

Comparison of Polyelectrolyte and Sodium Dodecyl Benzene Sulfonate as Dispersants for Multiwalled Carbon Nanotubes on Cotton Fabrics for Electromagnetic Interference Shielding

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ABSTRACT: Cotton fabrics with multiwalled carbon nanotubes (MWCNTs) dispersed by Nafion, a polyelectrolyte, and sodium dodecyl benzene sulfonate (SDBS), a surfactant, were prepared for electromagnetic interference (EMI) shielding. The fabrics were characterized by scanning electron microscopy and vector network analysis. The fabrics with the Nafion–MWCNT coating possessed a better shielding efficiency (SE) than those with the SDBS–MWCNT coating because of a more uniform dispersion of MWCNTs, which improved the electrical conductivity and EMI shielding properties. The maximum SE value of the fabric reached 11.48 dB, and the specific SE was 39.6 dB cm³/g. The reflectivity and absorptivity were calculated separately to determine the main mechanism of EMI shielding. The absorptivity was 68.6% at 12 GHz for the Nafion–MWCNT-coated fabric; this showed that the dominant mechanism of EMI shielding for the treated fabrics was absorption. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40588.

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INTRODUCTION

Electromagnetic interference (EMI) shielding fabrics have drawn more and more attention because electromagnetic (EM) radiation pollution is becoming a serious public health problem,^{1–4} especially for persons exposed to EM fields for a long time or those sensitive to EM radiation, such as pregnant women and young children, with the widespread use of cell phones, computers, and other electronic apparatuses, such as microwave ovens, TV sets, and refrigerators. To shield EM radiation, various metals, ferrites, and conductive polymers, including copper, silver, stainless steel, carbonyl iron, polypyrrole, and polyaniline,^{5–10} have been used in fabrics to obtain high EMI shielding efficiencies (SEs). Nevertheless, when either metal or conducting polymers are used, the EM power is most likely realized by a reflection mechanism, and this, consequently, causes secondary radiation in the environment. Moreover, these materials are also heavy, easily corroded, and poor in mechanical properties. Also, fabrics made of these materials are often thick, stiff, and heavy; this makes them uncomfortable or inappropriate for apparel.

Carbon nanotubes (CNTs) could be more attractive candidates for functional fabrics^{11,12} because of their light weight and unprejudiced mechanical, electrical, and thermal properties.^{13–15}

Although CNTs have been well documented as fillers in composites and macrofilms for EMI shielding applications,^{16–18} few studies have been published on CNT-coated fabrics as EMI shielding materials.¹⁹ Apart from CNTs' intrinsic characteristics, such as their aspect ratios and electrical conductivities, their dispersion is the most important factor influencing the EMI shielding properties of the substrate at a certain loading. Many relevant studies have shown that a homogeneous dispersion is necessary for producing a high conductivity with a low concentration of CNTs; this is critical for improving the EMI shielding properties.^{20–22} To acquire a stable CNT suspension for coating without damaging the CNT structure or sacrificing the electrical conductivity, researchers have used two systems for dispersing CNTs, that is, polyelectrolytes²³ and surfactants,²⁴ both of which have been applied to functional textiles by a dip-coating method because of the availability of equipment and effectiveness.^{25,26} Kotov et al.²⁵ found that cotton yarns coated with Nafion (a sulfonated tetrafluoroethylene)-stabilized CNTs had an electrical conductivity that was two orders of magnitude higher than those coated with polystyrene sulfonic acid (PSS)-stabilized CNTs at the same CNT–polymer ratio. Among the surfactants, sodium dodecyl benzene sulfonate (SDBS) exhibited the best dispersibility of CNTs because of the benzene rings and suitable length of alkyl chain in its structure.²⁴ Furthermore, a good

Table I. Masses of Coatings and Amounts of MWCNTs Dispersed by Nafion and SDBS with Various Numbers of Dip Coatings

Number of dip coatings	Mass of coating: Nafion-MWCNTs (mg/cm ²)		Amount of MWCNTs (mg/cm ²)			
	Mean	SD	Nafion-MWCNTs		SDBS-MWCNTs	
			Mean	SD	Mean	SD
1	0.63	0.033	0.11	0.006	0.10	0.004
2	1.02	0.052	0.18	0.009	0.15	0.005
3	1.24	0.058	0.22	0.010	0.19	0.009
4	1.56	0.074	0.28	0.010	0.24	0.010
5	1.84	0.083	0.33	0.013	0.28	0.011
6	2.09	0.088	0.37	0.016	0.32	0.013

SD, standard deviation.

dispersion of CNTs in solution improved the uniformity of CNTs on fabrics, but a well-dispersed CNT solution could not guarantee the homogeneous distribution of the CNTs onto fabrics.¹² However, few reports have been published on the comparison of the CNT dispersion performances of polyelectrolyte and surfactants with the same CNT concentration. Therefore, it is of significance to investigate the dispersion and electrical properties of CNT-coated fabrics with those two dispersant systems for EMI shielding applications.

In this study, Nafion was chosen as a polyelectrolyte dispersant; it endowed a polar side chain and a hydrophobic backbone, which were suitable for the preparation of a stable and homogeneous suspension of multiwalled carbon nanotube (MWCNTs) as reported by Wang et al.²³ Meanwhile, SDBS was selected as a surfactant dispersant because it had the best performance in the dispersal of CNTs among several surfactants.²⁴ The main objective of the study was to compare the dispersion of MWCNTs by Nafion and SDBS and the EMI SE properties of the corresponding MWCNT-coated cotton fabrics. The reflectivity and absorptivity of the fabrics coated with MWCNTs were evaluated to identify the main mechanism of the EMI shielding.

EXPERIMENTAL

Materials

The MWCNTs were purchased from Chengdu Organic Chemicals Co. (diameters = 8–15 nm, length \approx 50 μ m, and purity > 95%). Desized, scoured, and bleached plain woven cotton fabrics (330 \times 210/10 cm, thickness = 0.5 mm, 96.4 g/m²) were obtained from Shandong Lutai Textile Co., Ltd. A commercial Nafion dispersant with a concentration of 5 wt % and an average molecular weight of 70,000–120,000 Da (viscosity = 10–40 mPa·s) was purchased from DuPont Co. SDBS was provided by Sinopharm Chemical Reagent Co., Ltd. All of the chemicals were used without further purification.

Preparation of the MWCNT-Dip-Coated Cotton Fabrics

The MWCNT suspension was prepared as follows: 50 mL of Nafion solution (5%, 0.93 g/cm³) was first added to 150 mL of solvent, which was a mixture of 75 mL of deionized water and 75 mL of anhydrous ethyl alcohol. The suspension of MWCNTs at a concentration of 2.5 mg/mL was then treated in an ultra-

sonic cleaner (power = 50 W and frequency = 53 kHz) for 2 h. The stable suspension was used for the coating process.

The cotton fabric was first treated with acetone for 15 min to remove contaminants or impurities; it was then rinsed with deionized water several times and dried in an oven. A 15 \times 15 cm² cotton fabric was dipped in the aforementioned MWCNT suspension for 5 min. Then, the MWCNT-coated cotton fabrics were dried in an oven at 80°C for 10 min. This process was repeated to increase the MWCNT loading in the fabric up to six times, and no water or ethanol was used to wash the fabrics. For comparison, a 2.5 mg/mL MWCNT suspension dispersed with 10 mg/mL SDBS was also used to dip-coat the cotton fabric under the same experimental conditions. However, for the SDBS-MWCNT-coated fabrics, water was used to wash the SDBS away until no bubbles appeared when the fabric was dipped into water and pressed²⁶ to decrease the residual SDBS in the fabric, which could act as an insulator. For convenience, the samples named S1–S6 represented 1–6 dip coatings with Nafion-MWCNTs, and samples S1'–S6' represented 1–6 dip coatings with the SDBS-MWCNTs. The mass of the coating was obtained by the dry mass difference of the cotton fabric before and after deposition. The mass of coating and the add-on amount of the MWCNTs in terms of mass per square centimeter with various numbers of dip coatings are presented in Table I. We assumed that the MWCNT/Nafion mass ratio in the coating was maintained the same as the mass ratio of MWCNTs to Nafion in the suspension, namely 20:93, whereas for the SDBS-MWCNT-coated fabrics, the add-on mass of the MWCNTs was equal to the mass of the coating because the SDBS was almost completely washed away after the coating.

Scanning Electron Microscopy (SEM)

SEM analyses of the cotton specimens were carried out with a Hitachi S-4800 field-emission scanning electron microscope (Japan) at an accelerating voltage of 5 kV. Each specimen was coated with gold before observation.

Volume Resistivity

The volume resistivity of the samples was obtained as the surface resistance multiplied by the thickness of the fabric. Because there are two methods to test the surface resistance, that is, two-probe and four-probe methods, we measured our samples with both methods and found that the difference in the results

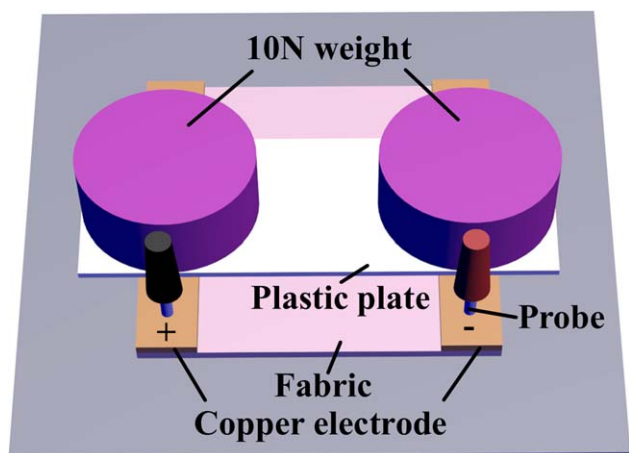


Figure 1. Schematic configuration of the measurement setup for the surface resistance of the fabrics. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the two methods was smaller than 5%. The two-probe method was finally adopted for the measurement of the surface resistance of the samples according to AATCC test method 76-2005, which is recommended for textile materials that are not highly conductive.²⁷ Two rectangular visually smooth and flat copper electrodes ($50 \times 10 \times 0.5 \text{ mm}^3$) separated by 50 mm were placed on the sample and pressed by a constant load (20 N) to ensure a good contact, as shown in Figure 1.²⁸ The resistance was recorded by a Fluke 15B multimeter with copper probes that were 2 mm in diameter and 20 mm in length and were placed on the copper electrodes. The surface resistance was calculated from the resistance value and probe dimensions according to the following equation:

$$R_s = RW/L \quad (1)$$

where R_s is the surface resistance (Ω/square , per any square as long as the measurement is related to a square), R is the resistance (Ω) of the fabric measured by the multimeter, and L and W are the length and width of the square between two probes (here, $L = W = 50 \text{ mm}$), respectively. The thickness (in millimeters) of the fabric was measured with a YG141N digital fabric

Table II. Thickness of the Fabrics Coated by the Nafion–MWCNTs and SDBS–MWCNTs with Various Numbers of Dip Coatings

Number of dip coatings	Thickness (mm)			
	Nafion–MWCNTs		SDBS–MWCNTs	
	Mean	SD	Mean	SD
0	0.500	0.015	0.500	0.015
1	0.491	0.012	0.507	0.021
2	0.482	0.019	0.516	0.023
3	0.471	0.014	0.523	0.020
4	0.463	0.017	0.528	0.019
5	0.455	0.018	0.537	0.021
6	0.446	0.011	0.542	0.025

SD, standard deviation.

thickness gauge (Nantong Hongda Experiment Instruments Co., Jiangsu, China) in accordance with ASTM D 1777-96 (“Standard Test Method for Thickness of Textile Materials,” 2011). The results are presented in Table II. To prevent the influence of the temperature and humidity change on the testing results, all measurements were carried out under standard textile testing conditions of $65 \pm 2\%$ relative humidity and $23 \pm 1^\circ\text{C}$.

EMI Shielding Testing

The EMI shielding effectiveness of MWCNT–cotton was measured with the waveguide method on an Agilent N5424A type vector network analyzer (VNA) in the frequency range 8–12 GHz. This frequency range was in the X band of the microwave and is widely used in many applications, such as Doppler radar, TV signal transmissions, mobile phone relay systems, and other communication technologies. The fabric ($22.86 \times 10.86 \text{ mm}^2$) was sandwiched between two waveguide adapters (black box, Figure 2) connected to separate ports of the VNA through a coaxial transmission line, and the assembly was tightened with two screws. The two waveguide adapters were the same, and one of them is shown in Figure 2. The VNA sent an EM wave signal, which was coupled by the adapter and could be reflected or transmitted when it encountered the sandwiched sample interface. Then, the reflected and transmitted signals were evaluated with the VNA.

RESULTS AND DISCUSSION

Distribution of the MWCNTs on Cotton

MWCNTs have a tendency to aggregate because of their large aspect ratio and specific surface area. Herein, we focus on the influence of two representative dispersants, namely, Nafion and SDBS, on fabric electrical conductivity and EMI shielding properties. To evaluate the distribution of MWCNTs on fabrics with different dispersion agents, coated fabrics were observed with SEM. The SEM images of the fabrics that were dip-coated six times with Nafion–MWCNTs and SDBS–MWCNTs are shown in Figure 3. MWCNTs dispersed by Nafion were distributed uniformly on the fiber surface with very little aggregation, whereas the MWCNTs dispersed by SDBS showed larger and more aggregation [Figure 3(b)]. A similar result was reported by Gonçalves et al.,¹² who also used a surfactant, Lev-egal RL, as the dispersant for MWCNTs. They attributed the variation in the uniformity of MWCNTs on the coated cotton fabrics to the difference in the dispersion of MWCNTs in the initial solutions; this suggested that the poor initial dispersion in the solution led to more aggregation on cotton fabrics coated with the MWCNT solution. For the same reason, it could have been possible that the MWCNTs were more homogeneously dispersed in the Nafion solution than in the SDBS solution; this generated a more uniform distribution of MWCNTs on the fiber surface. Moreover, for Nafion, its polar side groups could have been attached to the hydroxyl groups in cotton, and its hydrophobic backbone could have been attracted to the MWCNTs. This enhanced the stability and fastness of the MWCNTs onto cotton, as observed previously by Kotov et al.²⁵ On the other hand, for the SDBS–MWCNT system, SDBS was washed away after coating; this led to a poor attraction between the hydrophilic cotton surfaces and

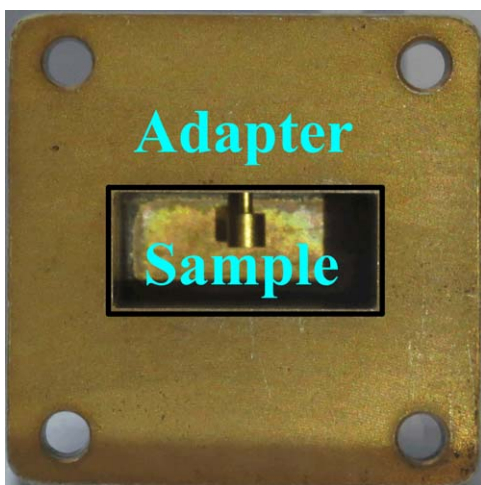


Figure 2. Photograph of one of the waveguide adapters. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrophobic MWCNTs so that the MWCNTs tended to rearrange and aggregate. It is well known that a uniform distribution of MWCNTs is crucial for electrical conductivity and EMI shielding.^{18,20–22,29}

The surface morphologies of the pristine cotton fiber, fibers dipped one time (S1), fibers dipped two times (S2), and fibers dipped five times (S5) with Nafion–MWCNTs are shown in Figure 4. We observed that the flexibility of the MWCNTs made them well conformed to the surface of the cotton fibers, which had a ribbonlike morphology with grooves. Moreover, it was also obvious that the amount of MWCNTs deposited on cotton fabric increased as the number of dipping increased; this was consistent with the results in Table I and resulted in an increased electrical conductivity in the fabrics (see Table III).

Volume Resistivity of Cotton with MWCNT Coating

The dispersion of the MWCNTs on cotton influenced the formation of the conductive network; this was verified by volume resistivity measurement. The variation of the volume resistivity with different numbers of Nafion–MWCNT or SDBS–MWCNT dippings is depicted in Table III. As expected, the volume resistivity of the cotton fabrics with the Nafion–MWCNT coating was much lower than that with the SDBS–MWCNT coating with the same number of dippings. In fact, the volume resistivity of the fabric with six dippings of the SDBS–MWCNTs was $3.40 \text{ } \Omega\cdot\text{m}$ (MWCNT loading = 0.32 mg/cm^2); this was just a little larger than that with only one dipping of the Nafion–MWCNTs, whose volume resistivity was $3.33 \text{ } \Omega\cdot\text{m}$ (MWCNT loading = 0.11 mg/cm^2). In comparison with other CNT-coated textiles, the surface resistance of the Nafion–MWCNTs ($<7 \text{ k}\Omega/\text{square}$) was much lower than that of nylon/CNT textiles ($31 \text{ M}\Omega/\text{square}$) reported in literature.³⁰ So, it was demonstrated that the better the dispersion of MWCNTs was, the greater the electrical conductivity of the fabric was. In addition, the volume resistivity decreased with increasing number of dippings for both the Nafion–MWCNT and SDBS–MWCNT coatings. This was attributed to the interconnection between the

MWCNTs, which could form conductive networks. When more MWCNTs were coated onto the fabric, denser conductive networks could be formed, and this led to the formation of more effective electrical carrier paths on the fabric surfaces, as shown in Figure 4. The volume resistivity values are not presented for the fabrics with one and two dippings with the SDBS–MWCNTs because their resistances were higher than $40 \text{ M}\Omega$, the multimeter's upper limit, and we were not able to measure them. The volume resistivity decreased three orders of magnitude from $12.7 \text{ k}\Omega\cdot\text{m}$ for three dippings to $14 \text{ } \Omega\cdot\text{m}$ for four dippings with the SDBS–MWCNT fabric. This was attributed to the percolation threshold³¹ of the SDBS–MWCNT-coated fabrics, which was reached after four dipping treatments. Although the electrical conductivities of the fabrics increased with increasing number of dippings with both types of coatings, the Nafion–MWCNT-coated fabrics had a much higher electrical conductivity. There were three potential reasons: (1) a better dispersion of MWCNTs with Nafion as the dispersant, which led to a more uniform distribution of MWCNTs on the fiber surfaces; (2) the fact that the Nafion solution (viscosity $>10 \text{ mPa}\cdot\text{s}$) was more viscous than the SDBS solution (viscosity $\approx 1 \text{ mPa}\cdot\text{s}$) was beneficial for more MWCNTs

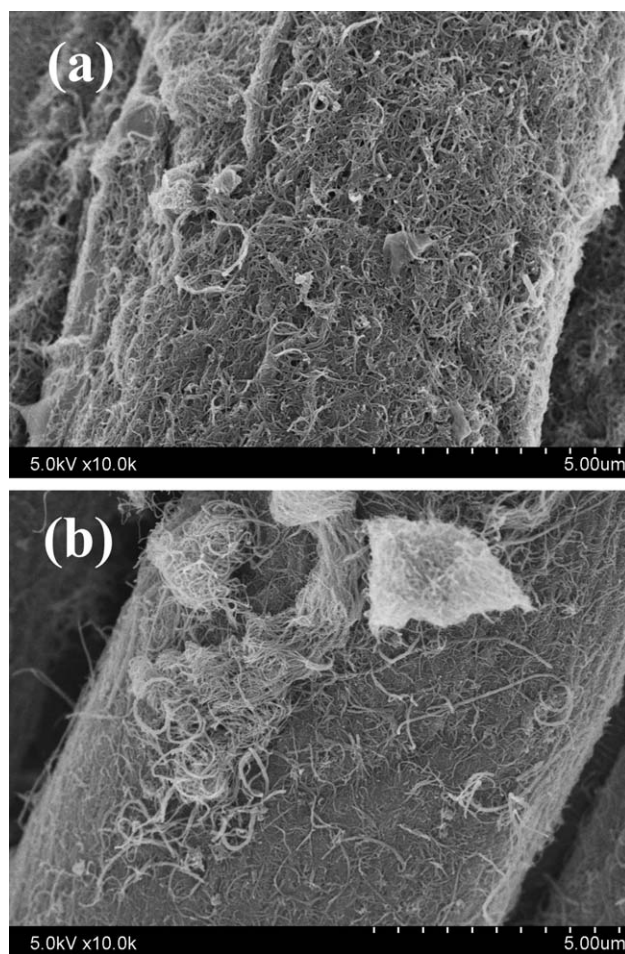


Figure 3. Cotton fiber surface morphology of six dip coatings with (a) Nafion–MWCNTs and (b) SDBS–MWCNTs.

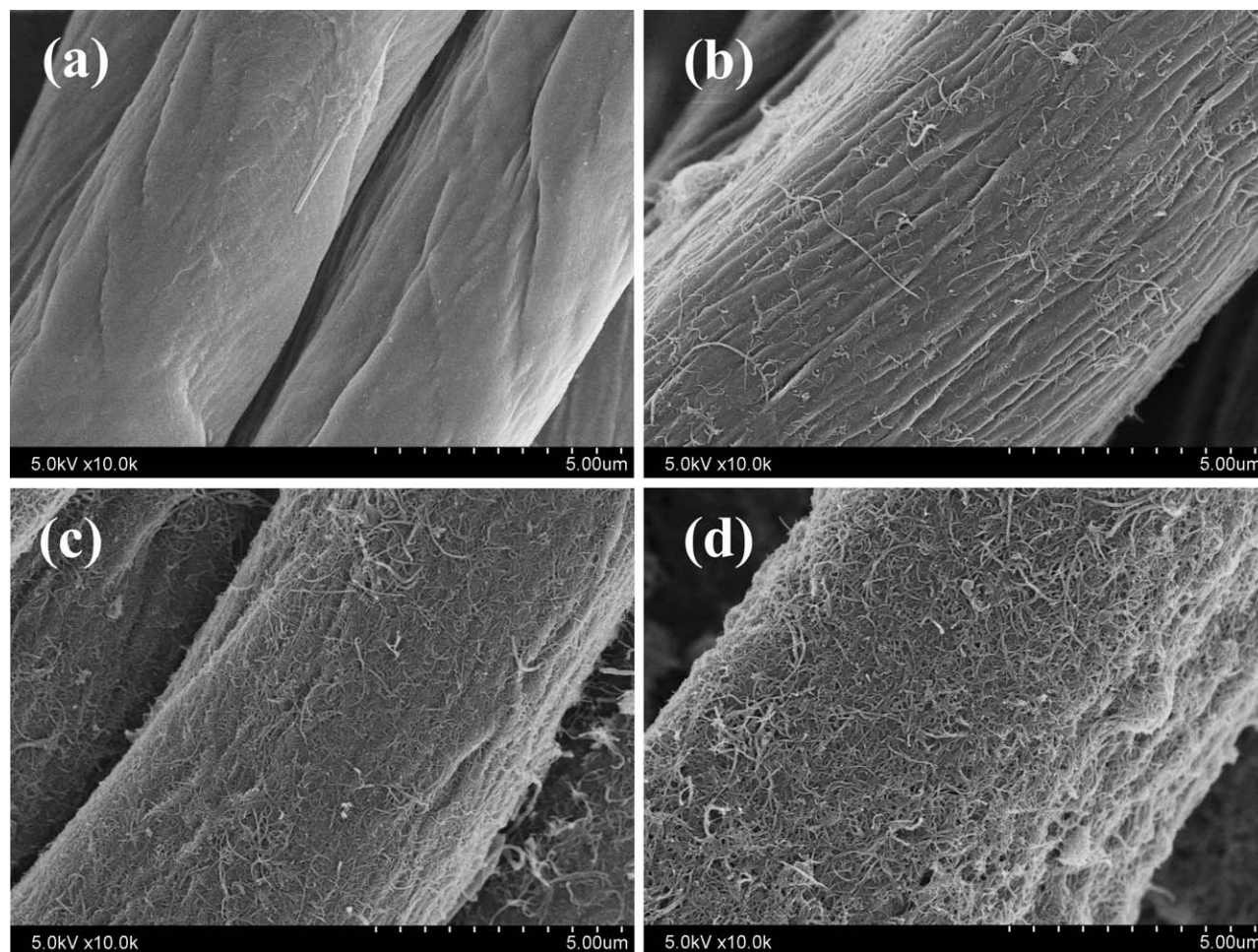


Figure 4. SEM images of the (a) pristine cotton fiber and cotton fibers treated with (b) one dip coating (S1), (c) two dip coatings (S2), and (d) five dip coatings (S5) of Nafion–MWCNTs.

being deposited onto the fabric; and (3) Nafion itself was more conductive (the surface resistance for the Nafion-coated fabric without MWCNTs was 600 k Ω /square) than cotton or air; this could have potentially reduced the percolation threshold of the

MWCNTs on the coated fabric surfaces. The improvement of the electrical conductivity in turn was expected to enhance the microwave shielding capability of the MWCNT-coated fabrics.

EMI SE of the MWCNT-Coated Cotton Fabrics

In Figure 5(a), the EMI SEs of the fabric dipped one time in Nafion–MWCNT and the fabric dipped six times in SDBS–MWCNT were compared because their electrical conductivities were similar. The EMI SE was calculated as the logarithmic function of the ratio of the transmitted power (P_t) to the incident power (P_i) of the EM wave, which was equal to that of S_{21} (or S_{12}) the scattering parameter of shielding material for transmission, representing the power transmitted from port 1 to port 2, with the following equation:³²

$$SE = -10 \log (P_t / P_i) \text{ (decibel, dB)} \quad (2)$$

As expected, the fabric with one Nafion–MWCNT dipping with 0.11 mg/cm² MWCNTs had almost the same EMI SE with the fabric dipped six times in SDBS–MWCNT with 0.24 mg/cm² MWCNTs. Moreover, Figure 5(b) shows that the EMI SE of the Nafion–MWCNT-coated fabrics exhibited a similar pattern of frequency dependency in the measured frequency range. All of the SEs (>3dB) in our study were higher than those of the

Table III. Volume Resistivity of the Fabrics Coated by the Nafion–MWCNTs and SDBS–MWCNTs with Various Number of Dip Coatings

Number of dip coatings	Volume resistivity (Ω -m)			
	Nafion-MWCNTs		SDBS-MWCNTs	
	Mean	SD	Mean	SD
1	3.33	0.11	Beyond range	—
2	0.91	0.04	Beyond range	—
3	0.53	0.02	12,708.9	641.6
4	0.39	0.02	14.17	0.71
5	0.27	0.01	7.44	0.31
6	0.17	0.01	3.40	0.16

SD, standard deviation.

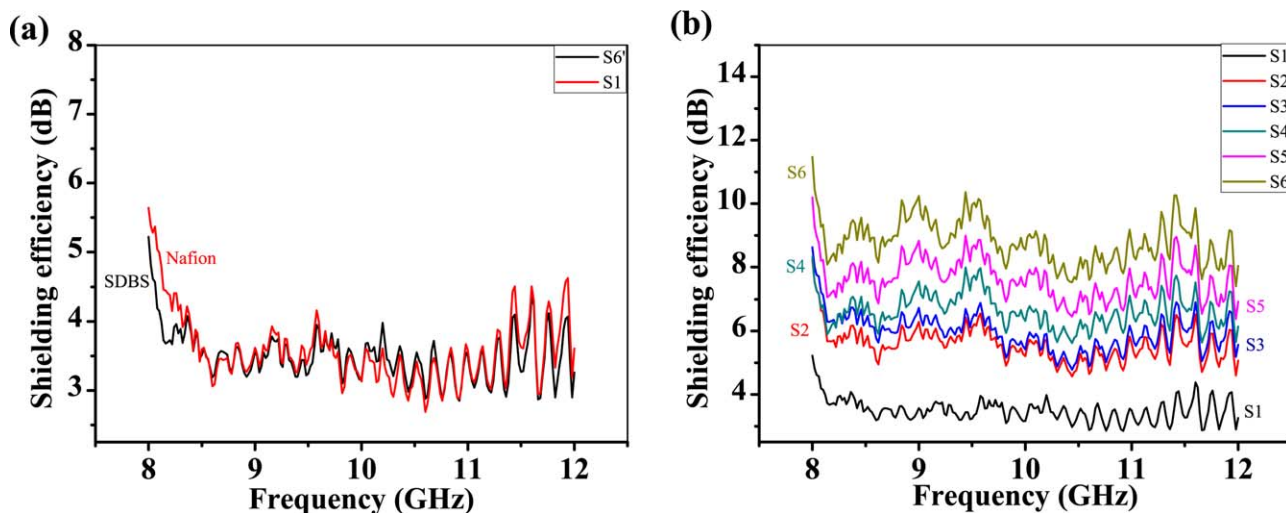


Figure 5. EMI SE of the fabrics with (a) six SDBS–MWCNT dip coatings ($S6'$) and one Nafion–MWCNT dip coating ($S1$) and (b) different numbers of Nafion–MWCNT dip coatings in the frequency range 8–12 GHz. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

MWCNT/butanetracarboxylic acid (BTCA)-coated cotton fabrics (the fabric with a surface resistance $\approx 2 \text{ k}\Omega/\text{square}$ exhibited an SE of about 1.5 dB) reported by Alimohammadi et al.¹⁹ To understand the EMI SE performance of the fabric with Nafion, we prepared fabric coated by Nafion only (surface resistance = $600 \pm 16 \text{ k}\Omega/\text{square}$, similar to the sheet resistance of a Nafion film³³) and found that the SE was below 0.5 dB. Therefore, the EMI shielding properties of the fabrics almost exclusively depended on the MWCNTs. The Nafion–MWCNT-coated fabric after one dipping possessed an SE of 3.57 dB; this ascended to 6.29, 8.83, and 10.24 dB at 10 GHz and corresponded to one, two, five, and six dippings, respectively. As discussed previously, with increasing dippings, the loading of the MWCNTs on fabric increased [Table I and Figure 4(b)]; this led to denser and more effective conductive networks and was beneficial for improving the EMI SE value. These results agreed well with what has been reported in the literature.^{20–22} The EMI

SE of a shielding material depends on the mobile charge carriers and the interfacial polarization in the shielding material.¹⁷ The greater the mobile charge carriers and interfacial polarization were, the larger the SE value was. With increasing MWCNT loading, the mobile charge carriers increased in the cotton fabric, and this gave a higher EMI SE value. In addition, when the MWCNTs were coated on both sides of the insulating cotton fiber, a large number of microcapacitors were formed, and this led to a high interfacial polarization and high EMI SE. In general, MWCNT products contain catalyst particles, such as Fe or Ni, but the concentrations of these catalyst particles or clusters were so low that the magnetic effect induced by these particles could be negligibly weak.¹⁴

In a comparison of the SEs for the fabrics with the two solution systems, with similar MWCNTs loadings, $S6'$ (six dippings with SDBS–MWCNTs) had an MWCNT loading of $0.32 \text{ mg}/\text{cm}^2$, an

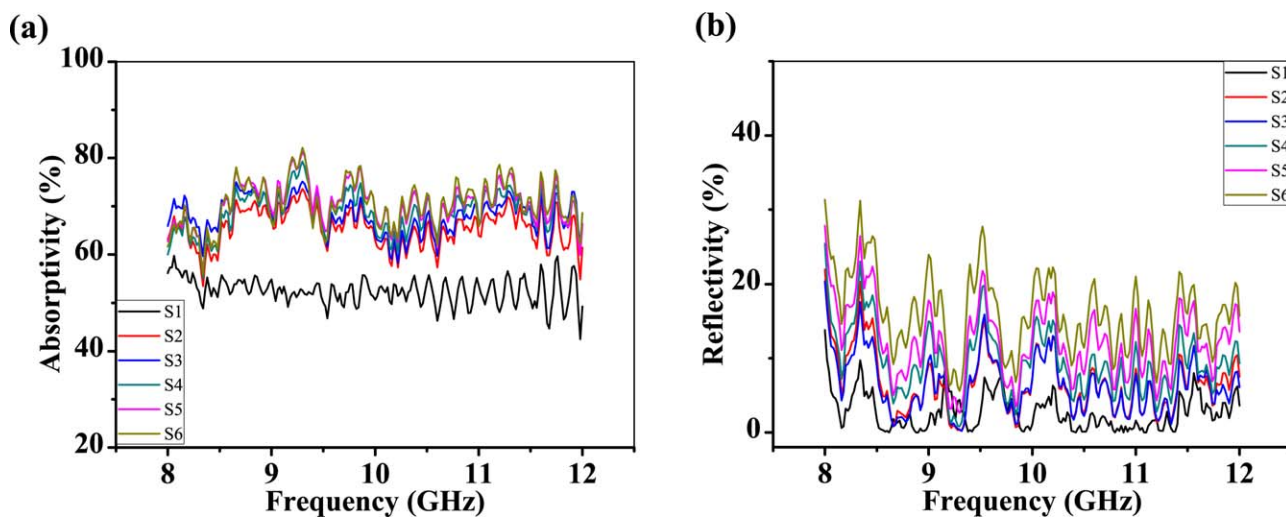


Figure 6. (a) Absorptivity and (b) reflectivity of fabrics with different numbers of Nafion–MWCNT dip coatings in the frequency range 8–12 GHz. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

average SE of 3.59 dB, and a volume resistivity of 3.4 $\Omega\cdot\text{m}$, whereas S5 (five dippings with Nafion–MWCNTs) had an MWCNT loading of 0.33 mg/cm², an average SE of 7.64 dB, and a volume resistivity of 0.27 $\Omega\cdot\text{m}$. This showed the great advantage of using Nafion as the dispersant. Here, the more uniformly distributed MWCNT conductive networks formed on the fiber surfaces in the Nafion–MWCNT-coated fabrics played a significant role in EMI shielding.¹⁴

In addition to the electrical conductivity of the samples, the thickness also played a significant role in the EMI shielding properties. The achieved SE for a single layer of the coated fabric was still low compared to those reported in prior works.^{17,20,22} However, in most previous reports, the materials were much thicker. Therefore, if more layers of the coated fabrics were stacked, the SE of the assembly could be greatly improved.³⁴ Furthermore, the specific EMI SE (per unit density) is a more appropriate index for comparing the shielding properties of various materials.³⁵ In our study, the specific EMI SE of the fabrics dipped six times was 39.59 dB cm³/g; this was much higher than that of typical metals, such as 10 dB cm³/g for copper.³⁵

Absorption and Reflection of the Nafion–MWCNT-Coated Fabrics

The shielding mechanisms of MWCNT-coated fabrics, to our knowledge, have not been well reported. To compare the contribution of reflection and absorption to the overall EMI SE of the MWCNT-coated cotton fabrics, the reflectivity and the absorptivity of the EM wave power of the Nafion–MWCNT-coated fabrics were analyzed. The SE included the shielding effectiveness due to reflection (SE_R), the shielding effectiveness due to absorption (SE_A), and shielding effectiveness due to multiple reflection (SE_M). The multiple-reflection effect was not discussed in this study because of the fact that it was usually a minor effect and because it was difficult to evaluate separately. The scattering parameters [S_{11} representing the power transmitted from port 1 to port 2 and S_{21} (dB)] of the VNA adopting two-port network test method were related to the reflectivity (RF) and transmissibility (T), respectively, that is, $T=10^{(S_{21}/10)}$, $RF=10^{(S_{11}/10)}$. Then, the absorptivity (A) of the EM wave power was calculated as follows:

$$A=1 - RF - T \quad (3)$$

Furthermore, the relative intensity of the EM wave inside the shield (by exclusion of the reflection wave from the incidence wave) was based on the value $1 - RF$, and the effective absorption (A_{eff}) was written as follows:

$$A_{\text{eff}} = (1 - RF - T)/(1 - RF) \quad (4)$$

So, SE_R and SE_A could be expressed as follows:¹⁴

$$SE_R = -10 \log(1 - RF) \quad (5)$$

$$SE_A = -10 \log(1 - A_{\text{eff}}) = -10 \log[T/(1 - RF)] \quad (6)$$

Figure 6(a) shows the absorptivity as a function of the frequency for the cotton fabrics treated with different numbers of Nafion–MWCNT dippings. For all of the coated fabrics, the absorptivity was above 50%, whereas for the fabrics dip-coated two or more times, their absorptivities were larger than 60%. The S1 sample had the lowest absorptivity because of the insufficient amount of MWCNTs so that EM wave could transmit the fabric easily. How-

ever, its absorptivity (57.8% at 8 GHz) was still much larger than its reflectivity [17.4% at 8 GHz; Figure 6(b)]. There are two ways to define the shielding mechanism. One is the comparison of the absorptivity and reflectivity (RF).^{15,21,36} The other is the comparison of SE_A and SE_R .^{14,37} Recently, Liu et al.³⁸ summarized the difference between the absorptivity and SEA, stated as “absorptivity is a value describing the ratio of power dissipated by the sample toward the overall incident power, while SEA is a measure of the ability to attenuate the electromagnetic power that has transmitted into the sample.” Thomassin et al.³⁹ reviewed carbon-based composites as EMI shielding materials and pointed out that the proportion of the EM power truly absorbed by the materials never surpassed 50% for carbon-based composites. In this way, we investigated the absorptivity ($A > 50\%$), which demonstrated that more than 50% of EM power was dissipated by the fabrics toward the overall incident power. Therefore, it was reasonable to conclude that the dominant shielding mechanism of the Nafion–MWCNT-coated fabric was absorption rather than reflection.

As shown in Figure 6(b), the reflectivities of the cotton fabrics with different numbers of dippings at different frequencies ranged from 31.3 to 4.7% (at 12 GHz). The low reflectivity demonstrated a better impedance match between air and the MWCNT-coated fabric surface; this provided a necessary condition for the absorption of EM energy. Thus, we concluded that EM wave power absorption was the dominant shielding mechanism.

The detailed data for SE_R and SE_A of the samples with Nafion–MWCNTs for five typical frequencies are listed in Table IV. It could be seen clearly that the value of SEA was at least five times higher than that of the corresponding SER for each sample at a given frequency. This again proved that the predominant function of shielding was realized by the absorption mechanism.

The absorption of EM waves was partially attributed to the moderate conductivity of the fabrics (Table III).¹⁴ Similar findings were also reported in the investigation of the shielding mechanism of PMMA/MWCNT coatings.^{14,15} This was different from fabrics woven with metal wires, in which reflection was the dominant shielding mechanism⁴⁰ because much higher electrical conductivity of metal enhanced the surface reflection effect and shallow skin depth.^{34,37} It was also reported that polymers reinforced with single-walled CNTs showed reflection as the dominant shielding mechanism.^{21,41} The reason could be that MWCNTs are not as conductive as single-walled CNTs, and the structures of the MWCNTs had more varieties, which ranged from metal-like to semiconductor-like. Therefore, it is possible that MWCNTs could have greater potential to absorb EM waves. EM wave absorption for MWCNTs should be investigated further to determine the exact mechanism. In addition to MWCNTs, polar groups, such as the hydroxyl groups in cotton and Nafion, may also play a role in EM wave absorption because they could be mobilized in an EM field and thus transfer EM energy into heat. The microporous structure of woven fabrics could also be a factor enhancing the absorption of EM waves because of the reflection and multiple absorptions, which could cause more energy to be dissipated inside the fabric because of a longer traveling distance

Table IV. SEA (dB) and SER (dB) Values of the Nafion-MWCNT-Coated Cotton Fabrics with Various Numbers of Dip Coatings

Frequency (GHz)	Sample																							
	S1			S2			S3			S4			S5			S6								
	SEA	SER	SD	SEA	SER	SD	SEA	SER	SD	SEA	SER	SD	SEA	SER	SD	SEA	SER	SD						
8	5.22	0.31	0.83	0.06	7.16	0.52	1.07	0.05	7.64	0.45	0.99	0.09	7.07	0.63	1.27	0.06	8.79	0.48	1.41	0.06	9.85	0.42	1.63	0.08
9	3.70	0.19	0.08	0.01	5.88	0.53	0.41	0.01	6.28	0.48	0.45	0.01	6.86	0.54	0.70	0.03	7.98	0.51	0.85	0.04	9.06	0.49	1.18	0.06
10	3.09	0.15	0.10	0.01	4.89	0.39	0.32	0.01	5.09	0.33	0.33	0.01	5.80	0.41	0.52	0.02	6.79	0.42	0.61	0.03	7.69	0.38	0.85	0.04
11	3.53	0.21	0.01	0.00	5.22	0.41	0.39	0.01	5.60	0.34	0.36	0.02	6.22	0.42	0.57	0.02	6.80	0.43	0.80	0.03	7.74	0.34	1.02	0.05
12	3.07	0.16	0.21	0.01	4.73	0.42	0.34	0.01	5.30	0.36	0.27	0.01	5.72	0.45	0.42	0.01	6.30	0.34	0.63	0.03	7.30	0.31	0.74	0.04

M, mean value; SD, standard deviation.

for the microwave. These are all potential mechanisms for EM wave absorption, although more studies need to be done to test these hypotheses.

Because absorption is the predominant mechanism of EMI shielding, this technique could be a more attractive alternative for the fabrication of EM-radiation-protection fabrics, which would absorb more EM energy instead of reflecting EMI, which leads to secondary EMI pollution.

CONCLUSIONS

Cotton fabrics with Nafion-MWCNT and SDBS-MWCNT coatings were fabricated. The distribution of MWCNTs on the fabric with Nafion as the dispersant was much more homogeneous than that with SDBS as the dispersant; this resulted in a greater electrical conductivity and EMI SE value. The SE value of the Nafion-MWCNT-coated cotton fabric increased with increasing deposition of MWCNTs and achieved a maximum value of 11.48 dB (92.9% of the EM energy was shielded by the fabric, and the specific EMI SE reached 39.59 dB cm³/g). The absorptivity of the Nafion-MWCNTs fabrics was much higher than 60%; this indicated that the main EMI shielding mechanism of the fabrics was absorption because of the moderate electrical conductivity and the formation of microcapacitors. The Nafion-MWCNT-coated fabric has potential as a promising EM wave-absorbing fabric.

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