases significantly with the increase of SWNT loading, the minimum reflection loss decreases for Z_{in} to be closest to Z_0 (i.e. highest absorption). This also indicates that, at 1-wt% loading, Z_{in} most closely matches Z_0 (i.e., the permeability and permittivity of the SWNT–epoxy composite are closest). As discussed above, SWNTs have extremely high electrical conductivity and can be homogeneously dispersed in the epoxy matrix, leading to the low loading (1%) necessary to reach relatively high permittivity and the most appropriate matching condition. Consequently, our SWNT–epoxy composites are provided with these striking microwave absorption properties at these very low loadings of SWNTs.

3.3. Mechanical performance of SWNT–epoxy composite

Generally speaking, the polymer materials, which are used as the matrix for microwave absorption composites, are insulators and thus are transparent to electromagnetic waves. Thereby, the microwave absorption performance mainly stems from the contribution of absorber fillers, and is strongly related to the dispersion state of absorber fillers in the polymer matrix. Although some reported polymeric composites utilizing carbon-based materials as absorber fillers can also achieve outstanding microwave absorption performance (i.e. higher than 15 dB), they always need quite a high weight fraction of the absorber fillers, and in some cases it is even higher than 30 wt% (Fig. 5).[1–3,6,8] From an economic point of view, due to the relatively high price of carbon-based absorber nanofillers, higher weight fraction of fillers leads to much higher production cost, which poses a significant hurdle for practical applications. Most importantly, while most carbon-based absorber fillers are able to act as mechanical reinforcement fillers to enhance the mechanical strength of their polymeric composites at appropriate loadings, too high filler loadings can cause processing difficulties and have a negative influence on the mechanical performance of the composites.[15,22] Thus, it is worth noting that our SWNT–epoxy composites with low loadings of SWNT also show enhanced mechanical properties, as indicated in Fig. 6. As can be seen, compared with the pure epoxy matrix, our composites can reach 40 and 25% increase in tensile strength by adding 0.51 wt% and 1 wt% of SWNTs respectively. These impressive results are attributed to the excellent intrinsic mechanical strength of the SWNTs and their good homogeneous dispersion state in the host polymer. Therefore, it is believed that our SWNT–epoxy composites are highly promising in the realm of microwave absorption materials.

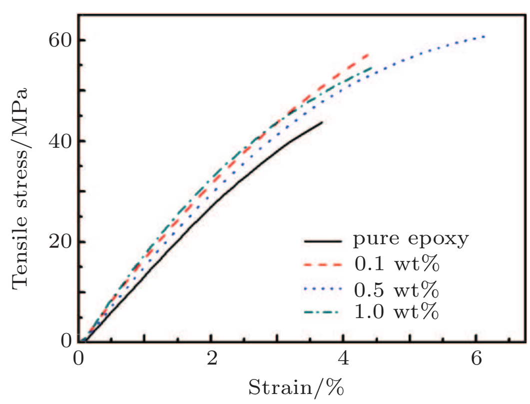

Fig. 6. (color online) Representative stress–strain behaviors for SWNT–epoxy composites with different SWNT weight loadings.

4. Conclusions

In this paper, SWNT–epoxy composites are fabricated through a facile and effective method, and their microwave absorption properties are investigated in a range of 2 GHz–18 GHz. The microwave absorption performances of the SWNT–epoxy composites can reach as high as 28 dB with only 1-wt% loading of SWNTs. This rather low loading of SWNTs can not only reduce the production cost, but also enhance the desired mechanical strengths of these composites. It is suggested that these impressive results are primarily due to the excellent intrinsic features of SWNTs and their homogeneous dispersion states in the host polymer, owing to our *in situ* solution process. Therefore, using the simple *in situ* process, these SWNT–epoxy composites have great potential to be exploited commercially as effective and lightweight microwave absorption materials.

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