



# High thermal and mechanical properties enhancement obtained in highly filled polybenzoxazine nanocomposites with fumed silica



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## ABSTRACT

Highly filled polybenzoxazine nanocomposites filled with nano-SiO<sub>2</sub> particles were investigated for their mechanical and thermal properties as a function of filler loading. The nanocomposites were prepared by high shear mixing followed by compression molding. A very low A-stage viscosity of benzoxazine monomer gives it excellent processability having maximum nano-SiO<sub>2</sub> loading as high as 30 wt% (18.8 vol%) with negligible void content. Moreover, thermal analysis of the curing process of the compound of the PBA-a/nano-SiO<sub>2</sub> composites was found to be autocatalytic in nature with average activation energy of 79–92 kJ mol<sup>-1</sup>. Microscopic analysis (SEM) performed on the PBA-a/nano-SiO<sub>2</sub> composite fracture surface indicated a nearly homogeneous distribution of the nano-scaled silica in the polybenzoxazine matrix. In addition, the enhancement in storage modulus of the nano-SiO<sub>2</sub> filled polybenzoxazine composites was found to be significantly higher than that of the recently reported nano-SiO<sub>2</sub> filled epoxy composites. The dependence of the nanocomposites' modulus on the nano-SiO<sub>2</sub> particles content is well fitted by the generalized Kerner equation. Furthermore, the relatively high micro-hardness of the PBA-a/nano-SiO<sub>2</sub> composites up to about 600 MPa was achieved. Finally, the substantial enhancement in the glass transition temperature (*T*<sub>g</sub>) of the PBA-a/nano-SiO<sub>2</sub> composites was also observed with the  $\Delta T_g$  up to 16 °C at the nano-SiO<sub>2</sub> loading of 30 wt%. The resulting PBA-a/nano-SiO<sub>2</sub> composite is a highly attractive candidate as coating material in electronic packaging or other related applications.

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## 1. Introduction

Polymer nanocomposites have been a subject of extensive study owing to their superior performance as compared to conventional filled polymer [1–3]. Firstly, the much higher specific surface area of these materials can promote stress transfer from matrix to nanoparticles. Various studies indicated that nanoparticles can improve Young's modulus of polymers more dramatically than micro-fillers [1,2]. Secondly, the required loadings of nanoparticles in polymer matrices are usually much lower than those of micro-fillers (typically 10–40 vol% for the latter) [4]. Therefore, many intrinsic merits of neat polymers, such as low weight, ductility, good processability, as well as transparency will be retained after the addition of nanoparticles. In recent years, nano-SiO<sub>2</sub> [1,4–6], Clay [7], carbon nanotube [8], carbon black [9], and other nanofillers [2,10] have been largely used as additive to achieve a significantly improved polymer performance.

Nano-SiO<sub>2</sub> is a very useful reinforcement of thermoplastic [9,11,12] and thermosetting polymers [1,4–8] and finds usage as

component material for dental filling, electronic packaging, thickeners of paints and coatings, reinforcement of rubbers etc. For industrial applications, nano-SiO<sub>2</sub> particles are often used to reduce the price, and also to improve mechanical and thermal properties of the product. Additionally, nano-SiO<sub>2</sub> particles can be used for reinforcement of polymer matrices to lower shrinkage upon curing, decreasing coefficient of thermal expansion [13], increasing fracture toughness, impact strength, and modulus [1], and improving adhesion property [6]. Concerning their mechanical properties, nano-SiO<sub>2</sub> particles have very high Young's modulus

(71.7 GPa), compressive strength (>1.1 GPa), and tensile strength (48.3 MPa) while it is a relatively light ceramic material because its density is only 2.203 g cm<sup>-3</sup> [14]. To obtain nanocomposite with good mechanical and thermal properties, large amount of silica is usually required, normally 5–30 wt% of total composite composition thus a choice of the matrix resin that can accommodate such high nanofiller loading is crucial to the success of the nanocomposite fabrication [1,4–6].

A number of papers reported on the improving composite performance by introduction of nano-SiO<sub>2</sub> nanoparticles into thermoplastic [9,11,12] and thermosetting matrices [1,4–8]. Thermosetting polymers such as epoxies [1,4,6], cyanate esters [5,7,13]

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and phenolic resins [15] have been often used for highly filled composite systems because of their lower viscosity compared to those thermoplastics. Goertzen and Kessler [5] investigated the effect of the distribution of nano-SiO<sub>2</sub> nanoparticles on thermo-mechanical properties of cyanate ester resin. The results revealed that the storage modulus enhancement of the cyanate ester was about 75% at 20.7 vol% of the fumed silica. Furthermore, the substantial reduction of the CTE with the fumed silica content was also observed in the cyanate ester nanocomposites [13]. However, this system showed only small changes in glass transition temperature ( $T_g$ ;  $\pm 4$  °C) for all volume fractions of the filler used. Moreover, the  $T_g$  was also adversely affected by a change in humidity. For example, the  $T_g$  in 1 vol% samples decreased about 2–3 °C for a change between 19% and 49% relative humidity [5]. In one of their report, the  $T_g$  of nanocomposites was also observed to decrease from 131 to 128 °C by an incorporation of the nano-SiO<sub>2</sub> content up to 25 wt% into epoxy matrix [16].

Polybenzoxazines are a relatively novel class of thermosetting phenolic resin that is recently attracting much attention industrially and academically as they possess various advantageous characteristics that overcome the limitations of conventional phenolic and epoxy resins [17–24]. A unique property of benzoxazine monomer is its very low A-stage viscosity. The low viscosity of this monomer gives it excellent processibility for fabrication of highly-filled composite system. In addition, the curing of benzoxazine resins can occur without any acid catalysts or producing any by-products thus minimizing void formation in the cured polymer [20]. Polybenzoxazines have been reported to exhibit a high thermal stability, high glass transition temperature, high modulus, low water absorption, low dielectric constant, and near-zero shrinkage upon curing [17–24]. Moreover, the polymers show a good adhesion with various type of filler such as boron nitride [21] and wood-flour [22], resulting in a substantial restriction of the molecular mobility of the polymer and, thereby, the substantial enhancement in the  $T_g$  of the obtained composite materials. Ishida and Low [23] used interlaminar short-beam shear (ILSS) as a screening method for evaluating fiber–matrix adhesion. The results revealed that the ILSS strength of the glass–cloth-reinforced polybenzoxazine composite was significantly higher than that of the novolac composite when no surface treatment of the glass fiber was applied. When glass fibers were surface-treated with 0.1% by weight of  $\gamma$ -amino-propyl-trimethoxysilane ( $\gamma$ -APS) aqueous solution, the authors concluded that  $\gamma$ -APS is not as effective on polybenzoxazine as it is on novolac. The high shear strength of the polybenzoxazine composites is due to a better wetting of the glass fiber by the low viscosity of the benzoxazine resin. This is an advantage in terms of processing.

The successful use of polybenzoxazine as a matrix for highly filled composite has also been reported [21,22]. Ishida and Rimdusit [21] investigated the effect of particle size and its distribution on the thermal conductivity of boron nitride-filled polybenzoxazine. The authors used large aggregates of flake-like boron nitride crystals and were able to make a composite with a maximum filler content up to 78.5 vol% (88 wt%). The extraordinary high thermal conductivity value of 32.5 W/mK was achieved at the maximum boron nitride content. The ternary systems of benzoxazine, epoxy and phenolic resins were also reported by Jubsilp et al. to be able to accommodate woodflour filler up to 70 wt% resulting in a substantial enhancement in flexural modulus and strength as well as glass transition temperature of the wood composites [22].

From those interesting characteristic of polybenzoxazine, it is chosen as a matrix for highly filled nanocomposite of fumed silica. Therefore, the aim of this work is to study the effect of nano-SiO<sub>2</sub> content at a high loading level on major composite properties of the highly processable polybenzoxazine. The obtained mechanical and thermal performance of their nano-SiO<sub>2</sub> composites will be evaluated.

## 2. Experimental

### 2.1. Materials

Benzoxazine monomer, bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane (BA-a), was synthesized from 2,2'-bis(4-hydroxyphenyl)-propane (bisphenol-A) with aniline and formaldehyde according to the solventless method described elsewhere [24]. Bisphenol-A (polycarbonate grade) provided by Thai Polycarbonate Co., Ltd. (TPCC) was used as-received. Para-formaldehyde (AR grade) and aniline (AR grade) were purchased from Merck Ltd.

Nano-SiO<sub>2</sub> or Fumed silica (Reosil<sup>®</sup> QS-20) from Tokuyama Co., Tokyo, Japan, was kindly provided by Cobra International Co., Ltd. Reosil<sup>®</sup> QS-20 has the density of 2.203 g/cm<sup>3</sup>. It is fluffy, white powder of amorphous structure. An average diameter of primary particles of the fumed silica is ranging from 5 to 50 nm and a specific surface area is approximately 200 m<sup>2</sup>/g.

### 2.2. Sample preparations

The benzoxazine (BA-a) resin was well dry-mixed with nano-SiO<sub>2</sub> at a desired weight fraction. The BA-a/nano-SiO<sub>2</sub> mixture was then heated up to 80–100 °C and mechanically mixed to ensure nano-SiO<sub>2</sub> particles wet-out by the BA-a resin. The nano-SiO<sub>2</sub>/BA-a compound in the form of paste was then compression-molded into various dimensions depending upon the types of experiments. All the specimens were thermally cured at 200 °C under a pressure of 0.1 MPa for 3 h. The fully cured specimens were left to cool down at room temperature before their characterizations.

### 2.3. Sample characterizations

#### 2.3.1. Density measurement

The density of the polymer composites were measured by water displacement method according to ASTM D792-08 (Method A). All specimens were prepared in a rectangular shape of 50 mm × 25 mm × 2 mm and weighed both in air and in water.

The density was calculated using the following equation:

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

where  $\rho$ ,  $\rho_0$  are density of the specimen and liquid at the given temperature, respectively (g/cm<sup>3</sup>).

$A$ ,  $B$  are weight of the specimen in air and in liquid, respectively (g).

#### 2.3.2. Fourier transforms infrared spectroscopy (FTIR)

Fourier transform infrared spectra of PBA-a, nano-SiO<sub>2</sub>, and nano-SiO<sub>2</sub>-filled PBA-a at 30% by weight of the filler were carried out on a Spectrum GX FTIR spectrometer from Perkin Elmer instrument with an ATR accessory. All obtained spectra were averaged from 64 scans at a resolution of 2 cm<sup>-1</sup> within a spectral range of 4000–650 cm<sup>-1</sup>.

#### 2.3.3. Differential scanning calorimetry measurements

Curing behaviors of BA-a/nano-SiO<sub>2</sub> molding compounds at various nano-SiO<sub>2</sub> contents were investigated by a differential scanning calorimeter (DSC, model 2910) from TA Instruments. Approximately 3–5 mg of the molding compounds was placed in an aluminum pan with lid and characterized at heating rates of 1, 2, 5, and 10 °C/min from 30 °C to 300 °C under nitrogen atmosphere (50 ml/min). The heat flow difference between reference blank and the sample pan was recorded.

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