

Development of preform moulding technique using expanded graphite for proton exchange membrane fuel cell bipolar plates

S.I. Heo^a, K.S. Oh^a, J.C. Yun^a, S.H. Jung^b, Y.C. Yang^b, K.S. Han^{a,*}

^a Department of Mechanical Engineering, Pohang University of Science and Technology, San 31 Hyoja-dong, Nam-gu, Pohang, 790-784, Republic of Korea

^b Fuel Cell Vehicle Team, Advanced Technology Center, Research & Development Division for Hyundai Motor Company & Kia Motors Corporation, 104, Mabuk-dong, Giheung-Gu, Yongin, 446-912, Republic of Korea

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Abstract

A preform moulding technique using expanded graphite is developed to manufacture composite bipolar plates for proton exchange membrane fuel cells (PEMFCs). The preform is composed of expanded graphite, graphite flake and phenol resin. Preforms utilizing the tangled structure of expanded graphite are easily fabricated at a low pressure of 0.07–0.28 MPa. A pre-curing temperature (100 °C) slightly above the melting point of phenol powders (90 °C) induces moderate curing, but also prevents excessive curing. After the preform is placed in a steel mould, compression moulding is carried out at high pressure (10 MPa) and temperature (150 °C). The fabrication conditions are optimized by checking the electrical conductivity, flexural strength and microstructure of the composite. The optimized electrical conductivity and flexural strength, 250 S cm⁻¹ and 50 MPa, respectively, met the requirements for PEMFC bipolar plates.

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1. Introduction

The fuel cell has received international attention for decades as a viable alternative to various electricity-generation facilities based on fossil fuels. Specifically, proton exchange membrane fuel cells (PEMFCs) have come into the spotlight because of their high specific energy and low operating temperature. A number of companies and other organizations have supported ongoing research into the development of PEMFCs for use in power generation as well as transportation and portable applications. However, the slow progress of fuel cell commercialization is a major barrier to the introduction of a hydrogen economy. This is due to the high cost and insufficient reliability of fuel cells [1,2].

One of the most costly components in manufacturing PEMFCs is the bipolar plate [3–5]. Bipolar plates perform a number of functions within PEMFCs. They distribute the fuel and oxidant within the cell, separate the individual cells in the stack, conduct current away from each cell, and carry water away from each

cell. The benefits and drawbacks of each type of bipolar plate material are summarized as follows. Traditionally, the most commonly used bipolar plate material is machined graphite because it has not only excellent chemical stability but also high electrical conductivity. However, its brittleness limits the extent to which plate thickness can be reduced and the machining of gas flow channels is an expensive process. Therefore, both coated metal plates and conductive polymer composites are being investigated as alternative materials. Metals offer higher mechanical strength, better durability to shocks and vibration, no permeability, and much superior productivity. Nevertheless, there are still some problems to solve, such as corrosion and contact resistance [6]. Conductive polymer composites with high filler loadings can be moulded into any shape and size, which makes them attractive for PEMFC stacks. Again, there are several problems, namely, low productivity (compression moulding) and insufficient electrical conductivity (injection moulding) [7,8].

The classical concept of composites was confined to mechanical strengthening [9,10]. Nowadays, though, carbon/graphite reinforced conductive polymer composites have brought much attention to multifunctional materials and are applied in various industrial fields because of their electromagnetic characteristics.

* Corresponding author. Tel.: +82 54 279 2163; fax: +82 54 279 5899.
E-mail address: kshan@postech.ac.kr (K.S. Han).

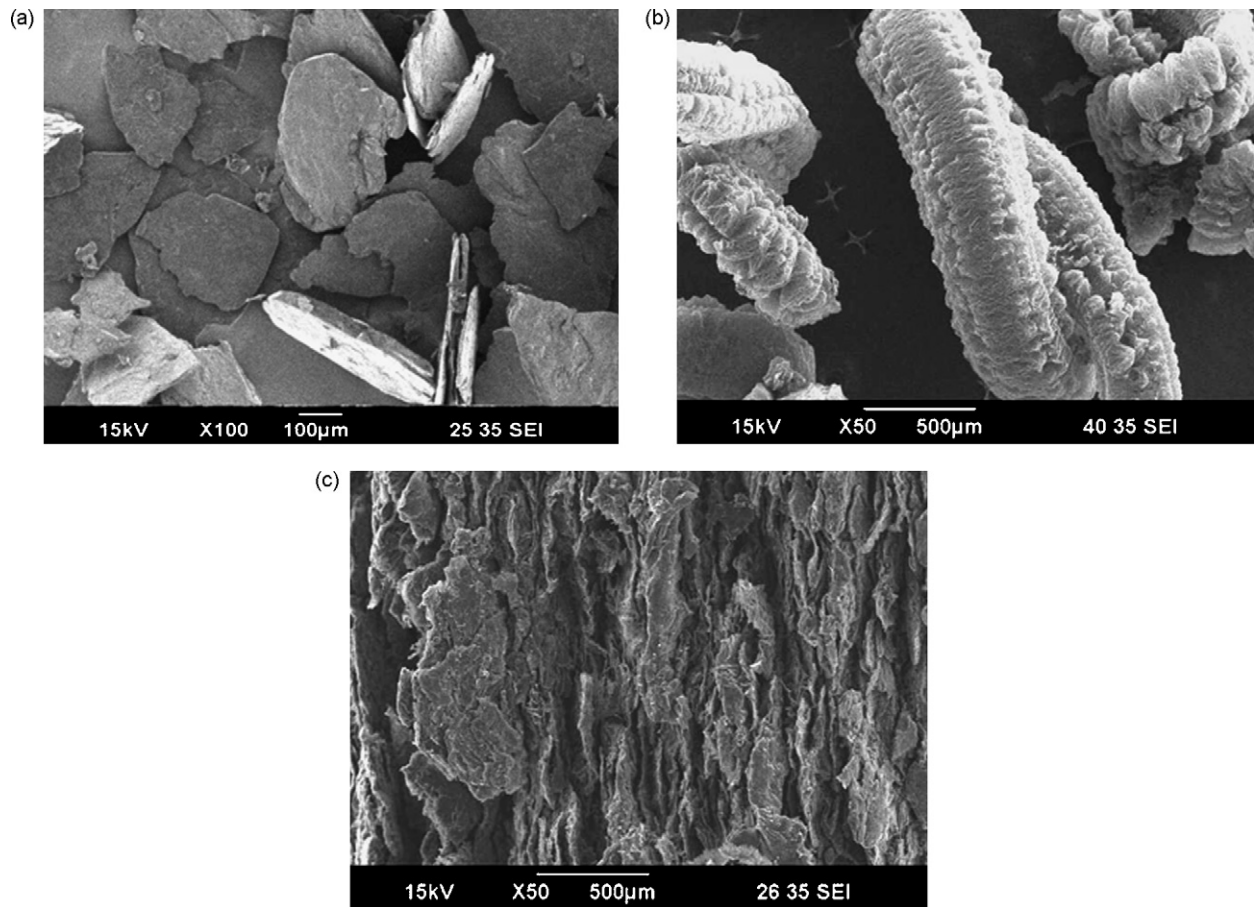


Fig. 1. Shape of conductive fillers: (a) graphite flake; (b) expanded graphite; (c) horizontally compressed expanded graphite at 7 MPa.

Research on conductive polymer composites for bipolar plates is reaching maturity. Most work has focused on carbon/graphite particles as conductive fillers on account of their good electrical conductivity and corrosion resistance [11–13]. Composite bipolar plates satisfy the development targets of bipolar plates for PEMFCs with regard to electrical and physical properties. In initial and long-term operation, their performance was comparable to that of machined graphite plates [14].

On the basis of the above results, optimization of the properties of composite bipolar plates has been vigorously pursued. Correlations between the morphology of graphite particles and the electrical conductivity have been found [15]. However, the application of the results of compaction without resin materials was restricted because many assumptions were made. Therefore, the influence of particle size and shape on electrical and mechanical properties of composite bipolar plates was studied experimentally [16–18]. Also, research to achieve high electrical conductivity at low filler loadings was attempted by using liquid crystal polymers which have a high glass transition temperature and good mechanical properties due to their molecular structure [19].

In addition to these efforts, production efficiency must be raised to commercialize composite bipolar plates. There is a limit to enhancing the productivity when general compression moulding is used. Therefore, many researchers have recently

focused on injection moulding as an alternative method for reducing manufacturing costs.

Recently, composite bipolar plates with graphite loadings above 80 wt.% have been produced by the injection moulding to satisfy the US Department of Energy specification of an electrical conductivity of 100 S cm^{-1} or above [20–22]. Large, thin plates comparable with existing machined graphite plates cannot easily be manufactured using injection moulding. Thus, another technique, such as wet-lay composites, is needed to improve manufacturing productivity [23].

Many researchers have been keenly interested in expanded graphite on account of its peculiar structure and excellent electrical conductivity and have used it to manufacture bipolar plates by several methods [24–26]. In this study, a preform moulding technique using expanded graphite was developed to reduce the manufacturing time and cost while maintaining plate performance. The electrical conductivity and flexural strength were measured to optimize fabrication conditions, and the results were supported by the microstructures and appearances of the specimens.

2. Experimental

2.1. Materials

The thermosetting resin used in this study was a novolak-type phenol resin (Kolon Chemical, Korea) which has a low shrink-

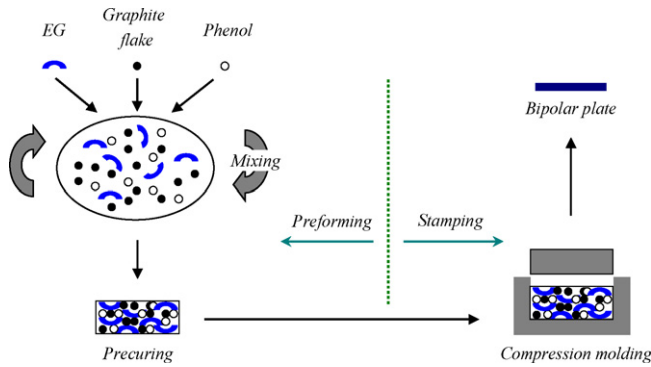


Fig. 2. Schematic diagram of manufacture of composite bipolar plates: preforming and stamping.

age rate and good chemical stability, thermal resistance and mechanical strength. Graphite particles were selected because they have high electrical conductivity, high mechanical strength, and immunity to corrosion.

Fig. 1a and b show the shape of graphite flakes and expanded graphite (EG), respectively. The density of graphite flake and EG was 2.2 and 0.015 g cm^{-3} , respectively. These graphite particles were supplied by Hyundai-kish, Korea. Industrial production of EG usually consists of exposing natural graphite flakes previously treated with sulfuric acid to a brutal thermal shock. The sudden volatilization of the intercalation induces a huge unidirectional expansion of the initial graphite plates. Raw uncompressed EG particles are highly porous and worm-like so they are easily tangled with each other. On account of these characteristics, it is easy to fabricate the preform at low pressure. At the beginning of the compaction of the loose-packed EG, the worm-like particles rearrange spatially, and then the rigidity threshold is met as the EG undergoes compaction [27]. As shown in Fig. 1c, the shape of the compressed EG returns to that of the original graphite flake. The density of the compressed EG was 1.68 g cm^{-3} at pressure of 7 MPa .

2.2. Fabrication

2.2.1. Preforming process

Preforming was composed of mixing and pre-curing, as shown in Fig. 2. Expanded graphite, graphite flake and phenol powder were mixed at an initial ratio of $7.5:67.5:25 \text{ wt.}\%$ and shaken for approximately 30 min to obtain a uniform graphite/phenol compound, which was then poured into an aluminum mould at room temperature. The mould was placed into a hot press (Tetrahedron 40ton, US) that was preheated at 100°C . The pre-curing time and pressure were varied from 3 to 20 min and from 0.07 to 0.7 MPa , respectively, to investigate their influence. The pre-curing temperature was fixed at 100°C , slightly above the melting point of phenol powder (90°C). This pre-curing process led to moderate curing, but prevented excessive curing of the phenol resin.

2.2.2. Stamping process

The fabricated preform was inserted into a steel mould preheated to 150°C , and the temperature was maintained in the

hot press for 30 s . The precured phenol resin resoftened during this preheating stage. The preheating time required would naturally vary with the mould shape, temperature, etc. The desired stamping pressure was then applied and caused the melted phenol resin to infiltrate into the voids of the preform. The main curing time and stamping pressure were varied from 1 to 3 min and from 0 to 20 MPa , respectively, to find optimum fabrication conditions. The dimensions of the fabricated specimens were $80 \text{ mm} \times 80 \text{ mm}$.

Existing composite bipolar plates, as a comparison group, were fabricated by general compression moulding at a temperature and time of 150°C and 10 min , respectively [18]. The ratio of graphite to phenol was $75:25 \text{ wt.}\%$. The moulds had to be cooled down to room temperature before dispersion of the graphite/phenol compound to prevent the compound from curing. This caused low productivity.

2.3. Measurements

The densities of samples were measured based on Archimedes's principle (ASTM D792-00) and the microstructures of samples were observed by means of a Philips XL 30S scanning electron microscope.

The electrical conductivity (in-plane) was measured by the well-known four-point probe technique. Samples were cut to a size of $80 \text{ mm} \times 12.7 \text{ mm}$ using a bandsaw and painted with conductive silver paste on the four regions to be contacted with probes. Specimens were then heat-treated at 50°C for 2 h . A current was applied stepwise through the two outermost probes and the resultant voltage across the two inner probes was measured by a multimeter 34401A (Agilent). The electrical conductivity was calculated according to the following equation:

$$\sigma = \frac{I L}{V A}, \quad (1)$$

where I is the applied current, V is the resultant voltage potential, A is the cross-sectional area of the specimen and L is the distance between the inner probes.

The three-point bending test was performed to measure the flexural strength. In accordance with ASTM D790-02, at least five tests were carried out using a universal testing machine (Shimadzu 5ton, Japan) in each case. Specimens used to measure the electrical conductivity were re-used to ensure experimental consistency. The support span-to-depth ratio (L/t) was 16 , and the cross-head speed was 1 mm min^{-1} , which corresponds to a strain rate of $0.01 \text{ mm mm}^{-1} \text{ min}^{-1}$. The flexural strength and flexural modulus were calculated according to the following equations:

$$\text{flexural strength} = \frac{3PL}{2Wt^2}, \quad (2)$$

$$\text{flexural modulus} = \frac{L^3 M}{4Wt^4}, \quad (3)$$

where P is the breaking force of the specimen, L is the support span, W is the width, M is the slope of the tangent of the initial straight-line portion of the load–deflection curve and t is the thickness of the specimen.

3. Results and discussion

3.1. Preforming process

The relevant pre-curing conditions were investigated under fixed stamping conditions. Preliminary experiments established the stamping conditions as follows: a main curing temperature of 150 °C, a main curing time of 3 min, and a stamping pressure of 10 MPa.

3.1.1. Pre-curing time

To find the appropriate pre-curing time, the pre-curing pressure was fixed at 0.28 MPa and the pre-curing time was increased from 3 to 20 min. Then the above-mentioned stamping process was applied.

Fig. 3 presents several material properties of composite bipolar plates according to the pre-curing time. There was only a slight decrease in both the electrical conductivity and the density, but a considerable change in the flexural strength with increasing pre-curing time. The data in Fig. 3b shows that optimum pre-curing time based on the flexural strength was around 5 min.

At a pre-curing time below 3 min, the flexural strength deteriorated owing to lack of curing of phenol resin. On the other hand, the flexural strength of samples gradually decreases as the pre-curing time increased beyond 5 min. This result is due to the difference in densification. When the pre-curing time reaches 10 min, excessive curing of phenol resin begins to occur. The excessively cured resin does not re-soften sufficiently during the preheating stage of the stamping process and cannot infiltrate into the gaps between the graphite particles or into the

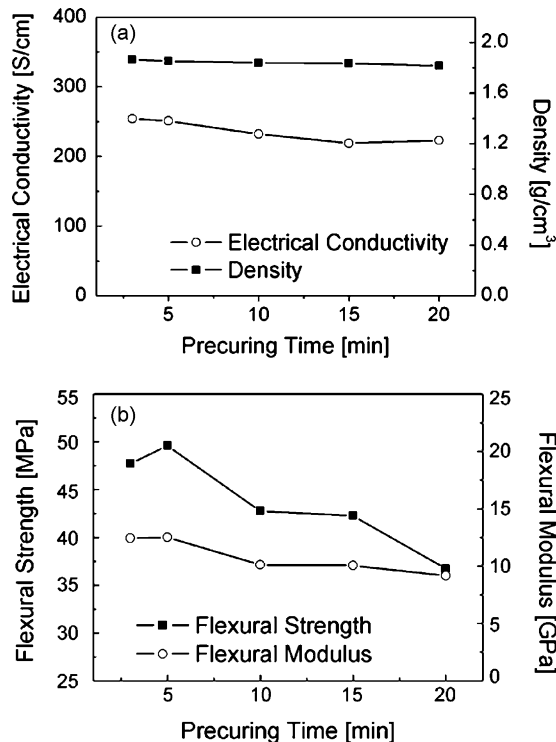


Fig. 3. Material properties of composite bipolar plates depending on pre-curing time: (a) electrical conductivity and density; (b) flexural strength and modulus.

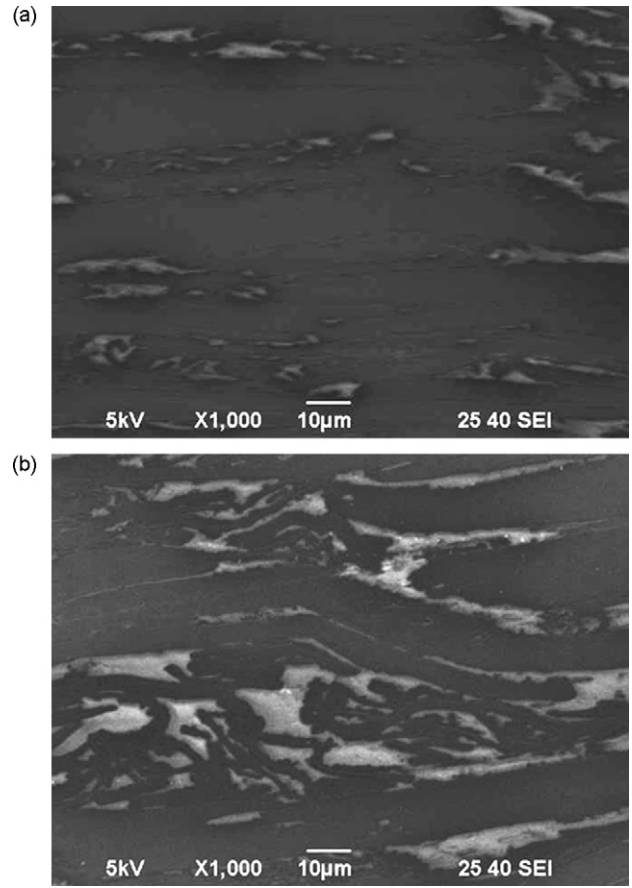


Fig. 4. Microstructure of composite bipolar plates depending on pre-curing time: (a) 5 min; (b) 15 min.

internal voids of the expanded graphite. Therefore, localized resin-rich regions and uncompressed EG remain after the stamping process, as shown in Fig. 4b. These defects obstruct smooth compaction of the preform and cause a falling-off in material properties of composite bipolar plates, particularly the flexural strength.

3.1.2. Pre-curing pressure

During pre-curing pressure tests, the graphite/phenol compound was exposed to pre-curing pressures of 0.07, 0.28, and 0.7 MPa. The pre-curing time was constant at 5 min. Then, the previously mentioned stamping process was applied.

Fig. 5 presents material properties of composite bipolar plates according to the pre-curing pressure. There is no particular change of density regardless of the pre-curing pressure, and the electrical conductivity and flexural strength decrease only slightly as the pre-curing pressure increased. This means that the pre-curing pressure variation, in the 0.07–0.7 MPa range, has an insignificant influence on the material properties of composite bipolar plates.

Productivity and formability are also important matters. The preform pre-cured below 0.07 MPa is likely to break because of a lack of compaction. Therefore, it is difficult to make a pre-form. As the pre-curing pressure increases from 0.07 MPa, the density of the preform increases and finally reaches as high as

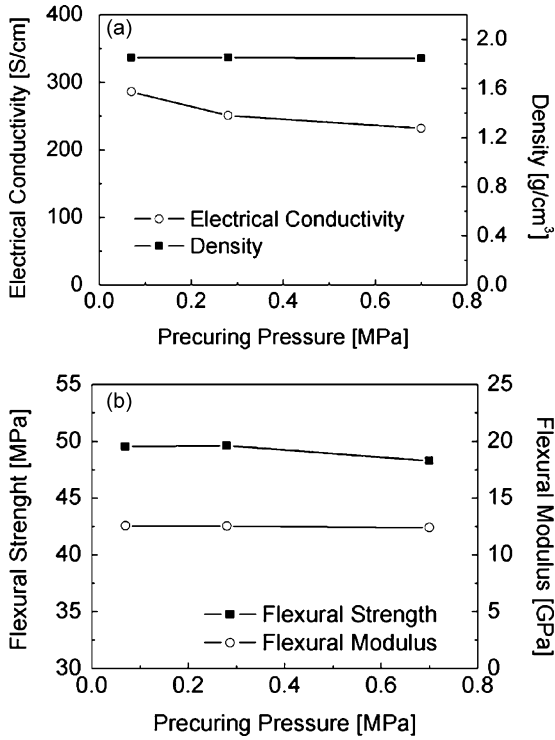


Fig. 5. Material properties of composite bipolar plates depending on pre-curing pressure: (a) electrical conductivity and density; (b) flexural strength and modulus.

1.26 g cm⁻³ at 0.7 MPa. At this point, the compression ratio falls to about 1.5, as shown in Fig. 6. The compression ratio is defined as:

$$\text{compression ratio} = \frac{\text{density of composite bipolar plate}}{\text{density of preform}} \quad (4)$$

A proper compression ratio is necessary to guarantee good formability of the preform. Here, the compression ratio should be at least 2 for the reliable preparation of composite bipolar plates with complicated gas flow channels. The ratio is also closely related to the flow and infiltration phenomena of melted phenol resin. Consequently, the optimum pre-curing pressure is between 0.07 and 0.28 MPa.

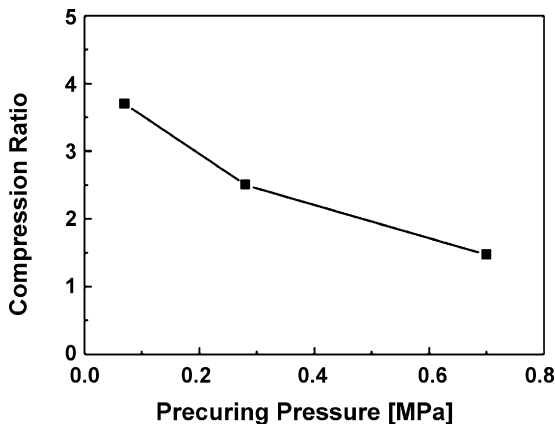


Fig. 6. Compression ratio according to pre-curing pressure.

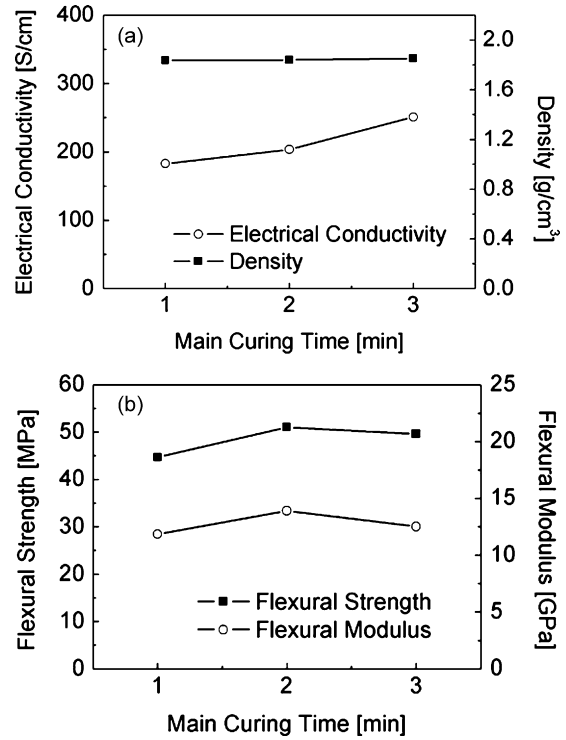


Fig. 7. Material properties of composite bipolar plates depending on main curing time: (a) electrical conductivity and density; (b) flexural strength and modulus.

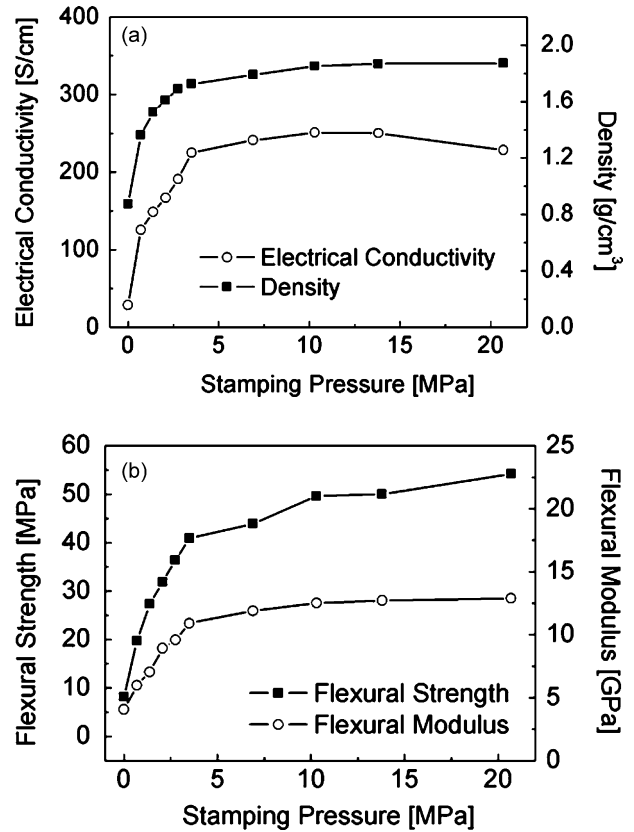


Fig. 8. Material properties of composite bipolar plates depending on stamping pressure: (a) electrical conductivity and density; (b) flexural strength and modulus.

3.2. Stamping process

The stamping conditions were optimized with the pre-curing conditions fixed at a temperature of 100 °C, a pressure of 0.28 MPa and a time of 5 min, in accordance with the former experimental results. The principal variables investigated were main curing time and stamping pressure.

3.2.1. Main curing time

The experimental method was similar to that of the pre-curing experiment. First, the main curing time was increased from 1 to 3 min at a constant stamping pressure of 10 MPa. Fig. 7 presents material properties of composite bipolar plates depending on the main curing time. At 1 min, the flexural strength is low owing to a lack of curing of the phenol resin. While the density is virtually constant, the flexural strength and electrical conductivity reach maxima at 2 and 3 min, respectively. The flexural strength changes very little above the main curing time of 2 min. Hence, a main curing time of 3 min is appropriate for this two-step (preforming and stamping) manufacturing process.

Besides merely reducing the high-pressure moulding time compared with existing compression moulding, the preform moulding technique removes the graphite/phenol dispersion process so that the moulds can always maintain the high temperature

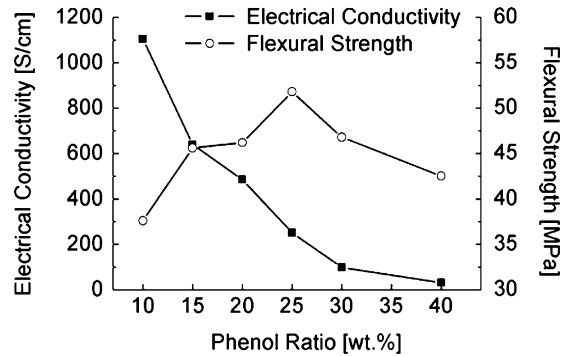


Fig. 9. Electrical conductivity and flexural strength depending on phenol ratio.

[28]. This induces a considerable increase in manufacturing efficiency.

3.2.2. Stamping pressure

The stamping pressure was optimized by varying it from 0 to 20 MPa with a main curing time of 3 min. Fig. 8 shows the material properties of composite bipolar plates with respect to the stamping pressure. The electrical conductivity and flexural properties follow the tendency of the density. These material properties rapidly increase until around 3.5 MPa and scarcely changed above 10 MPa. Therefore, the optimum stamping pressure is 10 MPa.

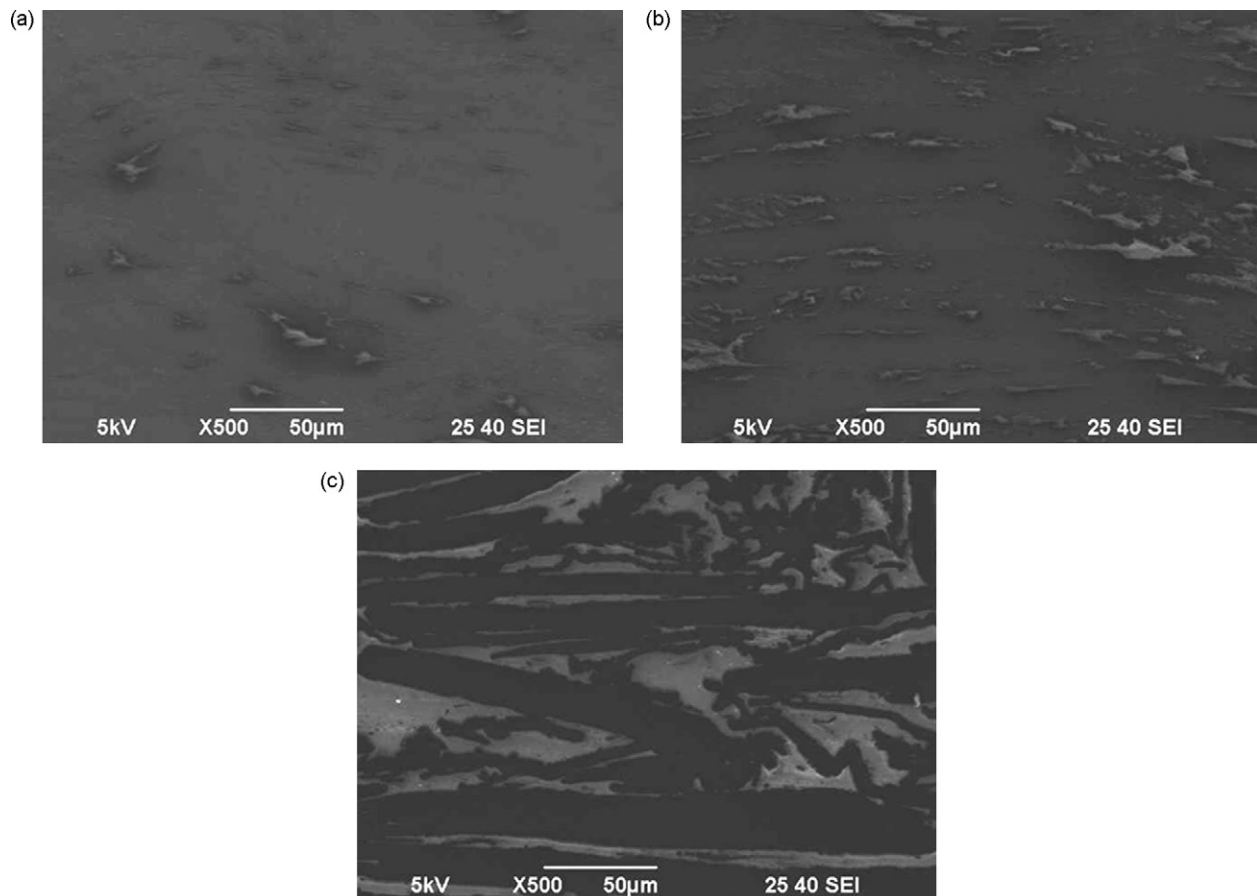


Fig. 10. Microstructure of composite bipolar plates depending on phenol ratio: (a) 10 wt.%; (b) 25 wt.%; (c) 40 wt.%.

3.3. Phenol weight ratio

The characteristics of the composite bipolar plates were observed at phenol ratios from 10 to 40 wt.% in steps of 5 wt.%. The weight ratio of expanded graphite to graphite flake was fixed at 1:9 wt.%. Pre- and main-curing conditions were fixed at the optimum conditions of 100 °C, 0.28 MPa and 5 min and 150 °C, 10 MPa and 3 min, respectively.

Fig. 9 presents the variation in electrical conductivity and flexural strength as a function of the phenol ratio. The electrical conductivity decreases continuously with increasing phenol ratio; it falls below the PEMFC specification at about 30 wt.%. This is closely associated with the conductive paths, or the direct contact between graphite particles. In Fig. 10a, every graphite particle (dark gray) is connected to neighbouring graphite particles and generally forms surface-to-surface contacts. In other words, full conductive networks are formed. Conductive networks, however, begin to be broken as the phenol ratio increases. Phenol resin, an insulating material, fills the gaps among graphite particles. These phenol resin regions (light gray) block the connection of the electrically conductive paths, as shown in Fig. 10b and c.

The flexural strength graph is more complicated than that of the electrical conductivity. When the phenol ratio is 10 wt.%, the preform is likely to break because of the lack of binder. As the phenol ratio is increased, the flexural strength reaches its highest value at a phenol ratio of 25 wt.% and then decreases afterwards. Additionally, the preform is difficult to de-mould at high phenol ratios. Therefore, the optimum phenol ratio is 25 wt.%.

The principal variables that affect the flexural strength of the composite bipolar plates are the bonding force by phenol resin and the stress concentration around the voids. The increase in the flexural strength in the low-resin section, below 25 wt.%, can be explained from a commonsense standpoint that the increase in the binder, phenol resin, causes a strengthening of the composite bipolar plates. However, excessive phenol resin induces voids in the composites [17,29]. Therefore, stress concentration effects due to the voids also increase while the bonding force between the graphite particles and the phenol resin increases as the phenol ratio increases. Then, the importance of the stress concentration increases above a phenol ratio of 30 wt.%, which causes deterioration of the flexural strength. This explanation is supported indirectly by the decrease in the relative density shown in Fig. 11. The relative density is defined as

$$\text{relative density} = \frac{\text{measured density}}{\text{theoretical density}} \quad (4)$$

Generally, the lower the relative density is, the higher the porosity is. Therefore, the decrease in relative density means an increase in the voids when the phenol ratio increases. The density of compressed EG is based on another Ref. [27].

3.4. Comparison with existing composite bipolar plates

In Table 1, the material properties of composite bipolar plates made using a preform moulding technique were compared against composites fabricated by the previously discussed

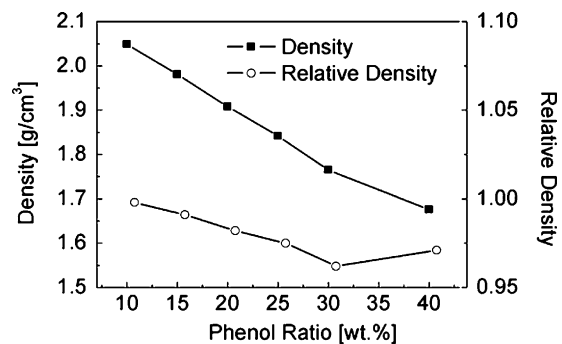


Fig. 11. Density according to phenol ratio.

Table 1

Material properties of composite bipolar plates (graphite:phenol = 75:25 wt.%)

	Electrical conductivity (S cm^{-1})	Flexural strength (MPa)
This study	251	50
Existing composites	180	53

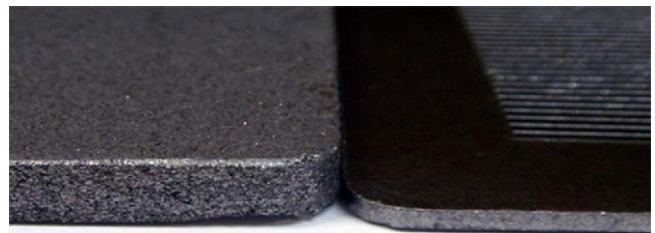


Fig. 12. Picture of specimens: preform (left) and composite bipolar plate (right).

compression moulding method. The ratio of graphite to phenol was 75:25 wt.%, i.e., the same as the optimum mixing ratio of the preform.

While the flexural strength is similar, the electrical conductivity of the composites fabricated by using the preform is about 1.4 times higher than that of existing composites because the tangled expanded graphite in the preform gives more efficient conductive networks.

A fabricated preform and a prototype composite bipolar plate are shown in Fig. 12. The pre- and main-curing processes were conducted at the previously optimized conditions. The compression moulded gas-flow channels are well-fabricated.

Therefore, the electrical conductivity, flexural strength and formability are good enough for bipolar plates for PEMFCs. The general industrial target for the flexural strength is around 40 MPa. For stability in fuel cell systems, however, it is desirable to enhance the flexural strength. The strengthening of composite bipolar plates by adding carbon fibres will be described in a forthcoming paper.

4. Conclusions

A preform moulding technique using expanded graphite has been developed to manufacture composite bipolar plates. This two-step manufacturing process consists of pre- and main-curing and has the potential to produce rapidly composite bipolar plates

because the graphite/phenol compound dispersion process is unnecessary and the high-pressure moulding time is reduced.

In this study, various fabrication conditions are investigated as basic research for mass production. The proper pre-curing time is determined to fabricate the preform stably because insufficient and excessive pre-curing deteriorates the flexural strength. A low pre-curing pressure is favoured to ensure good formability of the preform. The electrical conductivity and flexural strength increase as the stamping pressure and curing time increase, and reach maximum values. Therefore, a minimum stamping pressure and a main curing time to obtain satisfactory material properties are recommended.

The preform is sufficiently formable to be used for manufacturing PEMFC bipolar plates. The principal properties of the materials, such as the electrical conductivity and flexural strength, match those of existing composites. Future work will focus on improving the mechanical strength, through-plane conductivity and gas permeability.

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