

# Performance of Graphite Filled Composite Based on Benzoxazine Resin

Hajime Kimura, Keiko Ohtsuka, Akihiro Matsumoto

*Thermosetting Resin Lab, Organic Materials Research Division, Osaka Municipal Technical Research Institute, 1-6-50, Morinomiya, Joto-ku, Osaka 536-8553, Japan*

Received 1 September 2009; accepted 5 January 2010

DOI 10.1002/app.32057

Published online 29 March 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** In this study, we aimed to prepare and characterize graphite filled composites based on benzoxazine resin for the bipolar plate in fuel cell. Three kinds of graphite (synthetic graphite, natural graphite, and expanded graphite) were used for the preparation of the graphite filled composites. The composites were prepared by means of the compression molding of mixtures of graphite and benzoxazine resin. The properties of the graphite filled composites based on benzoxazine resin were estimated by mechanical property, gas permeability,

and electrical conductivity. As a result, it was found that graphite filled composites based on benzoxazine resin showed good gas impermeability, electrical conductivity and mechanical property compared with those of the graphite filled composites based on the conventional phenolic resin. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1711–1717, 2010

**Key words:** graphite; benzoxazine; composite; bipolar plate

## INTRODUCTION

During the past decade, polymer electrolyte fuel cells (PEFCs), as an alternative power source, have become the focus of very active research. The huge patent interest in this energy conversion technology arises mostly from promising applications in zero-emission vehicles and portable power generation, which could help address future environmental and energy supply challenges. The PEFC operation relies on the performance of the proton exchange membrane, electrode catalyst, and bipolar plates as components.

The bipolar plate separates one cell from the next, with this plate carrying hydrogen gas on one side and air (oxygen) on the other hand. The bipolar plate requires high electrical conductivity, low gas permeability, good mechanical properties, and good dimensional stability and so on.

To date, traditionally the most commonly used material for the bipolar plate have been graphite, because it has excellent chemical stability to survive the fuel cell environment. It also has good electrical conductivity, resulting in highest electrochemical power output. However, it is fraught with problems of high cost, low mechanical strength, and the need for machining to form the flow channels. Hence, the

metal-based bipolar plates have been focused recently. Metals, as sheet, are potential candidate for the bipolar plate material since they have good mechanical properties, electrical conductivity, and can be easily stamped to desired shape to accommodate the flow channel. However, for the metal-based bipolar plate, the corrosion of the plates in the fuel cell environment leads to a release of cations, which can result in an increase in a proton exchange membrane resistance as well as poisoning of the electrode catalysts. Moreover, a corrosion layer on the surface of a bipolar plate increases the electrical resistance and decrease the output of the fuel cell.

In contrast, graphite-based polymer composite bipolar plates have the advantage of low costs, low weight, good chemical stability, and can be molded into any shape and size (easy manufacturing). Thermosetting resins are usable as a binder resin of the graphite filled composite for the bipolar plate because of the excellent electrical conductivity. Phenolic resin has been commonly used as a binder resin of the graphite filled composite. However, there have been disadvantages that the phenolic resins produce volatiles by-products upon curing. Hence, it was difficult to produce the bipolar plate that had enough characteristics (high electrical conductivity, low gas permeability, good mechanical properties, and good dimensional stability and so on) for fuel cell.

It is well known that the benzoxazine ring is stable at low temperature, but the ring opening reaction occurs at high temperature and novolac type oligomer (benzoxazine based resin) having both the

Correspondence to: H. Kimura (kimura@omtri.city.osaka.jp).

phenolic hydroxyl group and the tertiary amine groups are produced.<sup>1</sup> We think that this benzoxazine based resin has attracted significant attention as a new material instead of conventional phenolic resin.

Benzoxazine based resin has such unique characteristic as dimensional stability, near-zero shrinkage, in addition to good heat resistance, water resistance, electrical insulation properties, mechanical properties, and flame resistance.<sup>2-8</sup> Furthermore, this benzoxazine based resin does not need strong acids catalysts for curing, and does not produce by-products during curing reaction.<sup>9</sup> We also have already investigated the curing behavior of the bisphenol-A, terpenediphenol, or poly(*p*-vinylphenol)-based benzoxazines with epoxy resin or bisoxazoline and the properties of the cured resins.<sup>10-14</sup>

To date, no papers have reported on graphite filled bipolar plate composite based on the benzoxazine resin. In this study, we aimed to prepare and characterize graphite filled bipolar plate composites based on benzoxazine resin. Therefore, in this study, three graphite based polymer composites using the benzoxazine resin were prepared, and the properties (mechanical property, gas permeability, and electrical conductivity) of the graphite filled composites based on benzoxazine resin were investigated.

## EXPERIMENTAL

### Materials

Three different types of graphite particles were used. Synthetic graphite GE-134 (Nippon Technocarbon Co., (Miyagi, Japan)) was pulverized by belt sander and used (size, average 30  $\mu\text{m}$ ). Expanded graphite BSP-2 (size, average 40  $\mu\text{m}$ ) and natural graphite CBR (size, average 18  $\mu\text{m}$ ,) was supplied by Chuetsu Graphite Works Co., (Osaka, Japan).

2,2-bis(3,4-dihydro-3-phenyl-1,3-benzoxazine)propane (bisphenol-A based benzoxazine, Ba) was supplied by Shikoku Chemicals Co., (Kagawa, Japan). Phenolic resin (#200) as a conventional phenolic resin was supplied from Lignyte Co., (Osaka, Japan).

All materials were used without further purification.

**TABLE I**  
Preparation of the Graphite Filled Composites Based on Benzoxazine Resin

Resin (20 wt %)	Graphite particles (80 wt %)	Molding conditions
Benzoxazine Ba	Synthetic graphite GE-134	180°C/60 min, 30 MPa
	Expanded graphite BSP-2	200°C/30 min, 30 MPa
	Natural graphite CBR	

**TABLE II**  
Preparation of the Graphite Filled Composites Based on Conventional Phenolic Resin

Resin (20 wt %)	Graphite particles (80 wt %)	Molding condition
Phenolic resin #200	Synthetic graphite GE-134	170°C/10 min, 30 MPa
	Expanded graphite BSP-2	
	Natural graphite CBR	

### Preparation of the molding graphite compounds and graphite filled composite based on benzoxazine resin

Three kinds of the molding graphite compounds containing 80 wt % graphite particles and 20 wt % Ba were prepared by blending with a mixer for 30 min. The preparation of graphite filled composites was carried out by compression molding method. Namely, the composites were molded using compression molder at 180°C for 60 min or 200°C for 30 min under the pressure of 30 MPa. This curing condition was determined from the results of measurements for melt viscosity as will become apparent below.

For comparison, the graphite filled composites based on the conventional phenolic resin were prepared using the same graphite particles by compression molding method at 170°C for 10 min under the pressure of 30 MPa. This curing condition was also determined from the results of measurements for melt viscosity as will become apparent below.

These experiments for preparation of the graphite filled composites are summarized in Tables I and II.

### Properties of graphite filled composite based on benzoxazine resin

To investigate the curing behavior of the composites, measurements for melt viscosity were conducted on a UBM Co. Dynamic Mechanical Spectrometer (Rheosol-G3000) by using a 25 mm parallel plate fixture at various temperatures. The plates were preheated to 100°C before the test. Next, the plates were heated from 100°C to the measuring temperature (170°C, 180°C, or 200°C) at a rate of 30°C/min. Melt viscosity for isothermal test at 170°C, 180°C, or 200°C were measured as a function of time.

The properties of the graphite filled composites were characterized by mechanical property, gas permeability, and electrical conductivity.

The flexural property, as mechanical properties, was measured on rectangular samples according to ASTM D790<sup>15</sup> (JIS K7055). A load was applied at its center by the loading nose and the load at the break

of the test piece was measured at the nearest 0.1 kgf. The flexural strength ( $\sigma_b$ ) was calculated with the following equations:

$$\sigma_b = 3P_b L / 2Wh^2$$

Where  $P_b$  is the load at break of test piece,  $L$  is the support span,  $W$  is the width of test piece,  $h$  is the depth of test piece. Five samples were tested, and then the average value was taken as the value of the flexural strength.

Gas permeability was measured by differential pressure method according to ASTM D1434<sup>16</sup> (JIS K7126 (A method)). In this method, the permeation cavity is divided into two independent parts by the sample package. Vacuate the two sides and then fill one side (side A is the high pressure side) with testing gas (He) of 1 atm (absolute pressure) and the other side keeps the vacuum state. Testing gas (He) between the two sides will form a pressure difference of 1 atm. The testing gas (He) transmits through the sample into the low-pressure side and causes a pressure change there. Through the following formula, He gas transmission rate (GTR) can be calculated with a high precision vacuum gage. The result unit is  $\text{cm}^3/\text{m}^2 \cdot 24 \text{ h} \cdot 1 \text{ atm}$ .

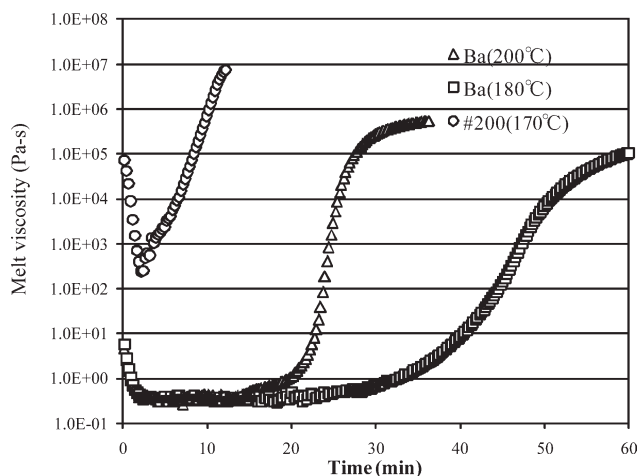
$$\text{GTR} = dp/dt \cdot V_c / (R \cdot T \cdot P_u \cdot A)$$

$V_c$  represents the volume of low-pressure side.  $T$  is the test temperature (thermodynamic temperature).  $A$  is the effective transmission area.  $dp/dt$  is the pressure variation on low pressure side per unit time after the transmission becomes stable.  $P_u$  is differential pressure of supplied gas.  $R$  is the gas constant. Three samples were tested, and then the average value was taken as the value of the gas permeability.

Electrical conductivity was estimated by measurement of resistivity with a four-point probe (probe A, B, C, D in order from the left) array according JIS K7194<sup>17</sup> on Mitsubishi Chemical Co. (Tokyo, Japan) Loresta-GP. Four needle electrodes are linearly placed on a test piece. When a current ( $I$ ) is passed between the probe A and the probe D, the resulting potential difference ( $V$ ) between the probe B and the probe C is measured, and the resistance  $R$  ( $V/I$ ) is obtained. Then, resistivity ( $\rho$ ) is calculated by multiplying the obtained resistance ( $R$ ) by the thickness of the test piece ( $t$ ) and correction factor ( $F$ ).

$$\rho = F \cdot t \cdot R$$

where correction factor ( $F$ ) is measured with a four-point probe array, which is a non-dimensional numerical value determined by the shape and dimensions of a test piece and position of the probe. Three samples were tested, and then the average value was taken as the value of the resistivity.



**Figure 1** Melt viscosity of benzoxazine resin (Ba) at 180°C or 200°C, and conventional phenolic resin (#200) at 170°C.

The morphology of the graphite filled composites was investigated by Scanning electron microscope (SEM). Scanning electron microscope (SEM, accelerating voltage was 10 or 15 kV) was used to confirm good resin distribution and interfacial adhesion between the resin and graphite particles on a JEOL (Tokyo, Japan) JSM-5800. The fracture surface of the samples fractured under flexural test was observed by SEM.

## RESULTS AND DISCUSSION

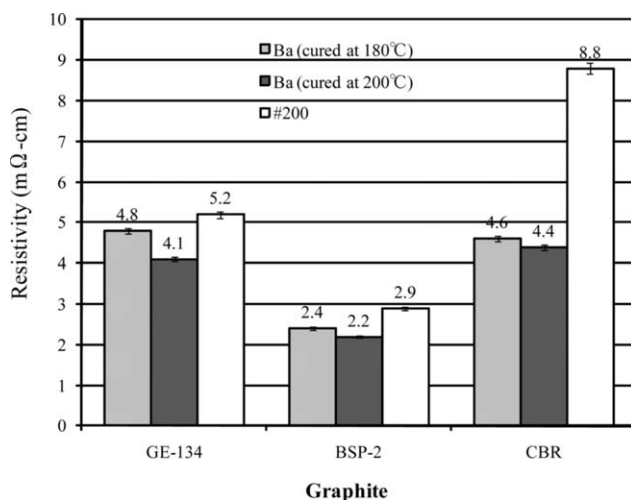
### Melt viscosity of Ba or conventional phenolic resin

Figure 1 shows the plot of the melt viscosity of benzoxazine based resin (Ba) and conventional phenolic resin (#200) vs. time at each curing temperature. The melt viscosity of Ba was kept a low value (0.3–0.4 Pa·s) at the curing temperatures (180°C or 200°C), and increased slowly. Ba showed low viscosity and good flowability at the curing temperature (180°C or 200°C) for a while, because the ring opening reaction (curing reaction) of the benzoxazine ring occurred difficulty. On the other hand, the melt viscosity of the conventional phenolic resin (#200) was kept not a low viscosity but a high viscosity (240–400 Pa·s) at the curing temperature (170°C), and increased rapidly because of the curing reaction. It was found that the conventional phenolic resin showed high viscosity and bad flowability at the curing temperature (170°C).

From the results of measurements for melt viscosity, the curing condition for benzoxazine resin (Ba) was determined as 180°C for 60 min or 200°C for 30 min. And the curing condition for conventional phenolic resin (#200) was also determined as 170°C for 10 min.

### Properties of graphite filled composites

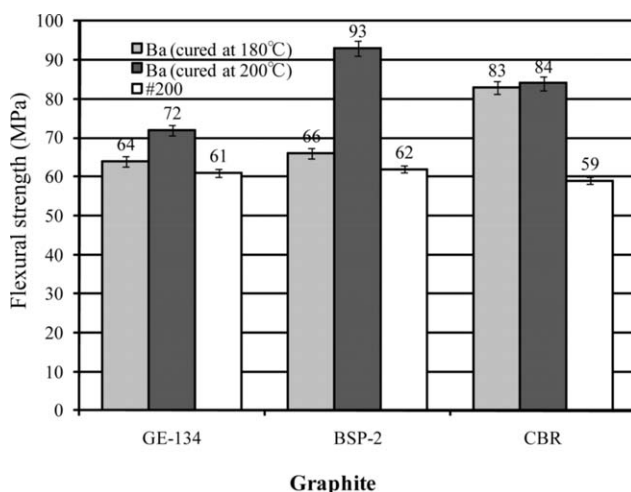
In general, the bipolar plates take a high proportion of the cost and volume of a fuel cell stack. The main



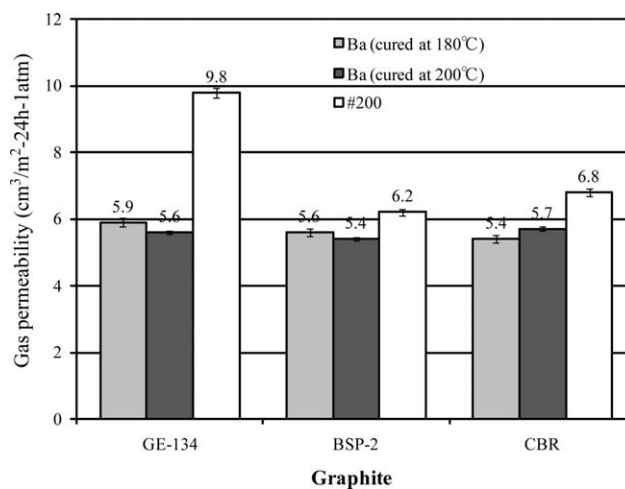
**Figure 2** Electrical conductivity of the graphite filled composites based on benzoxazine resin (Ba) cured at 180°C/60 min or 200°C/30 min, and conventional phenolic resin (#200).

roles of the bipolar plates are to collect and conduct the current from the anode of one cell to the cathode of the next cell. Therefore, the material for bipolar plate requires good electrical conductivity. Figure 2 shows the results of measurements for resistivity. The electrical conductivity of the graphite filled composite based on benzoxazine resin was higher than that of the graphite composite based on conventional phenolic resin in case of any kinds of graphite particles used. It was estimated that the higher electrical conductivity was probably due to the smaller gap between the graphite particles by low viscosity and good flowability of the benzoxazine based resin under the molding condition.

Bipolar plate also requires mechanical strength to withstand clamping forces of the package. The flex-



**Figure 3** Flexural strength of the graphite filled composites based on benzoxazine resin (Ba) cured at 180°C/60 min or 200°C/30 min, and conventional phenolic resin (#200).



**Figure 4** Gas permeability of the graphite filled composites based on benzoxazine resin (Ba) cured at 180°C/60 min or 200°C/30 min, and conventional phenolic resin (#200).

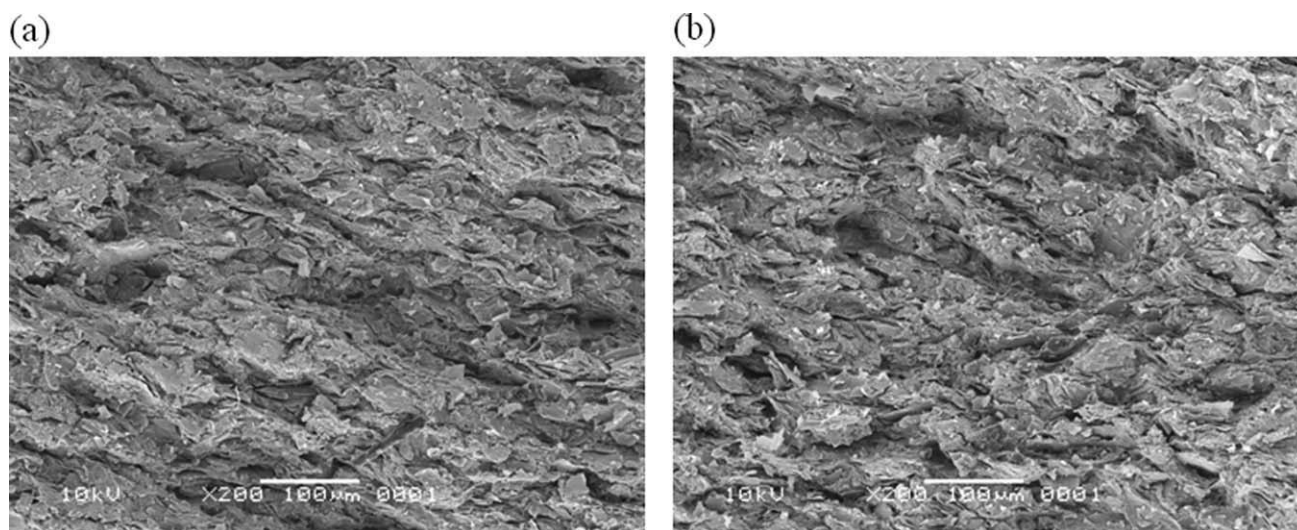
ural strength of the graphite filled composites based on benzoxazine resin and conventional phenolic resin is shown in Figure 3. As a result, the flexural strength of the graphite filled composite based on benzoxazine resin is higher than that of the graphite filled composite based on the conventional phenolic resin in the case of any kinds of graphite particles used. This higher flexural strength might be because the gap between the graphite particles was smaller by low viscosity and good flowability of the benzoxazine based resin under the molding condition.

As hydrogen flows through the anode side of the bipolar plates, and oxygen flows through the cathode side of the bipolar plates, the bipolar plates should have good gas impermeability to prevent the gas crossover through the bipolar plates. The gas permeability of the graphite filled composites based on benzoxazine resin and conventional phenolic resin is shown in Figure 4. As a result, the gas permeability of the graphite filled composite based on benzoxazine resin is smaller than that of the graphite filled composite based on the conventional phenolic resin in the case of any kinds of graphite particles used. When the phenolic resin was used, in curing process of phenolic resin, volatiles such as water or ammonia compounds, etc., are released. These volatiles sometimes reduce

**TABLE III**  
DOE Target Values for the Bipolar Plate

	DOE target
Flexural strength (MPa)	>25
Electrical conductivity (mΩ cm)	<10
Gas permeability (cm³/cm² s) <sup>a</sup>	<2 × 10 <sup>-6</sup>

<sup>a</sup> Gas; H<sub>2</sub>, at 80°C, 3 atm.



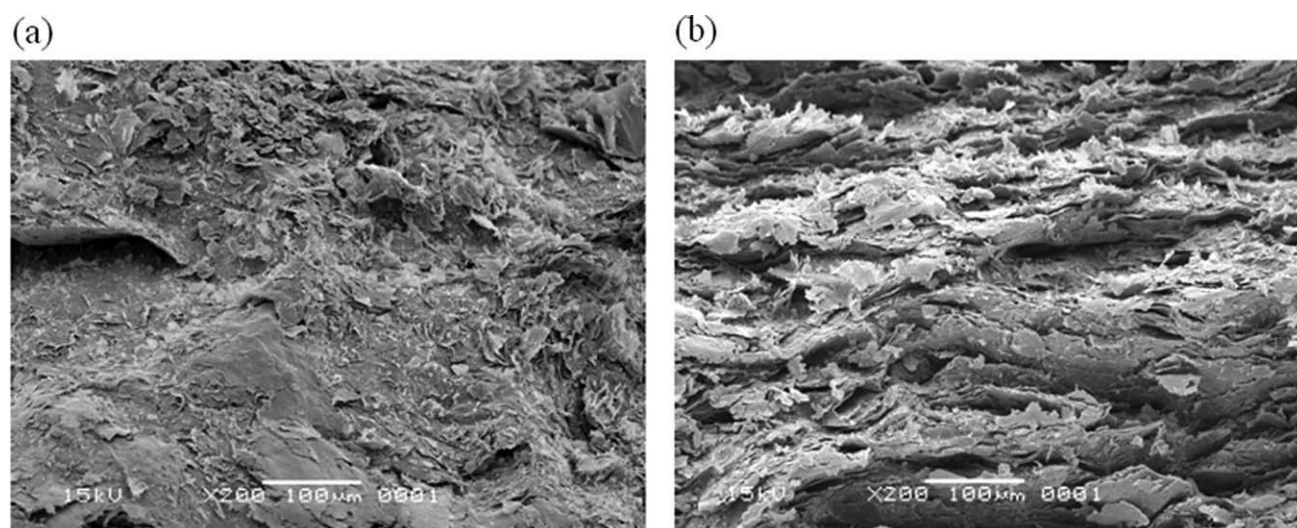
**Figure 5** SEM micrographs of fracture surface on the synthetic graphite (GE-134) filled composite based on (a) benzoxazine resin, (b) conventional phenolic resin: ( $\times 200$ ).

the properties of cured phenolic resin because of the formation of microvoid. Locally, these voids might connect with each other to form a gas permeation path. Also, low viscosity and good flowability allowed benzoxazine based resin to penetrate into the graphite gallery and fill the micro- and macro-pores of the graphite particles.

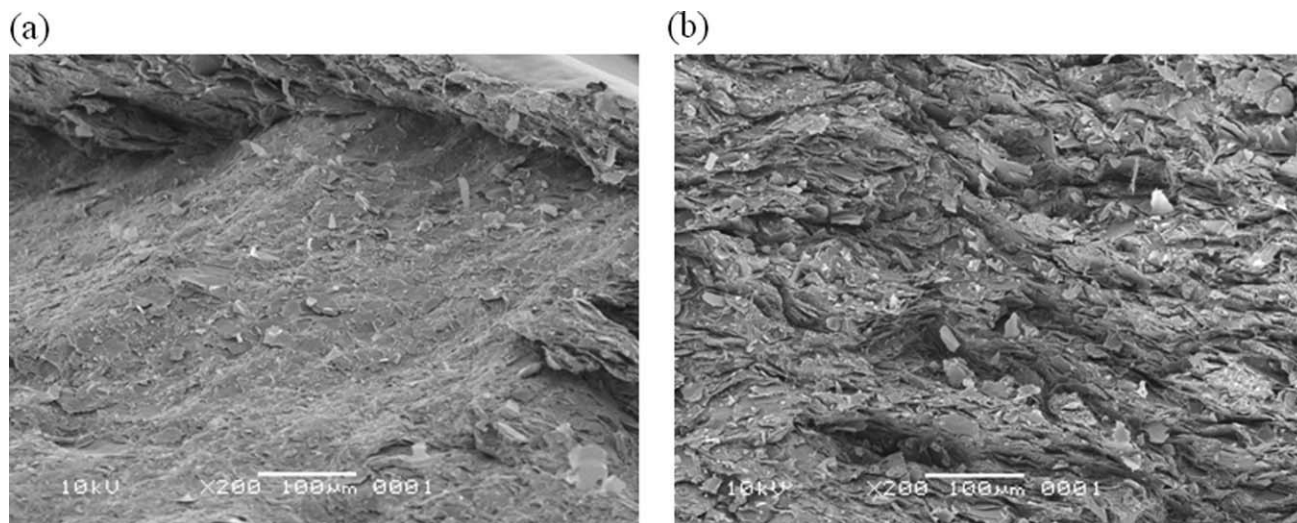
In this study, the influence of curing temperature ( $180^{\circ}\text{C}$  or  $200^{\circ}\text{C}$ ) on the mechanical property, gas impermeability and electrical conductivity for the graphite filled benzoxazine composites was investigated. The curing temperature significantly affected the mechanical properties of the composite based on benzoxazine resin. This might be due to the higher

crosslink density at higher curing temperature. On the other hand, the curing temperature did not almost affect the electrical conductivity and gas permeability.

The data on electrical conductivity and mechanical property of the graphite filled composites based on benzoxazine resin indicated the value that satisfied DOE (United States of Department of Energy) target<sup>18</sup> (Table III), though gas impermeability cannot be compared because of the measurement conditions different from DOE target. These graphite filled composites based on benzoxazine resin will be very suitable for bipolar plates in polymer electrolyte fuel cells (PEFCs).



**Figure 6** SEM micrographs of fracture surface on the expanded graphite (BSP-2) filled composite based on (a) benzoxazine resin, (b) conventional phenolic resin: ( $\times 200$ ).



**Figure 7** SEM micrographs of fracture surface on the natural graphite (CBR) filled composite based on (a) benzoxazine resin, (b) conventional phenolic resin: ( $\times 200$ ).

### SEM characterization of graphite filled composites

The morphology of the graphite filled composites was investigated by SEM. SEM images of fracture surface of the synthetic graphite (GE-134), expanded graphite (BSP-2), and natural graphite (CBR) filled composites (molded at 200°C for 30 min) based on benzoxazine resin (Ba) and conventional phenolic resin (#200) after flexural test are shown in Figures 5, 6, and 7. The microstructure of the composite based on benzoxazine resin was quite different from that of the composite based on the conventional phenolic resin. It can be observed that the graphite filled composite based on benzoxazine resin shows even fracture surface, but the graphite filled composite based on the conventional phenolic resin shows uneven fracture surface. It was suggested that the interfacial bond strength between the resin and the graphite of the composite based on the conventional phenolic resin was weaker than that of the composite based on benzoxazine resin. The graphite filled composite based on benzoxazine resin might show better resin distribution and interfacial adhesion between the resin and the graphite. These results might be attributed to low viscosity and good flowability of the benzoxazine resin at the molding temperature. And the interface debonding might cause the reduction of flexural property, gas impermeability and electrical conductivity of the composite based on the conventional phenolic resin.

### CONCLUSIONS

The purpose of this study was to prepare and characterize graphite filled composites based on benzoxazine resins for the bipolar plate in fuel cell. We investigated the properties of the three kinds of

graphite (synthetic graphite, natural graphite, and expanded graphite) particles filled composites based on benzoxazine resins. As a result, graphite filled composites based on benzoxazine resin showed good gas impermeability, electrical conductivity, and mechanical property compared with those of the graphite filled composites based on the conventional phenolic resin. These reasons were considered that benzoxazine resin does not produce by-products during curing reaction; the melt viscosity of benzoxazine resin is very low and benzoxazine resin shows good flowability at the molding temperature, different from the conventional phenolic resin. Then, the composite had more closely structures. The data on electrical conductivity, gas impermeability and mechanical property of the graphite filled composites based on benzoxazine resin indicate that these graphite filled composites based on benzoxazine resin will be very suitable for bipolar plates in polymer electrolyte fuel cells (PEFCs).

### References

1. Riess, G.; Schwob, J. M.; Guth, G.; Roche, M.; Lande, B. In *Advances in Polymer Synthesis*, Culbertson, B. M., Mcgrath, J. E., Eds. Plenum: New York, 1985.
2. Ning, X.; Ishida, H. *J Polym Sci Part B: Polym Phys* 1994, 32, 921.
3. Ning, X.; Ishida, H. *J Polym Sci Part A: Polym Chem* 1994, 32, 1121.
4. Ishida, H.; Allen, D. J. *J Appl Polym Sci* 2001, 79, 406.
5. Espinosa, M. A.; Cádiz, V.; Galià, M. *J Appl Polym Sci* 2003, 90, 470.
6. Ardhyantana, H.; Wahid, M. H.; Sasaki, M.; Agag, T.; Kawauchi, T.; Ismail, H.; Takeichi, T. *Polymer* 2008, 49, 4585.
7. Liu, Y.; Zheng, S. *J Polym Sci Part A: Polym Chem* 2006, 44, 1168.

8. Lee, Y. J.; Kuo, S. W.; Hung, C. F.; Chang, F. C. *Polymer* 2006, 47, 4378.
9. Ishida, H.; Low, H. Y. *Macromolecules* 1997, 30, 1099.
10. Kimura, H.; Matsumoto, A.; Hasegawa, K.; Ohtsuka, K.; Fukuda, A. *J Appl Polym Sci* 1998, 68, 1903.
11. Kimura, H.; Matsumoto, A.; Hasegawa, K.; Fukuda, A. *J Appl Polym Sci* 1998, 72, 1551.
12. Kimura, H.; Murata, Y.; Matsumoto, A.; Hasegawa, K.; Ohtsuka, K.; Fukuda, A. *J Appl Polym Sci* 1999, 74, 2266.
13. Kimura, H.; Matsumoto, A.; Sugito, H.; Hasegawa, K.; Ohtsuka, K.; Fukuda, A. *J Appl Polym Sci* 2001, 79, 555.
14. Kimura, H.; Taguchi, S.; Matsumoto, A. *J Appl Polym Sci* 2001, 79, 2331.
15. ASTM D 790: Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials, ASTM international, West Conshohocken, 2007.
16. ASTM D 1434: Standard test method for determining gas permeability characteristics of plastic film and sheeting, ASTM international, West Conshohocken, 2003.
17. JIS K 7194, Testing method for resistivity of conductive plastics with a four-point probe array, Japanese Industrial Standards Committee, Tokyo, 1994.
18. DOE Hydrogen Program 2008 Annual Progress Report, U.S. Department of Energy, Washington, DC, November 2008, 819.