

# Effect of Graphite Particle Size on Tribological and Mechanical Properties of Polybenzoxazine Composites

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The effect of size of natural graphite (NG) particles on the tribological and mechanical properties as well as thermal stability of polybenzoxazine composites with five different sized NG particles (32, 38, 45, 53, and 75  $\mu\text{m}$ ) was studied. The tribological performance of the composites performed in pin-on-disk tester was improved with adding larger NG particle size. It was found that the wear resistance of the composites was improved by increasing of the particle size. While, the increased NG particle size reduced the friction coefficient of the composites from 0.36 to 0.31. In term of mechanical properties under flexural test, i.e. flexural modulus and flexural strength, the NG particles with the largest size possessed the suitable reinforcement ability. Glass transition temperature evaluated by dynamic mechanical analysis and the degradation temperature at 5 % weight loss measured by thermogravimetric analysis of the composites was in a temperature range of 195  $^{\circ}\text{C}$  – 215  $^{\circ}\text{C}$  and 387  $^{\circ}\text{C}$  – 402  $^{\circ}\text{C}$ , respectively. Therefore, the obtained outstanding properties, i.e. friction coefficient, flexural modulus and strength, glass transition temperature, and degradation temperature make the polybenzoxazine composites highly attractive to be utilized as friction materials.

## 1. Introduction

Polymer-based materials are largely applied to industry products replacing traditional metallic materials, particularly in the fields of heavy pressure, load, impact, and wear because they possess excellent comprehensive properties such as high wear-, oil- and corrosion resistance, high elasticity and damping, good adhesion to other materials, low maintenance, and inexpensive prices. Moreover, mechanics of polymer-based materials are relatively well understood (Jinsong and Alan, 2011, Malvezzi et al., 2013). Therefore, the tribological properties of polymer-based materials of several engineering polymers, including virgin and composites, have been investigated (Jubsilp et al., 2015, Kalácska, 2013, Luo et al., 2010) because they have become elements of real machines and the tribological properties are required for the many friction applications especially for automotive mechanical parts. The friction materials in the automotive industry, i.e. brake pads and drum brakes have been designated for a long time. Most commercially available brake pad materials contain multiple components. They are often categorized into four classes of ingredients including of binders (phenolic and epoxy resins), fibers (aramid fiber, fly ash, asbestos fiber, etc.), friction modifiers (graphite, aluminum oxide, potassium titanate, etc.), and fillers (calcium hydroxide, barium sulphate, etc.) (Chan and Stachowiak, 2004). Phenolic resins offer a good combination of thermal, mechanical, and tribological properties and the resins can bind all of the ingredients strongly with cost effective. Therefore, they are generally selected as binders in a brake pad application. However, traditional phenolic resin still has some shortcomings, including the need of acid or alkaline catalysts in the synthesis step, the release of by-product such as water or ammonia during the processing step, short shelf-life, and their brittleness. Moreover, using the phenolic resin for friction materials, a moulding failure, i.e. cracks or bulges occur during a polymerization step because of a gas by-product generated from hexamethylenetetramine used as a curing agent. The epoxy resin has a problem that the heat resistance is insufficient, i.e. low glass transition temperature. This results in

heat fading, heat expansion, and heat cracks in brake pad materials. For solving these problems, recently, the use of polybenzoxazine, a novel class of phenolic type of thermosetting polymers, as a binder for polymer composite materials to overcome the inherent problems of the phenolic has been suggested (Ishida and Agag, 2011, Jubsilp et al., 2013, Rimdusit et al., 2013). In addition, as disclosed in US 8,227,390 B2 (Kurihara et al., 2012), they have reported that the benzoxazine resin that generates no gas in polymerization step and can give a friction composite material excellent in heat resistance. Its strength is used with an attempt to substitute for phenolic resin or epoxy resin as a binder resin of the friction composite materials.

To modify polymer composites for the friction application, graphite is widely used as it is able to form a lubricant layer on the opposing counter friction material rapidly. In friction materials, the graphite can be of natural or synthetic origin, and can exist in flake or particle form. Graphite in the flake form has improved lubrication properties, while graphite in the particle form is able to dissipate heat more effectively (Chan and Stachowiak, 2004). In this work, the size of the natural graphite particles is expected to show significant effects on tribological, mechanical, and thermal properties of polybenzoxazine composites. Therefore, the polybenzoxazine composites filled with the various natural graphite sizes will be prepared and their properties will be characterized for potential use as friction materials.

## **2. Experimental**

### **2.1 Materials**

BA-a-type benzoxazine resin based on bisphenol-A, formaldehyde, and aniline was synthesized in solventless condition (Ishida, 1996). The BA-a resin is a yellow clear solid at room temperature. Polycarbonate type bisphenol-A was provided by Thai Polycarbonate Co., Ltd. Paraformaldehyde and aniline was obtained from Merck Co., and Fluka Chemical Co., respectively. All chemicals were used as-received. Nitrile rubber (NBR) particle and natural graphite (NG) particles was supported by Compact International (1994) Co., Ltd. (Thailand). The Kevlar fiber with a length of 1 mm was provided by Du Pont, Japan. Alumina, Al<sub>2</sub>O<sub>3</sub> (A32) was purchased from Nippon Light Metal Co., Ltd. (Thailand). The density and an average diameter of particles of the alumina were 3.90 g/cm<sup>3</sup> and 1 μm, respectively. Calcium carbonate (CaCO<sub>3</sub>) with 6-9 μm in diameter was provided by Surintomya Chemical Co., Ltd. (Thailand).

### **2.2 Sample preparations**

BA-a compounds consisted of 5 wt % NBR, 5 wt % Kevlar short fiber, 10 wt % Al<sub>2</sub>O<sub>3</sub> powder, 45 wt % CaCO<sub>3</sub> powder, and 10 wt % natural graphite at various particle sizes of 32, 38, 45, 53, and 75 μm, and were prepared by mechanical mixing at 80 °C for at least 15 min to ensure ingredients wet-out by the BA-a. In the next step, the compounds were cured at 200 °C for 2 h in the hydraulic press using a pressure of 34 MPa. The samples were kept in a room to cool them to ambient temperature before any tests were carried out.

### **2.3 Sample characterizations**

Tribological test under dry sliding at room temperature of 25 °C was conducted on a high temperature tribometer having a maximum temperature of 950 °C from CSM Instrument Ltd., Switzerland. Equipment has a pin-on-disk configuration with 6-mm steel ball diameter. The test condition is 10 N for normal load and 0.366 m/s for sliding speed for 1,000 m distance.

Dynamic mechanical analyzer (DMA) from Netzsch Inc., model DMA 242 C in three-point bending mode, and a support span of 40 mm was used to examine loss tangent (tanδ) of the samples. The dimension of each sample in rectangular shape was 10 mm × 50 mm × 3 mm. The tests were performed in a temperature sweep mode with a fixed frequency of 1 Hz. Each sample was tested using a heating rate of 2 °C/min from 30 °C to about 250 °C.

Flexural properties were conducted by a Universal Testing Machine, Lloyd Instruments, Model LR 10 K. The measurement was carried out in a three-point bending mode, with a support span of 48 mm and at a crosshead speed of 1.2 mm/min. A minimum of five samples with a dimension of 25 mm × 60 mm × 3 mm was tested, and the average values for the specimens were determined.

The worn surface of the samples was evaluated with a JSM5410LV scanning electron microscopy (SEM) from JEOL Ltd. using an acceleration voltage of 15 kV. All samples were coated with a thin film of gold to make the surfaces conductive.

### 3. Results and discussion

#### 3.1 Friction coefficient and wear resistance

Figure 1 shows the friction coefficients at 25 °C as a function of sliding distance under the applied loads of 10 N of polybenzoxazine (poly(BA-a)) composites filled with 32, 38, 45, 53, and 75  $\mu\text{m}$  of natural graphite (NG).

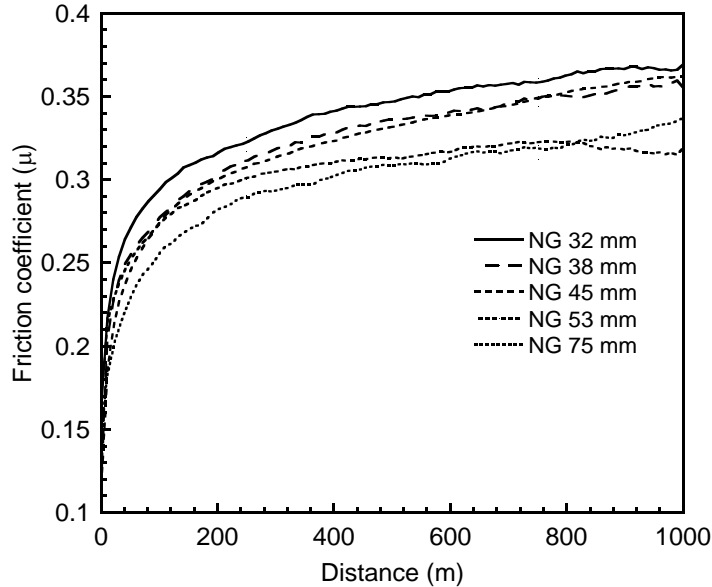


Figure 1: Friction coefficient of poly(BA-a) composites filled with various NG particle sizes.

It can be seen that the friction coefficient of all poly(BA-a) composites rose sharply at the run in a range of 0-100 m, and then a steady state was reached. The average friction coefficient ( $\mu_{\text{avg.}}$ ) of the poly(BA-a) composites is listed in Table 1. It was found that the friction coefficients of the poly(BA-a) composite increased with decreasing NG particle sizes, i.e. from 0.31 for 75  $\mu\text{m}$  NG-filled poly(BA-a) composite to 0.36 for 32  $\mu\text{m}$  NG-filled poly(BA-a) composite. This characteristic can be explained that the friction coefficient generally increases with an increasing of actual contact area of the higher surface area of the smaller NG particle sizes. In addition, it is possible that the more uniform transfer film of the poly(BA-a) filled with larger NG particle size was formed on the worn surface of the composites.

Table 1: Average friction coefficient and wear mass loss of poly(BA-a) composites filled with various NG particle sizes

NG particle size ( $\mu\text{m}$ )	Average friction coefficient	Wear mass loss (g/m)
32	$0.360 \pm 0.021$	$1.7 \times 10^{-6}$
38	$0.340 \pm 0.024$	$1.2 \times 10^{-6}$
45	$0.335 \pm 0.006$	$1.0 \times 10^{-6}$
53	$0.333 \pm 0.024$	$0.9 \times 10^{-6}$
75	$0.305 \pm 0.005$	$0.7 \times 10^{-6}$

Moreover, the wear mass loss of the poly(BA-a) composites is also detailed in Table 1. Wear is related to interactions between surfaces and specifically the removal and deformation of material on a surface as a result of mechanical action of the opposite surface. From the Table 1, the wear mass loss of the composites decreased with increasing NG particle size, that is, it decreased from  $1.7 \times 10^{-6}$  g/m to  $0.7 \times 10^{-6}$  g/m. Again, it is probable that lubricating film is formed to lower wear mass loss in the worn surface as the graphite particles size increases. It will be confirmed by observing the worn microstructure of the composites in Figure 2.

#### 3.2 Morphology of the worn surface

The effect of NG particle sizes on the wear behaviour of the poly(BA-a) composites was investigated by observation of wear track from tribological test as can be seen in Figure 2.

From the figure, worn surface morphologies of all composites showed regions of non-uniform roughness. However, resin-rich surface layer with less voids and debris on the worn surface of all composite was observed. This characteristic indicates good interfacial interaction between the poly(BA-a) and the ingredients for the poly(BA-a) composites. In Figure 2(a), it can be seen that the worn surface of the 32  $\mu\text{m}$  NG-filled composite was broken and a certain volume of surface material was removed. While, the removal surface materials was no observed for the composites filled with the larger than 32  $\mu\text{m}$  NG particles as can be seen in Figures 2(b)-2(e). This characteristic was related with the wear mass loss behavior of the composites. Furthermore, the plastic flow layer and friction film on the worn surface was clearly observed for the poly(BA-a) composites filled with the larger than 32  $\mu\text{m}$  NG particles. The plastic flow layer was formed on the worn surface. The detailed view of the plastic flow layer showed that a homogeneous and continuous thin friction film was formed on the worn surface that could decrease the friction between the friction pairs and increase the wear resistance of the composites.

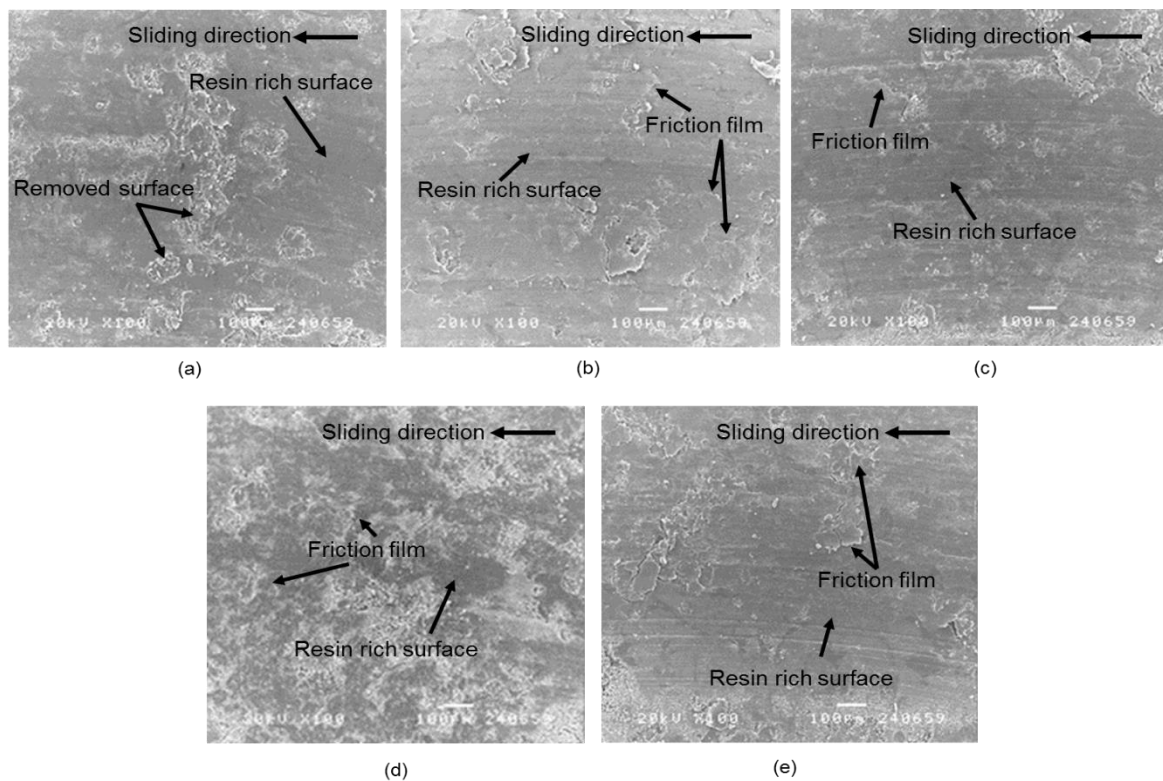


Figure 2: Wear micrographs (SEM) of worn surfaces of poly(BA-a) composites filled with various NG particle sizes. (a) 32  $\mu\text{m}$ , (b) 38  $\mu\text{m}$ , (c) 45  $\mu\text{m}$ , (d) 53  $\mu\text{m}$ , (e) 75  $\mu\text{m}$ . Each composite consisted of 25 wt % poly(BA-a), 5 wt % NBR, 5 wt % Kevlar short fiber, 10 wt %  $\text{Al}_2\text{O}_3$ , 10 wt % NG, and 45 wt %  $\text{CaCO}_3$ .

### 3.3 Flexural properties

Flexural properties, i.e. modulus and strength of the poly(BA-a) composites at different NG particle sizes, are depicted in Figure 3.

In this figure, the flexural modulus and strength of the composites were found to systematically increase with an increase NG particle size from 3.99 to 6.52 GPa and from 24.75 to 53.07 MPa, respectively. These observed trends are in agreement with the finding of NG-filled phenolic composites in the same NG particle size range (Kolluri et al., 2010).

The phenomenon was due to a result of particle geometry. According to mechanics of fiber-reinforced composite materials, one of important factors affecting their mechanical properties is a fiber aspect ratio defined as a fiber length-to-thickness ratio. Therefore, in this work, the enhancement of stress transfer from the polymer matrix to the reinforcing fillers and ultimately improved the composite mechanical properties may be due to the larger NG particle with a higher aspect ratio.

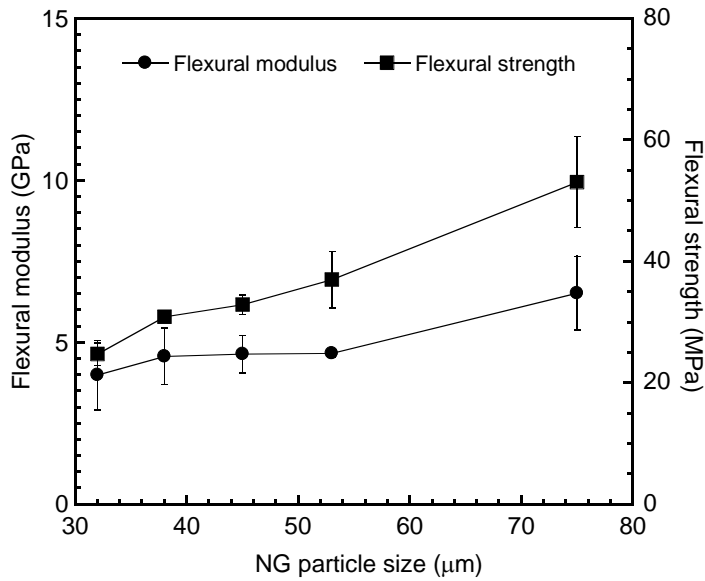


Figure 3: Flexural properties poly(BA-a) composites filled with various NG particle sizes.

### 3.4 Thermomechanical properties and thermal stability

The storage moduli ( $E'$ ) of the NG particle-filled poly(BA-a) composites at their glassy state were observed to systematically increase with increasing the NG particle size as tabulated in Table 2. At room temperature, the modulus value was raised from 14.7 GPa for the 32  $\mu\text{m}$  NG-filled poly(BA-a) composite to 17.7 GPa for the 75  $\mu\text{m}$  NG-filled poly(BA-a) composite. These values were in agreement with the modulus values under flexure mode as depicted in Figure 2.

Glass transition temperature ( $T_g$ ) of NG particle-filled poly(BA-a) composites was determined from the maxima peak of loss tangent ( $\tan\delta$ ) as presented in Table 2. The glass transition temperature was found to increase when the NG particle sizes were decreased. One reason for the improvement of the glass transition of the poly(BA-a) with an addition of the NG filler is attributed to an ability of the NG particles to substantially restrict the motion of the poly(BA-a) chains thus higher temperature is required to provide the requisite thermal energy for the occurrence of the glass transition in the composites. In addition, the significant interfacial adhesion between the poly(BA-a) and the ingredients was attributed to such strong restriction of the chains movements in the poly(BA-a) thus the substantial enhancement on its glass transition temperature.

Furthermore, degradation temperature ( $T_d$ ) is one of the key parameters used to determine the thermal stability of polymeric materials. Again, in Table 2, the degradation temperature at 5 % weight loss ( $T_{d5}$ ) of the composites trended to increase with a smaller NG particle size. This phenomenon is likely due to the significantly increased barrier effect of smaller NG particle size as well as the good interfacial interaction of the poly(BA-a) to the ingredients as similarly observed in alumina-filled poly(BA-a) composites (Kajohnchaiyagual et al., 2014). Moreover, the weight residue of the composites was similar for all composite samples suggesting uniform particle dispersion in the composites.

Table 2: Thermomechanical properties and thermal stability of poly(BA-a) composites filled with various NG particle sizes

NG particle size ( $\mu\text{m}$ )	$E'$ (GPa)	$T_g$ ( $^{\circ}\text{C}$ ) from $\tan\delta$	$T_{d5}$ ( $^{\circ}\text{C}$ ) residue	Weight residue
32	14.7	215	402	53.5
38	14.7	207	387	52.5
45	15.5	207	387	53.0
53	16.1	212	389	52.5
75	17.7	195	395	54.0

#### 4. Conclusions

In this work, an experimental program was conducted in order to determine the tribological and mechanical properties as well as thermal stability of friction composites base on polybenzoxazine filled with various sizes of natural graphite particles. It can be summarized that the natural graphite-filled polybenzoxazine composites showed a high frictional coefficient and significant wear mass loss. Increasing the size of natural graphite particle leads to slightly decrease in the friction coefficient and the wear mass loss. The mechanical properties of natural graphite particles-filled polybenzoxazine composites tended to increase with increasing natural graphite sizes. While, thermal properties was found to slightly increase with decreasing the particle sizes. Based on the findings in this work, it seems that the obtained natural graphite-filled polybenzoxazine composites would have high potential to be used for friction materials where high friction coefficient, high wear resistance, and modulus with good thermal property are required.

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