Synergistic Conductivity and Electromagnetic Interference Shielding Effectiveness of Epoxy/Carbon Fiber and Epoxy/Carbon Black Composites via Mixing with Bamboo Charcoal

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This study was aimed at preparing electromagnetic interference (EMI) shielding materials based on carbon black (CB), carbon fiber (CF), bamboo charcoal (BC), and epoxy resin. The effects of adding bamboo charcoal on the mechanical properties and electrical resistivity of epoxy composites were studied. Scanning electron microscopic (SEM) analysis, electrical resistivity, and electromagnetic interference (EMI) shielding effectiveness were also investigated. The composites were prepared at 120 °C by the curing-molding method through blending the fillers in epoxy resin. The results revealed that the BC/CB and BC/CF composites had perfect conductive network structure and resulted in better dynamic thermal mechanical properties. The electrical resistivity declined with the increase of bamboo charcoal contents; consequently, the EMI shielding effectiveness improved gradually. The lowest electrical resistivity, down to 0.071 Ω·m, corresponded to the best EMI shielding effectiveness of BC/CF composites, which could be above 60 dB over a frequency range of 30 MHz to 1500 MHz while the carbon fiber content was at 40 wt.%.

Keywords: Bamboo charcoal; Epoxy; Carbon black; Carbon fiber; EMI shielding effectiveness

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INTRODUCTION

With the development of broadcasting, television, and microwave technology, the power of radio frequency (RF) devices has increased exponentially, and thus elevated electromagnetic radiation on the ground has reached a harmful level for human health. Electromagnetic pollution is due to the massive release of harmful radiation, and it has been studied by the Biophysics department at Gazi University for more than 25 years (Seyhan 2010). Dhami (2012) had revealed that within some hospitals in the area there was a microwave/RF pollution power density of 11.48 MW/m², which is approximately 1148% of the biological limit based on readings from a TES 593 electrosmog meter from TES Electrical Electronic Corp. Infertility could result due to electromagnetic pollution, as reported by Lerchl (2013). Therefore, the use of electromagnetic interference shielding materials has been proposed. Researchers have used the strategy of compounding the resin as matrix with fillers such as iron powder (Hu et al. 2015), nickel (Kumar et al. 2014), and copper (Wetherhold and McManaman 2005). Also some shielding materials contained organic carbon nanotubes (Li et al. 2006, 2012; Kotsilkova et al. 2015), carbon black (Das et al. 2000; Alsaleh and Sundararaj 2008, 2013), and graphite (Liang et al. 2009; Morari et al. 2011; Song et al. 2014). Simultaneously, Song et al. (2016) have
prepared an acrylonitrile styrene acrylate copolymer (ASA), blending with graphite and carbon black composites, and showed that when carbon black loading was increased to 15% and graphite loading was at 25%, the EMI shielding effectiveness reached to more than 50 dB over the frequency range of 30 to 3000 MHz. Valentini et al. (2015) have presented that the commercial thermoplastic polyurethane filled with exfoliated graphite (EG) composites had a EMI shielding effectiveness of -20 dB with 20 wt.% EG in the frequency of 8.2 to 2.3 GHz. Joshi et al. (2013) reported a kind of thin film of graphene nanoribbon-polyvinyl alcohol composite with a high EMI shielding of 60 dB. Thomassin et al. (2013) showed different strategies of preparing EMI shielding composites, and the results on EMI shielding effectiveness with various fillers used in the study was ranked as: carbon black < carbon fiber < carbon nanotube < graphene sheet.

Epoxy resins also have been widely used as matrix for EMI shielding properties in many studies. Liang et al. (2009) adopted the epoxy filled with graphene sheet to produce good EMI shielding effective materials, and they also obtained a low percolation threshold of 0.52 vol.%. Wang et al. (2016) synthesized an electroactive shape memory composites by blending polybutadiene epoxy and bisphenol-A, and carbon black; the resultant composite was also characterized by dynamic mechanical analysis and scanning electron microscopy.

In order to achieve high-quality of EMI shielding effectiveness, various composites were fabricated in this work by adding bamboo charcoal, carbon black (CB), and carbon fiber (CF). Bamboo charcoal is a kind of cheap and green biomass resource with high porosity. In this work its usage improved the electromagnetic interference shielding effectiveness of composites. The CF and CB were adopted as fillers because of their good conductivity, and epoxy resin was selected as the polymer matrix. The curing-molding method was used for preparing the composites. This study investigated the electrical resistivity, morphology, dynamic thermal mechanical analysis, and mechanical properties of the CB and CF composites.

**EXPERIMENTAL**

**Materials**

Bamboo charcoal was produced by the Guilin Xinzhu natural functional material Co. Ltd. (China). Epoxy resin (Phoenix WSR618 E-51) was obtained from Nantong Xingchen synthetic material Co. Ltd. (China); carbon fiber(L/D=1428) with a diameter of 7 μm was bought from the Nanjing Weida composite material Co., Ltd (China); carbon black (EC-600 JD) with a high specific BET surface area of 1000 m²/g was purchased from Lion corporation (Japan).

**Samples Preparation**

The composites were blended uniformly with epoxy resin and carbon fiber or carbon black, respectively. The molding machine pressing was executed with a pressure of 2 MPa and a temperature of 120 °C for 20 min. The mass ratio of fillers loaded in BC/CF/epoxy and BC/CB/epoxy composites are documented in Table 1.
Characterization Methods

Flexural strength measurement

The samples prepared for flexural strength testing were cut into strips having dimensions of 80 mm × 10 mm × 4 mm. The flexural strength properties of BC/CF/epoxy and BC/CB/epoxy composites were measured using a material mechanical testing machine (Shenzhen SANS Company, China) with the standard of ISO 178 (2001). The cross-head speed used for testing was at 10 mm/min at room temperature and the span was 64 mm.

Table 1. The Mass Ratio of Each Component in Composites

<table>
<thead>
<tr>
<th>Number</th>
<th>BC (wt.%)</th>
<th>CB (wt.%)</th>
<th>CF (wt.%)</th>
<th>Epoxy (wt.%)</th>
<th>Curing Agent (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0CF</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>72</td>
<td>18</td>
</tr>
<tr>
<td>B1CF</td>
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<td>64</td>
<td>16</td>
</tr>
<tr>
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<td>10</td>
<td>56</td>
<td>14</td>
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<tr>
<td>B3CF</td>
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<td>0</td>
<td>10</td>
<td>48</td>
<td>12</td>
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<tr>
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<td>40</td>
<td>0</td>
<td>10</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>B0CB</td>
<td>0</td>
<td>10</td>
<td>0</td>
<td>72</td>
<td>18</td>
</tr>
<tr>
<td>B1CB</td>
<td>10</td>
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<td>16</td>
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<td>B2CB</td>
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<td>10</td>
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<td>56</td>
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<td>12</td>
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<tr>
<td>B4CB</td>
<td>40</td>
<td>10</td>
<td>0</td>
<td>40</td>
<td>10</td>
</tr>
</tbody>
</table>

Dynamic thermal mechanical analysis

The dynamic thermal mechanical properties were assessed by a dynamic mechanical analyzer DMA 242 E (NETZSCH Co., Germany). The specimens were cut into strips having a length of 40 mm. The testing temperature was over a range from 30 to 150 °C by three points bending mode, and the heating rate used was 3 K/min. The testing frequency was measured at one Hz, and the amplitude was set at 20 μm.

SEM morphology observation

The fracture surface of CF/epoxy and CB/epoxy composites was measured by scanning electron microscope (SEM, SU 8010), which was purchased from Hitachi Corporation (Japan). The accelerating voltage used was 20 kV, and the fracture surface was sprayed by gold particles.

Electrical resistivity test

A four-point probe tester (SZT-2A, Suzhou, China) used for this measurement was from Suzhou Tongchuang Electronics Co., Ltd. Three points on the disc sample were chosen randomly, and the mean value of the electrical resistivity was obtained.

EMI shielding measurement

The samples were prepared into discs with diameters of 12 cm and thickness of 1 mm. The EMI shielding effectiveness was measured with an Electromagnetic Shielding Measuring Instrument (DR-S02, Beijing Dingrong, China) and Vector Network Analyzer (TA7300A, Beijing Dingrong, China) with a frequency range of 30 to 1500 MHz.
RESULTS AND DISCUSSION

Mechanical Properties

Flexural strengths and moduli of composites were used to investigate the dispersion of fillers in the matrix (Zhang et al. 2011). Figure 1 manifests the effects of BC content on the flexural strengths of the CB and CF composites. It was evident from the results that the flexural strength of the CB composites decreased by 22 MPa with the increase of BC content from 0 wt.% to 40 wt.% The reason can be attributed to the high specific surface area of carbon black. The use of a large amount of carbon black causes the formation of CB aggregation, which worsens the interfacial properties between polymer and fillers (Song et al. 2015). But the flexural strength of the CF composite was increased from 28 to 112 MPa with a BC content increase of 0 wt.% to 40 wt.%. This is due to the fact that carbon fiber has a much lower specific surface area than carbon black. As a result, the added CB does not aggregate in the matrix. In addition, carbon fiber and bamboo charcoal can form a continuous network structure in matrix. Therefore, the flexural strength of the CF composites was much higher than the CB composites.

![Fig. 1](image1.png)

**Fig. 1.** The variation of flexural strengths of the CB and CF composites as a function of bamboo charcoal content

![Fig. 2](image2.png)

**Fig. 2.** The variation of flexural moduli of the CB and CF composites as a function of bamboo charcoal content
Figure 2 shows the effects of BC content on the flexural modulus of the CB and CF composites. The flexural modulus of the CB composites and the CF composites changed obviously with the increase of BC content. Both the CB composites and the CF composites reached a high value of modulus (3288 MPa and 3421 MPa), respectively when the BC content was at 20 wt.%. This case was attributed to the presence of fillers, which reinforced the flexural modulus of composites with increased BC content from 0 wt.% to 20 wt.%. When the BC content increased to 20 wt.%, the fillers got dispersed uniformly in the matrix, and the largest value of flexural modulus of composites was obtained with the good intermolecular interaction, indicative of the largest amount of fillers present in the composites. Once the BC content exceeded 20 wt.%, the flexural strength decreased considerably with poor dispersion, and many aggregates of fillers in the matrix were observed. Similar results have been reported (Song et al. 2015). Hence, the content of about 20 wt.% bamboo charcoal was the best content required in order to achieve a good flexural modulus.

![Graph showing the effects of BC content on the flexural modulus of the CB and CF composites.](image)

**Fig. 3.** Variation of the storage moduli and loss factor of the CB composite as a function of temperature: a) Storage modulus; b) Loss factor
Dynamic Thermo-Mechanical Analysis

DMA is a widely used technique to study the viscoelastic properties and mechanical behavior of wood-polymer composites (Jiang and Qin 2006; Cao et al. 2010; Koyun et al. 2012). The storage modulus revealed the elastic nature of composites, and the higher storage modulus corresponded to the higher resistance of deformation. Meanwhile, the loss factor showed the viscous aspect of composites, where the higher loss factor meant easier deformation (Cao et al. 2010). Figures 3 and 4 present the variation of storage modulus and loss factor with various contents of bamboo charcoal on the CB and CF composites as a function of temperature, respectively. For the CB composites, the storage modulus increased with increased BC content from 0 wt.% to 10 wt.%, then declined gradually over the content of bamboo charcoal in the range of 10 wt.% to 40 wt.%. The deformation temperature ranges of the composite were varied with the trends of the storage modulus. In general, the superior value of storage modulus of the CB composites obtained with 10 wt.% of carbon black was 4868 MPa at 40 °C (shown in Fig. 3a). On the other hand, for the CF composite, the storage modulus also increased with the content of the bamboo charcoal from 0 wt.% to 10 wt.%. Subsequently it decreased gradually over the bamboo charcoal range of 10 wt.% to 40 wt.% and almost had the same deformation temperature over a range of 60 to 100 °C. The high value of storage modulus of the BC/CF composite with 10 wt.% of carbon fiber was found to be 12039 MPa at 50 °C (shown in Fig. 4a).

![Graph 1](image1)

**Fig. 4.** The variation of the storage moduli and loss factor of the CF composite as a function of temperature: a) Storage modulus; b) Loss factor
The storage modulus of BC/CB composite was 147% compared with the BC/CB composites, because of the better interface surface combining power.

Figures 3b and 4b present the loss factor of the BC/CB and BC/CF composites, respectively. A giant relaxation peak was observed at 87.3 °C and 85.5 °C, which corresponded to 10 wt.% bamboo charcoal content of the composites. Figure 4 also illustrates the glass transition temperature (T_g) of the composites. For the BC/CB composites, the T_g decreased from 92.1 °C to 87.3 °C when the bamboo charcoal content changed from 0 wt.% to 10 wt.%. On the BC/CF composites, the T_g value decreased from 86.9 °C to 85.5 °C as the bamboo charcoal content changed from 0 wt.% to 10 wt.%. The T_g of BC/CB composites decreased by 4.8 °C as the bamboo charcoal content changed from 0 wt.% to 10 wt.%, whereas the T_g of BC/CF composites declined by 1.4 °C. These data indicate that there was little effect on the T_g values of the composites with the addition of bamboo charcoal. The increase of the T_g value suggests that the movements of the polymer chains were restricted. This was due to the porous structure of bamboo charcoal, in which the high specific surface area improved the intermolecular force between the polymer and fillers. Additionally, after bamboo charcoal was added, the height of T_g peaks was obviously increased first when the BC content changed from 0 wt.% to 10 wt.%; then the height of T_g peaks declined substantially when BC content changed from 10 wt.% to 40 wt.%, indicative of the enhancement in the rigidity. This result was due to the formation of the BC network, and the formed BC networks developed the elastic modulus and restrained the viscous deformation of the composites.

SEM Analysis

Figure 5 displays SEM pictures of the fracture surface of CB composite (shown in Fig. 5a) and CF composite (shown in Fig. 5b). Obviously, the presence of bamboo charcoal and carbon black uniformly dispersed in the epoxy matrix formed the network structure successfully. The carbon fiber was found to be in cross connection and buried throughout the matrix, and the bamboo charcoal powders were scattered around the carbon fibers in the epoxy, and formed into a conductive network.

![Fig. 5. The SEM images of BC composites: a: (8.9 mm × 35.0 k) the CB composites with 10 wt.% BC; b: (8.4 mm × 3.00 k) the CF composites with 10 wt.% BC](image)

The carbon black particles also possessed good electrical resistivity values. This was ascribed to their low density so that they could be in contact with each other and can...
form a conductive pathway network more readily. Therefore, these two kind of fillers with 10 wt.% bamboo charcoal exhibited smoother and more uniform fracture of composites with conductive pathway network.

**Electrical Resistivity Values**

It is well-known that the composites possess higher EMI shielding effectiveness because of the low electrical resistivity. Figure 6 shows the effect of BC content on the electrical resistivity values of the CB and CF composites. The electrical resistivity values of CB composites decreased from 2.128 to 0.785 Ω·cm as the BC content changed from 0 wt.% to 40 wt.%. However, the electrical resistivity of CF composites decreased from 0.538 to 0.071 Ω·cm over the BC content range of 0 wt.% to 40 wt.%.

![Graph showing the variation of electrical resistivity with BC content](image)

**Fig. 6.** The variation of the electrical resistivity of the CB and CF composites as a function of BC content

The electrical resistivity values for both composites declined obviously with the increasing content of bamboo charcoal, which indicated that the conductive network which formed gradually became more effective as the content of bamboo charcoal increased. And compared to the carbon black particles, the carbon fiber formed a tighter conductive network, which decreased the electrical resistivity of the CF composites. In addition, the electrical resistivity of the CF composites was generally lower than that of the CB composites. This was attributed to the fact that the ratio of length to diameter with the carbon fiber was larger than that of carbon black. This means that the bamboo charcoal and carbon fiber more easily formed a conductive network and achieved higher electrical resistivity values.

**Electro-Magnetic Interference Shielding Effectiveness (EMI SE)**

Electro-magnetic interference shielding effectiveness is an important factor for judging the shielding materials, and it strongly relies on the electrical resistivity of the materials used. In order to achieve higher EMI shielding effectiveness, lower electrical
resistivity is required. Hence, shielding materials with more than 20 dB of EMI shielding effectiveness is required for commercial application. The EMI SE quantified the ability of shielding materials stopping the transmission of the signal produced by the electromagnetic waves and was used to describe as the inverse of transmitted power (Thomassin et al. 2013; Song et al. 2015).

Figures 7 and 8 present the EMI SE of BC/CB composites and BC/CF composites over a frequency range of 30 to 1500 MHz, respectively. There was less than 20 dB with 0 wt.% bamboo charcoal of CB/BC composites. And when the content of bamboo charcoal was at 40 wt.%, the EMI SE of CB composites reached more than 30 dB. The CB/CF composites with 0 wt.% of carbon fiber showed about 42 dB of EMI shielding effectiveness. As the carbon fiber loading increased to 30 wt.% and 40 wt.%, effectiveness of EMI SE of CB/BC composites was achieved at about 60 dB. The electromagnetic shielding effectiveness was attributed to the conductive network formed by the interaction between bamboo charcoal and carbon black or carbon fiber.

![Figure 7](image_url)

**Fig. 7.** Variation of EMI SE of the CB composites as a function of frequency

![Figure 8](image_url)

**Fig. 8.** The variation of EMI SE of the CF composites as a function of frequency
These studies demonstrated that the bamboo charcoal could effectively contribute to the EMI SE as shielding materials. And with the bamboo charcoal content increasing, the EMI shielding effectiveness accordingly improved. This was attributed to the fact that the bamboo charcoal and carbon black or carbon fiber behave like mutual “bridges”, building the interworking conductive pathways, which resulted in favorable EMI shielding effectiveness. Comparing the two kinds of shielding materials, when there was 0 wt.% or 40 wt.% bamboo charcoal content, the content of carbon fiber was twice that of carbon black, and the EMI shielding effectiveness of CF composite was also about twice of CB composite. This phenomenon revealed that carbon fiber with bamboo charcoal achieved better shielding of electromagnetic wave effects.

CONCLUSIONS

1. BC/CB/epoxy and BC/CF/epoxy composites were prepared by a curing-molding method. The effects of adding BC on the mechanical properties, SEM, dynamic thermo-mechanical properties, electrical resistivity, and EMI SE of BC composites were investigated.

2. The flexural strength improved with the increase of the BC content. The SEM images showed the best smooth fracture surface at a BC content of 10 wt.% with the BC/CB and BC/CF composites, respectively. Meanwhile, a 10 wt.% content of BC in BC/CB and BC/CF composites exhibited the bigger storage modulus and loss factor with a uniform distribution of the fillers in the matrix.

3. The electrical resistivity of the CB composites decreased from 2.128 to 0.785 Ω·m as the BC content changed from 0 wt.% to 40 wt.%, which differed from the corresponding electrical resistivity from 0.538 to 0.071 Ω·m of the CF composites.

4. Generally, the EMI shielding effectiveness of the BC/CB composites was enhanced to above 30 dB over a frequency range of 30 to 1500 MHz. The EMI SE improved above 10 dB after adding 40 wt.% BC content. However, the EMI SE of the BC/CF composites was advanced to about 60 dB, and it improved to about 20 dB after adding 30 wt.% BC. The presence of two types of fillers in the matrix mutually affected and increased the contacts with each other, formed a more concentrated conductive pathway network, and then provided good EMI shielding effectiveness.

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