

Synthesis and characterization of boron-containing benzoxazine resins for advanced thermal protection systems

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The material systems used in aerospace and defense vehicles are of critical importance for ensuring reliable operation under both atmospheric and extra-atmospheric conditions. In particular, severe aerodynamic heating caused by surface friction during atmospheric entry and exit exposes these vehicles to extreme thermal loads. Preserving structural integrity and functional performance under such conditions requires the development of advanced thermal protection systems (TPS). Among the candidate materials, carbon fiber-reinforced phenolic resin composites have attracted considerable attention due to their high thermal resistance, ablative characteristics, and excellent mechanical properties. In this study, phenylboronic acid-modified benzoxazine resins were synthesized to enhance the thermal performance of composite materials intended for TPS applications. Neat benzoxazine and phenylboronic acid-modified benzoxazine resin systems were successfully prepared and comparatively investigated. The structural, morphological, and thermal properties of the synthesized resins were characterized using Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The incorporation of phenylboronic acid significantly improved the thermal behavior of the benzoxazine resin systems, indicating enhanced thermal stability and potential for high-temperature applications. The obtained results demonstrate that the developed resin systems are promising candidates for advanced thermal protection composites and contribute to the ongoing development of high-performance phenolic matrix materials for aerospace applications.

Keywords: Benzoxazine, Phenolic resin, Thermal properties, Phenylboronic acid

INTRODUCTION

The high velocities reached by spacecraft and aircraft during atmospheric flight expose these vehicles to severe environmental stresses. Aerodynamic heating, oxidative environments, high pressure, and plasma effects collectively threaten the structural and thermal integrity of the system [1]. The simultaneous presence of such extreme conditions necessitates the development of advanced engineering materials capable of maintaining performance under harsh operational environments.

In this context, thermal protection systems have been developed to provide effective thermal shielding by preventing excessive heat transfer from the vehicle's outer surface to its internal structure during hypersonic flight [2]. TPS materials are typically designed as multiphase composite systems consisting of a reinforcement phase (carbon, glass, or kevlar fibers) and a matrix phase (polymeric or ceramic resins) that provides structural cohesion and load transfer capability. Among these constituents, the matrix phase plays a critical role in determining overall performance, as it is the most susceptible

component to thermal degradation, ablation, and surface erosion under extreme temperature conditions. Therefore, the selection or modification of high-temperature-resistant polymer matrices is of paramount importance.

Thermoset and thermoplastic polymers are widely used as matrix materials in composite systems [3]. Among thermosets, phenolic resins exhibit superior thermal stability and high char yield compared to other polymer classes. Their dense aromatic structures provide resistance to thermal degradation, while their low thermal conductivity and ability to absorb heat generated during decomposition further enhance their suitability for high-temperature applications. Owing to these advantages, phenolic resins are commonly used as matrix materials in modern aerospace thermal protection systems.

However, inherent limitations such as brittleness and processing constraints have encouraged researchers to explore alternative high-performance polymer systems. In this regard, polybenzoxazine (PBZ) resins have emerged as promising candidates to replace or complement conventional phenolic

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resins. Benzoxazine monomers, synthesized *via* the Mannich reaction of formaldehyde, phenol (or phenol derivatives), and primary amines, undergo ring-opening polymerization to form phenolic-like PBZ networks under thermal curing conditions [4]. Compared to conventional phenolic systems, benzoxazine resins offer advantages such as reduced shrinkage, absence of volatile by-products during curing, and elimination of acidic catalysts. These characteristics make PBZ resins attractive candidates for advanced thermal protection composite applications.

In this study, boron-modified and unmodified benzoxazine resins were synthesized, and the resulting systems were characterized.

EXPERIMENTAL

Materials

Phenol (90%) supplied by Kimetsan Kimya, aniline ($\geq 99.5\%$) obtained from Merck, and 37% formaldehyde solution containing 10% by weight of methanol purchased from Tekkim Kimya were used as the primary precursors for benzoxazine synthesis. Magnesium hydroxide (95%) was supplied by Sigma-Aldrich, while N, N-dimethylformamide ($\geq 99\%$) was obtained from Carlo Erba and used as solvent without further purification. Phenylboronic acid (PBA) (98%) was purchased from BLDpharm and utilized as a thermal performance-enhancing modifier in the benzoxazine structure.

Synthesis of the resins

For the synthesis of benzoxazine resin, phenol and aniline were first weighed at appropriate molar ratios and mixed until a homogeneous solution was obtained. After continuous stirring for a predetermined period, formaldehyde solution was slowly added dropwise to the reaction medium using a burette under controlled conditions. Subsequently, magnesium hydroxide ($\text{Mg}(\text{OH})_2$) was introduced as a catalyst to promote the reaction and optimize the polymerization process. The pH of the reaction medium was adjusted to 6.0–6.5 to provide suitable synthesis conditions. The reaction mixture was then gradually heated to 80 °C and maintained at this temperature for a specific duration to complete the polymerization process [5]. Upon completion of the reaction, the reactor was cooled to room temperature, and the benzoxazine resin was successfully obtained.

For the modification process, phenylboronic acid was incorporated into the synthesized benzoxazine resin at predetermined concentrations. To ensure complete dissolution and homogeneous dispersion of phenylboronic acid within the resin matrix, the reaction

temperature was increased to 80–85 °C and the system was continuously stirred for approximately 1 h. After completion of the modification step, the resin mixture was cooled to room temperature, resulting in the successful synthesis of phenylboronic acid-modified benzoxazine resin.

Characterization of the resins

The synthesized benzoxazine resin systems were characterized to evaluate their structural, thermal, and morphological properties. Fourier transform infrared spectroscopy (FTIR) analyses were carried out using a Thermo Scientific Nicolet iS50 instrument to identify the chemical structures and functional groups present in the resins. The measurements were performed at room temperature within the scanning range of 4000–650 cm^{-1} .

Thermogravimetric analysis (TGA) was conducted to investigate the thermal stability and degradation behavior of the synthesized samples. The analyses were performed under a nitrogen atmosphere from room temperature to 900 °C at a heating rate of 10 °C min^{-1} .

The surface morphology of the samples was examined by scanning electron microscopy (SEM). Prior to SEM imaging, the sample surfaces were coated with a thin gold layer using a Leica ACE600 sputter coater to improve electrical conductivity and obtain high-quality micrographs.

RESULTS AND DISCUSSION

FTIR spectroscopy

The chemical bond structures and functional group properties of benzoxazine (BZ) resin and phenylboronic acid (PBA)-doped benzoxazine (PBZ) resin were investigated using FTIR. The measurements were performed at room temperature within a scanning range of 4000–650 cm^{-1} , and the FTIR spectra of benzoxazine resins containing BZ and 10% by weight of PBA are shown in Figure 1.

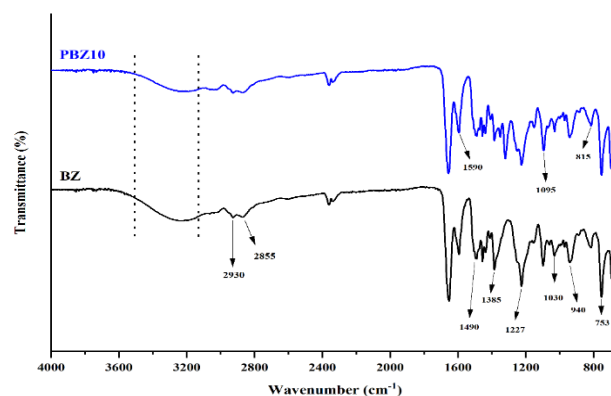


Figure 1. FTIR spectra of the resins

The FTIR spectra of the synthesized benzoxazine resin systems were analyzed to investigate the structural changes induced by phenylboronic acid modification. The broad absorption band observed in the 3500–3200 cm^{-1} region was attributed to hydrogen-bonding interactions between the phenolic hydroxyl groups formed after ring-opening polymerization of the benzoxazine ring and the B–OH functionalities of the PBA structure. The characteristic absorption bands detected at 2930 cm^{-1} and 2855 cm^{-1} correspond to the aliphatic C–H stretching vibrations of methylene groups and alkyl side chains associated with the oxazine ring structure, confirming the formation of methylene bridges within the polymer network [6]. The bands appearing in the 1590–1490 cm^{-1} range are assigned to aromatic C=C skeletal vibrations, indicating the preservation of the benzoxazine aromatic structure [7]. In addition, the band located at approximately 1385 cm^{-1} is related to methylene (–CH₂–) groups generated during the ring-opening polymerization process. The characteristic benzoxazine bands observed at 1227 cm^{-1} and 1030 cm^{-1} were attributed to asymmetric and symmetric C–O–C stretching vibrations, respectively, and were retained in all resin systems. Furthermore, the absorption band around 940 cm^{-1} , corresponding to out-of-plane bending vibrations of the oxazine ring C–H bonds, was clearly observed in the neat benzoxazine resin [8–9]. However, this band became weaker or partially disappeared in the PBA-containing samples, suggesting that boronic acid incorporation altered the chemical environment surrounding the oxazine ring [10–11]. Additional bands observed near 815 cm^{-1} and 753 cm^{-1} were attributed to aromatic C–H vibrations and ortho-disubstituted benzene structures containing oxazine functionalities [12–13]. Moreover, the relative intensity of the C–O–C vibrational band around 1095 cm^{-1} decreased after PBA modification, indicating possible intermolecular interactions between the benzoxazine network and phenylboronic acid molecules [14].

SEM analysis

The morphological properties of phenylboronic acid-modified benzoxazine resin systems were investigated by scanning electron microscopy (SEM) analysis of the fracture surfaces. SEM micrographs of the cured neat BZ resin and the BZ resin containing 10 wt.% phenylboronic acid (PBZ10) are presented in Figure 2.

As shown in Figure 2(a), the fracture surface of the cured neat BZ resin exhibits a relatively rough and heterogeneous morphology with noticeable

agglomerated domains distributed across the surface. In contrast, the PBZ10 sample displayed a more homogeneous and comparatively smoother fracture surface morphology, as illustrated in Figure 2(b). This morphological change suggests that phenylboronic acid was successfully incorporated, at least partially, into the benzoxazine network during the synthesis and curing processes.

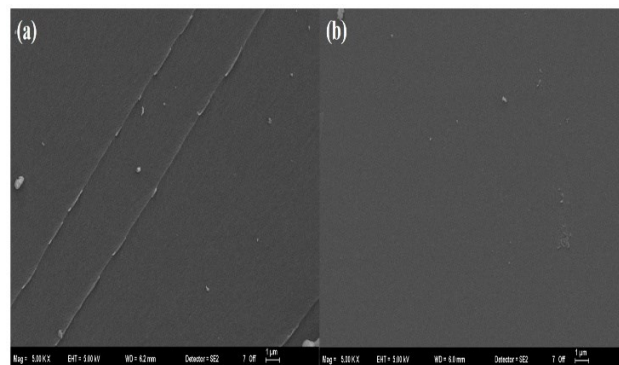


Figure 2. SEM images of resins (a) neat benzoxazine (b) benzoxazine resin containing 10 wt.% phenylboronic acid.

The improved surface homogeneity observed in the modified resin system may be attributed to enhanced intermolecular interactions and improved structural compatibility between the benzoxazine matrix and the phenylboronic acid component. These findings indicate that phenylboronic acid modification can influence the microstructural organization of the cured resin system and potentially contribute to improved thermal and structural properties.

TGA

The thermal decomposition behavior of neat BZ and phenylboronic acid-modified PBZ resins was investigated by thermogravimetric analysis (TGA) under a nitrogen atmosphere. The TGA curves presented in Figure 3 demonstrate that the incorporation of phenylboronic acid significantly influences the thermal degradation behavior of the benzoxazine resin systems.

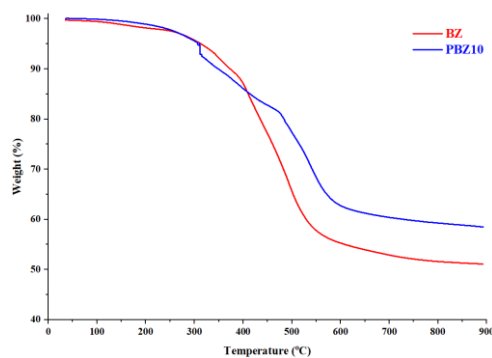


Figure 3. TGA results of the resins.

The results indicate that phenylboronic acid addition considerably enhances the char-forming ability of the benzoxazine matrix. While the neat benzoxazine resin exhibited a residual char yield of 51.08% at 900 °C, the residue amount increased to 58.49% for the resin containing 10 wt.% boron additive. This improvement suggests that boron-containing structures promote the formation of a more thermally stable carbonaceous layer during thermal decomposition and suppress the generation of volatile degradation products.

The primary weight loss region observed between approximately 400 and 600 °C corresponds to the pyrolytic decomposition of the benzoxazine-based polymer network. The higher char residue obtained at elevated temperatures for the boron-modified resin systems can be attributed to the relatively high bond dissociation energies of boron–oxygen (B–O) and boron–carbon (B–C) bonds introduced into the polymer structure [15]. These thermally stable boron-containing structures contribute to improved thermal resistance and enhanced carbonization behavior of the resin system.

CONCLUSION

In this study, phenylboronic acid-modified benzoxazine resin systems were successfully synthesized and evaluated for potential thermal protection system applications. The effects of phenylboronic acid incorporation on the structural, thermal, and morphological properties of benzoxazine resins were systematically investigated using FTIR, TGA, and SEM analyses.

FTIR results confirmed the successful modification of the benzoxazine structure through interactions between phenolic hydroxyl groups and boronic acid functionalities. Changes observed in the characteristic oxazine-related absorption bands indicated that the incorporation of phenylboronic acid altered the chemical environment of the polymer network. TGA analyses demonstrated that boron modification significantly enhanced the thermal stability and char-forming capability of the resin systems. The char residue increased from 51.08% for neat benzoxazine resin to 58.49% for the resin containing 10 wt.% phenylboronic acid, indicating the formation of more thermally stable boron-containing structures during decomposition. SEM observations further revealed that the modified resin exhibited a more homogeneous and smoother

fracture surface morphology compared to the neat benzoxazine resin, suggesting improved structural compatibility and network organization.

Overall, the obtained results demonstrate that phenylboronic acid incorporation effectively improves the thermal resistance and microstructural characteristics of benzoxazine-based resin systems. These findings indicate that the developed boron-modified benzoxazine resins are promising candidates for high-temperature composite and thermal protection applications in aerospace and defense industries. Future studies may focus on the incorporation of reinforcing fibers and ceramic fillers, as well as the evaluation of ablative and mechanical performance under extreme thermal environments.

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