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Designing Biobased Sulfur-Modified Benzoxazines for Enhanced Performance in Antimicrobials, Anticorrosion, and Dielectrics

Mohamed Mydeen K, Harinei Srinivasan, Subasri Appasamy, Balaji Krishnasamy,* and Shankar Ramasamy

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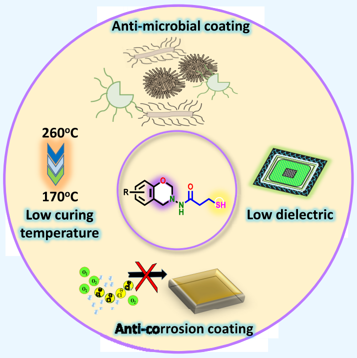
ABSTRACT: The future of benzoxazine research focuses on achieving a delicate balance between low curing temperatures and sustainability without compromising material performance. Advancing their molecular design to optimize these properties enables the way for advanced materials suitable for applications in coatings, adhesives, and advanced integrated circuits. Thus, in this study, sulfur-containing thiol-modified benzoxazines (-SH) were synthesized using 3-mercaptopropanehydrazide (MH) and different phenolic precursors such as bis-thymol, phenol, cardanol, guaiacol, eugenol, thymol, furfural bis-thymol, bis-thymol, and trifunctional thymol-containing phenol. All of the samples were characterized for their structural and thermal properties using techniques such as ^{1}H NMR, ^{13}C NMR, DSC, and TGA. Among the systems studied, C-MH exhibited the lowest curing temperature of 174 °C, while poly(TTP-MH) showed the highest thermal stability with a char yield of 40% at 850 °C. Electrochemical studies, including Tafel and Nyquist plots, revealed that all polybenzoxazines possess excellent anticorrosion properties, with poly(TTP-MH) exhibiting higher efficiency than the rest of the coated specimens. Dielectric measurements further exhibited that these materials possess low dielectric constants and minimum loss values, making them suitable for advanced electronic applications. The results of antimicrobial studies reveal that TTP-MH acts a good microbial agent. Also, neat polybenzoxazines and their coated cotton fabrics exhibited good hydrophobic nature. Data from this work bring out the potential of biobased sulfur-modified benzoxazines as next-generation materials for high-performance applications. By reducing the curing temperature and enhancing material properties, it addresses antimicrobial, anticorrosion, and dielectric properties by contributing to a sustainable future in polymer science.



KEYWORDS: *biobased benzoxazines, thiol, low-cure, high thermal stability, anticorrosion, DFT, low dielectric*

■ INTRODUCTION

Benzoxazines (Bzs) are emerging as a class of high-performance thermosetting resins that have shown enormous potential across industrial applications due to their excellent thermal stability, mechanical strength, and chemical resistance.[1,2] Despite these advantages, traditional Bzs face critical challenge mainly with regard to their high curing temperature.[3] This high curing temperature limitation in Bzs arises from the ring-opening polymerization (ROP) process, which limits industrial scalability and increases production costs.[4] The curing behavior of Bzs is highly influenced by the availability of free ortho- or para-positions in their phenolic precursors, which determines the ease and efficiency of ROP.[5,6] This structural dependency plays a crucial role in influencing the curing temperature, crosslinking density, and overall performance of the resulting polybenzoxazines (PBzs).

Further, the curing of Bzs involves a complex interplay of factors, including precursor reactivity, steric effects, and the presence of catalysts.[7] Addressing these issues requires targeted approaches, such as incorporating flexible linkages, reducing the crosslinking density, or blending Bzs with more flexible polymers.[8] Research efforts have progressively focused on modifying the chemical structure of Bzs to lower the curing temperature and enhance their processability.[9] Approaches include the incorporation of catalysts, such as Lewis acids or bases and the introduction of functional groups that promote ROP at lower temperatures.[10−12]

Sustainability is another concern due to their excessive utilization, and the reliance on fossil-derived phenols in their synthesis raises concerns about environmental sustainability, prompting the search for alternative biobased precursors and innovative structural designs.[13,14] By replacing petroleum-based phenols with biobased alternatives such as thymol, cardanol, guaiacol, and eugenol, researchers aim to create eco-friendly materials with enhanced properties.[15−18] Also, biobased Bzs have gained attention for antimicrobial applications in healthcare and food packaging due to their

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Table 6. Dielectric Constant (k) and Tan δ of MH PBzs

sample code	k value	tan δ
Poly(P-MH)	3.52	0.0041
Poly(G-MH)	3.46	0.0044
Poly(C-MH)	3.38	0.0060
Poly(E-MH)	3.42	0.0046
Poly(T-MH)	3.39	0.0045
Poly(BT-MH)	3.36	0.0052
Poly(FBT-MH)	3.32	0.0050
Poly(TTP-MH)	3.31	0.0056

dual crosslinking and rigidity. Similarly, the isopropyl structure in thymol increases free volume and reduces dielectric losses. C-MH PBzs, due to their long aliphatic hydrocarbon chains, demonstrate excellent hydrophobicity and low polarizability. The aliphatic chain increases the free volume and reduces dipolar interactions, resulting in a lower dielectric constant value of 3.38 and reduced dielectric loss. Comparatively, bifunctional and trifunctional PBzs resulted in a lower dielectric constant value compared to monofunctional systems. This may be due to the higher-order functionalities of the aromatic core that enhance conjugation and rigidity, with its furan-containing aromatic linker providing additional conjugation and chemical stability, ensuring that low dielectric losses demonstrate excellent sustainability and suitability for electronic insulation. Dielectric loss (tan δ) values for all samples remained below 0.0060, indicating minimal energy dissipation, which is a critical feature for electronic applications requiring low loss. This makes them suitable as dielectric materials in high-frequency and insulating applications.

CONCLUSIONS

In this study, sulfur-containing thiol-modified Bzs (-SH) were synthesized using MH and different phenolic precursors such as phenol, cardanol, guaiacol, eugenol, thymol, FBT, BT, and TTP. All of the samples were characterized for their structural and thermal properties using proper analytical techniques. Among the systems studied, C-MH exhibited the lowest curing temperature of 174 °C, while poly(TTP-MH) showed the highest thermal stability with a char yield of 40% at 850 °C. The activation energy (E_a) of T-MH was calculated using the Kissinger, Ozawa, and Flynn−Wall−Ozawa methods. From the curing kinetics, the calculated E_a values of T-MH were 141.20 and 142.29 kJ mol^{-1}, respectively. Electrochemical studies, including Tafel and Nyquist plots, revealed that all PBzs possess excellent anticorrosion properties, with poly(TTP-MH) exhibiting higher efficiency than the rest of the coated specimens. Dielectric measurements further showed that these materials exhibit a low dielectric constant and minimum loss values, making them suitable for advanced electronic applications. The results of antimicrobial studies reveals that all of the Bzs exhibited good antimicrobial behavior. Also, neat PBzs and their coated cotton fabrics studied exhibit good hydrophobic nature. Dielectric studies revealed that poly(TTP-MH) achieved the lowest dielectric constant value of 3.31 with minimal dielectric loss. Data from this work reveal the potential of biobased sulfur-modified Bzs as next-generation materials for high-performance applications.

ASSOCIATED CONTENT

Data Availability Statement

Data will be made available on request.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.5c03369.

Details of the characterization techniques (S1), preparation methods for Bz-coated water-repellent cotton fabrics (S2), and mild steel specimens (S3). Synthesis routes of MH, BT, FBT, and TTP precursors (Scheme S1) along with the ROP mechanism (Scheme S2). ATR-FTIR, ^{1}H NMR, ^{13}C NMR, and HMRS data for MH (Figure S1); ^{1}H NMR spectra of BT and TTP (Figure S2); thermal graphs including Kissinger, Ozawa, and Flynn−Wall−Ozawa plots and conversion behavior with temperature (Figures S3−S5); FTIR spectra of cured samples and coated fabrics, antimicrobial zone images, and solvent resistant tests (Figures S6−S10); DSC thermograms of PBzs (Figure S11); and dielectric property plots (Figure S12). Activation energies (Table S1), calculated reactivity parameters (Table S2), and swelling/gel data of MH PBzs (Table S3) (PDF)

AUTHOR INFORMATION

Corresponding Author

Balaji Krishnasamy − *Department of Chemistry, PSG Institute of Technology and Applied Research, Coimbatore 641 062, India;* orcid.org/0000-0003-0004-3863; Email: balaji.psgtech@yahoo.co.in

Authors

Mohamed Mydeen K − *Department of Chemistry, PSG Institute of Technology and Applied Research, Coimbatore 641 062, India*

Harinei Srinivasan − *Department of Chemistry, PSG Institute of Technology and Applied Research, Coimbatore 641 062, India*

Subasri Appasamy − *Department of Chemistry, PSG Institute of Technology and Applied Research, Coimbatore 641 062, India*

Shankar Ramasamy − *Molecular Simulation Laboratory, Department of Physics, Bharathiar University, Coimbatore 641 046, India;* orcid.org/0000-0001-8751-7827

Complete contact information is available at: https://pubs.acs.org/10.1021/acsapm.5c03369

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