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Thermoset composites functionalized with carbon nanofiber sheets for EMI shielding

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ABSTRACT: Carbon nanofiber sheets were developed through filtering well-dispersed carbon nanofiber (CNF) through filtering well-dispersed aqueous solution of CNF particles with 0.4 μm hydrophilic polycarbonate membrane by the aid of high-pressure air. They were used to functionalize composites by the resin transfer molding method. Their functionalized composites were characterized with scanning electron microscopy (SEM), four-point probes and a vector network analyzer to measure their morphologies, electrical conductivity, and electromagnetic interference (EMI) shielding performance over the frequency range of 8–12 GHz (X band), respectively. Their morphologies show that CNF particles are overlapped and tightly connected with each other in their interconnected networks. The CNF sheets are exposed on the surface, although their networks are partially penetrated by polyester resins. Their electrical conductivity can be 3.0 ± 0.2 Scm^{-1} or so, much higher by ten orders of magnitude than the reported electrical conductivity of CNF-filled composites. Their EMI shielding effectiveness slightly varies in a range of -30 dB to -35 dB as a function of frequency, much higher than that of most CNF or carbon nanotube–filled composites. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41873.

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INTRODUCTION

In recent decades, high-speed communication is rapidly developed over a wider frequency range from the microwave to the millimeter wave, based on which many electronic instruments have been applied, such as cellular phones, wireless local area network, aerospace, and military equipments. The electromagnetic waves produced from these electronic instruments have an adverse effect on the performance of other equipments or even cause harm to human body. This kind of "electromagnetic pollution" becomes one of public nuisances with a rapid growth of radiation sources and their EMI shielding is increasingly required by governments around the world.[1–4]

In order to alleviate these "electromagnetic pollution," great attention has been paid to develop EMI shielding materials, through which the penetration of the radiation is avoided.[5] Traditionally, metallic materials are utilized to supply good EMI shielding effectiveness (SE) in the form of bulk sheets, meshes, and plating coatings. However, these metallic shields have disadvantage of heavy weight, corrosion, degradation, and physical rigidity. Thus, their application has been limited, especially in the aeronautic applications.[6–8]

Recently, lightweight and highly conductive filler/polymer composites have been employed for EMI shielding applications, such as carbon fiber,[9–12] metal particles,[13–18] and carbon particles based materials.[19–35] These composites are attractive for EMI shielding due to their low density, easy processing, high strength, and good fatigue resistance. Although most polymer matrixes do not contribute to EMI shielding due to their electrical insulation, they can affect the EMI SE by determining the connectivity of the conductive fillers.[19–22] According to the percolation theory, the conductivity and SE of the composites are determined by the characteristics of the conductive network formed by the conductive fillers throughout the matrix. Thus, the fraction and aspect ratio of fillers plays a key role in providing high EMI SE. A high aspect ratio and high conductivity benefit the formation of a conductive network with much lower percolation threshold value (PTV) of fillers.[23–25] This is the reason why single-wall carbon nanotubes (SWCNT), multiwall carbon nanotubes (MWCNT), and CNF are superior over traditional fillers to improve the EMI SE of composites. Furthermore, CNF particles have attracted attention from both industrial and academic researches because they can be produced in a large amount at much lower cost, although SWCNT and MWCNT are excellent candidates for EMI shielding due to higher aspect ratio and larger surface area.

Although CNF, SWCNT, and MWCNT have been successfully used to enhance EMI SE of composites, the host materials are mostly thermoplastic polymers. Very few studies have been reported on their EMI shielding application in fiber-reinforced thermoset composites. They form cross-linked structures with high strength after being cured. These materials have been widely used in many important sectors of aircrafts, naval constructions, and ships. To obtain conductive composites, highly entangled agglomerates of CNF, SWCNT, or MWCNT have to be dispersed efficiently into the resin by shear mixing or ultrasonic processing due to their strong van der Waals force. In fact, the addition of these conductive filles can significantly increase the viscosity of polymer resins, which is detrimental to the process and uniform dispersion of nanofillers in polymer resins. As they are used in fiber-reinforced composites, much more problems occur such as heavy reagglomeration, poor compatibility, poor processability, leaching, and reduced mechanical properties.[36,37] In the case of CNF, high-loading levels will be required to achieve its theoretic PTV due to its lower efficiency, which would lead to even worse processing issues.

To avoid such problems, this article explores a novel method to functionalize the surfaces of fiber-reinforced thermoset composites with CNF sheets through the resin transfer molding method. This kind of CNF sheets, developed through filtering well-dispersed carbon nanofibers under well-controlled processing conditions, has a uniform network structure due to the entanglement of CNF particles with each other. They can be molded on the sample surface with much lower total concentration of CNFs (<1 wt % of total weight) through the resin transfer molding method. Theoretically, their uniform network structures should provide high EMI SE to fiber-reinforced composites according to the percolation threshold theory. To avoid the effect of fiber mats, the same molding method will be utilized to prepare thin thermoset composite slices without traditional fiber reinforcement. This kind of composite slices can be easily manipulated to characterize their EMI shielding performance and conductivity. It is supposed that these composite slices have the same structures with the exterior layers of CNF sheets functionalized fiber-reinforced composites and therefore have similar EMI shielding performance and conductivity when applied under identical conditions. Their measurements can be utilized to display the EMI shielding performance of CNF sheets in fiber-reinforced thermoset composites.

EXPERIMENTAL

Materials and Preparation of Samples

Vapor grown CNF (Polygraf III PR19-PS) particles have diameters of 50–150 nm and lengths of 30–100 μm (purchased from Applied Sciences, Inc). They could be dispersed in aqueous solution with the aid of a high-intensity sonicator. The unsaturated polyester resin (712–6117, Eastman Chemical Company) was used as matrix material with the MEK peroxide hardener at a weight ratio of 100 : 1. Surfactants (Nano Sperse AQ) were ordered from Nanolab Company.

The as-received CNF powders were grinded in a mortar with a small amount of de-ionized (DI) water. After being grinded, they were transferred into a 500-ml glass beaker, and 400 ml of water was added together with four drops of dispersing additives. Their mixture was subsequently sonicated using a high intensity sonicator (600 watt Sonicator 3000 from Misonix Inc.) for 20 min at a power of 30–50 watts. After the solution and probe were cooled down to room temperature, the solution was sonicated for 20 more minutes under the same condition. The as-prepared solution was allowed to settle overnight and 300 ml of the suspension was collected. The above process was repeated a few times. The final mixture was treated with the ultrasonic sonicator for 10 min before being filtered with 0.4 μm hydrophilic polycarbonate membrane by the aid of high-pressure air. After water is filtered completely, the specimen is placed on the smooth wax paper, and the polycarbonate membrane is carefully peeled off. Its two sides are covered with smooth plastic paper and dried in the air for 12 h. Finally, it should be dried in vacuum oven at 80°C for 12 h.

Resin transfer molding process was utilized to mold thin thermoset composite slices with the CNF sheet as an exterior layer. The CNF sheet was sealed on the bottom of mold, which would become the front surface after de-molding. With the aid of vacuum pump, polyester resin could fill the pores of the CNF sheets and finally be cured inside. The sample with a thickness of 0.61 mm was cured at room temperature for 24 h and post-cured in the oven for 2 h at 120°C.

Characterization

JEOL-6300F scanning electron microscopy (SEM) operated at 5 Kv was used to image the CNF sheets, the fracture crossing section and top surface of thermoset composite slices for their morphology analysis. Fracturing was performed in liquid nitrogen. Before imaging, samples were coated with gold to facilitate imaging and create conductive surfaces. Electrical conductivity measurements were conducted with four-point probes resistivity measurement system (RTS-9 model, four point probe science and technology co., China). Four-point probes were used to eliminate the effect of contact resistance. Their inter-point spacing is 1 ± 0.01 mm and the probe diameter is 0.5 mm. The operation was carried out at 23 ± 2°C with humidity of 15%. Their electrical conductivity measurements were tested six times, and the reported result was the average. HP 4339B high resistivity meter was utilized with 10 v for the conductivity measurements of highly insulative materials. EMI shielding measurements were performed on an Agilent-N5242A vector network analyzer over the frequency range of 8–12 GHz (X band), using a rectangular waveguide with a dimension of 22.86 mm $\times$ 10.16 mm.

RESULTS AND DISCUSSION

Morphologies of CNF Sheets

Polygraf III PR19-PS is one kind of oxidized CNF. Their stable dispersion in aqueous solution can be achieved through many function groups on their surfaces, such as phenolic (—OH) and carboxylic acid (—COOH). After being treated as described in the experimental section, their highly conductive sheets are obtained with a density of 0.40 g cm^{-3} and a thickness of 0.29 mm. Their morphologies are characterized with SEM (Figure 1). Although there are a few aggregates or ropes of CNF particles as shown by arrows in their SEM image at lower magnification (Figure 1a), most CNF particles are well-dispersed individually with larger length and smaller diameter (Figure 1b). They are randomly arranged and overlapped with each other to form an interconnected network.

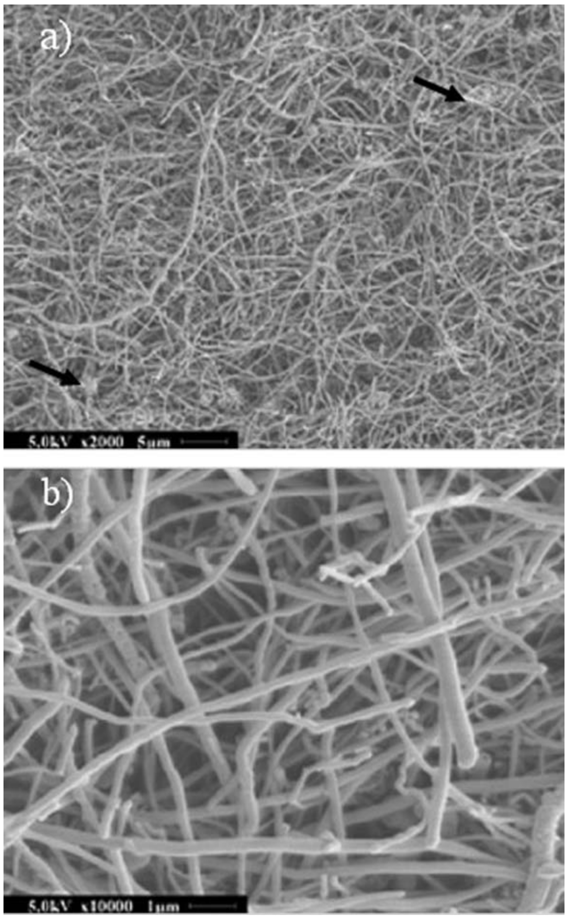

Figure 1. (a) Low-magnification SEM image of CNF sheets and (b) high-magnification SEM image of CNF sheet.

According to the percolation threshold theory, the formation of an interconnected network of CNF particles should be required to prepare CNF-filled polymer composites with a good conductivity and EMI shielding performance, in which high enough load of CNF particles is filled. For example, Yang Y.L. *et al* had fabricated CNF/polymer foam with a conductivity value of 2.6×10^{-3} Scm^{-1} with a PTV of 3 wt % CNFs.[28] Das A. *et al* prepared CNF/polymer film with a maximum conductivity value of 3.09×10^{-2} $S.cm^{-1}$ within a PTV of 1–2 wt % CNF particles.[29] However, their interconnected networks are different from CNF sheets shown by Figure 1. The mechanisms of the composite's electrical resistivity include tunneling and direct contact between the particles. In the CNF-filled composites, most of the CNF particles cannot tightly connect with each other because they are surrounded by the polymer resins. Tunneling is the dominant mechanism when the distance between the filler particles are close enough, roughly less than 10 nm.[38]

Their networks have a much larger pore size and a much lower bulk density of CNF particles than those of CNF sheets. Thus, their electrical conductivity only has slight enhancement above their PTV, even though their load is remarkably increased to 15–20 wt %. Figure 1 shows that CNF particles are tightly connected with each other in CNF sheets, which should be responsible for their much higher electrical conductivity. The electrical conductivity of CNF sheets is measured with four-point probes, and their averaged value is 3.0 ± 0.1 Scm^{-1} much higher by 10 orders of magnitude than the reported electrical conductivity of CNF-filled composites. Similar results are also found in various SWCNT- or MWCNT-filled composites. Table I summarizes the PTVs that have been reported so far in literatures for CNF-, SWCNT-, or MWCNT-filled polymer composites. Clearly, CNF sheets have much higher electrical conductivity than SWCNT- or MWCNT-filled polymer composites reported in the cited literatures, although single CNF particle has poorer electrical conductivity than SWCNT and MWCNT.

EMI Shielding Performance of CNF Sheets

Besides high electrical conductivity, carbon-based nanoparticles are good EMI shielding materials, whose EMI SE is defined as the ratio between the incoming power and outgoing power of an electromagnetic wave. Although high electrical conductivity is not necessary for good EMI shielding performance of CNF-, SWCNT-, and MWCNT-filled polymer composites, high enough load of these fillers, usually above their PTV, is required to achieve their applicable level of EMI SE (~-20 dB). Table I representatively displays EMI SE results of CNF-, SWCNT-, and MWCNT-filled polymer composites over the frequency range of X-band. Their high EMI SE usually could be achieved through filling much higher load of particles than their PTV. Polymer resins have no contribution to EMI SE so that their EMI shielding performance should derive from the existence of interconnected networks of nanoparticles.

Theoretically, CNF sheets should have good EMI shielding performance due to their even more compactly interconnected networks. Figure 2 presents the EMI SE of CNF sheets, measured over the X-band range. The results show that the SE of CNF sheets slightly varies in a range of −30 dB to −35 dB as a

Table I. Conductivity and EMI SE of Representative Composites in Open Literatures

Polymers	fillers	PTV (wt %)	Conductivity ($S.cm^{-1}$)	EMI SE (dB)	Frequency/load (wt)	References
PS	CNF	3	2.6×10^{-7}	19	8.2–12.4 GHz/15	[27, 28]
PTFE	CNF	1.1	3.06×10^{-2}	25	8.2–12.4 GHz/1.1	[29]
Epoxy	SWCNT	0.6	1.0×10^{-2}	20–30	8.2–12.4 GHz/15	[30]
EVA	SWCNT	3.5	1.0×10^{-4}	37	8–12 GHz/30	[32]
PS	MWCNT	3	1.0×10^{-2}	20	8.2–12.4 GHz/7	[33]
Epoxy	MWCNT	8	2.39×10^{-2}	60–90	8.2–12.4 GHz/8	[34]

Note: PS, polystyrene; PTFE, polytetrafluoroethylene; PAN, Poly(acrylonitrile); EVA, ethylene vinyl acetate.

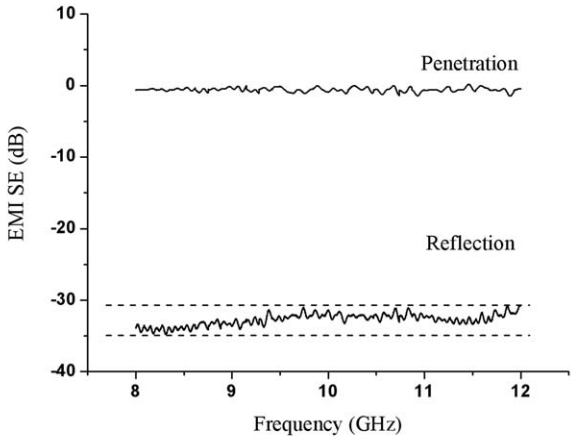

Figure 2. EMI SE of CNF sheets.

function of frequency. This SE value is much higher than those of CNF-, SWCNT-, or MWCNT-filled composites listed in Table I, except for that in Ref. 34. Indubitably, CNF sheets have good EMI shielding performance derived from their higher bulk density. Although their thickness is only 0.29 mm, the outgoing power of an electromagnetic wave is mostly shielded through reflection and there is nearly no penetration.

Morphologies of CNF Sheets Functionalized Composites

SEM was utilized to characterize the morphologies of CNF sheets functionalized composites, as shown in Figure 3. Figure 3a displays the top surface of CNF sheet functionalized composite slices. Although the interconnected networks of CNF sheets are filled with polyester resin after being molded on the surface of composites, a lot of CNF particles are still exposed on the surface of composite slices. The exposed CNF particles are uniformly dispersed on the surface. However, the morphologies of their crossing section show that these exposed CNF particles are part of CNF sheets (Figure 3b). Figure 3b also shows that the cross section of composite slices is composed of two zones. One zone belongs to the back surface of composite slices, in which there is no CNF particles. The other zone is part of CNF sheets filled with polyester resin. The latter has similar structures with CNF sheets before being molded on the surfaces of composites. This kind of structures plays an important role in controlling the electrical conductivity of composites. Both the top surface and back surface were characterized with four point probes and their electrical conductivity is measured to be 3.0 ± 0.2 Scm^{-1} and $1.5 \pm 0.2 \times 10^{-11}$ Scm^{-1}, respectively. Obviously, their back surface has very poor conductivity, slightly higher than the reported conductivity of pure polymer resins ($\sim 10^{-13}$ Scm^{-1}). But the CNF sheet–functionalized surface has much higher electrical conductivity, 11 orders of magnitude higher than that of the back surface. By comparison, the CNF sheet–functionalized surface has similar electrical conductivity with the CNF sheets before being molded. Both have much higher electrical conductivity than CNF-, SWCNT- or MWCNT-filled polymer composites listed in Table I. Clearly, the existence of polyester resin has no effect on the electrical conductivity of CNF sheet–functionalized composite surfaces and the exposure of CNF particles on the surface is a key factor to provide a highly conductive surface of composites. Furthermore, Figure 3b depicts that polyester resin penetrates the CNF sheets and they are molded together with each other. Thus, this kind of CNF sheets functionalized composites is structure materials, different from coating materials.

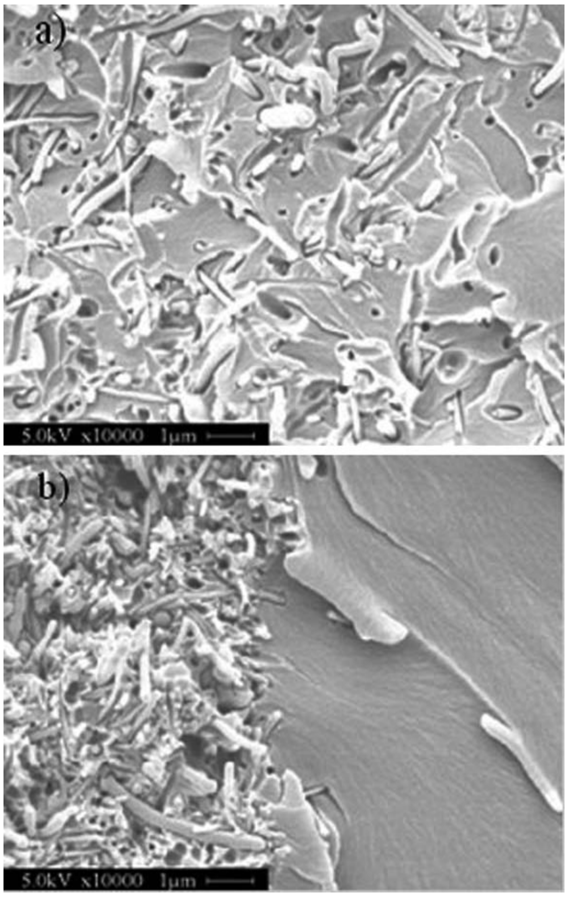

Figure 3. SEM images of CNF sheets functionalized composite slices (a) top view and (b) crossing section.

EMI Shielding Performance of CNF Sheets Functionalized Composites

As discussed previously, CNF sheets have good EMI shielding performance than most CNF-, SWCNT- or MWCNT-filled polymer

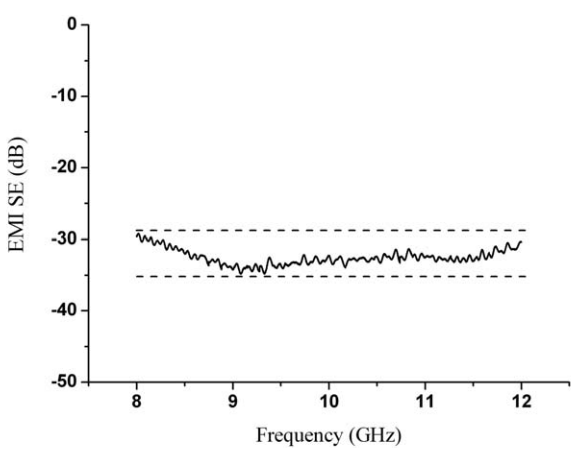

Figure 4. EMI SE of CNF sheets functionalized composites.

composites in the open literatures. Although polyester resins could be filled into the interconnected networks of CNF sheets through the resin transfer molding method, the EMI shielding performance would not be affected by the existence of polyester resins because polymer resin has no contribution to the EMI shielding performance of materials. Figure 4 displays the EMI SE of CNF sheets functionalized composites as a function of frequency over the X-band range. Their EMI SE is similar with that of CNF sheets presented in Figure 2. It experimentally proves that the existence of polyester resin has no effect on the EMI SE of CNF sheets. As a kind of structure materials, they have much wider potential application in the field of EMI shielding.

CONCLUSIONS

CNF sheets can be successfully developed through filtering well-dispersed aqueous solution of CNF particles with 0.4 μm hydrophilic polycarbonate membrane by the aid of high-pressure air. They have an electrical conductivity of 3.0 ± 0.1 Scm^{-1} and EMI SE of -30 dB $\sim$ -35 dB over the X-band range because their CNF particles are overlapped and tightly connected with each other in their interconnected networks. They can be utilized to prepare a kind of structure materials with good electrical conductivity and EMI shielding performance, in which polyester resins penetrate the interconnected networks of CNF sheets. Because CNF sheets are partially exposed on the surface of composite slices, both electrical conductivity and EMI shielding performance of CNF sheets are reserved in the CNF sheets functionalized composites. Similarly, the CNF sheets could be embedded onto the surface of fiber-reinforced composites by the same method. Thus, they also can be utilized to remarkably improve the electrical conductivity and EMI shielding performance of fiber-reinforced composites.

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