



## Effect of carbon fillers on properties of polymer composite bipolar plates of fuel cells<sup>☆</sup>

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### ABSTRACT

Bipolar plates are major components of fuel cell (FC) stacks and they make up a large portion of the stack volume and cost. In order to reduce their weight and fabrication cost, polymer composite materials with various carbon conducting fillers are tested for use as composite bipolar plates for FCs. The composite materials are prepared by using graphite with a small vol.% of carbon black (CB), multi-walled carbon nanotubes (MWNTs) or carbon fibres (CF) in an epoxy resin. The electrical conductivity and flexural properties of the composites are measured as a function of the carbon conductive filler content. The highest electrical conductivity is observed at a total conducting filler content of 75 vol.%. The addition of a small amount of hybrid conducting filler enhances the electrical conductivity up to certain threshold, viz. 5 vol.% of CB, 2 vol.% of MWNTs, and 7 vol.% of CF. Above these thresholds, the electric conductivity decreases with increasing filler content, due to the lack of sufficient resin to bind the fillers tightly. The hybrid filler system has better properties than the single filler system. The experimental results indicate that there is an optimum composition range with respect to electrical conductivity and mechanical properties.

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### 1. Introduction

Bipolar plates are important components of fuel cells (FCs). Traditionally, the most commonly used bipolar plate material is graphite plank because of its excellent resistance to corrosion and low bulk resistivity. On the other hand; it has disadvantages in terms of high cost, difficulty in machining and brittleness, as a result of which bipolar plates require a thickness of the order of several millimeters and thereby cause the fuel cell stack to be massive and voluminous. In order to overcome the issues relating to graphite plank bipolar plates, much effort has been made in recent years to use conducting polymer composites in the fabrication of bipolar plates [1–4]. Graphite/polymer composites were considered to be an ideal material for producing such plates. The advantages of these composites are their light weight, availability in different structural forms to provide enhanced electrical and mechanical properties [5–7], and the ease of fabrication of bipolar plates through injection molding or compression molding. Common conductive fillers such as graphite, carbon black (CB), multi-walled carbon nanotubes

(MWNTs) and carbon fibre (CF) have been introduced into polymeric materials to change their electrical properties in order to meet the optimum design requirements for bipolar plates. Combining graphite with other types of conducting fillers such as CB and MWNTs has been shown to be an effective way to develop composites with higher conductivity and better mechanical properties [8–11]. Nevertheless, systematic results which explain the effects of each of these carbon conductive fillers on the final composites have not been reported. In this study, the effects of the addition of CB, MWNTs, and CF to the graphite/polymer composite are investigated from the points of view of electrical conductivity and flexural properties.

### 2. Experimental

#### 2.1. Materials

##### 2.1.1. Carbon conducting fillers

Synthetic graphite powder (Timrex<sup>®</sup> KS-150) with a purity >95% and an average particle size of 180 μm was supplied by Timal Graphite & Carbon Inc., USA. Carbon black (EC-600JD) was obtained from Akzo Nobel Amides Co., Ltd., Korea. It had a purity of >99%, an aggregate size of 30–100 nm, a resistivity of 0.01–0.1 Ω cm and a BET surface area of 1250 m<sup>2</sup> g<sup>-1</sup>. Multi-walled carbon nanotubes (MWNTs, CM-95) were supplied by Hanwha Nanotech Co. Ltd.,

<sup>☆</sup> This paper is well written, with comprehensive grammar and sentence structure.

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**Table 1**  
Measured densities of materials used for volume fraction.

Materials	Density (g cm <sup>-3</sup> )
Epoxy (YSLV-80XY)	1.23
Hardener (Tamanol758)	1.2
Accelerator (TPP)	1.2
Graphite (KS-150)	2.2
Carbon black (EC-600JD)	1.73
Carbon nanotubes (CM-95)	1.72
Carbon fiber (S-231)	1.72

Korea and had a purity of >95%, a diameter of 10–15 nm, and a length of 10–20 μm. The carbon fibre (S-231) obtained from Osaka Gas Chemical Co. Ltd., Japan had a purity of >95%, a resistivity of 1 Ω cm, a length of 3 ± 0.4 mm, and a diameter of 13 μm.

### 2.1.2. Polymer resin

The powder epoxy resin (YSLV-80XY) was a bisphenol-F type and was obtained from Tohto Kasei Co., Ltd., Japan. It had an epoxide equivalent weight of 190–200 g eq<sup>-1</sup>, a density of 1.23 g cm<sup>-3</sup>, a molten viscosity of 0.1 Pa s at 150 °C, and a melting point of 78 °C. The phenol novolac hardener (TAMANOL758) was purchased from Arakawa Chemical Industries, Ltd., Japan. It had a molten viscosity of 0.25–0.35 Pa s at 150 °C, a melting point of 80–85 °C, density of 1.2 g cm<sup>-3</sup>, and an active hydrogen equivalent weight of 106 g eq<sup>-1</sup>. The accelerator (TPP: Triphenyl phosphine) was obtained from Arkema Inc., Canada. It had a density of 1.2 g cm<sup>-3</sup> and a melting point of 78.5–81.5 °C. The epoxy resin and hardener with 1% of accelerator were mixed in a ratio of 100:53 by weight.

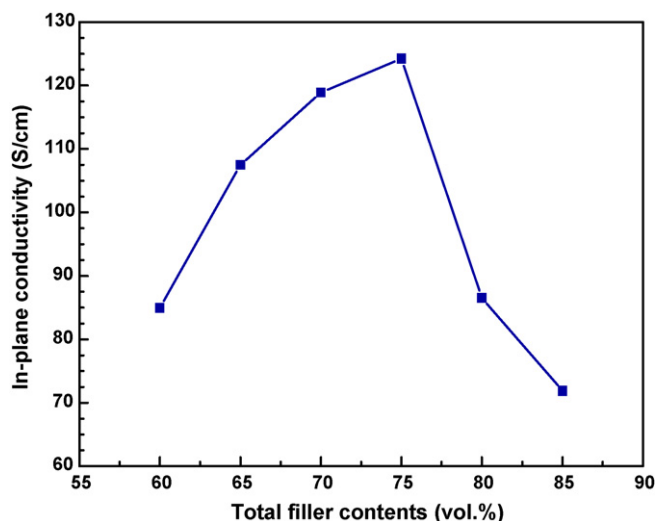
### 2.2. Preparation of composites

Since the electrical conductivity of the composites was strongly influenced by the volume of conducting filler involved in making conducting paths, the carbon fillers/epoxy composites were prepared with various volume fractions of conducting fillers and resin [12,13]. The densities of the conducting fillers were measured by a pycnometer. The measured densities are summarized in Table 1 and used to compute the volume fraction. Various volume percentages of CB, MWNTs, and CF were added to the graphite/epoxy composites to give graphite contents that ranged from 60 to 85 vol.%. The volume percentages of 2.5, 5.0, 7.5 and 10.0% of CB, 0.5, 1, 2 and 3 vol.% of MWNTs and 1, 3, 5, 7 and 9 vol.% of CF were tested to investigate the effects of the conducting fillers. The conductive fillers and powder resin were thoroughly mixed with a high speed mixer (M20, IKA, USA). The mixture was molded into composite samples of size 127 × 12.7 × 3.2 mm for measurements of the in-plane conductivity and flexural strength using a high temperature hydraulic press. The curing temperature of the composite was fixed at 190 °C, and pressure of 200 kg cm<sup>-2</sup> was maintained during the cycle.

### 2.3. Characterization of composite plates

The electrical conductivity of the composite plates was measured using the four-point probe method according to the ASTM D4496 procedure, A Keithley 6220 programmable current source was used to apply the current (10 mA) and the voltage drop was measured using a Keithley 2182A nanovoltmeter. The averaged value among 10 readings for each sample was taken as the conductivity of the composite. The resistivity ( $\rho$ ) and conductivity ( $\sigma$ ) were calculated as follows:

$$\rho = \frac{RWT}{L}, \quad \sigma = \frac{1}{\rho} = \frac{L}{RA} = \frac{L}{RWT} \quad (1)$$



**Fig. 1.** Electric conductivity of graphite/epoxy composites with various graphite contents.

where  $L$ ,  $W$  and  $T$  are the length, width and thickness of the specimen, respectively [14]. The flexural strength and modulus of the composite plate were measured by the three-point bending test on a Universal Testing Machine (STM-10, United, USA) as per ASTM standard D790. A rectangular plate with dimensions of 127 × 12.7 × 3.2 mm was used for the test. Six samples were tested under the same conditions. The punch speed for the test was kept at 1.15 mm min<sup>-1</sup> and the span length was 43.2 mm

## 3. Results and discussion

### 3.1. Effect of graphite on properties of composite plate

As shown in Fig. 1, the electrical conductivity of the graphite/epoxy composite increases with increasing graphite content in the range from 85 S cm<sup>-1</sup> (60 vol.%) to 124 S cm<sup>-1</sup> (75 vol.%), but when the graphite content exceeded 75 vol.%, the electrical conductivity decreases rapidly to 72 S cm<sup>-1</sup> (85 vol.%) with increasing graphite content. It is concluded that the amount of polymer resin is not sufficient to bind the fillers fully at graphite contents above 75 vol.%. The conducting fillers in the composite would not be kept tight enough to transfer electrons and, thus, the electrical conductivity of the composite would be decreased. Furthermore, an insufficient amount of epoxy resin might prevent full wetting of the graphite particles and induce holes in the composite. These holes would act as insulators and reduce the conductivity of the composite. The flexural strength and modulus of the composite decreases with increasing graphite content, as shown in Fig. 2(a) and (b), respectively. Because of the low aspect ratio of graphite particles, they do not act as a reinforcing material, but only as a conducting material. Increasing the loading of graphite would decrease the effective cross-sectional area of the composite and make its flexural properties weaker than those of the pure epoxy resin.

### 3.2. Effect of carbon black

The synergetic effects of the hybrid system of graphite and CB are shown in Fig. 3. By introducing CB into the graphite/epoxy system, a substantial reduction in the total filler loading required to reach the desired electrical conductivity is observed. Fig. 3 shows the electrical conductivity of the composites with various volume contents of

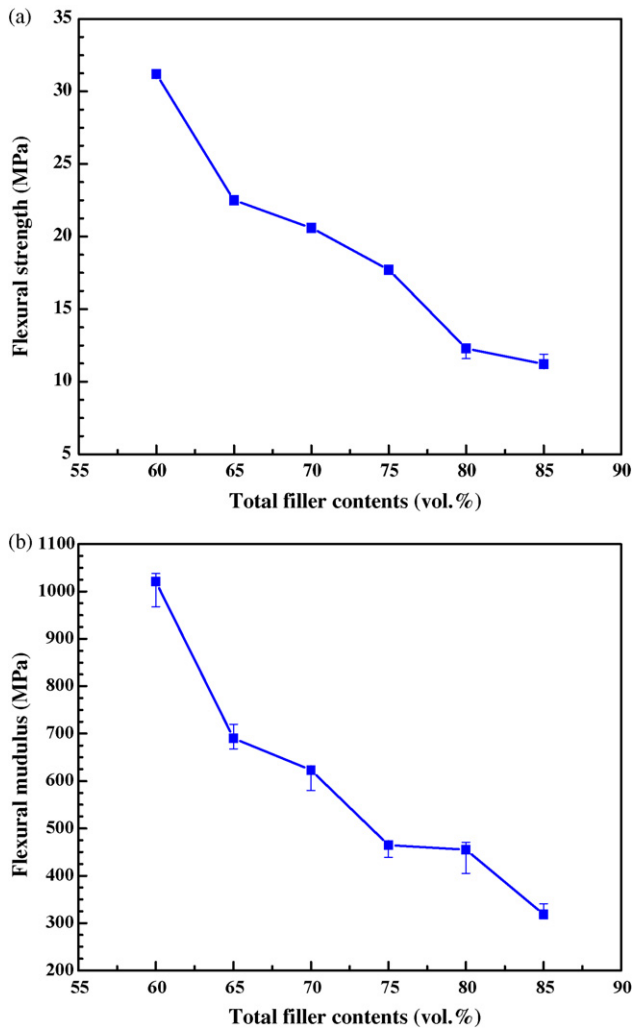


Fig. 2. Flexural (a) strength and (b) modulus of graphite/epoxy composites.

CB. When the CB contents are 2.5 and 5 vol.%, the conductivity of the composite improves with increasing CB content over the whole range of graphite contents. The comparatively small CB particles help to make conducting tunnels between the graphite particles, and thus increase the conductivity. For materials with CB contents

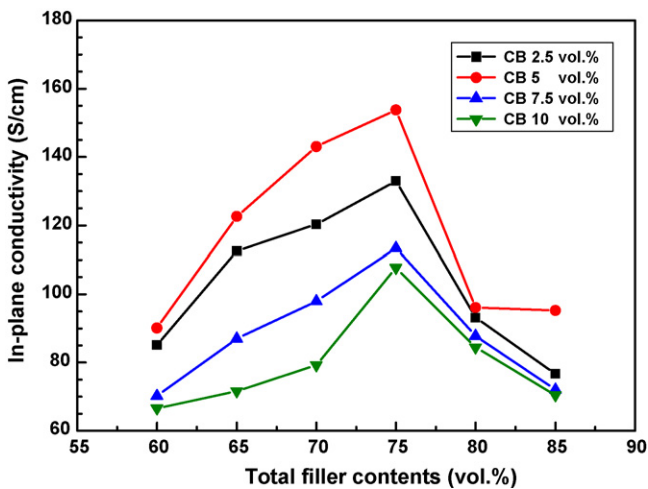


Fig. 3. Electrical conductivity of CB/graphite/epoxy composites with various CB contents.

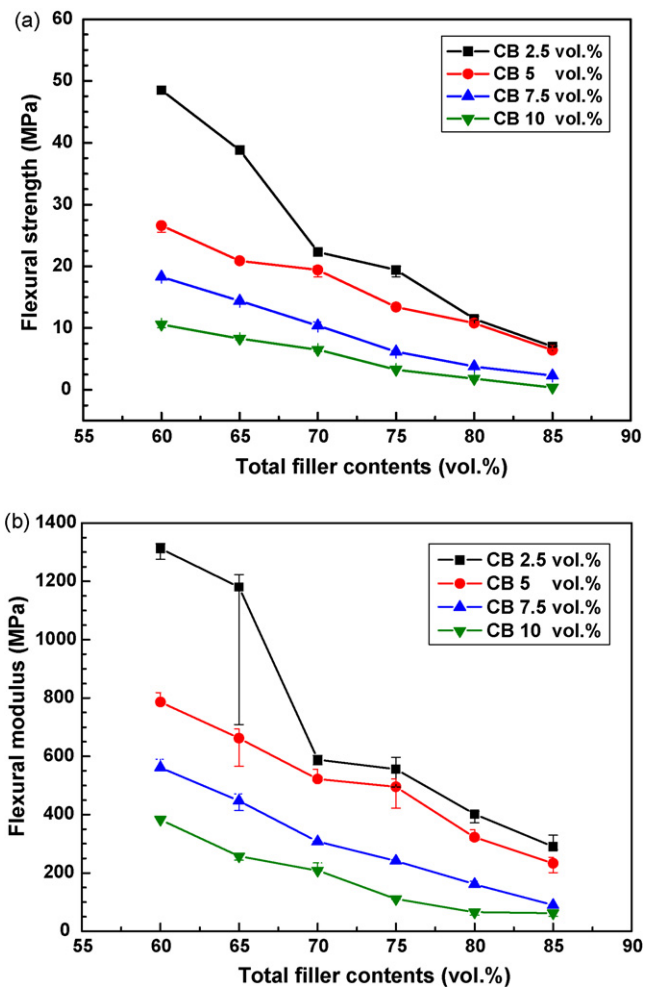


Fig. 4. Flexural (a) strength and (b) modulus of CB/graphite/epoxy composites with various CB contents.

of 7.5 and 10 vol.%, however, the electrical conductivity of the composite decreases with increasing CB loading. Above the critical CB content, the additional CB will not be wetted well with epoxy resin and will deteriorate the conductivity of the composite, because of its incomplete compaction.

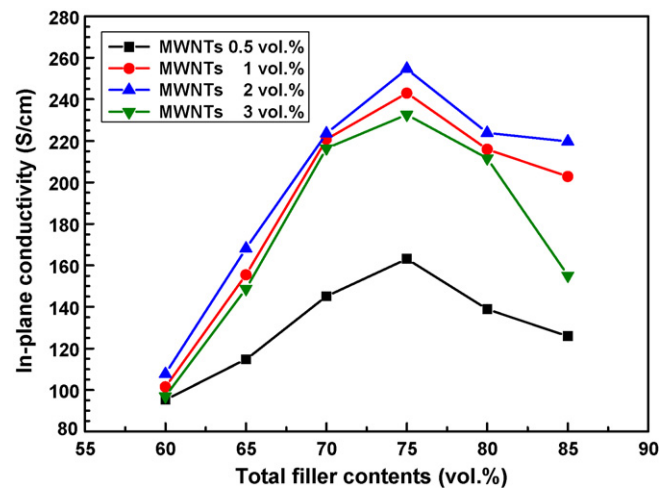


Fig. 5. Electrical conductivity of MWNTs/graphite/epoxy composites with various MWNTs contents.

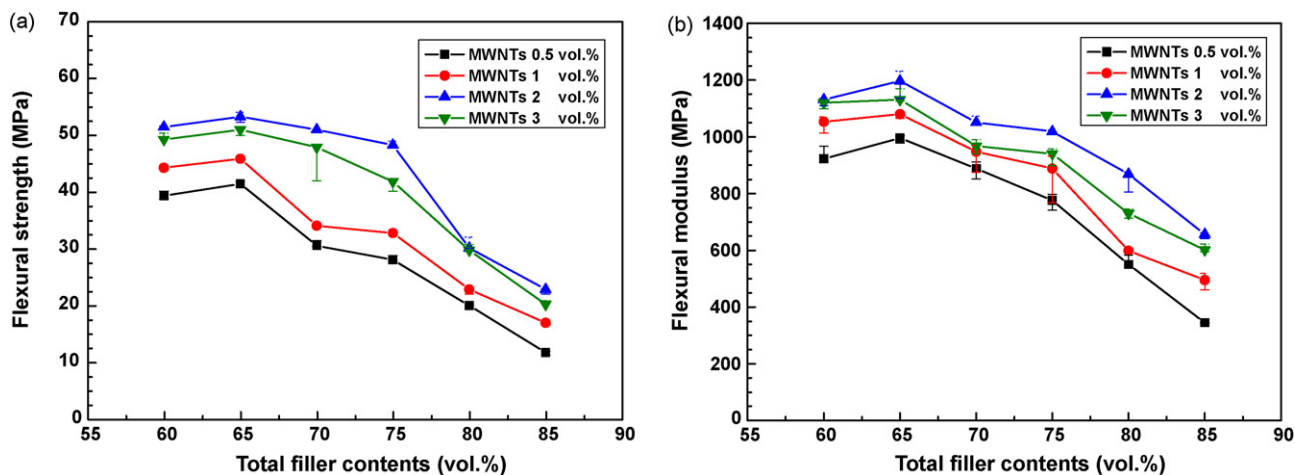


Fig. 6. Flexural (a) strength and (b) modulus of MWNTs/graphite/epoxy composites with various MWNTs contents.

When the CB content is 5 vol.%, the highest electrical conductivity of the CB/graphite/epoxy composite plate is observed, viz.  $153.8 \text{ S cm}^{-1}$ . This result indicates that an increase in the conductivity of the graphite/epoxy composite of about 24% is obtained at a total filler content of 75 vol.%. The flexural strength and modulus of the CB/graphite/epoxy composite plate is presented in Fig. 4. Compared with of the graphite/epoxy composite, the composite with 2.5 vol.% of CB has approximately 43% greater flexural strength. The flexural properties of the CB/graphite/epoxy composite decreases with increasing CB content. Since the CB and graphite particles are spherical or platelet shaped with almost the same dimensions in the planar direction, they do not act as reinforcing materials and cause a decrease in the effective cross-section area.

### 3.3. Effect of MWNTs

The effects of the addition of MWNTs to the graphite/epoxy composite on its flexural properties and electrical conductivity were studied. As shown in Fig. 5, the electrical conductivity of the composite rapidly increases with increasing MWNT content up to 2 vol.%, but then decreases as more MWNT is added. Among the tested samples, the composite with 2 vol.% of MWNTs has the highest electrical conductivity of  $254.7 \text{ S cm}^{-1}$ , which is 105% higher than that of the graphite/epoxy composite with the same amount of conducting filler. Compared with the CB/graphite/epoxy composite, a greater enhancement of the electrical conductivity is observed with the MWNTs/graphite/epoxy composite. Unlike the CB filler, MWNTs have a high aspect ratio with a very small diameter and

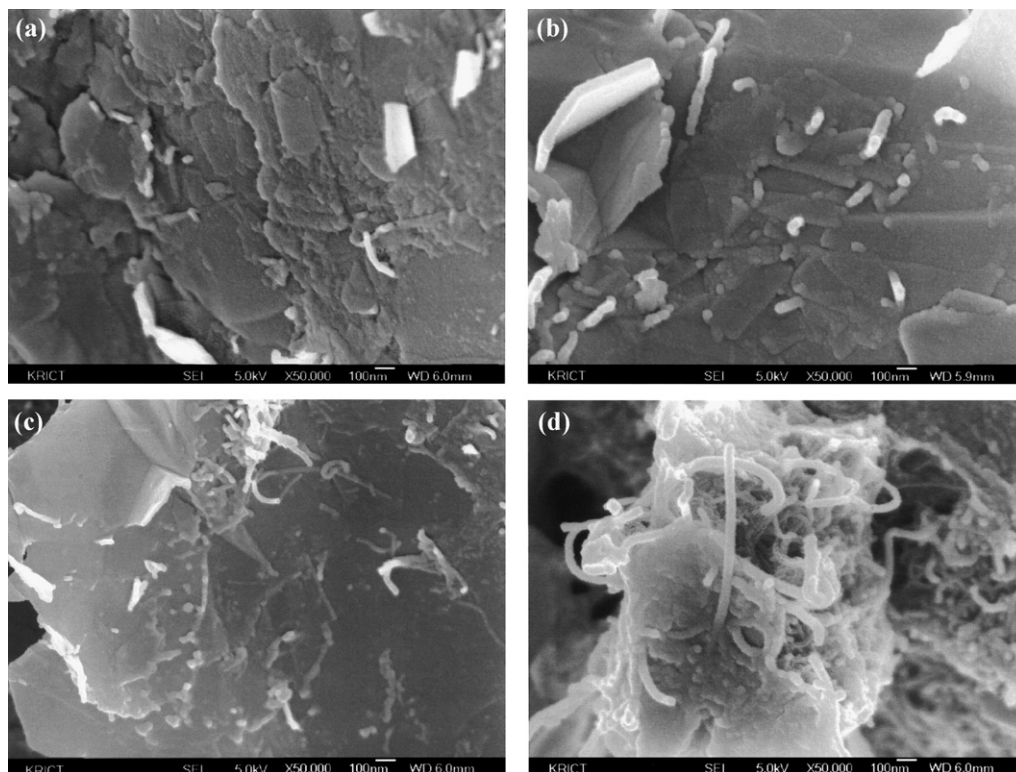


Fig. 7. Scanning electron micrographs of fractured surfaces of MWNTs/graphite/epoxy composites with contents (in vol.%) of (a) 0.5/59.5/40, (b) 1/59/40, (c) 2/58/40, and (d) 3/57/40, respectively.

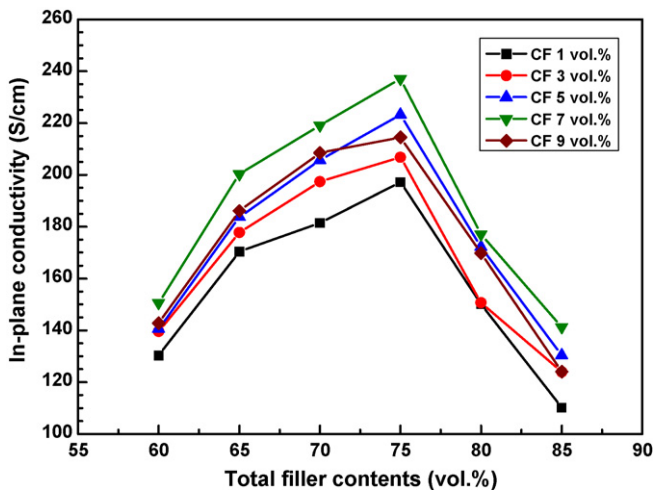


Fig. 8. Electrical conductivity of CF/graphite/epoxy composite with various CF contents.

this enables the MWNTs to make conducting channels between the graphite particles and act as a reinforcing material, thus enhancing the electrical conductivity and flexural properties of the composite. The flexural strength and modulus of the MWNTs/graphite/epoxy composite plate are shown in Fig. 6. A percolation threshold in

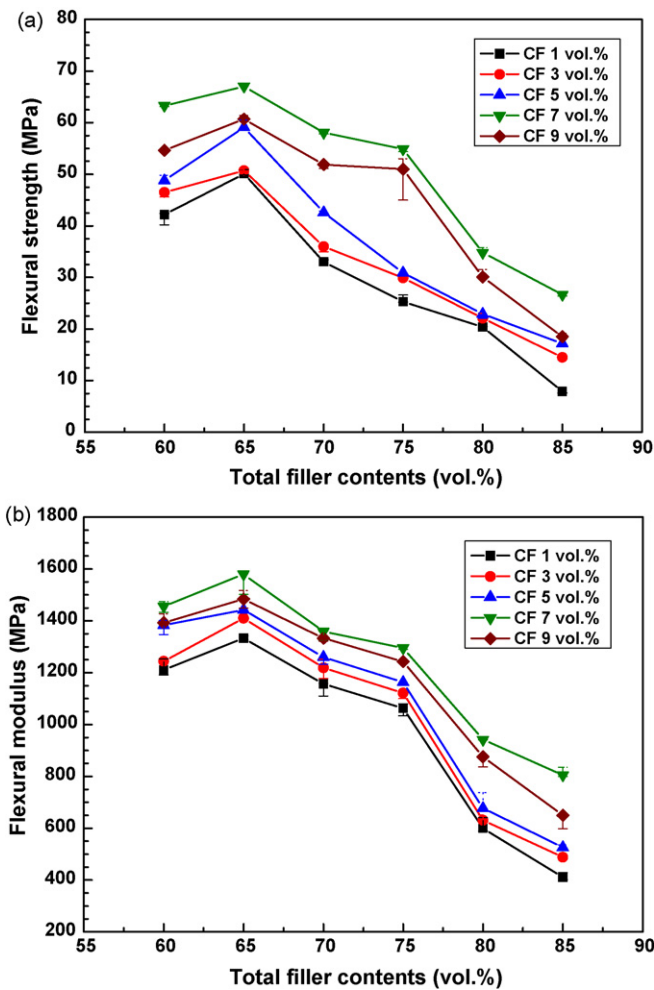


Fig. 9. Flexural (a) strength and (b) modulus of CF/graphite/epoxy composites with various CF contents.

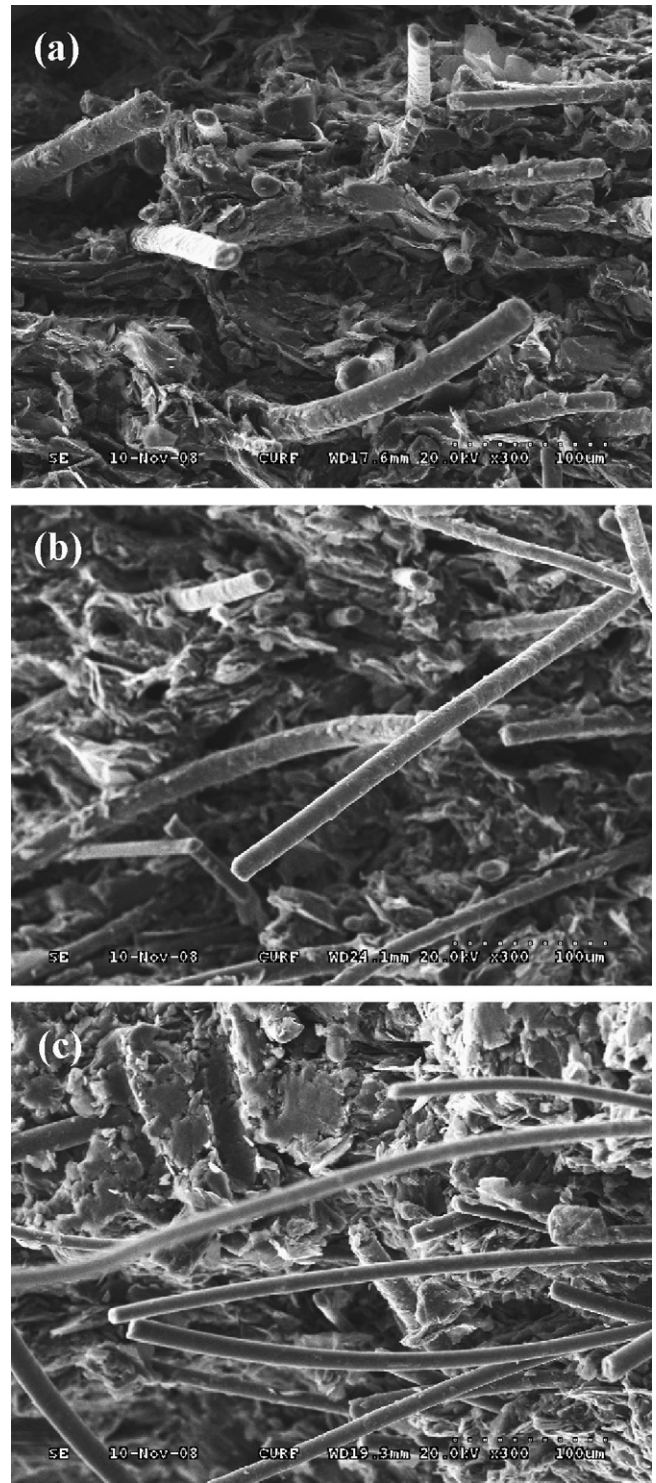


Fig. 10. Scanning electron micrographs of fractured surfaces of CF (5 vol.%) / graphite / epoxy composites for various graphite contents of (a) 60 vol.%, (b) 70 vol.%, and (c) 80 vol.%.

the electrical conductivity between 0.5 and 1 vol.% of MWNTs is observed in the composite. The flexural strength and modulus show a similar trend to that of the electrical conductivity. The flexural properties increases with increasing MWNT content up to 2 vol.% and decreases as the MWNT content is further increased. Different effects are observed for the MWNT/graphite/epoxy composite compared with the CB/graphite/epoxy composite. With increasing total filler content, the flexural properties initially tend to increase

slightly up to 65 vol.% content and, above this critical content, the flexural properties decrease slowly compared with those of the CB/graphite/epoxy composite. With only 2 vol.% of MWNTs, an 83% enhancement of the flexural strength is observed compared with that of the graphite/epoxy composite. In order to obtain higher electrical conductivity, the content of conducting fillers needs to be increased. In the case of CB and graphite, the flexural strength and modulus abruptly decreases with increasing filler content. In the case of MWNTs, however, the flexural properties do not decrease very much in the feasible range (up to 75 vol.%) and even slightly increases initially, along with a large enhancement in electrical conductivity.

The high aspect ratio and high strength of the MWNTs, as well as the good interfacial adhesion between the MWNTs and the matrix, also contribute to the enhancement of the flexural properties. On the other hand, the decrease in the strength with a high MWNT content can be attributed to the following effect. First, the dispersion of MWNTs is not good in the higher loading systems [15]. Second, due to a lack of resin to bind the fillers, incomplete packing occurs during the fabrication process and, thus, the fillers act as insulators and defects in the structure [16].

Scanning electron micrographs of the MWNTs/graphite/epoxy composites are given in Fig. 7. At 0.5 and 1.0 vol.% the MWNTs are reasonably well dispersed over the whole area and even between the graphite particles, but aggregated MWNTs are observed in the composites with higher MWNT contents of 2 and 3 vol.%. With increasing content of MWNTs, more aggregated MWNTs are observed. This aggregation is held responsible for the decrease in the electrical conductivity and flexural properties of the composites.

### 3.4. Effect of carbon fibre

The electrical conductivity of the CF/graphite/epoxy composite is shown in Fig. 8. The behaviour of the conductivity is similar to that of the MWNTs/graphite/epoxy composite. The electrical conductivity increases with increasing carbon fibre content up to 7 vol.% and then decreases with further increase in carbon fibre content. The flexural properties of the composites also increases with increasing CF content, as shown in Fig. 9. The flexural properties of the CF composite show similar trends to those of the MWNTs composite. Since MWNTs and CF are fibrous and have a high aspect ratio, they act as reinforcing materials and thus enhance the flexural properties as well as the electrical properties. The enhancement of the electrical conductivity of the CF/graphite/epoxy composite is lower than that of the MWNTs/graphite/epoxy composite, but the electrical conductivity continues to increase up to a high CF content of 7 vol.% (2 vol.% for MWNTs). The decreasing slope in the flexural properties of the CF/graphite/epoxy composite after the threshold point is steeper than that of the MWNTs composite. The highest flexural strength of the CF/graphite/epoxy composite of 6.7 MPa is observed at a CF content of 7 vol.% and is a 98% enhancement compared with that of the graphite/epoxy composite.

Fracture surfaces of the CF/graphite/epoxy composite are shown in Fig. 10 for various graphite contents with the same CF content. As the graphite content is increased, more pulled out fibres than broken fibres are observed. This indicates that there is incomplete bonding between the fibres and resin, thus making the former easy to pull out. This explains the decreasing trend in the flexural properties of the composites with high filler loadings. Fracture surfaces of the composites for various CF contents with the same total filler content are presented in Fig. 11. In the case of materials having the same total volume percent of fillers, the higher CF content composite has more pulled out fibres. This also indicates that achieving complete bonding with the resin is more difficult with CF fibres than with graphite particles.

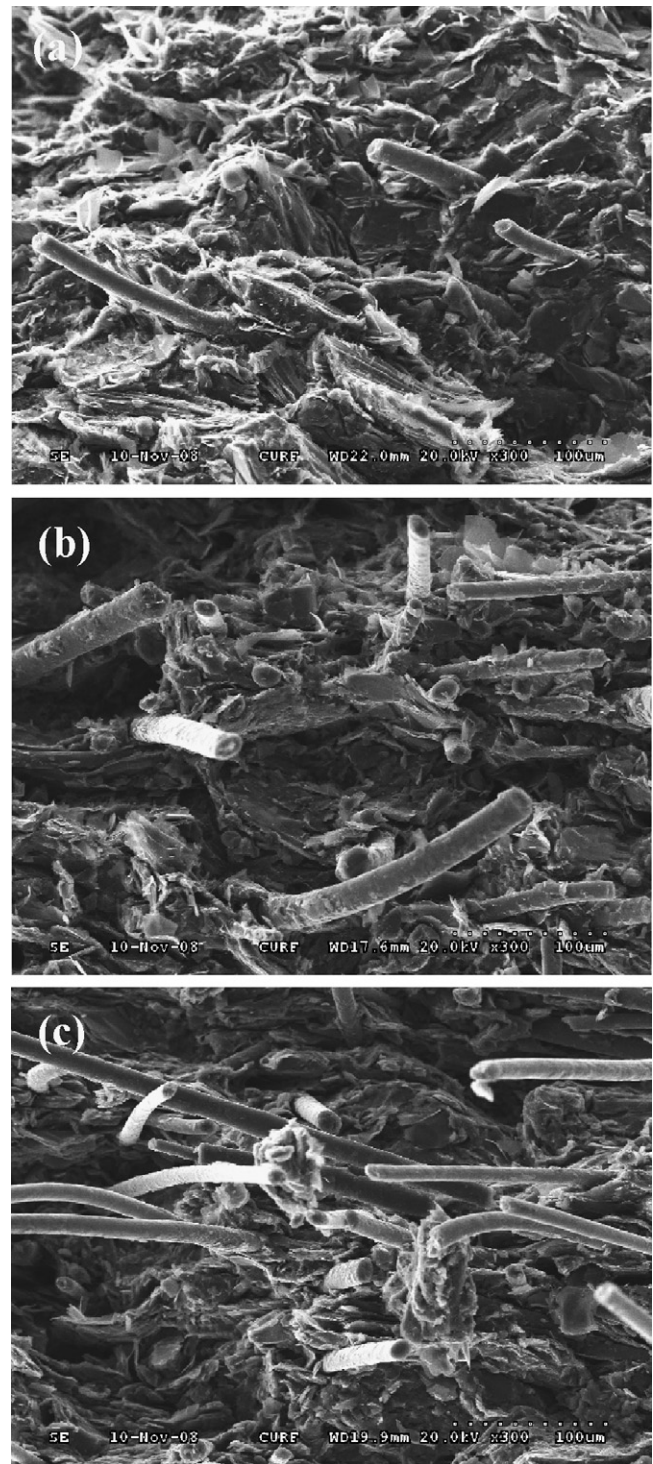


Fig. 11. Scanning electron micrographs of fractured surfaces of CF/graphite/epoxy composites with contents (in vol.%) of (a) 1/64/35, (b) 5/60/35, and (c) 9/56/35, respectively.

## 4. Conclusions

Composite materials with different types of conductive carbon filler have been fabricated by means of a compression moulding method. The properties of the composites that are particularly important for their use in bipolar plates are characterized, that is, their electrical and flexural properties. In general, when fibrous conducting fillers such as MWNTs and CF are added, both the elec-

trical conductivity and flexural properties increases initially up to a certain content with increasing content of the fillers. However, when particulate fillers such as CB and graphite are used, the electrical conductivity increases, but the flexural properties deteriorate with increasing filler content up to a certain content. Therefore, a hybrid system that is composed of fibrous and particulate fillers can be used to enhance both the electrical and flexural properties. The electrical conductivity continues to increase up to a filler content of 75 vol.%, and the flexural properties tend to decrease above a filler content of 65 vol.%, even with the fibrous fillers. A maximum value of the electrical conductivity of  $254.7 \text{ S cm}^{-1}$  is observed in a composite composed of 73 vol.% of graphite, 2 vol.% of MWNTs and 25 vol.% of epoxy resin. With the incorporation of a small amount of MWNTs, the electrical conductivity (about 105%) and flexural properties (about 173%) of the composites are greatly improved compared with those of the graphite/epoxy composites.

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