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RESEARCH ARTICLE

Vanillin and Guaiacol Based Trifunctional Polybenzoxazine Bio-Composites for Thermal and Corrosion Resistant Applications

A. Mohanraj[1] | M. Selvi[1] | S. Devaraju[2] | A. Kumaravel[3] | M. Alagar[1,2]

[1]Centre for Advanced Materials, Department of Chemistry, PSG College of Arts and Science, Coimbatore, India | [2]Polymer Engineering Laboratory, Department of Chemistry, PSG Institute of Technology and Applied Research, Neelambur, Coimbatore, India | [3]Functional Materials Laboratory, Department of Chemistry, PSG Institute of Technology and Applied Research, Neelambur, Coimbatore, India

Correspondence: S. Devaraju (subudeva@gmail.com) | M. Alagar (muthukaruppanalagar@gmail.com)

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ABSTRACT

In pursuit of sustainable and high-performance materials, bio-based trifunctional benzoxazine monomers (VG-Bz) were synthesized using eco-friendly sustainable vanillin and guaiacol-based trifunctional phenolic precursors with varied natures of primary amines, viz., aniline (a), furfuryl amine (fa), lauryl amine (la), and stearyl amine (sa), with paraformaldehyde through Mannich condensation reaction in the absence of solvent. The resulting benzoxazine monomers, VG-a, VG-fa, VG-la, and VG-sa, were thermally polymerized to obtain corresponding polybenzoxazines (PBZs) and comprehensively characterized for their curing behavior, thermal stability, flame retardancy, hydrophobicity, and corrosion resistance. Thermogravimetric analysis provides that poly(VG-a) and poly(VG-fa) exhibited superior thermal stability with high char yields, due to the presence of rigid aromatic structures. Data from water contact angle studies indicate that poly(VG-sa) possesses enhanced hydrophobicity due to the presence of long alkyl chains compared to those of other samples of polybenzoxazines. An incorporation of GPTMS-functionalized bio-silica (BS) into the poly(VG-sa) matrix further improved thermal resistance, water repellence, and anti-corrosive properties. Electrochemical impedance spectroscopy (EIS) and Tafel polarization studies in 3.5 wt% NaCl solution confirmed the exceptional corrosion protection efficiency of poly(VG-sa)/20% BS, achieving a maximum inhibition efficiency of 99%. These results highlight the potential of VG-Bz systems, particularly the poly(VG-sa)/BS hybrids, as environmentally benign coatings for advanced thermal and corrosion-resistant applications.

1 | Introduction

The growing environmental and health concerns associated with petroleum-based polymers have accelerated the development of bio-based sustainable polymeric materials derived from renewable resources. Among these, bio-based polymer composites reinforced with natural fillers offer a sustainable alternative for reduced ecological impact. These materials, synthesized from biomass-derived sources such as plant oils, lignin, carbohydrates, and agricultural residues, align with global efforts to reduce fossil fuel dependence and mitigate carbon emissions [1, 2].

Benzoxazine resins, a class of high-performance thermosetting polymers, are conventionally synthesized from fossil-based phenols, formaldehyde, and primary amines through

A. Mohanraj and M. Selvi contributed equally.

Mannich condensation [3]. Despite their favorable properties such as high thermal stability, near-zero shrinkage, and excellent mechanical strength, traditional benzoxazines present sustainability challenges [4–6]. These include reliance on nonrenewable feedstocks, a high carbon footprint, and the toxicity of monomers, like bisphenol-A (BPA), known for its endocrine-disrupting and teratogenic effects [7, 8]. To overcome these issues, extensive research has been focused on the synthesis of bio-based sustainable benzoxazine monomers using renewable bio-based phenols and primary amines as precursors. Bio-phenols, such as cardanol [9–11], guaiacol [11, 12], and urushiol [13], along with amines like furfuryl amine [12, 14], lauryl amine [15], and stearyl amine [16], have been utilized to partially or fully substitute petroleum-based feedstocks. Nevertheless, many such systems remain only partially bio-based, as fossil-derived constituents are still commonly involved.

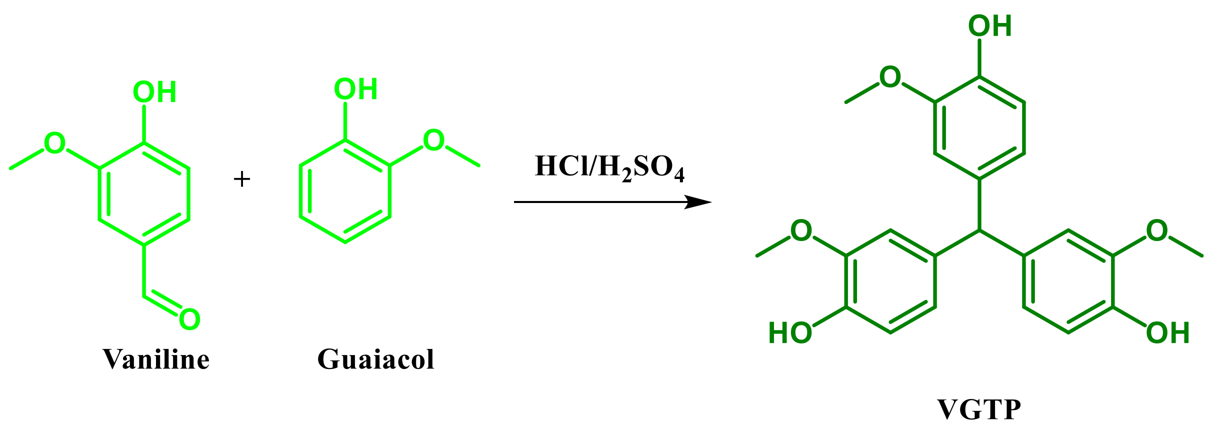
Recent studies demonstrate that the bio-based polybenzoxazines (PBZs) can match or exceed the performance of their petroleum-based analogs while offering superior environmental compatibility [1, 17–19]. Mohamed et al. [19] synthesized a multifunctional bisbenzoxazine (AP-fa-BZ) from natural flavonoids, achieving high T_g, excellent thermal stability, tunable surface properties, and intrinsic antibacterial activity. Chong et al. [20] reported difunctional and trifunctional benzoxazine monomers from guaiacol, vanillin, and furfuryl amine, which, when incorporated into epoxy blends, yielded polymers with tunable thermal stability, high stiffness, and improved fracture energies. Zhang et al. [21, 22] developed a fully bio-based trioxazine benzoxazine from resveratrol that produced polybenzoxazine with outstanding flame resistance, high char yield, and superior thermal stability. Similarly, Yang et al. [12] synthesized a tri-furan functional bis-benzoxazine resin with remarkable thermal stability (Tg 290°C, T_{d10} 375°C) and nonignitable flame-resistant properties. More recently, Yuan et al. [23] introduced a bio-based bisbenzoxazine (MH-fa) from vanillin and furfuryl amine and a Diels–Alder-based copolymer with DDM-BMI, achieving excellent thermal stability, high char yield, and ultra-low heat release. Collectively, these studies highlight the promise of fully bio-derived benzoxazines as sustainable, high-performance thermosetting resins required to eliminate fossil-derived feedstocks and to meet the various industrial applications.

In this context, in the present work, a bio-based trifunctional benzoxazine monomer was synthesized via Mannich condensation using renewable trisphenol synthesized from vanillin and guaiacol (Scheme 1), and three bio-derived primary amines, viz., furfuryl amine, lauryl amine, and stearyl amine with paraformaldehyde in the absence of solvent at appropriate experimental conditions. Aniline, a petroleum-derived primary amine, was also used for comparison. The trisphenol precursor was synthesized from vanillin and guaiacol, and its molecular structure was confirmed from Fourier-transform infrared (FT-IR) and proton nuclear magnetic resonance (^{1}H NMR) spectral analyses. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out to assess the curing behavior and thermal stability, respectively. The value of the water contact angle (WCA) was determined to evaluate the hydrophobic behavior, and electrochemical impedance spectroscopy (EIS) was used to assess the corrosion resistant properties. Based on superior EIS performance, the stearyl amine-based BZ system was selected and reinforced with varied weight percentages of GPTMS-functionalized bio-silica (BS) (0, 5, 10, 15, and 20 wt% w/w with respect to BZ monomers) to obtain hybrid composites. The resulting hybrid bio-composite exhibited markedly enhanced corrosion resistance, owing to the synergistic barrier effects of the long alkyl chain and bio-silica reinforcement. These improvements, combined with strong thermal and surface properties, underscore the promise of this bio-based hybrid material for sustainable, high-performance industrial applications. Data obtained from different studies are discussed and reported.

2 | Experimental

2.1 | Materials

Vanillin, guaiacol, furfuryl amine, lauryl amine, stearyl amine, paraformaldehyde, ethyl acetate, hexane, acetic acid, sulfuric acid, ethanol, 3,3′-dithiodipropionic acid, and gallic acid were procured from SRL Chemicals. Aniline, 2-mercaptonicotinic acid, and 3-glycidoxypropyltrimethoxysilane (GPTMS) were obtained from Sigma-Aldrich. Alumina-coated thin-layer chromatography (TLC) plates were procured from Merck. All chemicals were used as received without further purification.



SCHEME 1 | Synthesis of vanillin and guaiacol based trisphenol (VGTP).

protection. Electrochemical impedance studies confirmed that the poly(VG-sa)/20% BS coating achieved the highest impedance ($9.2 \times 10^7\,\Omega\,cm^2$) and corrosion inhibition efficiency (99.4%), due to the synergistic barrier effects of the hydrophobic matrix and bio-silica reinforcement. Overall, these results establish VG-Bz systems, particularly VG-sa/bio-silica hybrids, as promising eco-friendly coating materials for advanced thermal and corrosion-resistant applications. In summary, this work highlights the feasibility and advantages of using bio-derived benzoxazine systems, particularly the VG-sa/bio-silica hybrids, for the development of advanced coating materials with exceptional thermal stability, moisture resistance, and corrosion inhibition. These materials offer a sustainable and high-performance alternative to fossil-derived polymers, aligning well with green chemistry principles and industrial demands for environmentally friendly protective coatings.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. **Figure S1:** pat70381-sup-0001-Figures.docx. ^{1}H NMR spectrum of VGTP **Figure S2:** ^{13}C NMR spectrum of VGTP **Figure S3:** MASS spectrum of VGTP **Figure S4:** ^{1}HNMR spectra for VG-a **Figure S5:** ^{1}HNMR spectra for VG-fa **Figure S6:** ^{1}HNMR spectra for VG-la **Figure S7:** ^{1}HNMR spectra for VG-sa **Figure S8:** ^{13}C NMR spectrum of VG-a **Figure S9:** ^{13}C NMR spectrum of VG-fa **Figure S10:** ^{13}C NMR spectrum of VG-la **Figure S11:** ^{13}C NMR spectrum of VG-sa **Figure S12:** Equivalent circuit used for fitting of Nyquist plot **Figure S13:** XPS survey spectra of poly(VG-sa)/20% BS coated MS substrate before and after corrosion. **Video S1:** Poly(VG-sa)/20% BS composite coated on cellulose substrate for separation of oil–water mixture.