

Fabrication of Electrically Conductive Polymer Composites for Bipolar Plate by Two-Step Compression Molding Technique

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ABSTRACT: Electrically conductive polymer composites for bipolar plate were fabricated by two-step compression molding technique. Raw materials consisted of natural graphite flakes (G), expanded graphite (EG), carbon black (CB), and phenol resin (PF). The G/EG/CB/PF composites were first compressed at a temperature lower than curing point (100°C) and then cured at a high temperature above curing point (150°C) and high pressure (10 MPa). Results showed that G and EG are oriented in the direction parallel to the composite plate surface. CB is dispersed not only in the phenol resin matrix but also in the packing and porous space of G and EG. The addition of EG and CB significantly increases number of the electrical channels and thus enhances the electrical conductivity of the composite. Under optimal conditions, electrical conductivity and flexural strength of the composite were 2.80×10^4 S/m and 55 MPa, respectively, suggesting that the bipolar plates prepared by two-step compression molding technique are adequate to meet the requirement of proton exchange membrane fuel cells. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2296–2302, 2013

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INTRODUCTION

The proton exchange membrane fuel cells (PEMFC) have drawn a lot of attentions as alternative sources of energy due to their high energy density, high energy conversion efficiency, and low environmental pollution. The role of bipolar plates in PEM fuel cells is to distribute reactants gas uniformly over the active areas, collection of electrons, connection of two adjacent cells, removal of heat from adjacent cells, and preventing leakage of fuel gasses and coolant. They account for 60–70% of the weight and 40–50% of total cost in a fuel cell. Therefore, reducing weight and manufacturing cost of bipolar plates is of important significance for the commercialization of fuel cells.

In recent years, carbon/polymer resin composites are getting more attention in the development of bipolar plates for fuel cells.^{1–10} Their anti-corrosive properties and mechanical strength are respectively better than those of metal bipolar plates¹¹ and graphite bipolar plates¹² and give possibility of manufacturing more lightweight and low-cost bipolar plates. However, it is difficult to simultaneously satisfy electrical conductivity and mechanical strength requirements in bipolar plates. According to the function of bipolar plates, the raw material must have high mechanical strength, high electrical conductivity, low contact resistance, high thermal conductivity, uniform cooling channel,

and high corrosion resistance. A lot of researches have been done on the improvement of electrical conductivity and mechanical properties of carbon/phenol resin composite. By using several kinds of carbon materials, Yin et al.⁵ and Kakati and Mohan¹ simultaneously improved electrical conductivity and mechanical strength of the composite through curing temperature–time operation. Grundler et al.¹⁰ developed new compound materials with improved properties by mixing graphite and carbon black with CNT. Shen et al.¹³ tried to improve the characteristics of composites by mixing different size and different kind of fillers. Other bipolar plates have also been made using expanded graphite.¹⁴ Besides, there are studies on the injection molding¹⁰ and two-step molding technique, where good productivity and low cost¹⁵ bipolar plates has been produced. Currently, several kinds of carbon materials are being used for improvement of electric conductivity and mechanical strength of composite plates, however, research on the fabrication of several kinds of carbon filler based-composite plates using two-step compression molding technique, especially, on the design of composite molding has not been reported.

In this article, we present the fabrication of low-cost composite bipolar plates made of natural graphite flakes (G), expanded graphite (EG), and carbon black (CB) as electrical conductivity

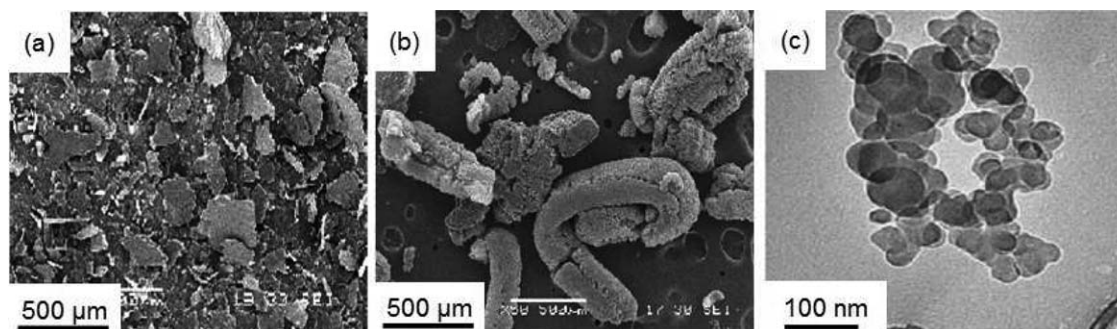


Figure 1. SEM and TEM micrographs of conductive fillers: (a) natural graphite (b) expanded graphite and (c) carbon black.

fillers and with Novlak-type phenolic resin as polymer matrix by using two-step compression molding technique.

EXPERIMENTAL

Raw Materials

A thermosetting Novlak phenolic resin powder (with an average size of $75\ \mu\text{m}$) composed of hexamethylenetetramine was supplied by Institute of Applied Chemistry, Shanghai. It cures within a short time and exhibits good chemical stability and high mechanical strength. Figure 1 shows SEM micrograph of electrical conductive filler used in the present experiment. The natural graphite supplied by Yifan Graphite Co. is in flake form with different particle sizes (75 , 150 , and $500\ \mu\text{m}$). The worm-like, highly porous expanded graphite was prepared by expanding the intercalated compound (provided by Yifan Graphite Co.) by thermal shock in the presence of concentrated nitric and sulfuric acid. It has V-shaped pores and the expanded volume is in the range of 238 – $242\ \text{mL/g}$. The density of natural graphite and the intercalated graphite is $2.2\ \text{g/cm}^3$. Particle size, density, and specific surface area of carbon black (XPB348, Degussa) are $45\ \text{nm}$, $1.8\ \text{g/cm}^3$, and $41\ \text{m}^2/\text{g}$, respectively.

Sample Preparation and Characterization

Electrically conductive fillers and phenol resin powder (Table I and III) were ball-milled for 2 h to obtain a uniform mixture, and were then poured into a mould at room temperature. Hot pressing was carried out in two steps, first pre-forming at a low temperature above the flow point (75°C) and lower than curing point (147°C) of the phenol resin and then compression at a high temperature (150°C) to obtain cured products.

The electrical conductivity of the composite plate was measured by a four-point probe technique. Samples were cut into specimens

Table I. Ingredients of the Composite Plates

No.	G-500 ^a (wt %)	G-75 ^a (wt %)	EG (wt %)	CB (wt %)	PF (wt %)
1	80				20
2		80			20
3	42	28	10		20
4	42	28		10	20

^aG-500 and G-75 indicate that the particle sizes of the graphite are 500 and $75\ \mu\text{m}$, respectively.

with a size of $80\ \text{mm} \times 12\ \text{mm} \times 2\ \text{mm}$ and painted with a conductive silver paste as electrodes. Keithley 6487 picoammeter and PZ158 DC digital voltmeter were employed to measure the sample's electrical properties under a DC power supply. The flexural strength of specimens was determined by the three-point bending test using a universal tester (SANS CMT-4000, New Sansi Group). The testing speed was $2\ \text{mm/min}$. The density of the composite plate was measured according to Archimedes law.

Morphology of the conductive filler and composites was observed via scanning electron microscope (SEM; JSM-6360, JEOL) at an accelerating voltage of $15\ \text{kV}$. Some specimens were fractured in liquid nitrogen.

RESULTS AND DISCUSSION

Analysis on Two-Step Compression Molding Process

Pre-Forming Process. In the pre-forming process, the phenol resin powder was liquefied to facilitate the dispersion and permeation of the conductive fillers. It might also be effective for easily orienting the conductive filling particles in the direction of the compression. During this process, the properties of composite bipolar plates are mainly influenced by molding pressure, temperature and time. Table I and Figure 2 show the composition of the mixtures and the variation of properties of composite plates with pre-forming pressure, respectively. (The main-forming temperature, pressure, and time were 150°C , $10\ \text{MPa}$, and $5\ \text{min}$, respectively.) For natural graphite filled phenol resin (No. 1 and 2), electrical conductivities of composites increase with increase in molding pressure up to $8\ \text{MPa}$. Dependence of electrical conductivity on molding pressure is more noticeable than the effect of particle size. This should be related to the high molding pressure induced orientation of graphite flakes. Molten phenol resin flows under pressure, while graphite flakes are oriented in the direction of compression. At this time, contact between graphite particles increase. Therefore, the larger size of filler particles and the higher pre-forming pressure contribute to more contact between graphite particles which results to better electrical conductivity of composite plate. However, when expanded graphite is added (No. 3), electrical conductivity decreases with pressure up to $4\ \text{MPa}$. Further increase in pressure leads to increase in electrical conductivity.

Electrical conductivity is maximum at $2\ \text{MPa}$ pressure due to high order porous structure of expanded graphite. When pressure is low, expanded graphite keeps its high ordered structure

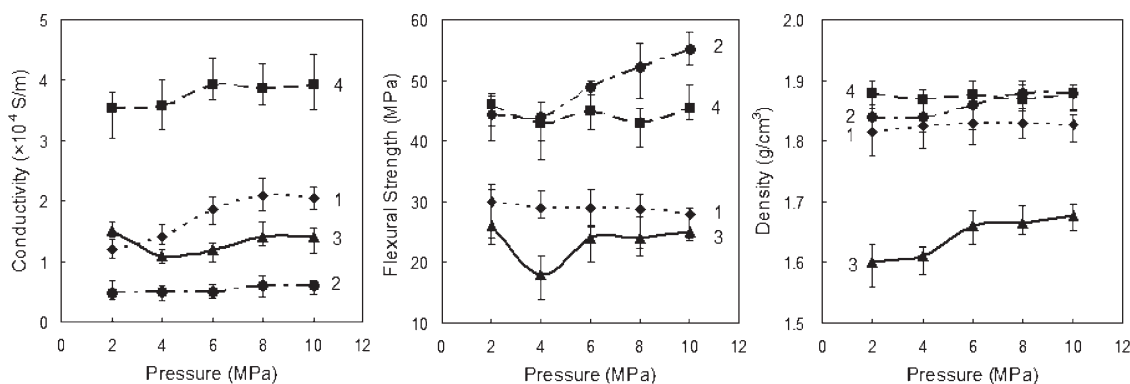


Figure 2. Variation of composite plate properties with pre-forming pressure for samples No. 1, 2, 3, and 4 as listed in Table I (compression temperature 80°C for 5 min).

and forms networks between electrical conductive filling particles. The network increases electrical channels and electrical conductivity. When pressure is applied, the high order structure of expanded graphite is easily destroyed, and hence the network between filling particles is constrained and electrical conductivity decreases. When the pressure is further increased, the porous structure becomes closed. The porosity is however regained slowly and the electrical conductivity tends to increase again.

Addition of both natural graphite and carbon black in the phenol resin for sample in No. 4, electrical conductivity increases with pressure to a maximum at around 6 MPa pressure. This is comparable with results for sample No. 1 and 2 and shows that carbon black does not affect the contact orientation, because its particles are spherical. Increase of electrical conductivity due to pressure is as a result of the contact orientation of natural graphite.

When natural graphite is used as filler material, the flexural strength slowly decreases with pressure for $500\ \mu\text{m}$ size of particles (relatively large), but increases for $75\ \mu\text{m}$ size of particles (relatively small). On the overall, the flexural strength of composite with large particles is lower than that with small particles.

Flexural strength is related to particle size in composite plate, filler materials, and binding power of resin matrix. In the case of large graphite flakes, which are oriented in the direction of compression, the contact area between particles is high, but the binding area between graphite particle and resin is low. This is main reason that the flexural strength of composite decreases with pressure.

When the particle size is $75\ \mu\text{m}$ (relatively small), flexural strength increases with pressure and the composite has greater strength than when large particles ($500\ \mu\text{m}$) are used. This might be ascribed to the smaller particles which have relatively large surface area and thus totally increase the binding area between filling particles and resin. When a mixture of natural graphite and expanded graphite is used as filler material, flexural strength decreases with increase in pressure. This is due to the change of high order porous structure of expanded graphite with increase in pressure. Under low pressure, expanded graphite keeps its high order porous structure and high surface area and therefore the binding area between expanded graphite and resin is high, hence high flexural strength of composite plates. When pressure is further increased the porous structures of expanded graphite is closed and the flexural strength of composite plates is enhanced. For sample No. 4 where carbon black was added, flexural strength is independent of pressure because of its high surface area and spherical shape. The densities of composite plates increased with pressure in all combinations of raw materials. From the experiments above, it was noted that the optimum processing pressure is 2 MPa initially and then at 8 MPa.

To investigate the effect of pre-forming temperature and time, the experiments were carried out at a pre-forming pressure of 2 MPa and then 8 MPa while the main forming conditions were maintained at 150°C , 10 MPa, and 5 min. According to DSC analysis, the melting range of phenol was $80\text{--}100^\circ\text{C}$. These two temperature extremes were used for the analysis below. Figure 3 shows the effect of pre-forming temperature and compression

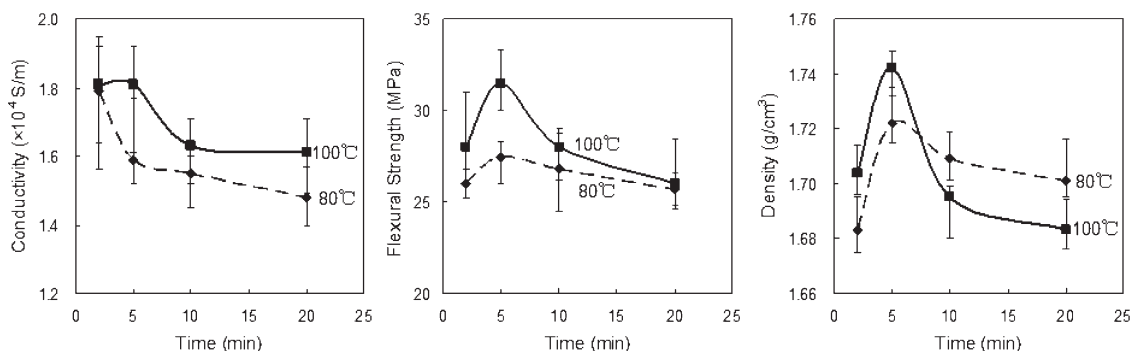


Figure 3. Variation of composite plate properties with pre-forming temperature and time for sample No. 3 (G-500/G-75/EG/PF = 42/28/10/20) as listed in Table I (compression at 2 MPa for 5 min then at 8 MPa for 1 min).

Table II. Variation of Composite Plate Properties with Change in Compression Time During the Main Forming Process for G-500/G-75/EG/PF with a Mass Ratio of 42/28/10/20

Time (min)	Electrical conductivity ($\times 10^4$ S/m)	Flexural strength (MPa)	Density (g/cm^3)
2	1.60	28	1.72
5	1.77	31.4	1.72
10	1.70	30	1.73
30	1.58	26.3	1.72

time on properties of composite plate. The electrical conductivity of composite plate decreases with increasing in compression time. Flexural strength and density initially increase, and then decrease having a maximum value at compression time of 5 min. Phenol resin melts at 80°C, and begins to cure at 100°C. When compression time is too short and temperature too low, the permeation of phenol resin in to porous structure of expanded graphite is difficult. However, when compression time is too long and temperature is too high, phenol resin begin to cure. Therefore, it loses fluidity and the permeation in to porous structure of expanded graphite becomes difficult. From the results of experiment, it can be seen that when compression time is very short or very long, insufficient permeation of phenol resin occur, pores form on composite plate, and flexural strength and density decrease. Thus, optimum pre-forming temperature and time are 100°C and 5 min, respectively.

Main-Forming Process. Main-forming process is a curing process after pre-forming. In the following experiments, the plates were preformed at 100°C under a pressure of 2 MPa for 5 min first, and then 8 MPa for 1 min again. The usual curing temperature of phenol resin is 150°C at a pressure of 10 MPa. The variations of electrical properties, flexural strength, and density with change in compression time during the main forming process are shown in Table II. Density is observed to be independent of the compression time but electrical conductivity and flexural strength have a maximum after compressing for 5 min.

This shows that compressing for 2 min, results to insufficiently curing and thus, electrical conductivities and flexural strengths are low. Hence the optimum compression time during the main forming process is 5 min when the resin has cured sufficiently.

Fabrication of G/EG/CB Composite Plate

The properties of the composite plates were further investigated by varying the composition of the filler material. The two-step compression molding technique was used and the total filler load was 80 wt % in all the plates. The changes in electrical properties, flexural strength, and density with different filler loadings are shown in Table III. It can be seen that the use of a combination of all the three carbon materials as filler results to plates with high electrical conductivity and high flexural strength. This is because of the higher conductivity of carbon black. Also, carbon black with nano-scale size is able to permeate into the porous structure of expanded graphite, filling up the pores as well as restraining the closure of the porous structure. Hence, the surface area and the binding area between the graphite and the resin increase. The flexural strength is lowest for a combination of natural graphite and expanded graphite (G/EG/PF) where formation of pores is evident. A combination of natural graphite and carbon black (G/CB/PF) gives high flexural strength but still lower than G/EG/CB/PF combination.

With increase of EG ratio in the combination of the filler material, defects occur at the surface of the plates (Figure 4) due to the high surface area of the expanded graphite, difficult in attaining uniform distribution in the resin and insufficiency of the resin.

It can further be seen from Table III that flexural strength increases with increase in the size of the main filler materials, natural graphite. When a 1 : 1 ratio of natural graphite of size 75 and 150 μm is used as the main filler material (G*), the composite plates obtained have a relatively high flexural strength and the lowest density compared to plates made from all other combination of the filler materials.

For application of bipolar plate as fuel cell, high electrical conductivity, high flexural strength, and low density is desirable. Therefore, the G*/EG/CB/PF composite with which consists of

Table III. Variation of Composite Plate Properties with Composition of Raw Materials Under Optimum Performing and Main Forming Conditions

Compositions of raw materials (wt %)	Electrical conductivity ($\times 10^4$ S/m)	Flexural strength (MPa)	Density (g/cm^3)	
G-75/EG/CB/PF	52.5/7.5/20/20	1.87	49	1.76
	72.5/7.5/0/20	0.79	36	1.75
	60/0/20/20	1.35	47	1.77
	80/0/0/20	0.56	56	1.88
G-150/EG/CB/PF	52.5/7.5/20/20	2.78	47	1.77
	72.5/7.5/0/20	0.88	35	1.80
	60/0/20/20	2.09	45	1.81
	80/0/0/20	0.74	51	1.85
G-500/EG/CB/PF	52.5/7.5/20/20	8.23	33	1.76
	72.5/7.5/0/20	2.83	25	1.82
	80/0/0/20	2.06	30	1.83
G*/EG/CB/PF	52.5/7.5/20/20	2.69	48	1.73

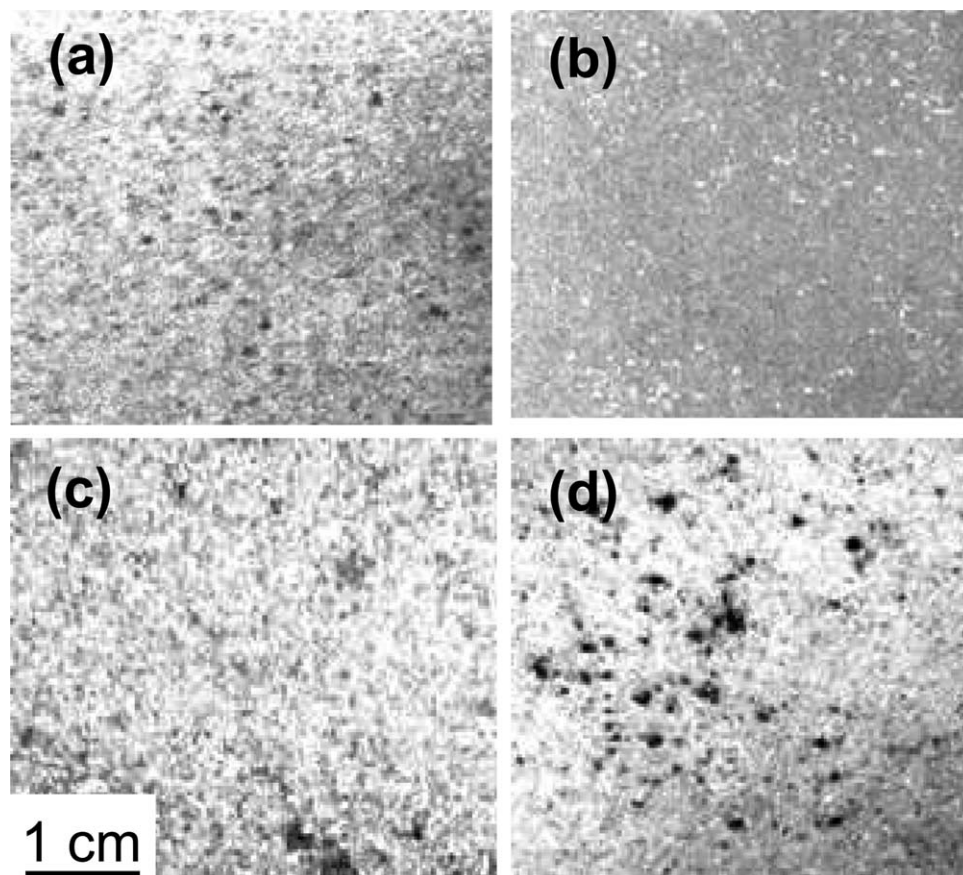


Figure 4. Influence of EG ratio on surface of composite plate (a: EG 5 wt %, b: EG 8 wt %, c: EG 10 wt %, d: EG 12.5 wt %).

natural graphite of 75 and 150 μm in the ratio 1 : 1 as main filler and with expanded graphite and carbon black as aid filler is the most suitable.

In order to determine the optimum amount of EG in the G*/EG/CB mixture, the amount of CB was fixed at 20 wt % while that of EG was varied from 5 wt % to 12.5 wt %. Figure 5 shows the variation of the composite plate properties with change in amounts of EG in the mixture. It can be seen that electrical conductivity, flexural strength, and density increase with increase in amounts of EG to a maximum at 8 wt % EG. When amount of EG is either 5 wt % or 10 wt %, pores are formed on the surface of the composite plates. However, no pores were observed when the amount of EG

is 8 wt %. This is due to the permeation of carbon black into porous structure of expanded graphite, and the change in surface area. When composite plate is fabricated using a combination of natural graphite, expanded graphite and carbon black, the nano-sized CB particles permeate into the pores of micro-size expanded graphite and these together with the blank pores are compressed and closed under high temperature and high pressure. Thus, the whole surface area decreases resulting to adequate binding between filler and resin and does not form pores on the surface of composite. If amount of expanded graphite is too little, excess carbon black exists because uniform mixing is difficult and lots of pores are formed on the surface of plates. If amount of expanded

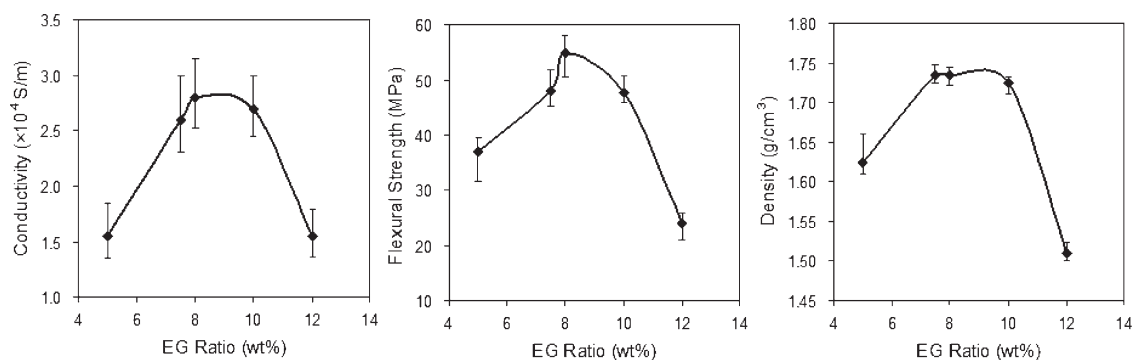


Figure 5. Variation of composite plate properties with EG content in G*/EG/CB/PF (CB and PF were fixed at 20 wt %, respectively).

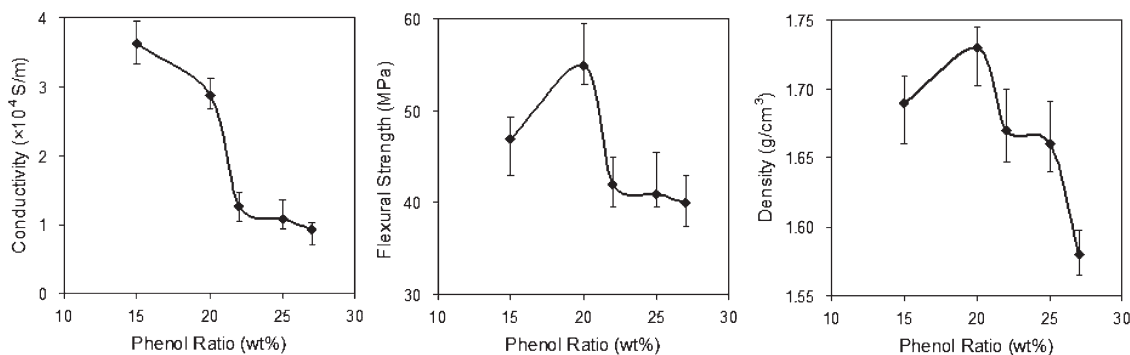


Figure 6. Variation of composite plate properties with amount of phenol in the mixture G*/EG/CB/PF (G*/EG/CB was fixed at 52/8/20).

graphite is too much, pores are also formed on the surface of composite plate owing to the high surface area of expanded graphite itself. Therefore, the optimum EG ratio is 8 wt %.

Figure 6 shows the variation of composite plate properties with change in the amount of phenol resin. Generally, with increasing the PF content, the conductivity, flexural strength, and density of composites decrease. It can be observed that above 25 wt %, the electrical conductivity does not satisfy the requirement of a bipolar plate. However, the amount is less than 20 wt %, the resin is insufficient and very few bonds are formed between the filler and the resin; hence, gaps are formed resulting to low densities and low flexural strength. It therefore shows that the most appropriate amount of phenol resin is 20 wt %.

Figure 7 shows SEM micrograph of G*/EG/CB/PF (52.5/7.5/20/20) composite plate. It can be seen that when hot-pressure is applied, natural graphite and expanded graphite are oriented in direction parallel to the surface of composite plate by fluiding of resin matrix. On the other hand, carbon black is dispersed in the phenol resin and covers the filling spaces between natural graphite and expanded graphite and the pores of expanded graphite itself. This indicates that carbon black is permeated into the gaps between fillers and the pores of expanded graphite and thus increases the electrical networks between natural graphite–natural graphite, expanded graphite–expanded graphite, natural graphite–expanded graphite, and expanded layer of expanded graphite. The well dispersion of filler increases the binding area

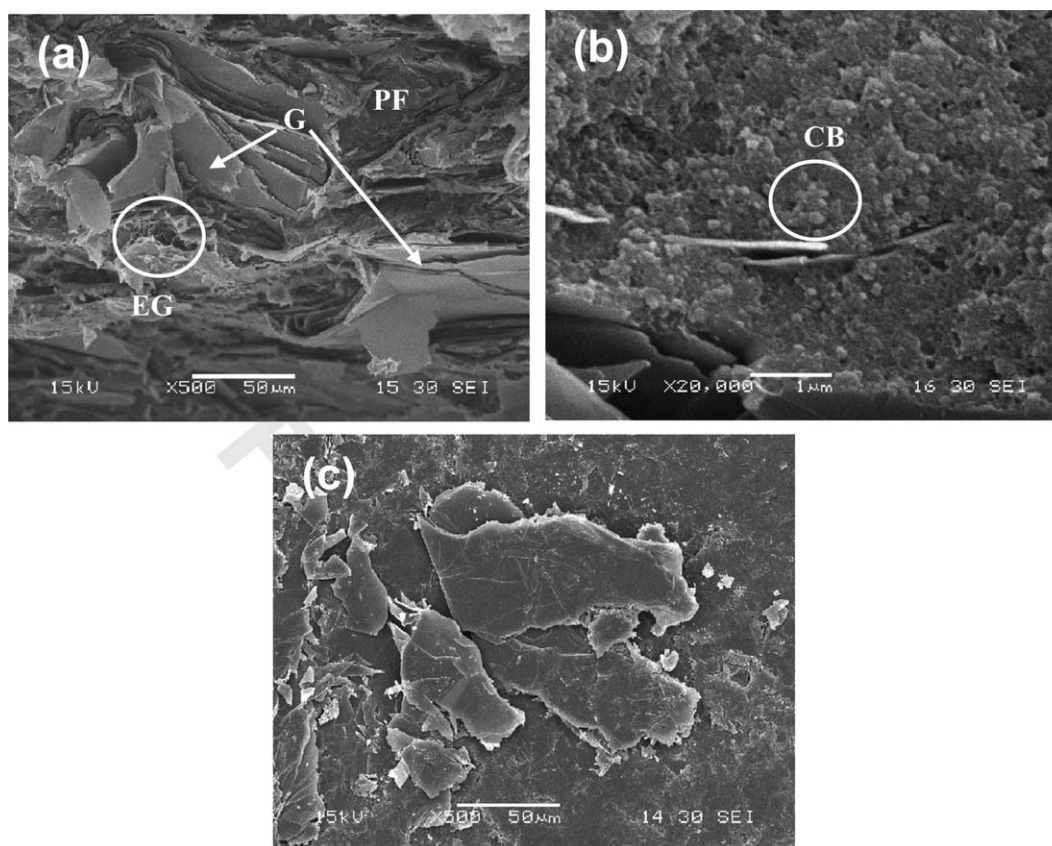


Figure 7. SEM micrograph of G*/EG/CB/PF (52.5/7.5/20/20) composite plate: (a) fracture (500 \times), (b) fracture (20,000 \times), and (c) surface (500 \times).

between filler and resin matrix, which enables the composite plate to have ideal electrical conductivity and flexural strength.

CONCLUSION

Based on the different shapes and structures of natural graphite, expanded graphite, and carbon black and the melting and curing characteristics of phenol resin, two-step compression molding optimum conditions and the effects of composition on the properties of composite plates were investigated. The pre-forming conditions for G/EG/CB/PF composite plates were optimized as molding temperatures at 100°C under a pressure of 2 MPa for 5 min and then at 8 MPa for 1 min, while for main forming process were compression at 150°C for 5 min under a pressure of 10 MPa. Electrical conductivity and flexural strength of composite plate made this technique were 2.80×10^4 S/m and 55 MPa, respectively. It has also been observed that carbon black permeates into the spaces between natural graphite and expanded graphite and the porous structure of expanded graphite. The addition of expanded graphite and carbon black increases the density of electrical network and enhances the electrical conductivity of composite.

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