Highly Filled Graphite Polybenzoxazine Composites for an Application as Bipolar Plates in Fuel Cells

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ABSTRACT: Highly filled graphite polybenzoxazine composites as bipolar plate material for polymer electrolyte membrane fuel cell (PEMFC) are developed. At the maximum graphite content of 80 wt % (68 vol %), storage modulus was increased from 5.9 GPa of the neat polybenzoxazine matrix to 23 GPa in the composite. Glass transition temperatures (T_g) of the composites were ranging from 176°C to 195°C and the values substantially increased with increasing the graphite contents. Thermal conductivity as high as 10.2 W/mK and electrical conductivity of 245 S cm^{-1} were obtained in the graphite filled polybenzoxazine at its maximum graphite loading. The obtained properties of the graphite filled polybenzoxazine composites exhibit most values exceed the United States department of energy requirements for PEMFC applications. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 3909–3918, 2013

INTRODUCTION

Polymer electrolyte membrane fuel cell (PEMFC) displays the most promising alternative source of energy for a variety of portable electronic devices, stationary, and vehicle applications.[1–4] The PEMFC operates at relatively low temperature (60–100°C) and has a high specific power and compactness. To generate useful current and voltage, individual single fuel cells are to be connected in series to form stack of cells. A bipolar plate is one of the key components of the fuel cells, which consumes around 38% of the total costs and may consume up to 80% of the total weight of the fuel cell stacks. Consequently, one of the main challenges in the development of PEMFCs is the reduction in cost as well as weight of the bipolar plate without compromising their performance and efficiency.[5] The bipolar plate's main functions include carrying current away from each fuel cell, distributing gas fuels within the cell and providing support for the membrane electrode assembly (MEA). The US department of energy (DOE) had proposed a technical target of bipolar plates for the year 2010, in which the main requirements are flexural modulus >10 GPa, flexural strength >25 MPa water absorption <0.3% at 24 h and electrical conductivity >100 S cm^{-1}.[6]

Nowadays, the most commonly used materials for a bipolar plate have been graphite-based polymer composite, because it has excellent chemical stability to survive the fuel cell environment. It also possesses good electrical conductivity, resulting in high electrochemical power output.

Graphite is the most commonly used material for a bipolar plate.[7–9] It has a good electrical conductivity and excellent corrosion resistance with a relatively low density of about 2.2 g cm^{-3}. However, it lacks mechanical strength and has poor ductility. These limit the minimum plate thickness to about 5–6 mm and machining is usually employed to fabricate the flow channels in the bipolar plate. Machining graphite into complex designs usually employed in bipolar plate fabrication is highly expensive and time-consuming therefore makes it unpractical for the full scale commercialization of fuel cells.[10]

Thermosetting resins are a highly attractive candidate as a binder resin of graphite filled composite especially for bipolar plate material because of their relatively ease of compounding with the filler comparing with thermoplastics. Benzoxazine resins are a novel kind of thermosetting phenolic resins that can be synthesized from phenol, formaldehyde, and primary amine. The curing process of benzoxazine resin into polybenzoxazine occurs via a ring-opening polymerization by thermal cure without a catalyst or curing agent and does not produce by-products during cure, which results in void-free products. Polybenzoxazines have been reported to possess outstanding properties such as near-zero volumetric shrinkage upon polymerization, ease of processing or compounding due to very low melt viscosity, high glass transition temperature (T_g), high thermal stability, and low water absorption.[11,12] Consequently, several highly filled and high performance polymer composites

from polybenzoxazines have been successfully developed and reported.[13,14] Henkel AG & Co. KGaA recently launches Henkel Benzoxazine Resin 99110[TM] for a wide range of aircraft applications.[15] Whereas Huntsman advanced materials has already commercialized five types of solid benzoxazine resins as a new generation of halogen-free materials for a broad range of advanced applications.[16]

Kimura et al. utilized three kind of graphite i.e., synthetic graphite, natural graphite, and expanded graphite, for the preparation of graphite/polybenzoxazine composites at the fixed graphite content of 80 wt %. It was found that the polybenzoxazine composites showed superior gas impermeability and mechanical property to conventional graphite/phenolic composites while electrical resistivity value as low as 2.2 mΩ cm from the graphite/polybenzoxazine composite was achieved.[17] However, the thermal properties such as thermal conductivity, thermal diffusivity, glass transition temperature, as well as thermal degradation behaviors of the graphite filled polybenzoxazine, which are also crucial for the successful bipolar plate application were not reported in their study.

In this study, we aim to prepare and characterize properties of graphite-filled composites based on polybenzoxazine at a relatively high graphite loading up to 80% by weight for bipolar plate application. Some essential properties such as mechanical properties, water uptake, thermal conductivity, thermal stability, and electrical conductivity of these highly filled composites will be evaluated.

EXPERIMENTAL

Materials
The materials in this research are benzoxazine resin and graphite. Benzoxazine resin (BA-a) is based on bisphenol-A, aniline, and formaldehyde. Thai Polycarbonate (TPCC) kindly supplied the bisphenol-A (polycarbonate grade). Paraformaldehyde (AR grade) and graphite powder (size: average 50 μm, purity: 95%) were purchased from Merck Ltd. whereas aniline (AR grade) was obtained from Panreac Quimica SA.

Benzoxazine Resin Preparation
Benzoxazine monomer (BA-a) was synthesized from bisphenol-A, aniline, and paraformaldehyde at a 1 : 2 : 4 molar ratio. The reactant mixture was constantly stirred at 110°C using the patented solventless technology.[18] Normally, the monomer is light yellow solid at room temperature. The resin was ground into fine powder and was kept in a refrigerator for further use.

Graphite-Polybenzoxazine Composites Preparation
The graphite-filled samples were prepared with graphite loadings of 0, 40, 50, 60, 70, 75, 80, and 85% by weight to yield molding compounds. The graphite was firstly dried at 110°C for 24 h in an air-circulated oven until a constant weight was achieved and was then kept in a desiccator at room temperature. The filler was mechanically stirred to achieve uniform dispersion in benzoxazine resin using an internal mixer at about 110°C. For thermal-cured specimen, the compound was compression-molded by hot pressing. The thickness was controlled using a metal spacer. The hot-press temperature of 150°C was applied for 1 h and 200°C for 3 h using a hydraulic

pressure of 15 MPa. All samples were air-cooled to room temperature in the open mold and were cut into desired shapes before testing.

Characterizations of the Highly Filled Graphite-Polybenzoxazine Composite
Curing characteristics of the benzoxazine-graphite composites were examined by a differential scanning calorimeter (DSC) model 2910 from TA Instrument. For each test, a small amount of the sample ranging from 5 to 10 mg was placed on the aluminum pan and sealed hermetically with aluminum lids. The experiment was done using a heating rate of 10°C/min to heat the sealed sample from 30°C up to 300°C under N₂ purging. The purge nitrogen gas flow rate was maintained at 50 ml/min.

The density of each specimen was determined by a water displacement method according to ASTM D792 (Method A). All specimens were prepared in a rectangular shape (50 × 25 × 2 mm³). Each specimen was weighed in air and in water at 23 ± 2°C. The density was calculated using eq. (1). An average value from at least five specimens was calculated.

$$\rho = \frac{A}{A-B} \times \rho_0 \qquad (1)$$

where ρ is the density of the specimen, A is the weight of the specimen in air, B is the weight of the specimen in liquid (water), and ρ_o is the density of the liquid (water) at the given temperature.

The dynamic mechanical analyzer (DMA) model DMA242 from NETZSCH Instrument was used to investigate dynamic mechanical properties of the composite samples. The dimension of each specimen was 50 × 10 × 2.5 mm³ (W × L × T). The test was performed under the three-point bending mode. A strain in the range of 0–30 μm was applied sinusoidally at a frequency of 1 Hz. The temperature was scanned from 30°C to 300°C with a heating rate of 5°C/min under nitrogen atmosphere.

A thermogravimetric analyzer model TGA/SDTA 851[e] from Mettler-Toledo (Thailand) was used to study thermal stability of graphite: polybenzoxazine composites. The initial mass of the composite to be tested was about 10 mg. It was heated from room temperature to 820°C at a heating rate of 20°C/min under nitrogen atmosphere. The degradation temperature at 5% weight loss and solid residue of each specimen determined at 800°C were then recorded.

Specific heat capacities of all samples were measured using a differential scanning calorimeter (DSC) model 2920 from Perkin-Elmer (Norwalk, CT) Instruments. All samples were crimped in nonhermetic aluminum pans with lids. The mass of the reference and sample pans with lids were measured to within 15–20 mg. The sample was purged with dry nitrogen gas at a flow rate of 60 mL min⁻¹. The test was performed from room temperature up to 200°C at a heating rate of 10°C/min.

Thermal diffusivity of the graphite-filled polybenzoxazine composites was measured by laser flash diffusivity instrument (Nano-Flash-Apparatus, LFA 447, NETZSCH). The composite specimens were prepared in a rectangular shape

$(10 \times 10 \times 1 \text{ mm}^3)$. All measurements were conducted from room temperature to 180°C.

Thermal conductivity (k) of the composite samples was calculated using the measured thermal diffusivity (α), specific heat capacity at constant pressure (C_p), and the measured density (ρ) of the sample according to eq. (2).

$$k = \alpha \times \rho \times C_p \qquad (2)$$

Flexural modulus and flexural strength of the composite specimens were determined utilizing a Universal Testing Machine (Instron Instrument model 5567). The dimension of the specimens was $50 \times 25 \times 2 \text{ mm}^3$. The test method used was a three-point bending mode with a support span of 32 mm. Bending was performed at a crosshead speed of 0.85 mm/min. The flexural modulus and the flexural strength were determined according to the procedure described in ASTM D 790.

Water absorption measurement was conducted following ASTM D570 using disk-shaped specimens having a diameter of 50 mm and a thickness of 3.0 mm. All specimens were conditioned, weighed, and submerged in distilled water at 25°C. The specimens were occasionally removed, wiped dry, weighed, and immediately returned to the water bath. The amount of water absorbed was calculated based on the initial conditioned mass of each specimen.

Electrical conductivity/resistivity of the samples was measured by a conventional probe method at a constant current supply. Kiethley 224 from Kiethley Instruments with programmable current source was used to provide a constant voltage drop (V) while current supply (I) in between two pinpoints was measured by Keithley 197A auto-ranging microvolt DMM. From the value of electrical resistance, electrical conductivity was calculated. An average value from 4 to 5 readings on each plate (in x–y plane) was then reported.

Interfacial bonding of a filled sample was investigated using an ISM-5400 scanning electron microscope (SEM), from JOEL, at an acceleration voltage of 15 kV. All specimens were coated with thin film of gold using a JEOL ion sputtering device (model JFC-1100E) for 4 min to obtain a thickness of ~30 Å and the micrographs of the specimen fracture surface were then taken. The obtained micrographs were used to qualitatively evaluate the interfacial interaction between the graphite filler and the matrix resin.

RESULTS AND DISCUSSION

Curing Behaviors of Graphite-Benzoxazine Molding Compounds

Curing condition of benzoxazine resin filled with different graphite contents was investigated by DSC with a temperature range of 30–300°C using a heating rate of 10°C/min. Figure 1(a) shows the curing exotherms of the neat benzoxazine resin (BA-a) and the benzoxazine molding compounds at different graphite contents. A maximum exothermic peak of benzoxazine resin was observed at 233°C, which is the characteristic of oxazine ring opening reaction.[11,12] Moreover, the thermograms of the molding compounds shows no peak shift with the amount of the graphite loading, indicating that graphite has no direct effect on crosslinking reaction during the curing process of the benzoxazine resins. This phenom-
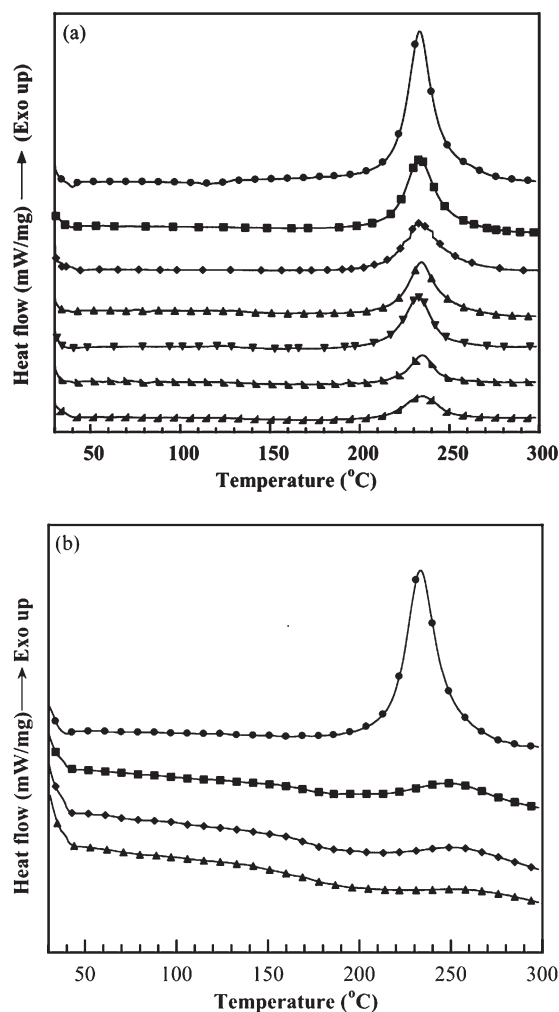
Figure 1. (a) DSC thermograms of benzoxazine molding compound at different graphite contents: (●) neat benzoxazine monomer, (■) 40 wt %, (◆) 50 wt %, (▲) 60 wt %, (▼) 70 wt %, () 75 wt %, () 80 wt %. (b) DSC thermograms of the composite (40 wt % graphite) at various curing times at 200°C: (●) Uncured molding compound, (■) 1 h, (◆) 2 h, (▲) 3 h. (The labeling symbols for the composites with the same graphite loadings in this figure can also be applied in Figures 3, 4, 6, 7, and 10).

enon implies that the graphite filler is relatively inert to the benzoxazine curing reaction. Figure 1(b) shows the DSC thermograms of the benzoxazine molding compound at 40 wt % of the graphite at various curing conditions. The heat of reaction was determined from the area under each exothermic peak. From the results, the value of the area under the exothermic peak decreased from 254 J/g of the uncured benzoxazine molding compound to 19, 11, and 4 J/g, after curing at 200°C for 1, 2, and 3 hr, respectively. The degree of conversion estimated by eq. (3) below was determined to be 98% after curing at 200°C for 3 h. Therefore, this curing condition was used for polymerization for all of our benzoxazine molding compounds.

$$\%\text{conversion} = \left[1 - \frac{H_{\text{rxn}}}{H_0} \right] \times 100 \qquad (3)$$

where H_{rxn} is the heat of reaction of the partially cured specimens and H_0 is the heat of reaction of the uncured resin.

Composite Density Measurement and Maximum Packing Density of Graphite in the Polybenzoxazine
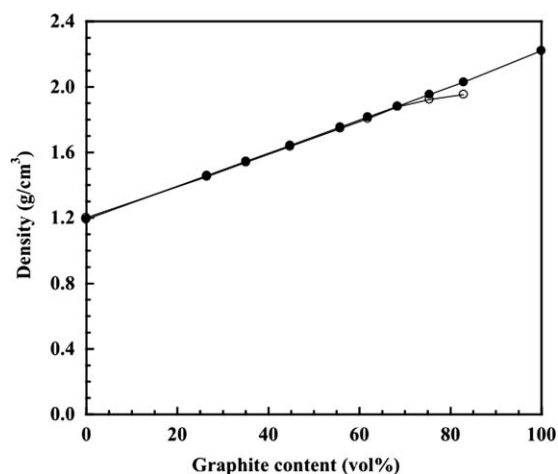
Figure 2 exhibits the density of the neat polybenzoxazine and graphite filled polybenzoxazine as a function of filler content. Density measurements of all composites were used to investigate the presence of void in the composite specimens, which can substantially deteriorate various properties of the resulting composites. One outstanding property of benzoxazine matrix resin is its low melt viscosity in which the highly filled composites can easily be obtained. This figure exhibits the theoretical density of the composites in comparison with their actual density. The theoretical density of the composites was calculated from eq. (4). The calculation is based on the basis that the densities of the graphite and of the polybenzoxazine are 2.22 and 1.20 g/cm^3, respectively. Because of the higher density of graphite, the results revealed that the theoretical and actual density of the polybenzoxazine composites was increased with the graphite content following a rule of mixture when adding graphite up to 68 vol % or 80 wt %. The attempt to add graphite higher than 68 vol % was found to provide the lower experimental density value than the theoretical value possibly because of the presence of void or air gap in the sample. Therefore, the maximum graphite loading between the graphite filler and the polybenzoxazine matrix was found to be 68 vol %.

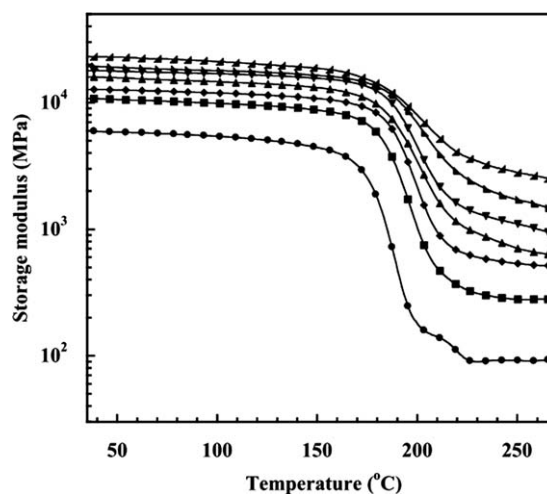$$\rho_c = \frac{1}{\dfrac{W_f}{\rho_f} - \dfrac{(1-W_f)}{\rho_m}} \qquad (4)$$

where ρ_c is the composite density, ρ_f is the filler density, ρ_m is the matrix density, and W_f is the filler weight fraction.

Dynamics Mechanical Properties of Highly Filled Polybenzoxazine Composites as a Function of Graphite Contents

Figures 3 and 4 illustrate the dynamic mechanical properties of the graphite filled polybenzoxazine composites with the graphite contents ranging from 0 to 80 wt %. At room temperature, the storage modulus (E') of the graphite filled polybenzoxazine composites increased with increasing graphite content as seen in

Figure 3. DMA thermograms of storage modulus of graphite filled polybenzoxazine composites.

Figure 3. The modulus value was raised from 5.9 GPa for the neat polybenzoxazine to the very high value of 23 GPa for the 80 wt % graphite filled composite, which is about 290% enhancement in the polybenzoxazine stiffness. The modulus of the graphite filled polybenzoxazine in the rubbery plateau region was also found to increase significantly with increasing amout of the graphite. The influence is possibly attributed to the addition of rigid particulate filler into the polymer matrix was able to improve the stiffness of the polymer composite. The results indicate the substantial reinforcing effect of the graphite filler on both in the rubbery and the glassy state modulus implying strong interfacial bonding between the polybenzoxazine matrix and the graphite filler.

Figure 4 exhibits the loss modulus (E'') curves of the graphite filled polybenzoxazine as a function of temperature. The temperature at the maximum of the loss modulus curve was assigned as a glass transition temperature (T_g) of the specimen.
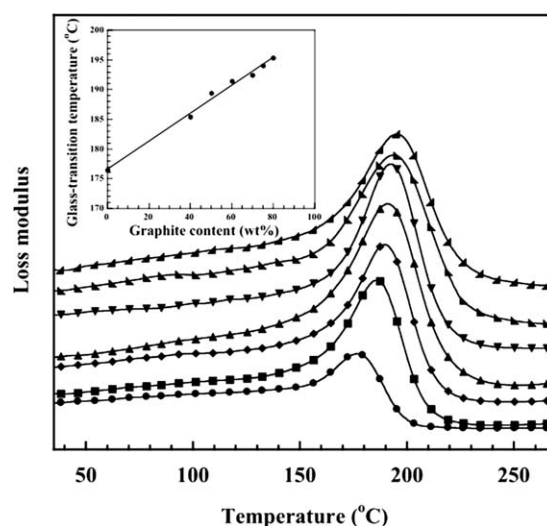

Figure 2. Theoretical and actual density of graphite filled polybenzoxazine composites at different content of graphite: (●) theoretical density, (○) actual density.

Figure 4. DMA thermograms of loss modulus of graphite filled polybenzoxazine composites. Inset: glass transition temperature of graphite filled polybenzoxazine composites at various graphite contents.
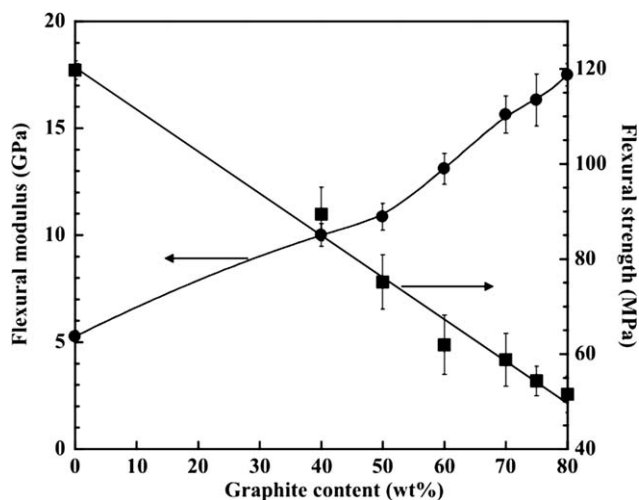
Figure 5. (●) Flexural modulus and (■) flexural strength of graphite filled polybenzoxazine composites.

As seen in this figure and its inset, the linear relationship between the glass transition temperature and the filler content was observed. The glass transition temperature of the neat polybenzoxazine was determined to be 176°C whereas the glass transition temperature of the 80 wt % graphite filled polybenzoxazine is about 195°C. An increase of the T_g with an addition of the graphite is likely due to the good interfacial adhesion between the graphite filler and polybenzoxazine matrix, which can highly restrict the mobility of the polymer chain. This behavior also confirmed the high reinforcing effect of the graphite to provide a substantial enhancment in the storage modulus of the obtained polybenzoxazine composites.

Effect of Graphite Loadings on Flexural Properties of Highly Filled Polybenzoxazine

Bipolar plates require good mechanical properties to withstand the high clamping forces of the stacking and vibrations during vehicular applications.[19,20] Flexural modulus and flexural strength of the neat polybenzoxazine and graphite-filled polybenzoxazine composites are illustrated as a function of graphite content in Figure 5. From this plot, the flexural modulus values of the composites were found to be substantially improved by the presence of the graphite up to 80 wt %. The modulus of the neat polybenzoxazine was determined to be 5.2 GPa whereas at 40–80% by weight of graphite, the modulus of the polybenzoxazine composites increased from 10.0 to 17.5 GPa. The phenomenon was attributed to the substantial interfacial interaction between the filler and the matrix thus the addition of rigid particulate graphite into the polybenzoxazine matrix was able to substantially improve the stiffness of the resulting polymer composites. In addition, it was also found that the modulus of the composites tended to follow a rule of mixture. In this work, the flexural modulus of graphite filled composite at 80 wt % was 236% higher than that of neat polybenzoxazine.

However, as shown this figure, at graphite filled polybenzoxazine composites of 40–80% by weight, it was observed that the flexural strength of the composite bipolar plates decreased with increasing graphite content. At maximum graphite content of

80 wt %, the flexural strength of our polybenzoxazine composite was determined to be 52 MPa. The value is more than two times greater than the target strength value set by DOE i.e., 25 MPa. It was postulated that the aggregation and agglomeration that may present in the graphite may cause some microscopic defects in the composites thus lowering the strength values. These observed phenomena are similar to those observed in the systems of graphite-epoxy,[21] graphite-phenolic resin,[22] graphite-phenol formaldehyde resin, and graphite-novolac epoxy.[23] However, our graphite-polybenzoxazine composites still showed the flexural strength value significantly higher than that of other graphite composite systems.[21–23] The highest reported flexural strength obtained for graphite-polymer composites was 45 MPa at 80 wt % of total filler (i.e., 5 wt % of carbon nanotube mixed with 75 wt % of graphite) in novolac epoxy[23] whereas those of the 85 wt % graphite-filled poly(phenylene sulfide), graphite-filled poly(vinylidene fluoride), and graphite-filled poly(propylene glycol) provided that flexural strength values of only 30, 31, and 37 MPa, respectively.[24]

Effect of Graphite Loadings on Thermal Stability of Graphite-Filled Polybenzoxazine

Degradation temperature (T_d) is one of the key parameters used to determine thermal stability of polymeric materials. Figure 6 and its inset exhibit TGA thermograms of the neat polybenzoxazine and graphite filled polybenzoxazine composites at various graphite contents in nitrogen atmosphere. It was observed that pure graphite exhibits outstandingly high thermal stability with negligible weight loss up to 800°C. On the other hand, the polybenzoxazine matrix possesses a degradation temperature at its 5% weight loss of 320°C and the char residue at 800°C of 25% as seen in Figure 6. Additionally, the degradation temperature at 5% weight loss of the graphite filled polybenzoxazine composites was found to systematically increase with increasing graphite content as seen in inset of Figure 6. The decomposition temperature at the highest graphite content of 80 wt % in the
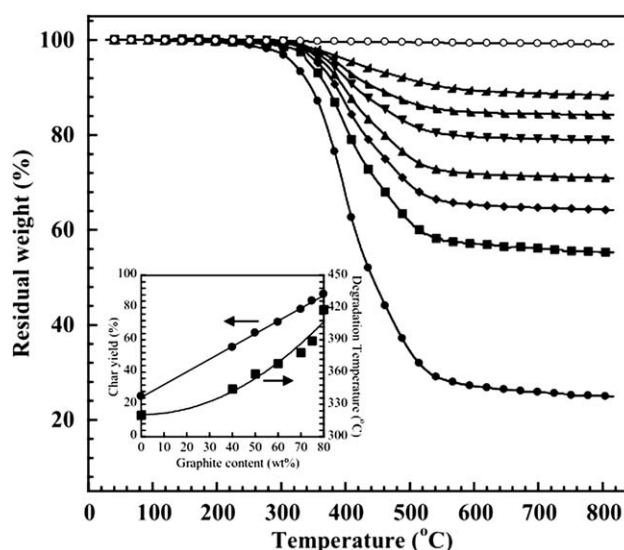
Figure 6. TGA thermograms of graphite filled polybenzoxazine composites. Inset: (●) char yield (800°C) and (■) degradation temperature (5%Wight loss) of graphite filled polybenzoxazine composites.
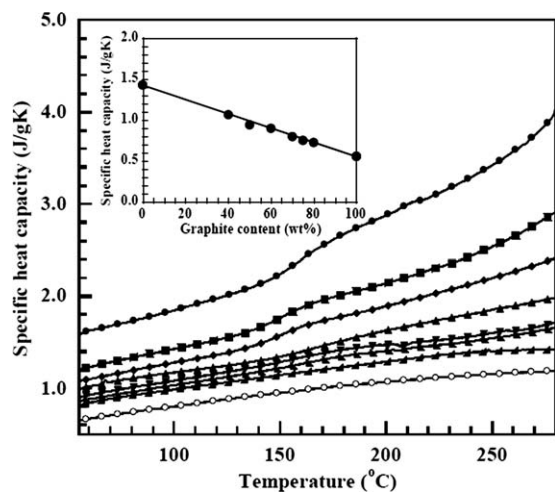
Figure 7. Specific heat capacity of graphite filled polybenzoxazine composites, (○) neat graphite at various temperature. Inset: specific heat capacity of graphite filled polybenzoxazine composites at various graphite contents.

polybenzoxazine was determined to be about 420°C, which is about 100°C greater than that of the unfilled polybenzoxazine. This extraordinary enhancement in the thermal properties of the highly filler polybenzoxazine is likely due to the outstanding barrier effect of the graphite, which minimize the permeability of volatile degradation products out from the material, as well as the strong bonding of the benzoxazine resin to the graphite. When the temperature was raised to 800°C, only the polybenzoxazine fraction was decomposed thermally and formed char. Therefore, the amounts of solid residue in this case can be approximated to correspond to the content of the graphite filler plus char residue of the polybenzoxazine fraction.

Specific Heat Capacity from DSC of Graphite-Polybenzoxazine Composites

Specific heat capacity (C_p) is a thermodynamic property that describes the ability of a material to store thermal energy. In particular, heat capacity dictates the amount of energy one must put into the system in order to heat the material to a certain temperature.[25] The effect of temperature on composite specific heat capacity at different filler loading is shown in Figure 7. From this figure, an addition of graphite in polybenzoxazine decreased its specific heat capacities as expected due to the lower specific heat capacities of the graphite as compared to the polymer. In the observed temperature range, the specific heat was found to increase with increasing temperature. The effect of temperature on the specific heat capacities of the composites can be determined from the slope of the plots. From the experimental results, we observed fairly low and stable slopes in our composite systems up to about 140°C. This is due to the high thermal stability and T_g of the polybenzoxazine matrix used. However, within this temperature range, we observed the inflection of the slope of the plot at the temperature about 160°C and higher, which is the glass transition of the polybenzoxazine and its composites. The plot also reveals a linear relationship between the specific heat capacity and the filler loading as illustrated in an inset of Figure 7.

Because of the structure-insensitive characteristic of composite specific heat capacity,[26] the effect of filler loading on the composite heat capacity should be predicted by a rule of mixture as expressed in eq. (5).

For a two-phase system,

$$C_{pc} = C_{pf} W_f + C_{pp}(1 - W_f) \tag{5}$$

C_{pc}, C_{pf}, and C_{pp} are the specific heat capacities of the composite, filler, and polymer, respectively, W_f is the mass fraction of the filler.

The inset of Figure 7 shows the plot of the composite specific heat capacity as a function of filler loading ranging from 40 to 80% by mass of filler at 25°C. We obtain the specific heat capacity value of the pure graphite and neat polybenzoxazine with the value of 0.753 and 1.756 J K^{-1} g^{-1}, respectively. The values were then substituted in eq. (5) to yield heat capacity of the composites i.e.,

$$C_{pc} = 0.753 W_f + 1.756(1 - W_f) \tag{6}$$

The plot reveals a linear relationship between specific heat capacity and filler loading as suggested by eq. (6). The specific heat capacity values at different filler contents from the experimental results are therefore in good agreement with those predicted by the rule of mixture with an error within ±1.0%. Heat capacity and density are important parameters used to convert thermal diffusivity to thermal conductivity, a very useful transport property of material.

Thermal Diffusivity and Thermal Conductivity of Graphite-Filled Polybenzoxazine at Varied Graphite Contents

Thermal diffusivity of graphite filled polybenzoxazine composites as a function of filler content at room temperature is shown in Figure 8. As seen in this figure, an addition of highly thermally conductive graphite enhanced the thermal diffusivity of the neat polybenzoxazine significantly, particularly, at high contents of the graphite. At below 50% by weight of graphite, thermal diffusivity of the composites increased slightly with the amount of the filler; however, beyond 50% by weight, the sharp increase in the diffusivity values was clearly observed. Similar behavior was also observed and reported in the highly filled
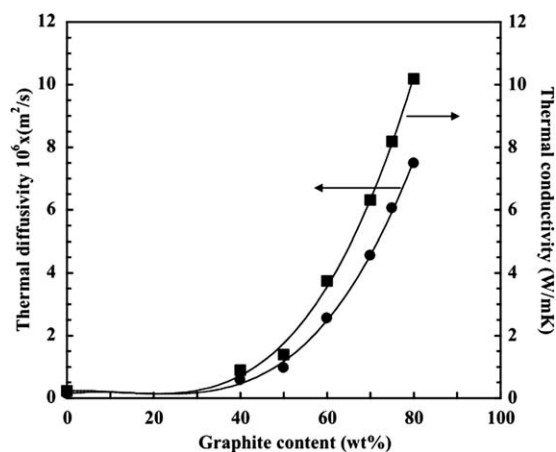
Figure 8. (●) Thermal diffusivity and (■) thermal diffusivity at 25°C of graphite filled polybenzoxazine as a function of filler contents.

Table I. Thermal Conductivity of Graphite-Filled Polybenzoxazine

Filler content (wt %)	$\alpha \times 10^6$ (m²/s)	C_p (J/kg K)	ρ (g/m³)	k (W/mK)
0	0.133	1.427	1.200	0.228
40	0.577	1.063	1.452	0.890
50	0.963	0.942	1.537	1.394
60	2.546	0.900	1.635	3.744
70	4.550	0.795	1.746	6.314
75	6.051	0.749	1.806	8.185
80	7.482	0.725	1.877	10.185

$$k = 0.014129 * (\phi - \phi_c)^{(1.7033)} \quad R = 0.99844$$

Figure 9. Percolation theory of thermal conductivity of graphite filled polybenzoxazine.
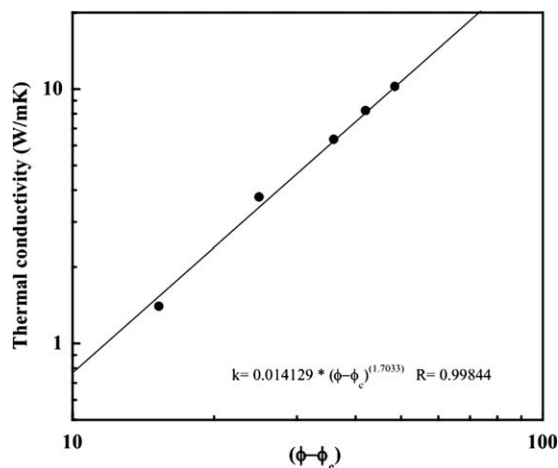
systems of boron nitride and polybenzoxazine,[13] graphite/polystyrene system,[27] or glass/ethylene vinyl acetate system.[28] The behavior was attributed to the formation of tremendous amount of conductive paths in the filled systems with the loading approaching their maximum packing i.e., highly filled composites. In theory, thermal diffusivity can be converted into thermal conductivity by the relationship expressed in eq. (2). To determine the thermal conductivities of the composites, densities, and heat capacities of the composite are thus needed.

Thermal Conductivity Determination of Graphite Filled Polybenzoxazine Composites

In practice, a bipolar plate must be thermally conductive to dissipate the generated heat (reaction by-product) from an active part of the fuel cell to a cooling channel, to control the stack temperature and to achieve a homogeneous temperature distribution in each cell and over the whole active area, therefore; thermal conductivity is one critical bipolar plate characteristic. Table I shows the thermal diffusivities, heat capacities, and composite densities of the highly filled composite specimens at different graphite compositions as well as the corresponding values of thermal conductivities determined from eq. (2). The calculated thermal conductivity values of the composites were also plotted in Figure 8.

As it can be seen from the figure, thermal conductivity increased as the graphite content increased. When the graphite concentration reached 80 wt %, thermal conductivity of the resulting composite increased to 10.2 W/mK or more than 44 times greater than that of the pure polybenzoxazine (0.23 W/mK). This substantial increase in the k-value is attributed to the significant amount of conductive pathways formed in the composite. As per the recent benchmark given by the US DOE, the recommended value of thermal conductivity for bipolar plate material is to be greater than 10 W/mK.[6] Our highly filled graphite-polybenzoxazine composites at 80% by weight of graphite content are, therefore, a promising bipolar plate for the fuel cell application with the thermal conductivity value meets that of DOE requirement.

Bond percolation theory gives a phenomenological description of the conductivity of a disordered system near the insulator-conductor transition relatively well, especially, in path-dependent properties of materials such as electrical conductivity. The filler content (ϕ) at the insulator-conductor transition point is called the percolation threshold, ϕ_c a point at which the first conductive path is formed. However, thermal conduc-

tivity seems to be an intermediate property between a path-dependent property and a bulk property.[13] Hence, the thermal conductivity value in the composite material tends to depend on both the formation of the filler network and the filler loading. Generally, the percolation threshold of thermally conductive composite is difficult to define. In our system, we use a percolation threshold of 0.198, which is the currently accepted percolation threshold for a three dimensional network.[13,29] Figure 9 is the plot between log k and $\log(\phi - \phi_c)$. The slope of the plot is the critical percolation exponent. From the plot, we obtained the critical exponent having the value of 1.703, which is close to the theoretical universal value of 2.0 in bond percolation for a three-dimensional system.[13,29]
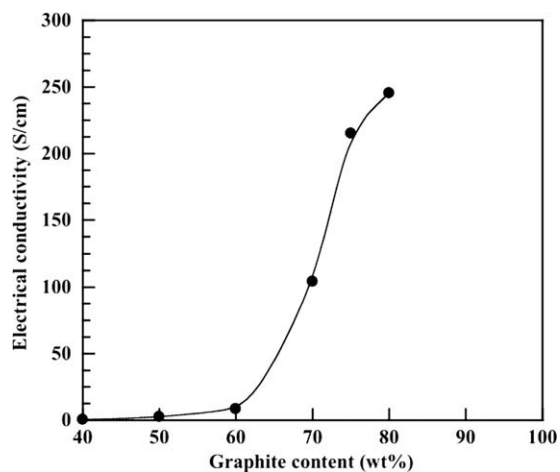
Water Absorption Property of Graphite-Polybenzoxazine Composites for Bipolar Plate Material

In this experiment, water absorption of each specimen was calculated from eq. (7):
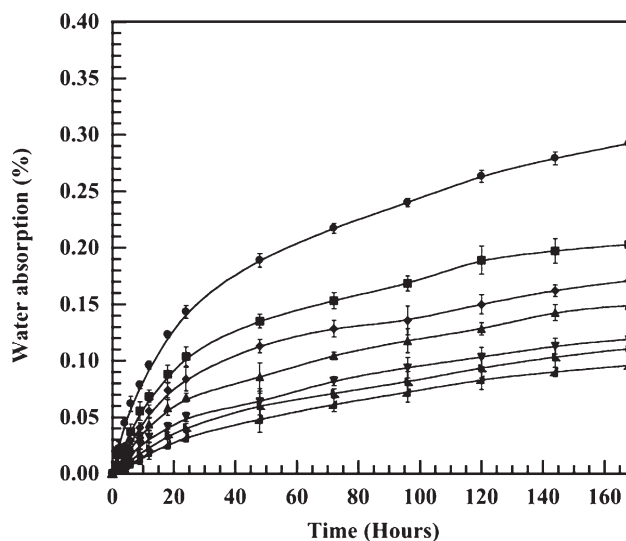
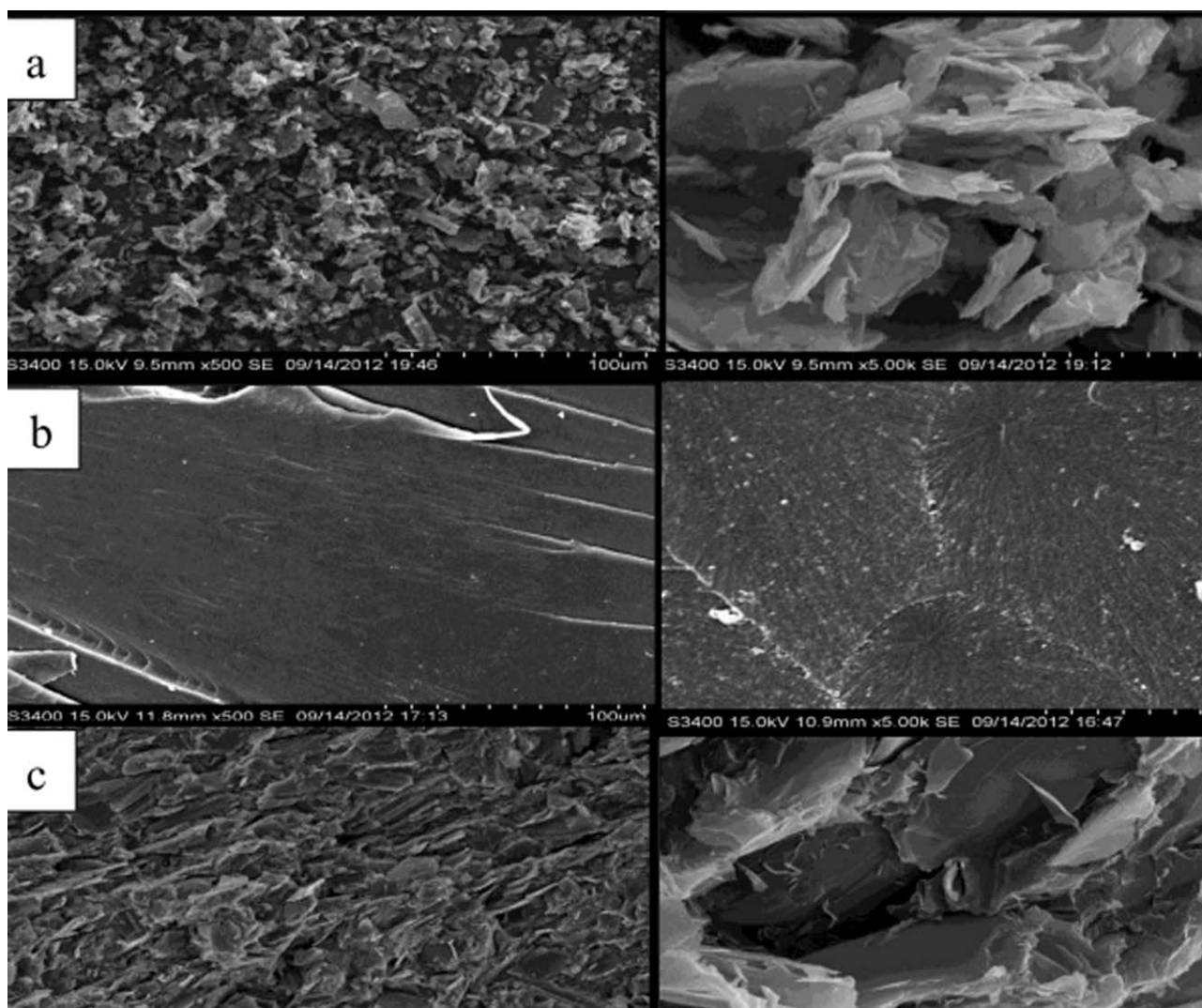**Figure 10.** Water absorption of graphite filled polybenzoxazine composites.

Figure 11. Effect of the graphite content on electrical conductivity (in-plane) of graphite filled polybenzoxazine composites.

$$\text{Water}\quad \text{absorption}\,(\%) = \frac{W - W_d}{W_d} \times 100 \qquad (7)$$

In eq. (7), W is the weight of the specimen at time t, and W_d is the weight of the dry specimen.

Water absorption values of the graphite filled polybenzoxazine composites at different graphite contents are exhibited in Figure 10. The percentage of water absorbed plotted against time of all specimens revealed a similar behavior i.e., the specimens absorbed water more rapidly during first stages (0–24 h). The water adsorption values of all graphite-polybenzoxazine composites at different filler contents ranging from 40 to 80% by weight were recorded up to 168 h of the immersion i.e. beyond their saturation points. These composites showed very low room temperature water uptake having values of much less than 0.3%, which is the value desired in the industrial standard of typical composites for bipolar plate.[6] The water uptake of all compositions at 24 h is <0.11% and only about 0.03% at a

Figure 12. SEM micrographs of fracture surface of graphite-filled polybenzoxazine composites: (a) pure graphite, (b) neat polybenzoxazine (PBZ), and (c) 80 wt % graphite-filled PBZ.

filler content of 80% by weight. Furthermore, the water uptake up to 168 h is only 0.2% at graphite content of 40% by weight and steadily lower at higher graphite contents. These values were also significantly lower than water absorption values of other composite systems such as those of graphite filled with epoxy.[30] For example, Du and Jana reported a 24 h water uptake of about 1.8% for graphite-epoxy composite (at 50 wt % graphite). The decrease of water absorption with increasing graphite content is attributed to the presence of the more hydrophobic nature of the graphite filler in the polymer composites. The water absorption study in our work also confirms the good wetting of the benzoxazine resin with the graphite filler thus resulting in a very low water uptake at 24 h of only 0.08% by weight at 50% by weight of graphite and only 0.03% by weight at the maximum graphite content of 80% by weight. While in the 50% by weight of graphite filled epoxy i.e., the highest reported graphite content in this study, the water uptake at 24 h was reported to be significantly higher with the value of 1.8%.[30] Our result also suggests good interfacial interaction of the polybenzoxazine with the graphite.

Electrical Conductivity of Highly Filled Polybenzoxazine as a Function of Graphite Contents

Major function of bipolar plates is to collect and transport electrons generated by the electrochemical reaction in fuel cell stacks. The materials for bipolar plate fabrication require high electrical conductivity to minimize voltage loss. As a consequence, the electrical conductivity is one of the most important characteristics among those requirements for a bipolar plate application. The property is largely influenced by the total filler loading and an ability to form a conductive network of the conductive filler used.[23] Figure 11 depicts electrical conductivity of the graphite filled polybenzoxazine composites at different weight fraction of graphite. It is evident that the conductivity of the composite increased with an increase in graphite content up to 80% by weight. This is due to the gradual formation of the percolating network of graphite particles within the polybenzoxazine matrix with increasing the graphite content.[31] As per the recent benchmark given by DOE, USA, the recommended value of electrical conductivity for bipolar plate is >100 S cm^{-1}.[6] Our highly filled graphite-polybenzoxazine composites at 70–80% by weight of graphite content were found to be a promising candidate for bipolar plate for the fuel cell application as they showed relatively high electrical conductivity of 104 to 245 S cm^{-1}, which evidently meet that of DOE requirements. Moreover, our polybenzoxazine composites showed greater enhancement in electrical conductivity than those in other graphite/polymer systems such as novolac epoxy,[32] phenol formaldehyde,[33] and epoxy[21,23] comparing at the same graphite loading.[21,23,32,33] That is in the case of resole-typed phenol formaldehyde resin, the electrical conductivity value was reported to be 125 S cm^{-1} for the 65 vol % graphite whereas at the graphite content of 85 vol %, the highest electrical conductivity value was reported to be 235 S cm^{-1}.[33]

Fracture Surface of Graphited-Filled Polybenzoxazine Composites

Figure 12(a–c) exhibits interfacial characteristics along the fracture surface at the magnification of 500 times and 5000 times

of the pure graphite, the neat polybenzoxazine and the graphite filled polybenzoxazine. SEM micrographs of the graphite platelets are shown in Figure 12(a). These platelets are flake-like structure consisting of stacks of thin plates. Figure 12(b) shows the fracture surface of pure polybenzoxazine revealing relatively smooth fracture surface as compared to that of the graphite filled polybenzoxazine composite. Figure 12(c) illustrates the SEM micrographs of the graphite filled polybenzoxazine composites with graphite content of 80 wt %. The graphite-filled composite based on polybenzoxazine shows relatively good distribution of graphite particles in the matrix with substantial interfacial adhesion between the matrix and the graphite. These results might be attributed to the very low viscosity and good flow ability or wettability of the benzoxazine resin to the graphite at the molding temperature. Only thin layer of the polybenzoxazine covered those graphite particles with minimal void formation. At the high level of the graphite particles, they tend to be in good contact with each other to give a well-developed electrical pathway and an obtained high electrical conductivity with substantial mechanical integrity of the resulting composites.

CONCLUSIONS

Bipolar plate based on highly filled systems of graphite and polybenzoxazine have been developed. The graphite content is varied between 0 and 80 wt %. The resulting composite's flexural modulus was enhanced from 5.2 to 17.5 GPa at a maximum graphite loading of 80 wt %. The water absorption of the polybenzoxazine composites was significantly suppressed with the addition of the graphite. Thermal conductivity and electrical conductivity of the composites having 80 wt % of graphite was determined to be as high as 10.2 W/mK and 245 S cm^{-1}. The obtained thermal properties, mechanical properties, and electrical conductivity of the highly filled graphite-polybenzoxazine composites were found to be highly attractive for bipolar plates in polymer electrolyte fuel cell application. The obtained properties were found to meet those requirements set by the US DOE.

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