



# Mechanical and thermal properties of silicon nitride reinforced polybenzoxazine nanocomposites



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## ABSTRACT

Silicon nitride (SN) nanoparticle-reinforced polybenzoxazine nanocomposites were produced with good processability at various fractions of nano-SN ranging between 0 and 30 wt% via a compression molding technique. At the maximum nano-SN loading, the DMA of the nanocomposites showed an increase of 2 GPa and 47 °C in stiffness and glass transition temperature ( $T_g$ ), respectively. In addition, increasing the nano-SN fraction to 30 wt% significantly enhanced both the tensile strength and the micro-hardness of the nanocomposites. The TGA results revealed that the thermal stability of these nanocomposites was highly improved upon the addition of the reinforcing phase. The enhancements in the thermal and mechanical properties of these nanocomposites are attributed to the uniform nanoparticle dispersion and to the strong matrix–particle interactions based on the SEM and TEM results. Therefore, these nanocomposites are more suitable for high performance coating applications.

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## 1. Introduction

Over the past few decades, polymer–inorganic nanocomposites have been attracting significant scientific research and technological interests. The incorporation of inorganic particles including ceramics, metal powders, metallic oxides, non-metal oxides and natural fillers into polymeric matrices proves their effectiveness to produce high-performance materials that are suitably applicable in various industrial fields [1]. In addition, the selection of the inorganic fillers depends on the preferred property that is required such thermal, mechanical, or electrical.

Polybenzoxazine resins are promising matrices for producing nanocomposites materials due to their advantageous properties such as high thermal stability, high char yields, high glass transition temperature ( $T_g$ ), near-zero volumetric change upon curing, good mechanical and dielectric properties, low water absorption, good optical properties, and low flammability [2–9]. These characteristics promote the polybenzoxazine over epoxies and phenolic resins in the area of electronics and the aerospace sector. However, there are some shortcomings associated with these thermosets such as their brittleness, lack of toughness and limited impact strength for hard applications, which are the most serious

problems that polybenzoxazine researchers have to consider [10]. To overcome these concerns, the alloying with inorganic fillers to prepare high performance nanocomposites appears as one of the most preferred approaches because this approach is the easiest route compared to the synthesis of bulky benzoxazine structures that is very expensive and difficult to achieve [11–13].

Recently, an extensive research to explore polybenzoxazine-based nanocomposites with different inorganic fillers has been conducted [14]. Particularly, ceramics fillers have been widely used to enhance the thermal and mechanical properties of polybenzoxazine matrix [15]. Agag et al. have found that the addition of TiO<sub>2</sub> into the polybenzoxazine via a sol–gel technique increased both the storage modulus and the thermal stability of the pristine polybenzoxazine [16]. Also, high thermal and mechanical property enhancements have been obtained in highly filled polybenzoxazine nanocomposites with SiO<sub>2</sub> and fumed silica [17,18]. In addition, aiming to improve the thermal conductivity of the polybenzoxazine matrix highly filled system with boron nitride (BN) has been recently published [19]. On the other hand, nano-ZrO<sub>2</sub> improved the wear properties of the polybenzoxazine matrix as reported by Wu et al. [20].

Silicon nitride (Si<sub>3</sub>N<sub>4</sub>) nanoparticles are promising ceramic fillers that were developed in a search for high strength and high toughness ceramics that could replace metals in providing much higher operating temperatures and efficiencies. These nanofillers have been explored in different ways such as improving the

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fracture toughness and lowering the brittleness of materials, as well as reducing the friction and enhancing the wear resistance [21]. Silicon nitride has been recognized as one of the most important materials for high temperature and mechanical strength applications [22] due to its advantageous characteristics such as a good resistance to corrosion, better wear properties with a low dielectric constant, and superior hardness with a low density [23]. Albeit these outstanding properties, high performance nanocomposites have been prepared using various polymers matrices such as epoxy [24,25], polypropylene [26], polyethylene [27], polyimide 6 [28], cyanate ester [29], polyetherether-ketone (PEEK) [30,31], and bismaleimide [32], which are actually the main objectives. However, there has been no study which explored the effect of silicon nitride on the thermal and mechanical properties of the polybenzoxazine matrix until now.

In the current study, a novel series of nanosized silicon nitride (SN) reinforced typical polybenzoxazine nanocomposites was prepared initially using a solvent mixing method followed by a compression molding technique. The effects of the SN nanoparticles on the thermal and mechanical properties of the polybenzoxazine matrix are scrutinized in terms of its nano-SN content.

## 2. Experimental

### 2.1. Materials

The bisphenol A–aniline-based benzoxazine monomer was synthesized according to the solventless technique reported by Ning and Ishida [33]. The silicon nitride nanoparticles ( $\alpha$ - $\text{Si}_3\text{N}_4$ ) were produced by Hefei Kaier Nanometer Technology and Development (China). These nanofillers are in the form of a white powder with a crystalline structure having a density of  $3.44 \text{ g/cm}^3$ , an average diameter of particles of 50 nm, and a nominal surface area of approximately  $121 \text{ m}^2/\text{g}$  (measured by BET method). The silane coupling agent, KH-550 ( $\text{NH}_2-(\text{CH}_2)_3\text{Si}-(\text{OC}_2\text{H}_5)_3$ ), was purchased from Nanjing Union Silicon Chemical Co., Ltd., PR (China). The  $\alpha$ - $\text{Si}_3\text{N}_4$  nanoparticles were mixed with KH550 silane coupling agent (5 wt% of filler) in ethanol and stirred for 4 h. The collected nanoparticles from filtration were then dried under vacuum at  $80^\circ\text{C}$  for 12 h. Dichloromethane was purchased from the Aladdin Co. and used without further purification.

### 2.2. Preparation of polybenzoxazine/silicon nitride nanocomposites

The polybenzoxazine nanocomposites were produced by adding the necessary amounts of the treated nano-SN that ranged between a 5 wt% and 30 wt% with increments of 5 wt% into a glass vessel containing about 2 g of (BA-a) monomers, that was previously dissolved in 50 ml of dichloromethane (DCM). The composite mixtures were vigorously stirred using a mechanical agitator for 3 h and then sonicated at the rate of 4000 r/min to provide a much better dispersion of the nano-SN into the polybenzoxazine matrix. The afforded mixtures were then heated at  $60^\circ\text{C}$  for 24 h under vacuum to evaporate the DCM solvent.

In the appropriate steel mold, the dried mixtures were first reheated at  $120^\circ\text{C}$  under vacuum to evaporate any residual solvent and avoid any entrapped bubbles, which have a detrimental effect on the mechanical properties of the cured specimens, since they act at stress concentration and crack initiation sites. The dried nanocomposites were then compression-molded following an isothermal heating program at  $180^\circ\text{C}$  for 6 h under a pressure of 10 MPa using a hydraulic hot-press apparatus. The thickness of the cured samples was limited to 2 mm via a polishing process. Hereafter, both the uncured and the cured nanocomposites were labeled as (BA-a)/SN and P(BA-a)/SN, respectively.

### 2.3. Characterization

Fourier transform infrared (FTIR) spectra were recorded by a Perkin–Elmer Spectrum 100 spectrometer. Transmission spectra were obtained in the range of  $4000\text{--}400 \text{ cm}^{-1}$  with a resolution of  $4 \text{ cm}^{-1}$  after averaging two scans by casting a thin film on a KBr plate. DSC measurements were evaluated using a TA Q200 differential scanning calorimeter under a 50 mL/min constant flow of nitrogen. The instrument was calibrated using a high-purity indium standard, and  $\alpha$ - $\text{Al}_2\text{O}_3$  was used as the reference material. A sample of about 4.5 mg was weighed into a hermetic aluminum sample pan at  $25^\circ\text{C}$ , which was then sealed and immediately tested. The dynamic scanning experiments ranged from 40 to  $350^\circ\text{C}$  at a heating rate of  $20^\circ\text{C}/\text{min}$ . The dynamic mechanical thermal properties of the cast blends were carried out by a TA Q800 dynamic mechanical analyzer. The rectangular samples ( $20 \text{ mm} \times 5 \text{ mm} \times 2 \text{ mm}$ ) were previously polished before being loaded in a single cantilever mode at a temperature ramp of  $3^\circ\text{C}/\text{min}$  in the range of  $30\text{--}250^\circ\text{C}$  using a frequency of 1 Hz in air. The fracture surface morphology of the P(BA-a)/SN nanocomposites from the DMA test was investigated using a scanning electron microscope (JOEL, model JSM-5800LV) at 20 kV with gold coating on the samples. The inorganic phase dispersion was examined by a JEM-2100 TEM (JEOL, Japan) at an accelerating voltage of 120 kV. The thin sections for the TEM tests were cut by a microtome at  $-100^\circ\text{C}$  and placed on copper grids. The cross-sectional fracture surfaces of the DMA samples were obtained by cooling in liquid nitrogen followed by breaking. The microhardness of the nanocomposites specimens was evaluated using the Impressor Hand-Held Portable 0558298254 Hardness Tester (American Standard ASTM B648), with the average of 10 measurements reported. The tensile tests were carried out using an INSTRON 4505 at a crosshead speed of 1 mm/min of specimens of about  $45 \text{ mm} \times 10 \text{ mm} \times 2 \text{ mm}$ . A thermogravimetric analysis (TGA) was performed by a TA Instruments Q50 at a heating rate of  $20^\circ\text{C}/\text{min}$  from 50 to  $800^\circ\text{C}$  under a nitrogen atmosphere at a flow rate of 50 mL/min.

## 3. Results and discussion

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

Fig. 1 shows the FTIR spectra of the surface-treated nano-SN, (BA-a) benzoxazine monomer and some of their cured nanocom-

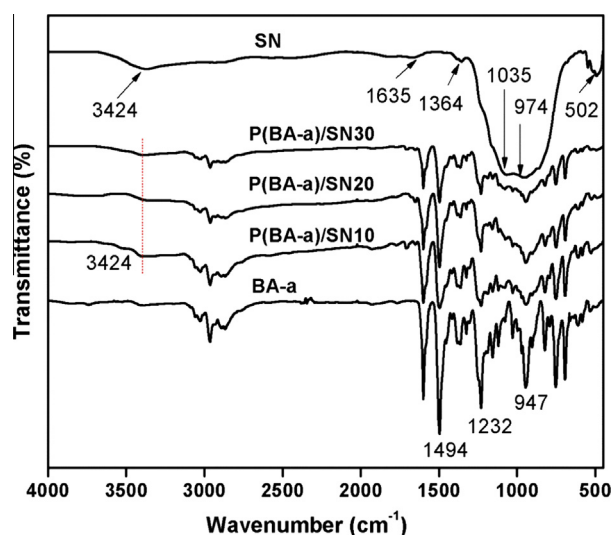


Fig. 1. The FTIR spectra of BA-a, nano-SN, and some of P(BA-a)/SN nanocomposites.

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