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Preparation and Characterizations of Highly Filled Graphene-Polybenzoxazine Composites

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Abstract

In recent years, graphene has been extensively utilized in electronic applications due to its superior electrical conductivity, high thermal conductivity and excellent mechanical properties(1,2). This research emphasized on the development of graphene (xGnP Grade H, XG Science, USA) filled composites based on polybenzoxazine particularly at high graphene loading (0-60wt%)(3,4). It was found that the density of the obtained composites was linearly increased with graphene content and the values were determined to be 1.185-1.637 g/cm^3 which followed the rule of mixture suggesting negligible void in the composites samples. Mechanical and thermal properties of the graphene filled polybenzoxazine composites were examined by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). The curing temperature of the composites was observed to remarkably reduce from 233°C for the as-synthesized benzoxazine resin to 196°C at 60wt% of the graphene content suggesting curing acceleration with the presence of graphene. The storage modulus (E') at room temperature of the composites was considerably enhanced with the amount of the graphene i.e. from 5.9GPa of the neat polybenzoxazine to about 25.1 GPa at 60wt% of graphene. The glass-transition temperatures (T_g) obtained from the maximum peak of loss modulus of the graphene-filled polybenzoxazine composites were observed to be in a range of 174°C to 188°C. The T_g values increased substantially with increasing graphene content implying good interfacial interaction between the graphene filler and the polybenzoxazine matrix. Other essential properties of these highly filled composites including gas permeability, electrical and thermal conductivity are also evaluated for potential use as a bipolar plates for proton exchange membrane fuel cells.

Keywords : Highly Filled, Graphene, Polybenzoxazine
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Introduction

The polymer electrolyte membrane fuel cells (PEMFC) have been known as the most promising alternative source of energy due to their high efficiency and zero emission(5). The features of PEMFC are high power density, low temperature operation (50-80°C) and no pollutant release(2).

The bipolar plate is an important part of PEMFC which account for 45% of cost and 80% of total weight of fuel cell stacks(6). Therefore, the bipolar plate needs to be lightweight and inexpensive but should have good chemical compatibility with the oxidation/reduction environment of PEMFC(7).

The main functions of bipolar plate include carrying current away from each fuel cell, distributing gas fuels within the cell and providing support for the Membrane Electrode Assembly (MEA)(7).

Graphene, two-dimensional (2-D) sheet composed of sp^2 carbon atoms arranged in a honeycomb structure, has been explored to be an excellent material due to it has been reported to possess excellent mechanical strength (Young's modulus of 1 TPa, ultimate strength of 130 GPa), large specific area (theoretical limit: 2630 m^2/g) and low gas permeability. Especially, graphene exhibits a superior electrical conductivity and high thermal conductivity (5000 W/mK) thus gains much attention for bipolar plate utilization(2).

Polybenzoxazines are a novel class of thermosetting polymers which offer a number of attractive properties such as very low melt viscosity, high glass transition temperature, high thermal stability, good mechanical strength and modulus, low water absorption, low dielectric constant, good adhesive properties, high resistance to burning and chemicals and no by-product release during cure(8). The very low melt viscosity and good adhesion of benzoxazine resin results in

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its ease of filler mixing during the molding compound preparation thus giving its outstanding characteristics as matrix materials for composite fabrication.

In this research we aim to prepare and characterize properties of highly filled system of graphene-polybenzoxazine composites. Physical, mechanical and thermal properties of the composites will be investigated.

Materials and Experimental Procedures

Materials

The materials in this research are benzoxazine resin and graphene nanoplatelets. Benzoxazine resin (BA-a) is based on bisphenol-A, para-formaldehyde and aniline. The bisphenol-A (polycarbonate grade) was kindly supplied by Thai Polycarbonate Co., Ltd. (TPCC). Para-formaldehyde (AR grade) was purchased from Merck Company and aniline (AR grade) was obtained from Panreac Quimica SA Company. XGnP graphenenanoplatelets (Grade H, size: average particle diameters of 15 µm, 15 nm in thickness, surface area of 50-80 m^2/g, purity: more than 99.5% and density is 2.2 g/cm^3) was purchased from XG Sciences, USA.

Methods

Preparation of Benzoxazine Resin

Benzoxazine resin is synthesized from bisphenol-A, para-formaldehyde and amine at 1 : 4 : 2 molar ratio. It can be prepared by using solventless technology(9). The monomer is light yellow solid at room temperature. The resin was ground in to powder and kept in a refrigerator prior to use.

Preparation of Graphene Filled Polybenzoxazine Composites

The graphene filled polybenzoxazine composites were prepared by varying compositions of graphene from 0-60wt% to yield molding compounds. The graphene powder was firstly dried at 110°C overnight in an air-circulated ovenand kept in a desiccator at room temperature. The molding compound was prepared using an internal mixer at temperature of 90°C to 100°C and a mixing speed of 40 rpm for 30 minutes. A compression molder at temperature of 200°C and hydraulic pressure of 15 MPa for 3 hours was then used to fabricate graphene filled polybenzoxazine composites. All samples were air-cooled to room temperature in the open mold and were cut into desired shapes before testing.

Density Measurement

The density of each specimen was determined by water displacement method according to ASTM D 792 (Method A). The specimens were prepared in a rectangular shape with 50 mm in length, 25 mm in width and 2.0 mm in thickness. Each specimen was weighed in air and in water at 23±2°C.

Differential scanning calorimeter DSC

The curing characteristic of the benzoxazine -graphene composites were examined using a differential scanning calorimeter (DSC) model 2910 from TA Instrument. For each test, a small amount of the sample ranging from 5-10 mg was placed on the aluminum pan and sealed hermetically with aluminum lids. The experiment was done using a heating rate of 10°C/minute to heat the sealed sample from 30°C to 300°C under N_2 purging. The purge nitrogen gas flow rate was maintained to be constant at 50 ml/minute. The curing condition and percentage of resin conversion were determined from the DSC thermograms.

Dynamic mechanical analysis (DMA)

Dynamic mechanical property i.e. storage modulus (E′), was measured with dynamic mechanical testing apparatus (model DMA 242C, Netzsch). The dimension of the specimens was rectangular with 50 mm in length, 10 mm in width, and 2.5 mm in thickness at temperature range of 30°C to 300°C with a heating rate of 5°C/minute.

Results and Discussion

Curing Behaviors of Graphene - Benzoxazine Molding Compounds

The curing condition of benzoxazine resin filled with high loadings of graphene was examined using a differential scanning calorimeter in a temperature range of 30°C to 300°C and at a heating rate of 10°C/minute. Figure 1 presents the curing exotherms of the neat benzoxazine resin (BA-a) and the benzoxazine-graphene molding compounds at different graphene contents. The thermograms of the molding compounds evidently shows peak shift to lower temperature with the amount of graphene loading. The curing temperature of the composites was remarkably reduced from 233°C for the as-synthesized benzoxazine resin to 196°C at 60wt% of the graphene content. The result indicated that graphene could act as a catalyst for oxazine ring-opening reaction. Moreover, the area under the curing peaks was found to decrease with increasing the graphene content. This expected phenomenon is related to the decreasing amount of benzoxazine resin in the molding compounds with an increase of the graphene content

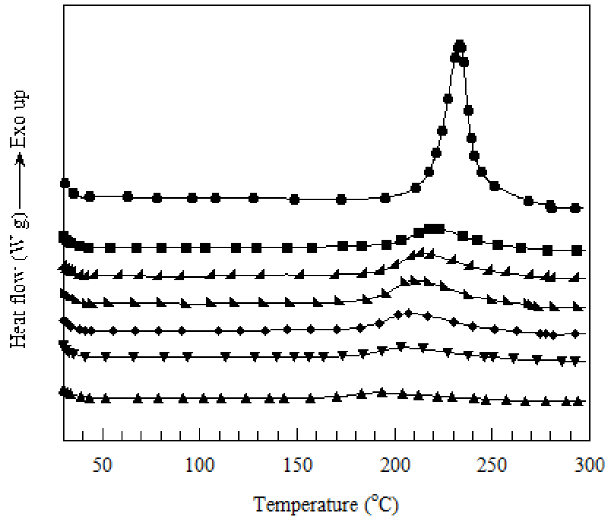

Figure 1. DSC thermograms of benzoxazine molding compound at different graphene contents: (●) neat benzoxazine monomer, (■) 10wt%, (◢) 20wt%, (◣) 30wt%, (♦) 40wt%, (▼) 50wt%, (▲) 60wt%.

Figure 2 exhibits the DSC thermograms of graphene filled benzoxazine molding compound at 10wt% of the graphene. The measurement was performed at 200°C with various curing times. From the results, the heat of reaction of the uncured benzoxazine molding compound determined from the area under the exothermic peak is 245 J/g and the value decreases to 19, 11 and 4 J/g, after curing at 200°C for 1 hour, 2 hours and 3 hours, respectively. The degree of conversion estimated by Equation 1 was calculated to be 98% after curing at 200°C for 3 hours. Therefore, a curing temperature at 200°C for 3 hours was used as curing condition for every molding compound to provide the composite specimens for further investigation

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

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

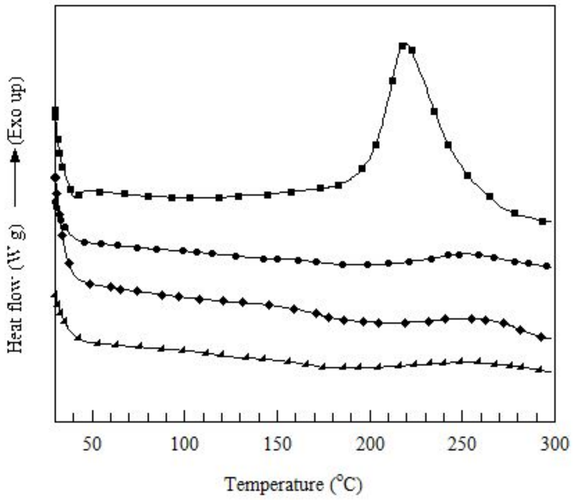

Figure 2. DSC thermograms of polybenzoxazine composite (10wt% of graphene) at 200°C as a function of curing times: (■) Uncured molding compound, (●) 1 hour, (♦) 2 hours, (◢) 3 hours.

Density Measurement

Density data of composite is a major characteristic used to approximately evaluate the quality of composites due to the void formation. The theoretical density of graphene filled polybenzoxazine composites with different graphene contents were calculated from Equation 2. The densities ofpolybenzoxazine and graphene are 1.19 and 2.20 g/cm^3, respectively. Figure 3 shows the theoretical density of the graphene filled polybenzoxazine composites at 0-60wt% of graphene contents compared with their actual density. From the results, the density of the graphene-filled polybenzoxazine composites was linearly increased with increasing graphene content which follows the rule of mixture suggesting negligible void in the composites samples. The actual densities of the composites were determined to be 1.247, 1.310, 1.377, 1.455, 1.540 and 1.637 at 10, 20, 30, 40, 50 and 60wt% of graphene content, respectively. Due to the aforementioned very low melt viscosity and good adhesion of benzoxazine resin, the highly filled composite with no void formation was thus provided. However, the experimental density of the composite with 65wt%

of graphene contents was found to be slightly lower than that of the theoretical density value due to the presence of small content of void or air gap in the composite specimen. As a result, the maximum graphene loading in polybenzoxazine composite was determined to be 60wt% or about 44.8vol%

$$\rho_c = \frac{1}{\frac{W_f}{\rho_f} - \frac{(1-W_f)}{\rho_m}} \qquad (2)$$

where, ρ_c is the theoretical density of composite (g/cm^3), ρ_f is filler density (g/cm^3), ρ_m is matrix density (g/cm^3), W_f is the filler weight fraction.

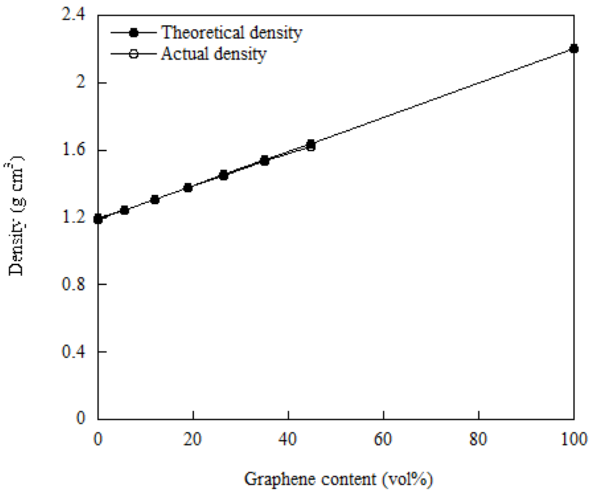

Figure 3. Theoretical and actual density of graphene-filled polybenzoxazine composites at different content of graphene: (●) theoretical density, (○) actual density.

Dynamic Mechanical Properties of Graphene-Filled Polybenzoxazine Composites.

The dynamic mechanical analysis plots of the storage modulus (E′) and loss modulus (E″) of the graphene filled polybenzoxazine composites with the graphene content ranging from 0 to 60wt% are shown in Figure 4 and 5, respectively. As seen in Figure 4, the storage modulus at room temperature of the composites was considerably enhanced with the presence of the graphene i.e. from 5.9 GPa of the neat polybenzoxazine to about 25.1 GPa at 60wt% of graphene, which was about 322% enhancement in the polybenzoxazine stiffness. Furthermore, the modulus of the graphene filled polybenzoxazine in the rubbery plateau region was also found to increase significantly with increasing amount of the graphene. These results implied the strong interfacial interaction between the graphene and the polybenzoxazine matrix with the addition of rigid particulate filler into the polymer matrix.(3,4)

Figures 5 exhibits the loss modulus curves of graphene filled polybenzoxazine at 0-60wt% of graphene contents as a function of temperature. The glass-transition temperatures (T_g) obtained from the maximum peak of loss modulus of the graphene filled polybenzoxazine composites were observed to be in the range of 174°C to 188°C. It could be seen that the T_g values increased with increasing graphene content. This phenomenon also suggests good adhesion between the graphene filler and the polybenzoxazine matrix. (3,4)

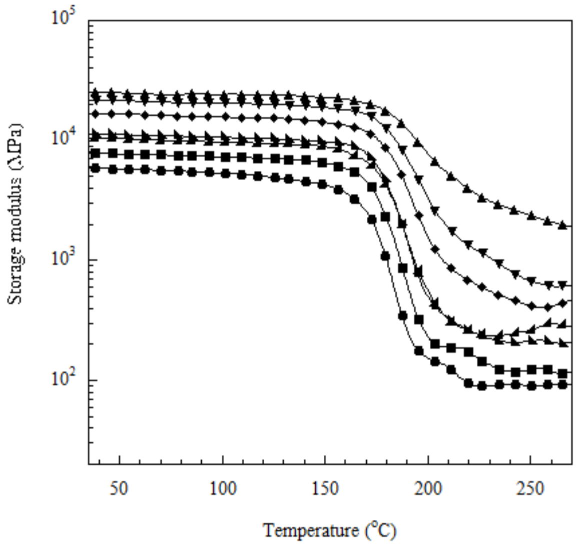

Figure 4. DMA thermograms of storage modulus of graphene-filled polybenzoxazine composites: (●) neat benzoxazine monomer, (■) 10wt%, (◢) 20wt%, (◣) 30wt%, (♦) 40wt%, (▼) 50wt%, (▲) 60wt%.

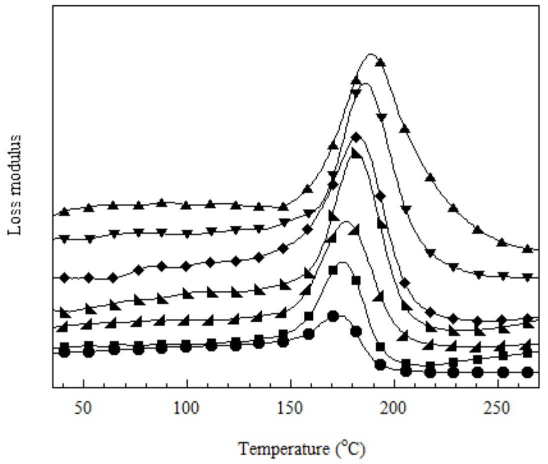

Figure 5. DMA thermograms of loss modulus of graphene-filled polybenzoxazine composites: (●) neat benzoxazine monomer, (■) 10wt%, (◢) 20wt%, (◣) 30wt%, (♦) 40wt%,(▼) 50wt%, (▲) 60wt%.

Conclusions

The graphene-filled polybenzoxazine composites with graphene content of 0-60wt% were prepared using internal mixer. The presence of graphene was found to substantially accelerate the curing reaction of the benzoxazine resin. At a curing temperature of 200°C for 3 hours, the fully cured specimens were achieved with the conversion up to 98%. The density of the obtained composites was linearly increased with graphene content. The incorporation of graphene contents in graphene-filled polybenzoxazine composites contributed to significant enhancement in the storage modulus and the glass-transition temperatures, which made the obtained sample attractive as a good candidate for e.g. bipolar plate applications.

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