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# Preparation and Characterization of Highly Filled Graphite-Based Polybenzoxazine Composites

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## Abstract

This research aims to study suitable preparation methods and to characterize highly filled graphite composites using polybenzoxazine as a matrix. The high loading of graphite filler was attained in the range of 40 to 80% by wt. due to the very low a-stage viscosity of the benzoxazine resin (BA-a) used. The suitable condition for the compression molding of the highly filled graphite-polybenzoxazine (PBA-a) composites was at temperature of 200°C, and pressure of 15 MPa in the hydraulic hot-press machine for 3 hours to assure a fully cured specimen. The densities of the obtained composites were found to be in a range of 1.19-1.88 g/cm$^3$. Mechanical and thermal properties of these composites were studied by dynamic mechanical analysis (DMA), and differential scanning calorimetry (DSC). The experimental results revealed that at the maximum content of 80wt% or 68vol% of graphite filled in the polybenzoxazine, storage modulus at room temperature of the specimen was raised from 5.9 GPa of the neat polybenzoxazine to about 21.9 GPa in the composites. Finally, glass-transition temperatures ($T_g$) of the prepared composites were observed to be ranging from 174 to 194°C. The Tg values substantially increased with increasing the graphite contents implying substantial interfacial interaction between the filler and the matrix.

**Key words**: Benzoxazine, Graphite, Mechanical properties, Thermal properties

## Introduction

Graphite-polymer composites have been found to possess outstanding physical, chemical and mechanical properties.(1-2) Graphite is a highly prospective filler material for polymer composites due to the high ratio of hexagonal carbon layer, high strength, high thermal conductivity and high electrical conductivity, low coefficient of thermal expansion, as well as high chemical and corrosion resistance.(1, 5) Recently, various approaches for making graphite-based composites have been developed. The methods include blending polymer and graphite particles, and intercalating the polymers into interlayer of graphite. The availability of graphite-polymer composites is an essential requirement for the construction of bipolar plate in fuel cell, batteries and molding.(3-4)

Recently, a new thermoset resin namely benzoxazine resin have been developed and used as matrix for composites material. Polybenzoxazine, a novel class of phenolic resins, has a wide range of mechanical and physical properties that can be tailored to various needs. The polymer can be synthesized by ring-opening polymerization of the aromatic oxazines with no by-products released upon curing, no catalysts needed, no solvent elimination, and no need of monomer purification.(6) The property balance of the material renders the polymer with good thermal, chemical, electrical, mechanical, and physical properties including very low A-stage viscosity, near-zero shrinkage, low water absorption, high thermal stability, good fire-resistant characteristics, and fast development of mechanical properties as a function of curing conversion.(7)

In this study, we aim to prepare and characterize properties of graphite-based composites from highly filled polybenzoxazine i.e. density, mechanical properties, and thermal properties.

## Materials and Experimental Procedures

### *Materials*

The materials in this research are benzoxazine resin and graphite. Benzoxazine resin is based

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on bisphenol-A, aniline, and formaldehyde. Thai Polycarbonate Co., Ltd. (TPCC) supplied bisphenol-A (commercial grade). Paraformaldehyde (AR grade) and graphite powder (size, average 50 µm) were purchased from Merck Company whereas aniline (AR grade) was obtained from Panreac Quimica SA Company.

### *Benzoxazine Resin Preparation*

Benzoxazine monomer (BA-a) was synthesized from bisphenol-A, aniline, and paraformaldehyde at a 1:2:4 molar ratio. The mixture was constantly stirred at 110°C using the patented solventless technology.(6, 10) Normally, the monomer is solid powder at room temperature with yellow color. The powder was ground into fine powder and was kept in a refrigerator for further use without purification.(9-11)

### *Graphite Polybenzoxazine Composites Preparation*

The composite samples were prepared at filler loadings of 0, 40, 50, 60, 70, 75 and 80% by wt. to yield molding compound. The graphite was firstly dried at 110°C for 24 hours in an air-circulated oven until a constant weight was achieved and was then kept in a desiccator at room temperature. In the molding compound preparation, graphite was thoroughly mixed by hand with benzoxazine resin in an aluminium container at about 120°C and mechanically stirred to achieve good dispersion of the filler in benzoxazine resin. For thermal-cured specimen, the compound was compression-molded by hot pressing. The thickness was controlled by using a metal spacer. The hot-press temperature of 150°C was applied for 1 hr and 200°C for 3 hr at a hydraulic pressure of 15 MPa. All samples were air-cooled to room temperature in the open mold before testing.

### *Characterizations of the Graphite-Polybenzoxazine Composite*

#### *Differential Scanning Calorimetry (DSC)*

The curing characteristic of the benzoxazine-graphite composites were examined by 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 10oC/min to heat the sealed sample from 30oC up 300$^{o}$C under $N_2$ purging. The purge nitrogen gas flow rate was maintained to be constant at 50 ml/min. The processing temperature, time and glass transition temperature were obtained from the thermograms while the percentage of resin conversion was calculated from the DSC thermograms.

#### *Density Measurement*

##### Actual Density Measurement

The density of each specimen was determined by water displacement method according to ASTM D 792 (Method A). All specimens were prepared in a rectangular shape (50 mm × 25 mm × 2 mm). Each specimen was weighed in air and in water at 23±2°C. The density was calculated using Equation (2.1). An average value from at least five specimens was calculated.

$$\rho = \frac{A}{A - B} \times \rho_0 \qquad (2.1)$$

where $\rho$ = density of the specimen (g/cm$^3$)
A = weight of the specimen in air (g)
B = weight of the specimen in liquid (water) at 23 ± 2°C (g)
$\rho_o$ = density of the liquid (water) at the given temperature (g/cm$^3$)

## Results and Discussion

### *Differential Scanning Calorimetry (DSC)*

The curing condition of benzoxazine resin filled with different graphite contents was investigated by DSC with a temperature range of 30 to 300°C using a heating rate of 10°C/min. Figure 1a shows the curing exotherms of the neat benzoxazine resin (BA-a) and the benzoxazine molding compounds at different graphite contents. A maximum exotherm peak of benzoxazine resin was observed at 233°C, which is the characteristic of oxazine ring opening. 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 chemical reaction during the curing process of the benzoxazine resins. It is due to the fact that the graphite filler is relatively inert to the benzoxazine curing reaction. Figure 1b shows the DSC thermograms of the benzoxazine molding compound at 40% by wt. of the graphite at various curing conditions. The heat of reaction determined from the area under the exothermic peak. From the results. The value 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 hour, 2 hours and 3 hours , respectively. The degree of conversion estimated by Equation (3.1) was determined to be 98%.after curing at 200°C for 3hours. Therefore, this curing condition was used for polymerization of our benzoxazine molding compound.

$$\%\ \text{conversion} = 1 - \frac{(H_{rxn})}{H_0} \times 100 \qquad (3.1)$$

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

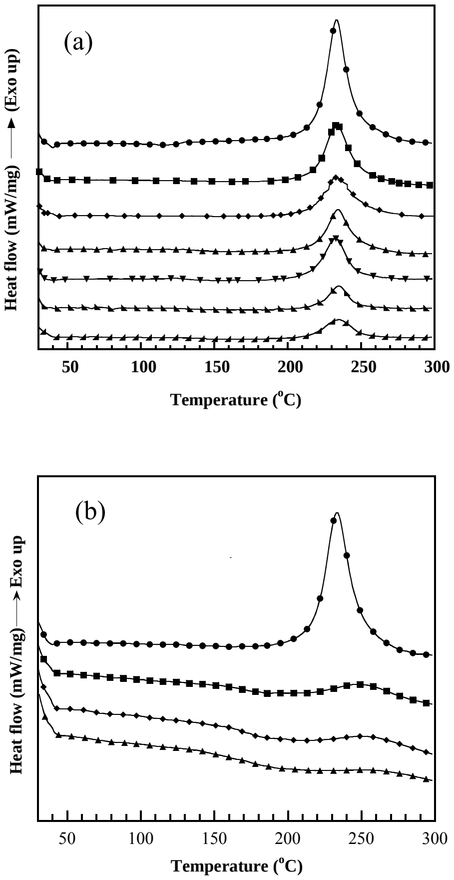


**Figure 1.** DSC thermograms of (a) benzoxazine molding compounds with various graphite contents: (●) neat benzoxazine monomer, (■) 40wt%, (♦) 50wt%, (▲) 60wt%, (▼)70wt%, (○) 75wt%, (□) 80wt% and (b) benzoxazine molding compounds with 40wt% of graphite cured at 200°C at various curing times: (●) Uncured molding compound, (■) 1 hour, (♦) 2 hours, (▲) 3 hours.

## Density Measurement

Figure 2 exhibits the density of the neat polybenzoxazine and graphite filled polybenzoxazine as a function of filler content. Density measurements of all composite were used to investigate the presence of void in the composite specimens. One outstanding property of polybenzoxazine matrix is its low melt viscosity in which the highly filled composite can easily be obtained. This figure shows the theoretical density of the composite in comparison with their actual density. The theoretical density of the composites was calculated from Equation (3.2). The calculation is based on the basis that the densities of the graphite and of the polybenzoxazine are 2.22 g/cm$^3$ and 1.20 g/cm$^3$, respectively. Due to the higher density of graphite, the results reveal that the theoretical and actual density of the polybenzoxazine composites was increased with the graphite content following the rule of mixture. Furthermore, it can be observed that when adding graphite up to 68% by vol or 80% by wt. The attempt to add graphite higher than 68% by vol. was found to provide the lower experimental density value than the theoretical value possibly due to the presence of air gap. Therefore, the maximum graphite loading between the filler and the matrix resin was found to be 68% by vol..

$$\rho_c = \frac{1}{\dfrac{W_f}{\rho_f} - \dfrac{(1-W_f)}{\rho_m}} \qquad (3.2)$$

where $\rho_c$ = composite density, g/cm$^3$
$\rho_f$ = filler density, g/cm$^3$
$\rho_m$ = matrix density, g/cm$^3$
$W_f$ = filler weight fraction
$(1-W_f)$ = matrix weight fraction

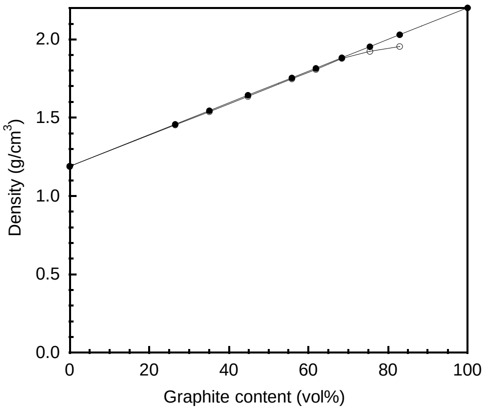
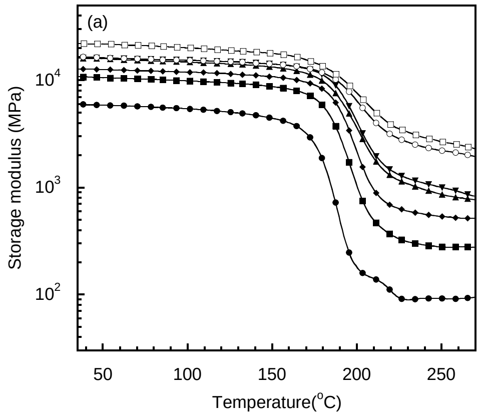


**Figure 2.** Theoretical and actual density of graphite filled polybenzoxazine composites at different content of graphite: (●) theoretical density, (○) actual density.

### *Dynamics Mechanical Measurement*

Figures 3a and 3b illustrate the dynamic mechanical properties of the graphite filled polybenzoxazine composites with the graphite ranging from 0 to 80wt%. At room temperature, the storage modulus (E') of the graphite filled polybenzoxazine composites increased with increasing graphite content as seen in Figure 3a. 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, which imply strong interfacial bonding between the matrix and the reinforcing filler.

Figure 3b exhibits the loss modulus (E") curves of the graphite filled polybenzoxazine as a function of temperature. The maximum peak temperature in the loss modulus curve was assigned as a glass transition temperature ($T_g$) of the specimen. As seen in this figure, 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 174°C whereas the glass transition temperature of the 80% by weight of graphite filled polybenzoxazine is about 194°C. An increase of the $T_g$ with an addition of the graphite is due to the good interfacial adhesion between the graphite filler and polybenzoxazine matrix which can highly restrict the mobility of the polymer chain.



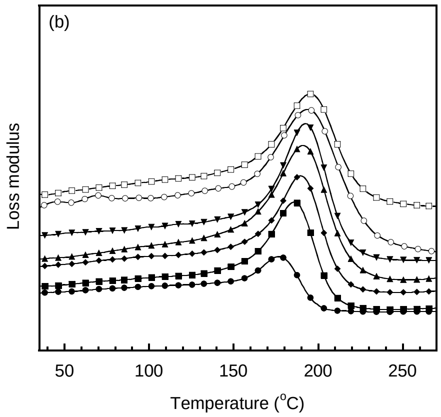


**Figure 3**. DMA thermograms of highly filled graphite-polybenzoxazine (a) storage modulus and (b) loss modulus composites: (■) 40wt%, (♦) 50wt%, (▲) 60wt%, (▼) 70wt%, (○) 75wt%, (□) 80wt%

## Conclusions

Graphite filler showed no adverse effect on curing reaction of benzoxazine resin. The conversion of suitable curing condition was achieved up to 98%. A large increase in storage modulus at room temperature of the obtained polybenzoxazine composites implied substantial interfacial interaction between the graphite filler and the polybenzoxazine matrix.

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