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Letters to the editor

Increasing the electromagnetic interference shielding effectiveness of carbon fiber polymer–matrix composite by using activated carbon fibers

Junhua Wu, D.D.L. Chung*

Composite Materials Research Laboratory, State University of New York at Buffalo, Buffalo, NY 14260-4400, USA

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Electromagnetic interference (EMI) shielding is increasingly needed for electronics and radio frequency sources, due to the interference of radio frequency waves (such as those from cellular telephones) to digital electronics [1]. In particular, electronic enclosures, as well as rooms, vaults and aircraft that house electronics, need to be able to provide EMI shielding.

Due to the desire for light weight for avionic electronics, laptop computers, aircraft and many other devices, polymer-matrix composites are increasingly important for EMI shielding [2–4]. Furthermore, these composites are attractive due to their moldability and processability.

The polymer matrix in the composites is typically electrically insulating, so it is not able to provide shielding. However, the use of electrically conducting fillers renders the composites the ability to shield. Both discontinuous and continuous fillers are used for this purpose. The discontinuous fillers are advantageous in that they are amenable to the use of extrusion, injection molding and other conventional polymer processing methods for composite fabrication. However, continuous fillers, namely fibers, are needed to provide high strength and high modulus, as required for structural applications, such as aircraft.

Among the continuous fibers, carbon fibers are dominant, due to their low density, high modulus, high strength and wide availability. Compared to glass fibers, carbon fibers are attractive in their electrical conductivity, which relates to EMI shielding effectiveness. Therefore, this

 $\hbox{\it E-mail address:} \ ddlchung@acsu.buffalo.edu \ (D.D.L.\ Chung).$

paper is focused on continuous carbon fiber polymer-matrix composites.

The mechanisms of EMI shielding are reflection, absorption and multiple reflections. Reflection is usually the dominant mechanism, especially for carbon fibers. The contribution by multiple reflections is usually relatively small for carbon composites. To improve the contribution by reflection, previous work has emphasized the use of nickel-coated carbon fibers, as nickel is more conductive than carbon [5,6]. However, the enhancement of the contribution by multiple reflections by fiber modification has not received previous attention. In this work, we found that appropriate activation of the carbon fibers enhances the contribution of multiple reflections without degrading the mechanical properties.

Activation is a method of fiber surface modification that involves a chemical reaction which causes increase of the specific surface area through the formation of surface pores. Activated carbon fibers with specific surface area typically exceeding 1000 m²/g are used for adsorption, which is relevant to fluid purification. They are also used for the storage of hydrogen, natural gas and other fuels. In addition, they are used as electrodes for double-layer capacitors and for industrial processes. However, they have not been previously investigated for use in electromagnetic applications such as EMI shielding.

Epoxy (a thermoset) is the dominant matrix used for carbon fiber polymer—matrix structural composites. The epoxy used in this work was EPON Resin 862 together with EPI-CURE 3234 curing agent in the weight ratio 100:15.4 (Shell Chemical Co., Houston, TX).

The carbon fiber used in this work was Thornel P-25 (without sizing or twist) from Amoco Performance Products Inc., Alpharetta, GA. The diameter was $11~\mu m$.

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^{*}Corresponding author. Tel.: +1-716-645-2593; fax: +1-716-645-3875.

Carbon fiber activation was conducted by (i) washing the fiber with acetone for the purpose of surface cleansing, (ii) heating the fibers in flowing nitrogen from room temperature to 1000°C at a heating rate of 10°C/min , (iii) maintaining the temperature at 1000°C for 1 h for the purpose of removal of surface volatile components, if any, (iv) introducing CO_2 gas $(0.6 \text{ vol.}\% \text{ in N}_2)$ for 1 h while the temperature remained at 1000°C for the purpose of activation, and (v) cooling to room temperature at 10°C/min in flowing nitrogen.

Unidirectional carbon fiber epoxy-matrix composites with a fiber volume fraction of 34.5% were fabricated by (i) preparing the prepreg (i.e. immersing the fibers in the resin, with curing agent, and then immediately squeezing the fibers between glass tubes (to remove excessive resin) and then winding the fibers onto a mandrel), (ii) after about 30 min, cutting the prepreg into sheets, (iii) stacking eight prepreg sheets in a steel mold of size 178×101 mm, such that the fibers in all the layers were in the same direction, (iv) initial curing of the resin by heating from 25 to 121° C at a heating rate of 4° C/h and at a pressure of 2.0 ± 0.2 MPa, and (v) post curing of the resin by heating at 121° C and 2.0 ± 0.2 MPa for 2 h. Composites were fabricated using separately as-received fibers and activated fibers.

Electromagnetic testing using the coaxial cable method was conducted using an Elgal (Israel) SET 19A shielding effectiveness tester, which was connected to a Hewlett-Packard (HP) 8752C network analyzer (Fig. 1). A HP 85032B type N calibration kit was used to calibrate the system. The frequency was scanned from 1.0 to 1.5 GHz, while 200 data points were taken in reflection and also in transmission. The specimens were annular, with outer diameter 97 mm, inner diameter 32 mm and thickness 3 mm.

The attenuation upon transmission (the EMI shielding effectiveness) is significantly increased by activating the fibers, whereas the attenuation upon reflection is not much

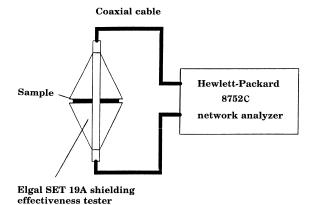


Fig. 1. Set-up for electromagnetic shielding effectiveness measurement.

Table 1
Attenuation under transmission and under reflection of carbon fiber composites

Fiber type	Attenuation upon transmission (dB)	Attenuation upon reflection (dB)
As-received	29.6±0.9	1.3±0.2
Activated	38.8±0.8	1.2±0.2

affected by activation (Table 1). This means that the shielding effectiveness is increased by activation, not because of increased reflectivity, but because of increased multiple reflections and/or increased absorption. Since the activation has minor effect on the overall dipole concentration in the composite (in spite of the functional groups formed on the fiber surface after activation), the enhanced shielding effectiveness is mainly attributed to increased multiple reflections.

Single fiber tensile testing was performed on as-received and activated fibers, using a screw-action mechanical testing system (2/D, Sintech, Stoughton, MA) at a crosshead speed of 1 mm/min. The gage length was 128 mm. Activation has little effect on the tensile strength or modulus of the fibers (Table 2). It probably increases both strength and modulus slightly, as made possible by the heating at 1000°C in step (iii) of the activation process.

The BET specific surface area of the fibers was determined by nitrogen adsorption and gas pressure measurement, using ASAP 2010 (Micromeritics, Norcross, GA). The specific surface area is 7.6 and 90 m²/g before and after activation, respectively. Though the specific surface area is significantly increased by the activation, the area after activation is low compared to that of typical activated carbon fibers. Thus, the absence of tensile property degradation by activation is not unreasonable. The main (or mean) pore size of the fibers is 19.3 and 20.1 Å before and after activation, respectively. Hence, activation increased the specific surface area, with little effect on the pore size.

In conclusion, the use of activated carbon fibers with specific surface area $90~\text{m}^2/\text{g}$ as a continuous reinforcement (35 vol.%) in a polymer–matrix composite enhances the EMI shielding effectiveness of the composite due to multiple reflections. The shielding effectiveness at $1.0{-}1.5~\text{GHz}$ is 39 dB, compared to a value of 30 dB when

Table 2
Tensile properties of carbon fibers before and after activation.
Standard deviations are shown in parentheses

Fiber type	Strength (MPa)	Modulus (GPa)
As-received ^a	665 (87)	126 (7)
Activated ^b	727 (151)	138 (15)

^a Six specimens tested.

^b Eight specimens tested.

untreated fibers are used. The activation treatment does not degrade the tensile properties of the fibers.

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References

- [1] Chung DDL. Materials for electromagnetic interference shielding. J Mater Eng Perform 2000;9(3):350-4.
- [2] Luo X, Chung DDL. Electromagnetic interference shielding

- using continuous carbon-fiber carbon-matrix and polymer—matrix composites. Comp Part B: Eng 1999;30(3):227–31.
- [3] Sau KP, Chaki TK, Chakraborty A, Khastgir D. Electromagnetic interference shielding by carbon black and carbon fibre filled rubber composites. Plastics Rubber Comp Process Appl 1997;26(7):291–7.
- [4] Ramadin Y, Jawad SA, Musameh SM, Ahmad M, Zihlif AM, Paesano A et al. Electrical and electromagnetic shielding behavior of laminated epoxy–carbon fiber composite. Polymer Int 1994;34(2):145–50.
- [5] Huang CY, Pai JF. Studies on processing parameters and thermal stability of ENCF/ABS composites for EMI shielding. J Appl Polym Sci 1997;63(1):115–23.
- [6] Shui X, Chung DDL. Submicron diameter nickel filaments and their polymer–matrix composites. J Mater Sci 2000;35:1773–85.

A comparative study of carbons for use as an electrically conducting additive in the manganese dioxide cathode of an electrochemical cell

Weiming Lu, D.D.L. Chung*

Composite Materials Research Laboratory, University at Buffalo, The State University of New York, Buffalo, NY 14260-4400, USA

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Due to the fact that some electrochemical electrode materials are not conductive electrically, a conductive additive is added to the electrochemically active species in forming the electrode [1-6]. An example is manganese dioxide (MnO_2) , which is not conducting and serves as the cathode of various electrochemical cells, including lithium cells. Due to the chemically inert and electrically conductive nature of carbons, carbon is used as the conductive additive. Among the carbons, carbon black is particularly common for this purpose.

Other than the electrochemically active materials and the conductive additive, the electrode contains a binder, which is commonly a thermoplastic polymer, such as polytetra-fluoroethylene (PTFE, or teflon) and polyvinylidenefluoride (PVDF) in the form of particles. The binder serves to bind the ingredients together to form a shaped object (such as a disc) that can be handled. The type and amount of binder are expected to affect not only the bindability, but also the distribution of the carbon additive.

E-mail address: ddlchung@acsu.buffalo.edu (D.D.L. Chung).

The primary objective of this work is to investigate the effect of the type of carbon additive on the electrical resistivity of the MnO_2 cathode. The types of carbon include graphitized mesophase pitch, natural graphite, graphitized carbon filaments (0.1 μ m diameter, as made catalytically from carbonaceous gases), carbon filaments without graphitization, and carbon black. These types of carbon differ in their particle size, aspect ratio and degree of crystallinity, so their dispersion, connectivity and effectiveness as a conductive additive are expected to differ.

The secondary objective of this work is to investigate the effect of binder content on the effectiveness of carbons as a conductive additive.

Previous work has shown that carbon black is more effective than submicron carbon filaments without graphitization as a conductive additive for the MnO_2 cathode [7], even though a carbon black compact without MnO_2 exhibits higher resistivity than a carbon filament compact without MnO_2 [8]. Thus, a low resistivity for a carbon compact does not imply a low resistivity for an MnO_2- carbon composite. This is because the resistivity of an MnO_2- carbon composite depends on the dispersion and connectivity of the carbon in the midst of MnO_2 particles.

^{*}Corresponding author. Tel.: +1-716-645-2593x2243; fax: +1-716-645-3875.