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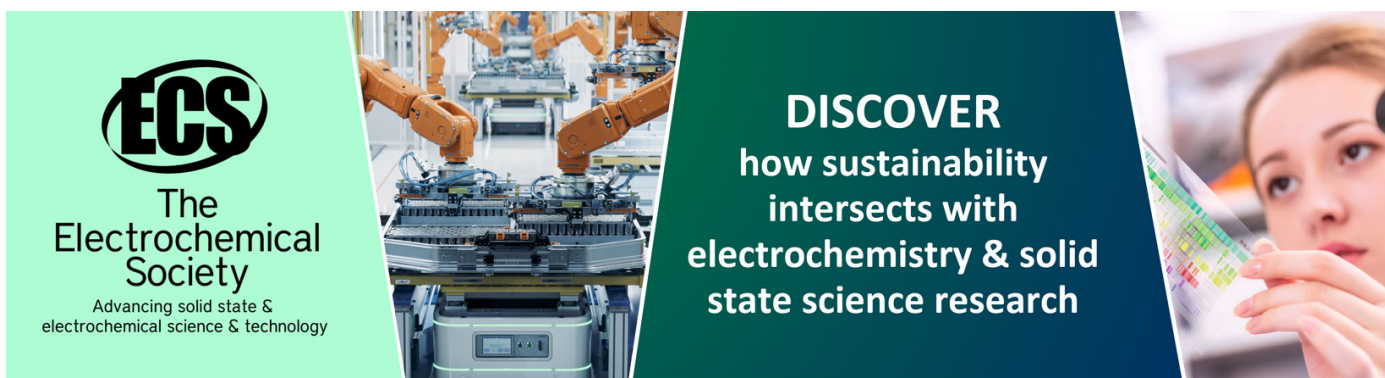
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Comparison of electromagnetic interference shielding properties between single-wall carbon nanotube and graphene sheet/polyaniline composites

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Abstract

Single-wall carbon nanotube/polyaniline (SWCNT/PANI) and graphene sheet/polyaniline (GS/PANI) composites were prepared by a simple alcohol-assisted dispersion and pressing process. The SWCNTs and GSs were synthesized by the dc arc-discharge method. The dc electrical conductivity and the electromagnetic interference (EMI) shielding effectiveness (SE) of these two kinds of composites were measured. The experimental results reveal that the conductivity and the EMI SE of the GS/PANI composite are better than that of the SWCNT/PANI composite, and the absorption proportion of the SWCNT/PANI composite is higher than that of the GS/PANI composite. The EMI shielding results (2–18 GHz) also show that both composites present an absorption-dominant mechanism and present a wide application prospect in the field of EMI shielding and microwave absorption.

(Some figures may appear in colour only in the online journal)

1. Introduction

Single-wall carbon nanotubes (SWCNTs) and graphene sheets (GSs) are quasi-one-dimensional structure and two-dimensional lattice structure of sp^2 hybridized carbon atoms, respectively. They have markedly different geometric shapes; but both of them have exceptional electrical transport, thermal and mechanical properties [1–3], which make them excellent fillers to enhance the conductivity of composites [4, 5]. Polyaniline (PANI) is the most versatile conducting polymer owing to its cheapness and desirable properties, such as low specific mass, thermal and chemical stability and high conductivity at microwave frequencies [6]. So far, many theoretical and experimental investigations on polymer composites using CNTs as electrically conductive fillers for the application of electromagnetic interference (EMI) shielding and microwave absorption have been carried out by several groups recently [7–10]. As we know, the EMI shielding effectiveness (SE) of a composite material

depends on many factors, including the filler's intrinsic conductivity, dielectric electrical constant, aspect ratio and so on [11, 12]. A theoretical study has shown that GS-filled composites have higher electrical conductivity and can form conductive networks more easily than CNT-filled composites in the same filler weight fraction [13]. However, there are only a few reports about the EMI shielding property of GS-filled polymer composites [14], and no paper reports the comparison of the EMI shielding properties between SWCNTs and GSs as fillers in conductive polymers. In this paper, we used a simple alcohol-assisted dispersion and pressing process to prepare SWCNT/PANI and GS/PANI composites. A comparative study on the electrical properties and the EMI shielding properties of SWCNT/PANI and GS/PANI composites is carried out. Consistent with theoretical predictions, the GS/PANI composite has higher electrical conductivity and higher EMI SE than the SWCNT/PANI composite. The EMI shielding of these two composites presents an absorption-dominant mechanism, and the absorption proportion of the SWCNT/PANI composite is higher than that of the GS/PANI composite.

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2. Experiment

2.1. Materials and composite preparation

The SWCNTs and GSs were both prepared by the hydrogen arc-discharge method [15]. The PANI was supplied by the Alfa Aesar Company; its electrical conductivity is 1 S cm^{-1} . The SWCNT/PANI and GS/PANI composites were prepared by a simple alcohol-assisted dispersion and pressing process [16]. To achieve a uniform dispersion, mixed powders (SWCNTs and PANI or GSs and PANI) were first ground for 10 min, and smashed by an ultrasonic cell crusher for 5 min in alcohol, and then further dispersed by ultrasonic mixing for 1 h to acquire SWCNT/PANI and GS/PANI suspensions. Thus, the composite powders were obtained by a thermostatic water bath (at 95°C). Subsequently, parts of these composite powders were compressively moulded into $\text{Ø}12 \text{ mm}^2$ sheets at room temperature with a pressure of 3 MPa for 1 min. The sheets were used for the measurement of electrical conductivity, and the other parts of the composite powders were moulded into ring-type samples for the EMI SE test. The average densities of the SWCNT/PANI and GS/PANI composites are about 1.3 g cm^{-3} and 1.2 g cm^{-3} , respectively. Finally, all the samples were placed in an oven at 60°C for 2 h. The samples for EMI shielding were named as follows: P1 (pure PANI); C1, C2 and C3 (SWCNT/PANI composite); G1, G2 and G3 (GS/PANI composite), the doping quantity ratios were 1 : 5, 1 : 4 and 1 : 3, respectively.

2.2. Measurements

The graphite structures were examined by Raman analysis with an excitation power of 10 mW at 514 nm (RENISHAW, Invia plus). The morphological observations of the samples were performed using a fielding emission scanning electron microscope (FE-SEM, JEOL-6700F) equipped with an energy dispersive spectroscopy analyser (EDS, Oxford Inca), a transmission electron microscope (TEM, JEOL JEM-200CX) and a high-resolution transmission electron microscope (HRTEM, JEOL JEM-2010F and Tecnai G2 F20 S-Twin).

The conductivities of all samples (including SWCNTs, GSs, pure PANI and composites) were measured by the four-probe method at room temperature using a surface low-impedance analyser (Loresta EPMCP-T360). The conductivity (σ) was calculated using the following two equations:

$\rho = R_s \times t (\Omega \text{ cm})$, $\sigma = 1/\rho (\text{S cm}^{-1})$ [17], where ρ is the bulk resistivity and t (cm) is the sample thickness.

The EMI SE of all samples with different doping ratios was calculated by the S parameters, measured by the HPE8363B vector network analyser using the coaxial method in the range 2–18 GHz [18, 19]. The specimen size is $\text{Ø}3.05 \text{ mm}$ (inner), $\text{Ø}7.00 \text{ mm}$ (outer); the thickness is about 2.4 mm.

3. Results and discussion

3.1. Morphology and microstructure

Figure 1 shows the TEM, HRTEM images and the Raman spectra of the SWCNTs and the GSs. In figure 1(a), we see the

SWCNT bundles with amorphous carbon and Fe nanoparticles adhering to the surface, which are shown in dark and bright points. The image in figure 1(b) shows that the GSs are flaky structure, they overlap each with other, like folds of tissue slice. The inset in figure 1(b) shows the HRTEM image of the GSs, from which we can see that the GSs consist of 2–4 layers. In fact, the number of layers is mainly in the range 2–10 and the sheet thickness is in the range 0.4–3 nm. Figures 1(c) and (d) are the Raman spectrum of the SWCNT and GSs, respectively. As we know, the ratio of D band and G band intensity (I_D/I_G) represents the defects or crystallinity in the carbon materials. The smaller the ratio, the smaller the defect, and the better the crystallinity. The ratio of G band and 2D band intensity I_G/I_{2D} is related to the graphene layers; the smaller the ratio, the fewer the graphene layers. In figure 1(c), the ratio of the peak intensity I_D/I_G is about 0.043, which demonstrates that the SWCNTs have good crystallinity and purity [20]. From the inset, we can see that three RBM peaks appear at 133, 184 and 261 cm^{-1} . Using the relation between the diameter d (nm) and the RBM peak frequency ω (cm^{-1}): $d = 224/(\omega - 14)$ [21], the calculated result indicates that these three peaks should originate from the SWCNTs with diameters 1.8, 1.3 and 0.9 nm, respectively. Namely, the diameter of the SWCNTs is in the range 0.9–2 nm and the average length is about tens of microns. As shown in figure 1(d), the I_D/I_G value of the GSs is 0.21 and the I_G/I_{2D} value is 0.98. These indicate that the prepared GSs have good crystallinity and are composed of a few (2–10) layers.

To examine the dispersion of SWCNTs and GSs in the PANI matrix, the composite powders were analysed by FE-SEM. Figure 2(a) shows that the pure PANI powder has a blocky structure; figure 2(b) clearly reveals that the SWCNTs (entangled filamentous structures with impurity particles, as the arrows point) are inserted into the PANI block layer, and seem not very uniform. However, as shown in figure 2(c), the GS/PANI composite seems uniform; it is difficult to distinguish the GSs and PANI. Moreover, the size of the GSs/PANI composite is smaller than that of the SWCNT/PANI composite; this shows that the GSs help in reducing the particle size, because they are inserted into polyaniline and are distributed evenly. Compared with the GS/PANI composite, the SWCNTs are quasi-one-dimensional structure and are easy to aggregate, which means that they are hard to be distributed, so the size of the SWCNT/PANI composite powder is still large.

3.2. Raman spectra analysis

Figure 3 shows typical Raman spectra of the composites. According to Lindfors's work, the Raman spectrum at 514 nm for different PANI forms is different [22]. Here, the remarkable characteristic peaks of PANI are at 1188, 1344 (coincides with peak D of the GSs) and 1604 cm^{-1} . After doping the SWCNTs or the GSs, the Raman spectra of the composites are changed: (i) for PANI, the C–H bond of the quinoid ring is at 1188 cm^{-1} , after doping the SWCNTs or the GSs, this peak is slightly decreased; (ii) the peak of 1344 cm^{-1} comes from C–N⁺, but coincides with the D band of graphene (represents defects and disordered crystal structure), results in an increase

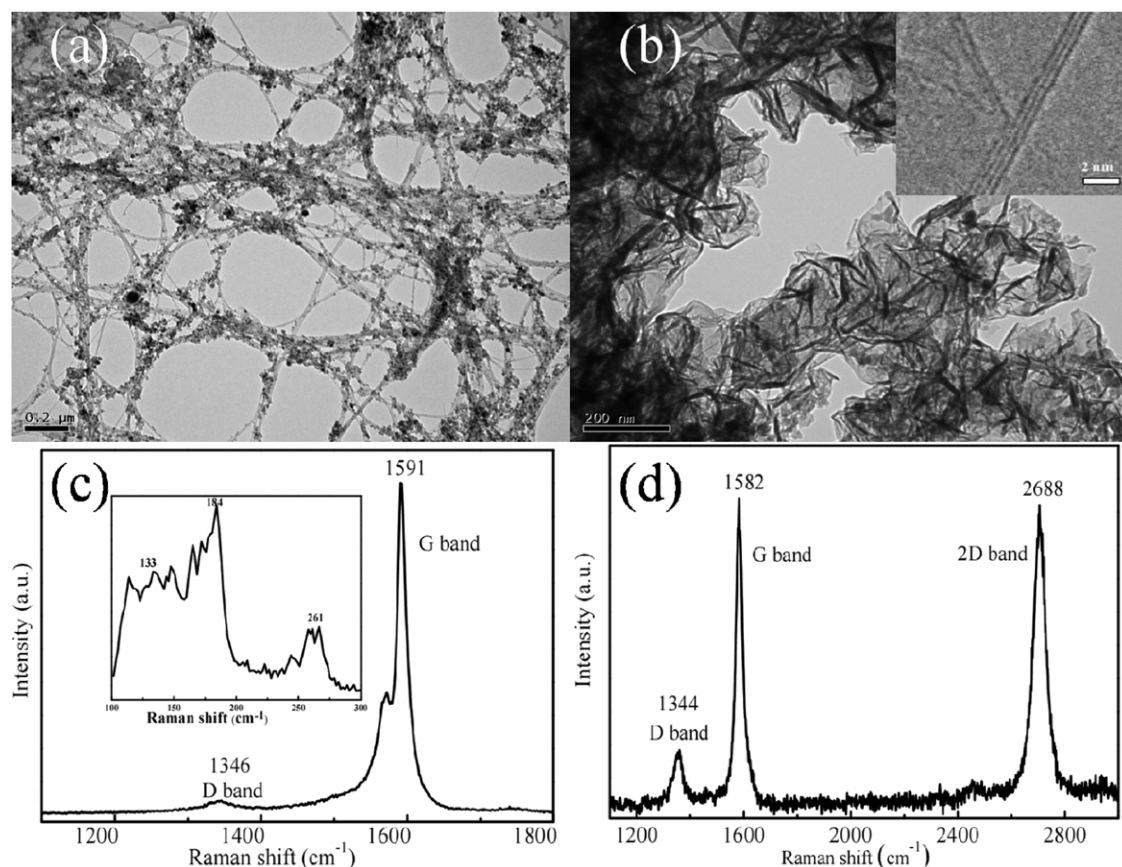


Figure 1. TEM image of the SWCNTs (a) and GSs (b); (c) and (d) show the Raman spectra of the SWCNTs and the GSs, respectively. The inset in (b) shows the HRTEM image of the GSs.

in this peak value in the GS/PANI composite and little change in the SWCNT/PANI composite; (iii) band around 1604 cm^{-1} in PANI is close to the G band of the SWCNT (1591 cm^{-1}) and the GSs (1582 cm^{-1}). In these two kinds of composites, this band shifted to a low wave number and the peak becomes sharper compared with the pure PANI sample, which may have resulted from the π - π^* electron interaction between PANI and SWCNTs or GSs [23].

Obviously, because of the interaction with the SWCNTs and GSs, the Raman spectrum of the PANI is changed, and the interaction effect in the GS/PANI composite is stronger than that in the SWCNT/PANI composite.

3.3. Electrical properties

Figure 4 shows the electrical conductivities of these two composites versus filler weight fraction. The electrical conductivity of pure PANI is 1 S cm^{-1} , and the experimental results show that the electrical conductivities of the SWCNTs and GSs are about 34 S cm^{-1} and 20 S cm^{-1} , respectively. By adding the SWCNTs or GSs, the electrical conductivities of the composites are both improved and increase with the filler weight fraction. The differences between these two kinds of composites are as follows: the electrical conductivity of the GS/PANI composite is higher and changes more quickly than that of the SWCNT/PANI composite at the same filler weight fraction. The main reasons can be ascribed to the

following facts: (1) as the Raman spectra in figure 3 show that the π - π^* electron interaction between GS and PANI is stronger than that of SWCNT and PANI, which causes the GS/PANI composite to form a more stable dispersion system; (2) the SWCNTs prepared by the arc discharge method are of better crystallinity and apt to winding with each other, so it is difficult to disperse them in PANI than the GSs; (3) during the manufacturing process of the composites, the GSs or SWCNTs act as an electron acceptor while PANI acts as an electron donor, which forms a weak charge transfer [24, 25]. Based on the above reasons, the GSs with the two-dimensional lattice sheet structure lead to a larger contact surface area when the GSs disperse into PANI. Thus, the electrostatic attraction force between adjacent GSs and PANI is stronger than that between SWCNTs and PANI. The stronger interaction will enhance the interface contact between the GSs and PANI, which can help in forming a conductive network [25]. So the electrical conductivity of the GS/PANI composite is extraordinarily more enhanced than that of the SWCNT/PANI composite.

3.4. Shielding effectiveness

EMI shielding is defined as the attenuation of the propagating electromagnetic waves produced by the shielding material [26]. Shielding is a direct consequence of reflection, absorption and multiple internal reflection losses at the existing

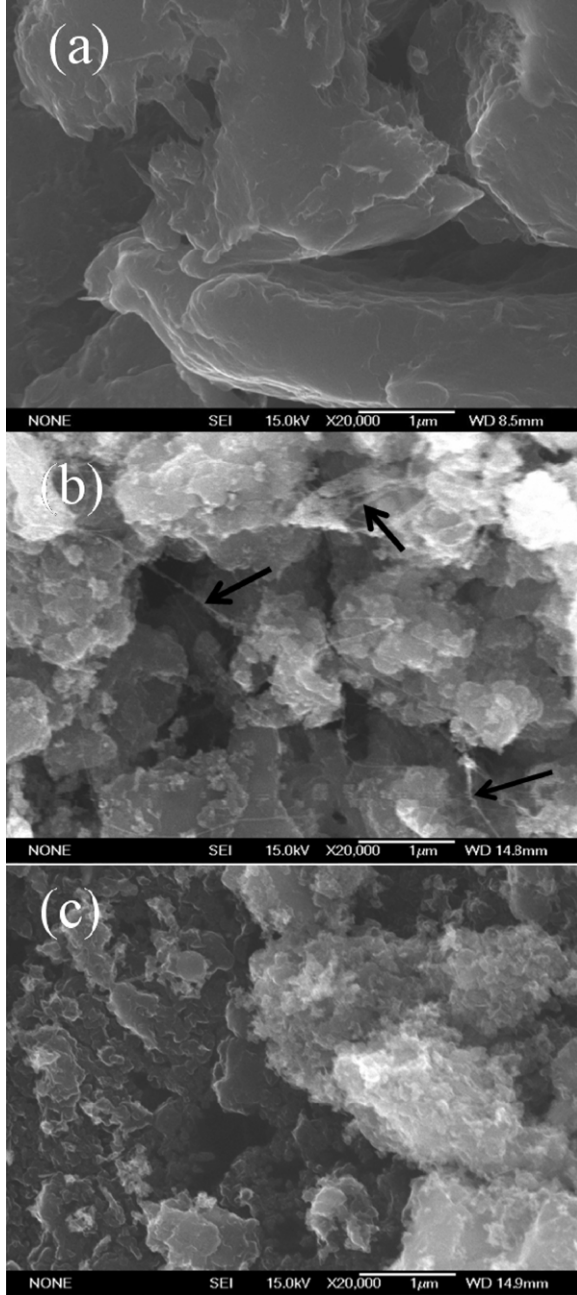


Figure 2. SEM images of (a) pure PANI (P1), (b) C2 and (c) G2.

interfaces [27]. The EMI SE can be expressed as follows:

$$SE_T = 10 \log \frac{P_I}{P_T} = 20 \log \left| \frac{E_I}{E_T} \right| = 20 \log \left| \frac{H_I}{H_T} \right| \text{ (dB)} \quad (1)$$

where $P_I(E_I, H_I)$ and $P_T(E_T, H_T)$ are the power of the incident and transmitted EM waves, respectively. For a single layer of shielding material, the total EMI SE obtained from equation (1) is described as the sum of the contribution due to reflection (SE_R), absorption (SE_A) and multiple reflections (SE_M). When SE_A is higher than 10 dB, SE_M can be ignored [28]. For an effective and lightweight shielding material, the useful value of the EMI SE is around 20 dB [29]. In order to investigate the contribution of absorption and reflection to SE_T , the reflection (SE_R) and absorption (SE_A) were also calculated from the S

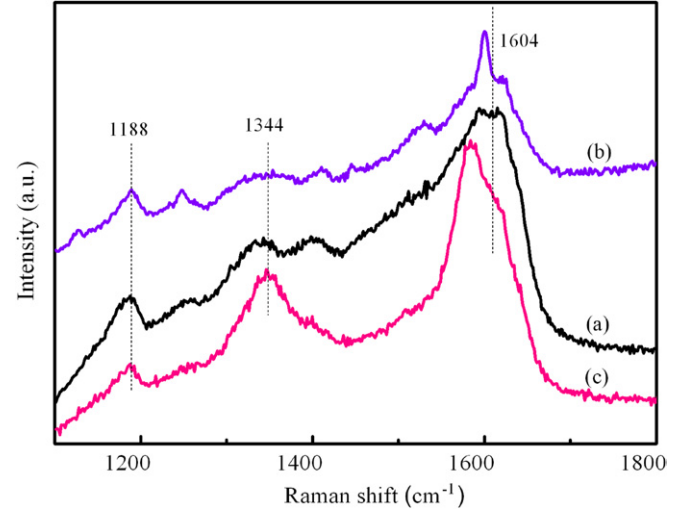


Figure 3. Raman spectra of (a) sample P1; (b) C1 composites; (c) G1 composites.

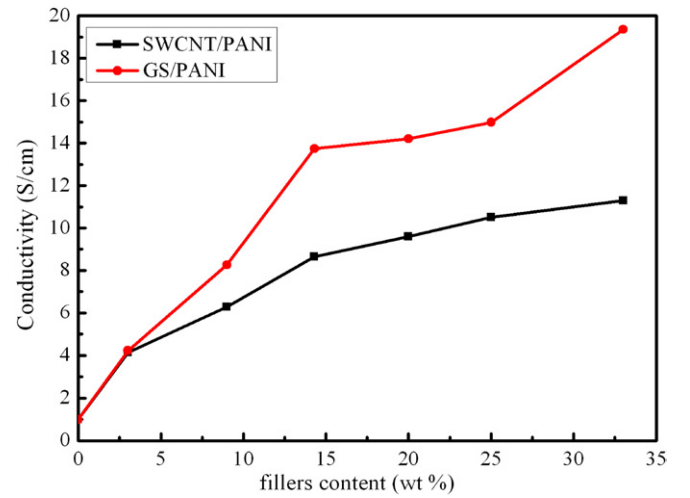


Figure 4. Electrical conductivities of the SWCNT/PANI and GS/PANI composites versus filler weight fraction.

parameters by the following equations [30]:

$$SE_R = 10 \log \frac{1}{1 - |S_{11}|^2} \quad (2)$$

$$SE_A = 10 \log \frac{1 - |S_{11}|^2}{|S_{21}|^2} \quad (3)$$

$$SE_T = SE_R + SE_A = 10 \log \frac{1}{|S_{21}|^2}. \quad (4)$$

Here, S_{11} , S_{22} , S_{12} , S_{21} are the surface reflection coefficients at both ends of the sample, transmission coefficient of the forward and reverse transmission coefficients. In theory, for a plane wave radiation, the far field reflection loss (SE_R) is given by [31]

$$SE_R = 39.5 + 10 \log \frac{\sigma}{2\pi f \mu}. \quad (5)$$

And the absorption loss (SE_A) is given by

$$SE_A = 8.7d\sqrt{\pi f \sigma \mu} \quad (6)$$

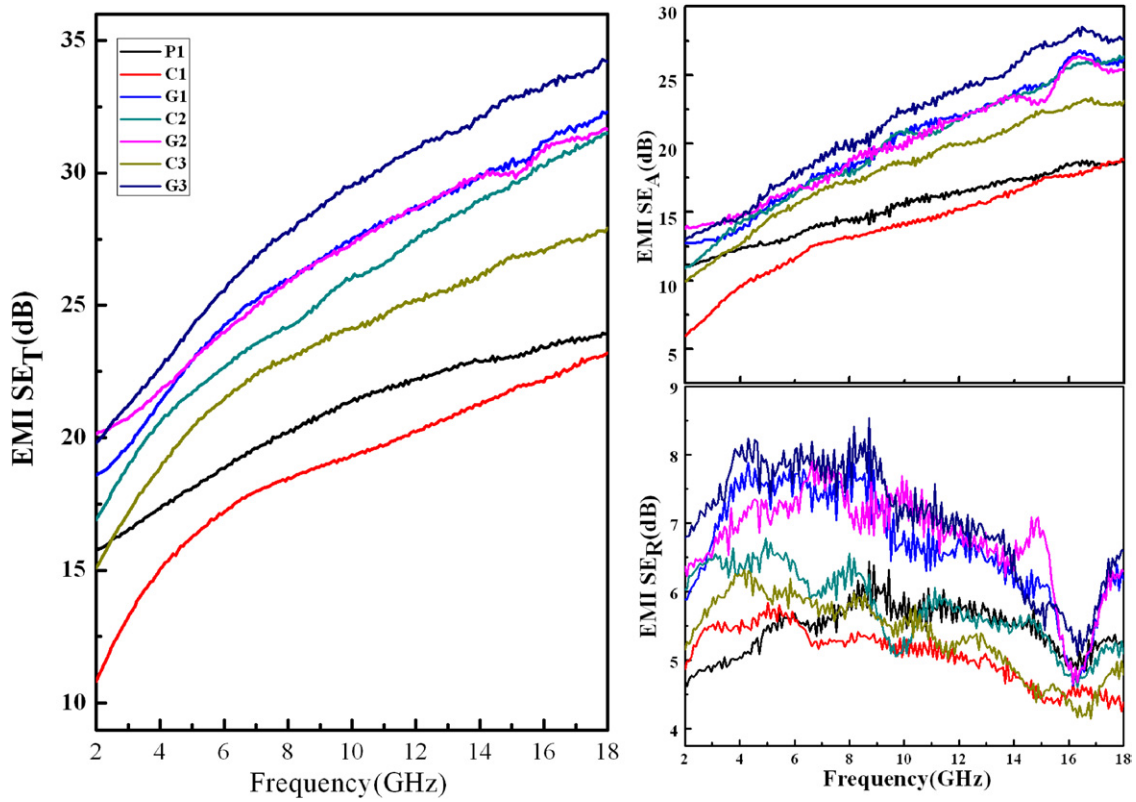


Figure 5. EMI SE of SWCNT/PANI and GS/PANI composites in the range 2–18 GHz.

where f is the frequency, $\mu = \mu_0\mu_r$ is the magnetic permeability, μ_r is the relative magnetic permeability, $\mu_0 = 4\pi \times 10^{-7} \text{ H m}^{-1}$ for nonmagnetic materials, μ_r can be taken as 1, d is the thickness of the sample and σ is the electrical conductivity in $\Omega^{-1} \text{ m}^{-1}$.

Figure 5 shows the comparison of the EMI SE_T , SE_R and SE_A between these two composites in the range 2–18 GHz. Firstly, SE_T and SE_A of all the samples increase as the frequency increases, and SE_R changes slightly, which are consistent with theoretical formulae (5) and (6). Secondly, SE_T of all the composite samples improves compared with pure PANI (as shown in black), except the composite C1. SE_A , SE_R and SE_T of all the GSs/PANI composites are larger than that of the SWCNT/PANI composite at the same doping ratio in the range 2–18 GHz. The best EMI SE of the SWCNT/PANI composite is 31.5 dB at 25 wt% and the GS/PANI composite is 34.2 dB at 33 wt%. Compared with pure PANI, the EMI SE of the SWCNT/PANI composite and the GS/PANI composite increases to about 32% and 42%, respectively. These results can be attributed to the following reasons: (1) the electrical conductivity of the GS/PANI composite is higher than that of the SWCNT/PANI composite; (2) the GSs are easily dispersed in PANI than SWCNTs. So, the GS/PANI composite is more uniform than the SWCNT/PANI composite; (3) the powder sizes of the GS/PANI composite are smaller than those of the SWCNT/PANI composite, which benefits the absorption and reflection of the EM wave. Thirdly, SE_A of all these composites is far larger than SE_R ; therefore, we can conclude that microwave absorption is the main contributor to the EMI SE_T of these two kinds of composites.

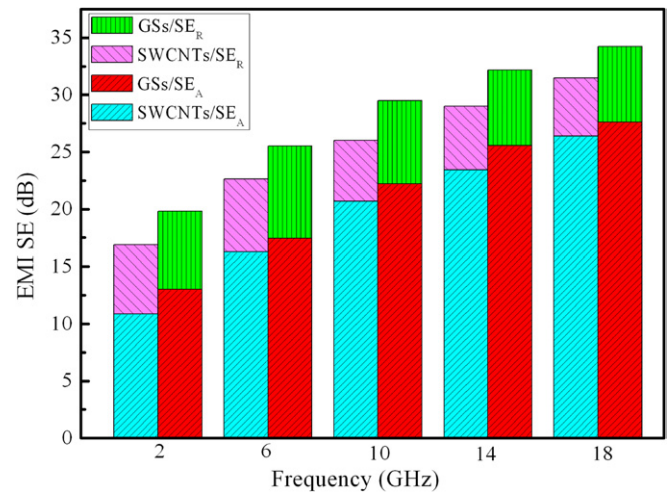


Figure 6. EMI SE with the fraction of reflection and absorption effects at several frequency points.

Moreover, in order to compare the absorption to the total EMI SE_T , we made a distribution strip figure, setting the best samples (C2, G3) as an example. The EMI SE for the reflection and absorption are presented in figure 6. For both composites, as the frequency increases, the absorption proportion increases. For the GS/PANI composite, SE_A values against the total SE were 66%, 68%, 75%, 79% and 81% at frequencies of 2 GHz, 6 GHz, 10 GHz, 14 GHz and 18 GHz, respectively, while the absorption proportions of the SWCNT/PANI composite were 64%, 72%, 80%, 81% and 84%. Obviously, the absorption share of the SWCNT/PANI composite is larger than that

of the GS/PANI composite at all frequencies except at low frequencies. The most likely reason is that there are some Fe nanoparticles in the SWCNT/PANI composite, which exhibit magnetic properties, present hysteresis loss and enhance the absorption of microwave [18].

4. Conclusions

Highly crystalline SWCNTs and GSs were prepared by the hydrogen arc-discharge method. Highly conducting SWCNT/PANI and GS/PANI composites were synthesized by a simple alcohol-assisted dispersion and pressing method. With the filler fraction, the electrical conductivities of the two kinds of composites increase, and the electrical conductivity of the GS/PANI composite is larger than that of the SWCNT/PANI composite at the same filler fraction. SE_T of both composites increases with frequency; the EMI SE_R , SE_A and SE_T of the GS/PANI composite are higher than those of the SWCNT/PANI composite in the range 2–18 GHz, but the absorption share of the SWCNT/PANI composite is higher than that of the GS/PANI composite. The EMI SE results show that both composites present an absorption-dominant mechanism and can be used as lightweight, effective EMI shielding or microwave absorption materials. Moreover, we can combine SWCNTs and GSs as hybrid conductive fillers in various thermoplastic matrices to make a new microwave shielding material in the future.

Acknowledgments

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