European Polymer Journal 234 (2025) 114017

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Sustainable benzoxazine materials from renewable sources: Synthesis, corrosion resistance, dielectric and superhydrophobic studies

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ARTICLE INFO

Keywords:
Predominantly bio-based benzoxazines
Superhydrophobic
Antimicrobial
Anticorrosion
DFT
Dielectric

ABSTRACT

The study explores predominantly bio-based benzoxazines, in order replace conventional/petroleum based benzoxazines. In this aspect, developing bio-based benzoxazines using furfural bis-thymol (FBT) and renewable amine derivatives, including 1-aminododecane (ad), 1-aminooctadecane (ao), 1-amino-9-octadecene (ae), 2-aminomethylfuran (af) and dehydroabietylamine (da). These plant-derived precursors provide an eco-friendly approach to developing advanced benzoxazine materials. Comprehensive characterization of the synthesized benzoxazines was performed using FTIR, ^{1}H NMR and ^{13}C NMR techniques. Curing studies were assessed using DSC, notably, FBT-ae exhibit the dual curing nature with temperature of 210 °C and 243 °C. Among the cured samples, poly(FBT-af) resulted highest char yield of 50 % due to the additional cross-linking nature of furan ring. The superhydrophobic nature was achieved by coating FBT-ao containing benzoxazine on cotton fabric which showed the WCA value of 156°. All the polybenzoxazines possesses enhanced corrosion resistant behavior which was supported by the DFT results. Moreover, the samples resulted better antimicrobial nature against *S.aureus and E.coli*. Further, low dielectric constant value of 3.39 with minimum dielectric loss has been noticed. The obtained results demonstrates the potential of bio-based benzoxazines as a sustainable and high-performance alternative for diverse industrial and engineering applications, contributing to the growing global demand for greener material solutions.

1. Introduction

The increasing awareness of environmental sustainability has significantly influenced advancements in material science, particularly in polymer technology [1]. The reliance on fossil-based polymers, despite their versatility and widespread use, has resulted in severe ecological concerns, including resource depletion, pollution and prolonged persistence in ecosystems [2]. To address these issues, researchers and industries have turned their focus toward the development of sustainable and bio-based materials, aiming to replace conventional polymers with environmentally friendly alternatives [3]. Bio-based polymers derived from renewable resources have emerged as a viable solution to mitigate the environmental challenges associated with traditional materials [4,5]. Among these, polybenzoxazines (PBzs) stand out due to their remarkable thermal stability, mechanical strength and chemical resistance [6,7]. Unlike conventional polymers, benzoxazines (Bzs) offer unique properties, such as tunable cross-linking density and surface functionality, making them suitable for various applications ranging from coatings and adhesives to electronics and biomedical materials [8].

The utilization of bio-phenols such as thymol, eugenol, cardanol and vanillin offer an eco-friendly route for sustainable material design [9–12]. These naturally derived phenolic compounds not only reduce the dependency on fossil fuels but also provide inherent bioactivity, such as antimicrobial and antifouling properties [13–15]. In recent years, there has been a growing interest in developing multifunctional bio-based materials that combine hydrophobicity, antimicrobial activity and corrosion resistance [16,17]. For instance, thymol, a phenolic compound abundantly found in thyme plants, exhibits exceptional antimicrobial properties, making it suitable choice for the preparation of Bzs [18]. These properties are particularly valuable for applications in environments, such as marine coatings, or in healthcare, where resistance to microbial colonization is crucial [19]. Similarly, bio-phenols like pyrogallol, curcumin, vanillic acid, tyrosine and eugenol contribute to enhanced hydrophobicity and corrosion resistance, addressing critical challenges in marine and industrial environments [20–23]. Furthermore, bio-based Bzs obtained from rosins, resveratrol, hordenine have shown potential in advanced electronic applications due

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https://doi.org/10.1016/j.eurpolymj.2025.114017
Received 14 March 2025; Received in revised form 29 April 2025; Accepted 13 May 2025
Available online 14 May 2025

to their low dielectric constants and exceptional insulating properties, which are essential for modern microelectronic devices [24–26].

In order to align with the above said objectives some of the studies pertaining to the fully bio-based Bzs deals with the naturally sourced phenol and amines. Thymol is considered a bio-phenol because it is a naturally occurring phenolic compound found in various plants. It is commonly found in the essential oil of thyme (Thymus vulgaris) and other plants like oregano [27]. Furfural is derived from pentosan-rich agricultural biomass like corncobs, sugarcane bagasse, and rice husks through acid hydrolysis and dehydration of pentose sugars, primarily xylose [28]. 2-aminomethylfuran has also shown to be derived from furfural, which can be obtained from the sugars of agricultural waste [29]. 1-aminooctadecane, 1-aminododecane can be synthesized from naturally occurring fats and oils, which are commonly derived from plant and animal sources [30]. These fats and oils serve as the feedstock for the production process. 1-amino-9-octadecene is often produced by the reaction of oleic acid with ammonia or other amination agents. Oleic acid is a fatty acid found in various vegetable oils, making it a renewable and bio-based material [31]. Dehydroabietylamine is obtained from rosin, a natural resin extracted from pine trees, through chemical modification processes such as amination of dehydroabietic acid, a primary component of rosin [32]. Bio-refinery syngas can be fermented to produce bio-methanol, which has the potential be used to produce paraformaldehyde. These methods reduce the reliance on synthetic chemistry and petrochemical feedstock [33].

However, collective utilization of all the above mentioned five amines and its comprehensive studies for the preparation of bio-based Bzs are not found in most of the literature as per our knowledge. Hence this study aims to utilize the naturally sourced precursors as much as possible and focuses on the synthesis of bio-based Bzs using furfural bis-thymol and renewable amine derivatives. These plant-derived precursors provide an eco-friendly approach to developing advanced benzoxazine materials. Comprehensive characterization of the synthesized Bzs was performed using FTIR, ^{1}H NMR and ^{13}C NMR techniques. The thermal, hydrophobic, antimicrobial, dielectric and corrosion-resistant properties were systematically evaluated to study their multifunctional performance. Also, experimental corrosion resistant results were theoretically corelated with the DFT results. This work demonstrates the potential of bio-based Bzs as a sustainable and high-performance alternative for diverse industrial and engineering applications, contributing to the growing global demand for greener material solutions.

2. Experimental

2.1. Materials

Thymol (≥99 %), 1-aminododecane (98 %), 1-aminooctadecane (98 %), 1-amino-9-octadecene (95 %), 2-aminomethylfuran (97 %) and dehydroabietylamine (96 %) were obtained from SRL, India. Sodium sulphate (anhydrous, ≥99 %) and ethyl acetate (HPLC grade) were purchased from Isochem, India. Furfural bis-thymol was synthesized as per the earlier report [34].

2.2. Characterization techniques

The detailed analyses, characterization and testing techniques are provided in the supporting information file S1.

2.3. Syntheses of FBT bio-based Bzs

FBT bio-based Bz monomers were synthesized via Mannich condensation reaction involving FBT, paraformaldehyde and five different bio-amines such as 1-aminododecane (ad), 1-aminooctadecane (ao), 1-amino-9-octadecene (ae), 2-aminomethylfuran (af) and dehydroabietylamine (da). The general synthetic method involved using FBT (1 mmol), paraformaldehyde (4 mmol) and the respective amine (2 mmol) under controlled heating and stirring conditions, as described below (Scheme 1).

2.4. Synthesis of FBT-ad

In a 100 mL round-bottom flask, FBT (1 mmol, 0.37 g), paraformaldehyde (4 mmol, 0.12 g) and 1-aminododecane (2 mmol, 0.37 g) were combined. The mixture was stirred continuously and slowly heated to 80 °C for 1 h to achieve a homogeneous solution. Subsequently, the temperature was increased to 110 °C and maintained for an additional 6 h to complete the reaction. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate, washed thoroughly with distilled water and 1 M NaOH to remove any unreacted materials, dried over anhydrous sodium sulfate. The organic layer was evaporated under reduced pressure and the obtained product was further dried in a hot-air oven at 50 °C to yield the FBT-ad monomer as a viscous solid.

ATR-FTIR (ν cm^{-1}): 2956–2834 (–CH_2-), 1480 (C–H bend), 1080,1233 (C-O-C), 1122 (C-N-C), 940 (oxazine ring), 750 (Ar-H out-of-plane).

^{1}H NMR ($CDCl_3$), δ ppm: 1.20–1.50 (Aliphatic –CH_2), 2.24 (–CH_3), 3.25 (–CH), 4 (O-CH_2-C), 5.01 (O-CH_2-N), 5.3 (=CH–), 5.5 (–CH), 5.90–6.50 (furan), 6.5–7.6 (Ar-H).

^{13}C NMR ($CDCl_3$), δ ppm: 26–34 (Aliphatic –CH_2), 16–20 (Aliphatic –CH_3), 40 (–CH-), 50 (Ar-C-N), 80 (O-C-N), 129–131 (=C-), 110–139 (furan), 115–155 (Ar-C).

2.5. Synthesis of FBT-ao

Following a similar procedure, FBT (1 mmol, 0.37 g), paraformaldehyde (4 mmol, 0.12 g) and 1-aminooctadecane (2 mmol, 0.53 g) were reacted. After sequential heating at 80 °C and 110 °C, the reaction mixture was subjected to extraction with ethyl acetate, followed by aqueous washing and drying. Solvent removal under reduced pressure and drying in a hot-air oven at 50 °C provided the FBT-ao resin.

ATR-FTIR (ν cm^{-1}): 2956–2834 (–CH_2-), 1480 (C–H bend), 1080,1233 (C-O-C), 1122 (C-N-C), 940 (oxazine ring), 750 (Ar-H out-of-plane).

^{1}H NMR ($CDCl_3$), δ ppm: 1.20–1.50 (Aliphatic –CH_2), 2.24 (–CH_3), 3.25 (–CH), 4 (O-CH_2-C), 5.01 (O-CH_2-N), 5.3 (=CH–), 5.5 (–CH), 5.90–6.50 (furan), 6.5–7.6 (Ar-H).

^{13}C NMR ($CDCl_3$), δ ppm: 26–34 (Aliphatic –CH_2), 16–20 (Aliphatic –CH_3), 40 (–CH-), 50 (Ar-C-N), 80 (O-C-N), 129–131 (=C-), 110–139 (furan), 115–155 (Ar-C).

2.6. Synthesis of FBT-ae

For the synthesis of FBT-ae, FBT (1 mmol, 0.37 g), paraformaldehyde (4 mmol, 0.12 g) and 1-amino-9-octadecene (2 mmol, 0.47 g) were used. The reaction mixture was initially stirred and heated to 80 °C for 1 h, then further heated to 110 °C for 6 h. Post-reaction, the product was extracted, washed and dried similarly and the resulting FBT-ae monomer was isolated as a resin.

ATR-FTIR (ν cm^{-1}): 2956–2834 (–CH_2-), 1480 (C–H bend), 1080,1233 (C-O-C), 1122 (C-N-C), 940 (oxazine ring), 750 (Ar-H out-of-plane).

^{1}H NMR ($CDCl_3$), δ ppm: 1.20–1.50 (Aliphatic –CH_2), 2.24 (–CH_3), 3.25 (–CH), 4 (O-CH_2-C), 5.01 (O-CH_2-N), 5.3 (=CH–), 5.5 (–CH), 5.90–6.50 (furan), 6.5–7.6 (Ar-H).

^{13}C NMR ($CDCl_3$), δ ppm: 26–34 (Aliphatic –CH_2), 16–20 (Aliphatic –CH_3), 40 (–CH-), 50 (Ar-C-N), 80 (O-C-N), 129–131 (=C-), 110–139 (furan), 115–155 (Ar-C).

2.7. Synthesis of FBT-af

In the case of FBT-af, FBT (1 mmol, 0.37 g), paraformaldehyde (4 mmol, 0.12 g) and 2-aminomethylfuran (2 mmol, 0.19 g) were reacted

properties suitable for replacing conventional fossil-based Bzs. Among the developed samples, poly(FBT-af) exhibited better thermal stability, with the highest char yield of 50 %. The superhydrophobic nature of poly(FBT-ao) was evident from its WCA value of 156° when applied as a coating on cotton fabric, showing its water-repellent behavior. Furthermore, antimicrobial studies showed the effectiveness of these materials in inhibiting microbial growth. Dielectric analysis revealed low dielectric constants ranging between 3.39 and 3.54, enhancing their suitability for electronic applications. Further, the polybenzoxazine coatings provided exceptional corrosion resistance on mild steel, achieving an efficiency of 99 % and aligns with the DFT results. From, these results the developed materials suitably exploited for industrial applications, including adhesives, sealants and high-performance coatings.

CRediT authorship contribution statement

K.Mohamed Mydeen: Writing - original draft, Methodology, Analysis. **Balaji Krishnasamy:** Supervision, Project administration, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The authors express their gratitude to the PSG Management, Secretary, Principal, and PSG Institute of Technology and Applied Research, Coimbatore-641062, India, for their invaluable moral and financial support. One of the authors Mohamed Mydeen K thank the PSG Management for providing full-time research fellowship.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2025.114017.

Data availability

Data will be made available on request.

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