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# Design and development of disulfide and thioether-linked bio-based bisbenzoxazines for low-curing, thermally stable and corrosion-resistant coating applications

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A B S T R A C T

Polybenzoxazines derived from green precursors face significant challenges due to the high temperatures required for ring-opening polymerization (ROP), limiting industrial scalability. To address this, the present study introduces two novel series of bisbenzoxazine monomers containing disulfide (-S-S-) and thioether (-C-S-C-) linkages, synthesized from bio-based phenolic precursors (guaiacol, cardanol, eugenol, thymol) were paired with dihydrazides (thiodipropionate and dithiodipropionate). The structural confirmation of these monomers was confirmed by ATR-FTIR, $^{1}H$ NMR and $^{13}C$ NMR spectral techniques. Thermal properties were studied using DSC and TGA analyses. The synergistic combination of -S-S-, C-S-C and hydrazide groups have enabled the development of novel benzoxazine systems with lower curing behavior and higher thermal stability. Also, from curing kinetics the ROP temperature of benzoxazine monomers were reduced to 142 °C and subsequently confirmed through ATR-FTIR. Further, TGA results revealed that eugenol containing polybenzoxazines possess higher thermal stability among the series. Additionally, the corrosion resistant performance of polybenzoxazines was carried out using electrochemical methods on mild steel (MS) substrates. Results indicated excellent anti-corrosion properties with better corrosion inhibition efficiency of 99 %. All the results were compared with conventional phenol-based monomers containing same functionalities. This work highlights the potential utility of sustainable feedstocks for benzoxazine with lower energy demands and high-performance coating applications.

## 1. Introduction

The development of sustainable polymer systems has become a critical focus in materials science, driven by the need to balance performance and environmental responsibility [1]. Among these, benzoxazine monomers (Bzs) are a class of compounds explored significantly due to their exceptional thermal stability, flame retardancy and mechanical properties [2–5]. These monomers are synthesized through a condensation reaction involving phenols, amines and formaldehyde, resulting in the formation of a reactive 1,3-oxazine ring [6–8]. Their polymerized form, polybenzoxazines (PBzs), are renowned for their thermal stability [9,10], molecular design flexibility [11,12], moisture resistant [13], inter/intra molecular hydrogen bonding [14,15], low outgassing [16] and zero shrinkage [17] properties offering solutions for high-performance applications. These attractive properties make them suitable for corrosion resistant coatings [18]. Recently more studies focused on enhancing corrosion resistance for high-performance coatings through various strategies due to the need arises from the damage caused by corrosion to metal substrates [19,20]. Chemical modifications, such as incorporating silane, amine or polar groups, improve adhesion to metal substrates [21]. Structural modifications, including pendant groups with corrosion-inhibiting properties like long alkyl chains, enhance hydrophobicity. Addition of nanoparticles, blending with polymers and copolymerization method coatings to improve adhesion and barrier properties [22–25]. Nevertheless, the bio-based benzoxazines have been explored diversely but the applications in the field of corrosion resistant coatings with low temperature curable are highly warranted [26].

Conventional Bzs systems requires high temperatures (≥250 °C) for effective polymerization [27]. This high-temperature normally limits their processing efficiency and increases energy consumption. Several studies have been reported to lower the ROP temperature by using

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bisbenzoxazine monomers obtained from sustainable phenolic precursors have been compared with phenol based bisbenzoxazine monomers. Among them, the eugenol-based TH and DH benzoxazines exhibit lowest curing temperature 171 °C and 165 °C respectively. While, P-TH and P-DH monomers resulted in curing temperatures of 229 °C and 217 °C respectively. The activation energy ($E_a$) of *E*-TH and E-DH monomers was calculated using Kissinger, Ozawa and Flynn-Wall-Ozawa methods. From the curing kinetics the calculated $E_a$ of E-TH and E-DH were 98.19 kJ $mol^{-1}$, 98.29 kJ $mol^{-1}$ and 95.09 kJ $mol^{-1}$, 93.99 kJ $mol^{-1}$ respectively. The results revealed that the presence of dynamic sulfur linkages efficiently influences the $E_a$. Further, the poly (E-TH) and poly(E-DH) exhibits higher char yield and thermal stability than the phenol based polybenzoxazines. Corrosion resistance studies showed a high inhibition efficiency of 99 % on MS due to the formation of a dense polymer network. This work establishes a sustainable route for advancing coating materials for industrial applications.

## CRediT authorship contribution statement

**K. Mohamed Mydeen:** Writing – original draft, Methodology, Investigation, Formal analysis. **Balaji Krishnasamy:** Writing – review & editing, Supervision, Resources, Conceptualization. **Harinei Srinivasan:** Visualization, Validation. **Subasri Appasamy:** Data curation.

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## 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.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.porgcoat.2025.109356.

## Data availability

Data will be made available on request.

## References

[1] A. Dotan, Biobased Thermosets, Elsevier Inc., 2013, https://doi.org/10.1016/B978-1-4557-3107-7.00015-4.
[2] H. Ishida, Overview and Historical Background of Polybenzoxazine Research, Elsevier B.V, 2011, https://doi.org/10.1016/B978-0-444-53790-4.00046-1.
[3] N. Teng, S. Yang, J. Dai, S. Wang, J. Zhao, J. Zhu, X. Liu, Making benzoxazine greener and stronger: renewable resource, microwave irradiation, green solvent, and excellent thermal properties, ACS Sustain. Chem. Eng. 7 (2019) 8715–8723, https://doi.org/10.1021/acssuschemeng.9b00607.
[4] Y. Lu, J. Liu, W. Zhao, K. Zhang, Bio-benzoxazine structural design strategy toward highly thermally stable and intrinsically flame-retardant thermosets, Chem. Eng. J. 457 (2023) 141232, https://doi.org/10.1016/j.cej.2022.141232.
[5] C. Zhang, Y. Zhang, Q. Zhou, H. Ling, Y. Gu, Processability and mechanical properties of bisbenzoxazine modified by the cardanol-based aromatic diamine benzoxazine, J. Polym. Eng. 34 (2014) 561–568, https://doi.org/10.1515/polyeng-2014-0018.
[6] C. Wang, J. Sun, X. Liu, A. Sudo, T. Endo, Synthesis and copolymerization of fully bio-based benzoxazines from guaiacol, furfurylamine and stearylamine, Green Chem. 14 (2012) 2799–2806, https://doi.org/10.1039/c2gc35796h.
[7] P. Thirukumaran, A.S. Parveen, M. Sarojadevi, Synthesis and copolymerization of fully biobased benzoxazines from renewable resources, ACS Sustain. Chem. Eng. 2 (2014) 2790–2801, https://doi.org/10.1021/sc500548c.
[8] W. Zhao, B. Chen, K. Zhang, Biobased bisbenzoxazine resins derived from natural renewable Monophenols and diamine: synthesis and property investigations, ACS Sustain. Chem. Eng. 10 (2022) 14783–14793, https://doi.org/10.1021/acssuschemeng.2c04103.
[9] C.T. Vijayakumar, S. Shamim Rishwana, R. Surender, N. David Mathan, S. Vinayagamoorthi, S. Alam, Structurally diverse benzoxazines: synthesis, polymerization, and thermal stability, Des. Monomers Polym. 17 (2014) 47–57, https://doi.org/10.1080/15685551.2013.797216.
[10] T. Periyasamy, S.P. Asrafali, S. Muthusamy, S.C. Kim, Replacing bisphenol-a with bisguaiacol-F to synthesize polybenzoxazines for a pollution-free environment, New J. Chem. 40 (2016) 9313–9319, https://doi.org/10.1039/c6nj02242a.
[11] S. Niyomsin, T. Hirai, A. Takahara, S. Chirachanchai, Incorporation of benzoxazine pendants in polymer chains: a simple approach to add-up multi-responsive functions, Macromol. Chem. Phys. 220 (2019) 1–12, https://doi.org/10.1002/macp.201800526.
[12] T. Agag, T. Takeichi, Synthesis and characterization of novel benzoxazine monomers containing allyl groups and their high performance thermosets, Macromolecules 36 (2003) 6010–6017, https://doi.org/10.1021/ma021775q.
[13] W. Zhang, X. Lu, Z. Xin, C. Zhou, Development of a superhydrophobic polybenzoxazine surface with self-cleaning and reversible water adhesion properties, RSC Adv. 6 (2016) 106054–106063, https://doi.org/10.1039/C6RA22524A.
[14] S. Ren, F. Tian, S. Zhang, W. Zhou, Y. Du, Bio-based benzoxazine from renewable L-tyrosine: synthesis, polymerization, and properties, J. Polym. Sci. 60 (2022) 1492–1500, https://doi.org/10.1002/pol.20210786.
[15] N. Faiza, B. Hardacre, C. Scott, S. Winroth, H. Ishida, Synthesis of bio-based and intrinsically flame-retardant benzoxazine containing dynamic ester bond that quantitatively satisfies all twelve principles of green chemistry, ACS Sustain. Chem. Eng. 12 (2024) 13525–13534, https://doi.org/10.1021/acssuschemeng.4c03838.
[16] K. Uenishi, A. Taden, T. Huver, (12) United States Patent, 2 (2012).
[17] H. Ishida, D.J. Allen, Physical and mechanical characterization of near-zero shrinkage polybenzoxazines, J. Polym. Sci. Part B Polym. Phys. 34 (1996) 1019–1030, https://doi.org/10.1002/(SICI)1099-0488(19960430)34:6<1019::AID-POLB1>3.0.CO;2-T.
[18] R. Malekkhouyan, M.G. Olivier, A review on the application of benzoxazine as coatings and corrosion inhibitors for corrosion protection of metallic substrates, Mater. Today. Chem. 45 (2025) 102614, https://doi.org/10.1016/j.mtchem.2025.102614.
[19] M. Ates, A review on conducting polymer coatings for corrosion protection, J. Adhes. Sci. Technol. 30 (2016) 1510–1536, https://doi.org/10.1080/01694243.2016.1150662.
[20] X. Lu, Y. Liu, C. Zhou, W. Zhang, Z. Xin, Corrosion protection of hydrophobic bisphenol A-based polybenzoxazine coatings on mild steel, RSC Adv. 6 (2016) 5805–5811, https://doi.org/10.1039/C5RA22980D.
[21] C. Zhou, X. Lu, Z. Xin, J. Liu, Corrosion resistance of novel silane-functional polybenzoxazine coating on steel, Corros. Sci. 70 (2013) 145–151, https://doi.org/10.1016/j.corsci.2013.01.023.
[22] C. Zhou, X. Lu, Z. Xin, J. Liu, Y. Zhang, Hydrophobic benzoxazine-cured epoxy coatings for corrosion protection, Prog. Org. Coatings. 76 (2013) 1178–1183, https://doi.org/10.1016/j.porgcoat.2013.03.013.
[23] Y. Cao, C. Chen, X. Lu, D. Xu, J. Huang, Z. Xin, Bio-based polybenzoxazine superhydrophobic coating with active corrosion resistance for carbon steel protection, Surf. Coatings Technol. 405 (2021) 126569, https://doi.org/10.1016/j.surfcoat.2020.126569.
[24] J. Ye, X. Lu, Z. Xin, Cardanol-based polybenzoxazine coatings: crosslinking structures, hydrophobicity and corrosion protection properties, J. Polym. Sci. 62 (2024) 2936–2944, https://doi.org/10.1002/pol.20240139.
[25] M. Damej, R. Hsissou, A. Berisha, K. Azgaou, M. Sadiku, M. Benmessaoud, N. Labjar, S. El hajjaji, New epoxy resin as a corrosion inhibitor for the protection of carbon steel C38 in 1M HCl. Experimental and theoretical studies (DFT, MC, and MD), J. Mol. Struct. 1254 (2022) 132425, https://doi.org/10.1016/j.molstruc.2022.132425.
[26] C. Chen, Y. Cao, X. Lu, X. Li, H. Yao, Z. Xin, Copolymer of eugenol-based and pyrogallol-based benzoxazines: low curing temperature and enhanced corrosion resistance, Colloids Surfaces A Physicochem. Eng. Asp. 609 (2021) 125605, https://doi.org/10.1016/j.colsurfa.2020.125605.
[27] L. Han, M.L. Salum, K. Zhang, P. Froimowicz, H. Ishida, Intrinsic self-initiating thermal ring-opening polymerization of 1,3-benzoxazines without the influence of impurities using very high purity crystals, J. Polym. Sci. Part A Polym. Chem. 55 (2017) 3434–3445, https://doi.org/10.1002/pola.28723.
[28] B. Lochab, M. Monisha, N. Amarnath, P. Sharma, S. Mukherjee, H. Ishida, Review on the accelerated and low-temperature polymerization of benzoxazine resins: addition polymerizable, Polymers 13 (2021) 1260, https://doi.org/10.3390/polym13081260.
[29] N.P. Tarasova, A.A. Zanin, E.G. Krivoborodov, Y.O. Mezhuev, Elemental sulphur in the synthesis of sulphur-containing polymers: reaction mechanisms and green prospects, RSC Adv. 11 (2021) 9008–9020, https://doi.org/10.1039/d0ra10507d.
[30] A. Trejo-Machin, J.P. Cosas Fernandes, L. Puchot, S. Balko, M. Wirtz, M. Weydert, P. Verge, Synthesis of novel benzoxazines containing sulfur and their application in

rubber compounds, Polymers 13 (2021), https://doi.org/10.3390/polym13081262.
[31] P. Verdugo, D. Santiago, S. De la Flor, À. Serra, A biobased epoxy vitrimer with dual relaxation mechanism: a promising material for renewable, reusable, and recyclable adhesives and composites, ACS Sustain. Chem. Eng. 12 (2024) 5965–5978, https://doi.org/10.1021/acssuschemeng.4c00205.
[32] M. Monisha, S. Sahu, B. Lochab, Self-polymerization promoting monomers: in situ transformation of disulfide-linked benzoxazines into the thiazolidine structure, Biomacromolecules 22 (2021) 4408–4421, https://doi.org/10.1021/acs.biomac.1c00981.
[33] O. Bayram, B. Kiskan, E. Demir, R. Demir-Cakan, Y. Yagci, Advanced thermosets from sulfur and renewable benzoxazine and ionones via inverse vulcanization, ACS Sustain. Chem. Eng. 8 (2020) 9145–9155, https://doi.org/10.1021/acssuschemeng.0c02773.
[34] Y. Lyu, Y. Zhang, H. Ishida, Intrinsically noncombustible polymers without flame retardant additives: sulfur-containing and bio-based benzoxazines, Eur. Polym. J. 133 (2020) 109770, https://doi.org/10.1016/j.eurpolymj.2020.109770.
[35] K. Bayram, B. Kiskan, Y. Yagci, Synthesis of thioamide containing polybenzoxazines by the Willgerodt-Kindler reaction, Polym. Chem. 12 (2021) 534–544, https://doi.org/10.1039/d0py01381a.
[36] Y. Lyu, H. Fan, L. Qiu, Intrinsically noncombustible thermosets from sulfur-containing epoxy resin and benzoxazines: evaluation of thermal and mechanical properties, Adv. Polym. Technol. 2023 (2023), https://doi.org/10.1155/2023/1686001.
[37] S. Sahu, B. Lochab, Sustainable benzoxazine-sulfur copolymer with dynamic linkages: recycling, reprocessing, self-healing, and shape recovery (R2S2), ACS Sustain. Chem. Eng. 12 (2024) 7126–7135, https://doi.org/10.1021/acssuschemeng.4c01317.
[38] X. Zhao, X.Z. Wang, X.K. Jiang, Y.Q. Chen, Z.T. Li, G.J. Chen, Hydrazide-based quadruply hydrogen-bonded heterodimers. structure, assembling selectivity, and supramolecular substitution, J. Am. Chem. Soc. 125 (2003) 15128–15139, https://doi.org/10.1021/ja037312x.
[39] F. Zamboni, C. Okoroafor, M.P. Ryan, J.T. Pembroke, M. Strozyk, M. Culebras, M. N. Collins, On the bacteriostatic activity of hyaluronic acid composite films, Carbohydr. Polym. 260 (2021), https://doi.org/10.1016/j.carbpol.2021.117803.
[40] S. Nalakathu Kolanadiyil, M. Minami, T. Endo, Implementation of meta-positioning in tetrafunctional benzoxazines: synthesis, properties, and differences in the polymerized structure, Macromolecules 53 (2020) 6866–6886, https://doi.org/10.1021/acs.macromol.0c00947.
[41] Y.E. Dogan, B. Satilmis, T. Uyar, Synthesis and characterization of bio-based benzoxazines derived from thymol, J. Appl. Polym. Sci. 47371 (2018) 1–10, https://doi.org/10.1002/app.47371.
[42] S. Abdous, M. Derradji, O. Mehelli, R. Belgacemi, S. Soudjrari, N. Ramdani, K. Khiari, M.E.A. Kadi, W. Liu, Synthesis and characterization of nitrogen-rich polybenzoxazines for energetic applications, High Perform. Polym. 34 (2022) 455–464, https://doi.org/10.1177/09540083211073654.
[43] A. Trejo-Machin, L. Puchot, P. Verge, A cardanol-based polybenzoxazine vitrimer: recycling, reshaping and reversible adhesion, Polym. Chem. 11 (2020) 7026–7034, https://doi.org/10.1039/d0py01239d.
[44] M. Monisha, S. Sahu, B. Lochab, Self-polymerization promoting monomers: in situ transformation of disulfide-linked benzoxazines into the thiazolidine structure, Biomacromolecules 22 (2021) 4408–4421, https://doi.org/10.1021/acs.biomac.1c00981.
[45] J. Liu, Y. Wuliu, J. Dai, J. Hu, X. Liu, Synthesis and properties of the bio-based isomeric benzoxazine resins: revealing the effect of the neglected short alkyl substituents, Eur. Polym. J. 157 (2021) 110671, https://doi.org/10.1016/j.eurpolymj.2021.110671.
[46] M. Mydeen K, H. Arumugam, B. Krishnasamy, A. Muthukaruppan, Development of hybrid polybenzoxazine composites from sustainable bio-phenol for dielectric and superhydrophobic water repellent utilizations, Polymer 283 (2023) 126287, https://doi.org/10.1016/j.polymer.2023.126287.
[47] M. Arslan, B. Kiskan, Y. Yagci, Combining elemental sulfur with polybenzoxazines via inverse vulcanization, Macromolecules 49 (2016) 767–773, https://doi.org/10.1021/acs.macromol.5b02791.
[48] A. Suesuwan, N. Suetrong, S. Yaemphutchong, I. Tiewlamsam, K. Chansaenpak, S. Wannapaiboon, N. Chuanopparat, L. Srathongsian, P. Kanjanaboos, N. Chanthaset, W. Wattanathana, Partially bio-based benzoxazine monomers derived from thymol: photoluminescent properties, polymerization characteristics, hydrophobic coating investigations, and anticorrosion studies, Polymers 16 (2024), https://doi.org/10.3390/polym16131767.
[49] K. Mohamed Mydeen, B. Krishnasamy, H. Arumugam, A. Muthukaruppan, Eco-friendly bio-based polybenzoxazine composites derived from sustainable thymol: a versatile approach and multifaceted study for enhanced applications, J. Polym. Sci. (2024), https://doi.org/10.1002/pol.20230904.
[50] C.R. Arza, P. Froimowicz, H. Ishida, Triggering effect caused by elemental sulfur as a mean to reduce the polymerization temperature of benzoxazine monomers, RSC Adv. 6 (2016) 35144–35151, https://doi.org/10.1039/c6ra04420d.
[51] K. Mohamed Mydeen, B. Krishnasamy, H. Arumugam, K. Saravana Mani, A. Muthukaruppan, Sustainable strategies for fully biobased polybenzoxazine composites from trifunctional thymol and biocarbons: advancements in high-dielectric and antibacterial corrosion implementations, ACS Sustain. Chem. Eng. 12 (2024) 2225–2240, https://doi.org/10.1021/acssuschemeng.3c06314.
[52] M. Arslan, B. Kiskan, Y. Yagci, Recycling and self-healing of polybenzoxazines with dynamic sulfide linkages, Sci. Rep. 7 (2017) 1–11, https://doi.org/10.1038/s41598-017-05608-2.
[53] Y. Tang, H.E. Symons, P. Gobbo, J.S. Van Duijneveldt, I. Hamerton, S. Rochat, Properties and curing kinetics of a processable binary benzoxazine blend, ACS Appl. Polym. Mater. 5 (2023) 10404–10415, https://doi.org/10.1021/acsapm.3c02221.
[54] T. Chang, K.H. Hsueh, C.C. Liu, C.R. Cao, C.M. Shu, A method to derive the characteristic and kinetic parameters of 1,1-bis(tert-butylperoxy)cyclohexane from DSC measurements, Processes 10 (2022) 1–20, https://doi.org/10.3390/pr10051026.
[55] D.W. van Krevelen, Some basic aspects of flame resistance of polymeric materials, Polymer 16 (1975) 615–620, https://doi.org/10.1016/0032-3861(75)90157-3.