

## Synthesis, spectral, and thermal studies on eugenol based hydrophobic polybenzoxazines

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### Abstract:

A new class of the thermally stable, hydrophobic, sustainable and renewable eugenol (E) based benzoxazines were synthesized using 4-aminobenzonitrile (abn) isophoronediamine (ipda) separately. Polybenzoxazines were formed by thermal ring-opening polymerization of respective monomers and confirmed by spectral analyses. TGA results indicated that residual char yield value obtained at 850°C for poly(abn) and poly(ipda) are 36% and 32%, respectively. Poly(E-abn) showed better thermal stability than poly(E-ipda) due to the presence triazine cross-linkages in the matrix system. The water contact angle studies showed that poly(E-ipda) possesses better hydrophobic character than poly(E-abn), due to the presence of isophorone (alicyclic) group and allyl substitutions.

**Keywords:** Eugenol, benzoxazine, thermal stability, water contact angle, hydrophobic behaviour.

### Introduction

Polybenzoxazine is one of the most important and versatile classes of thermosetting high performance polymers which possesses the good mechanical and thermal properties<sup>[1][2]</sup>, low moisture uptake, high carbon residue, good resistance to flame, low surface free energy and excellent dielectric properties<sup>[3, 4]</sup>. These properties make them useful as sealants and encapsulants in fabrication of electronic devices, adhesives and coatings for different industrial and engineering applications<sup>[5]</sup>. Despite, polybenzoxazine possesses some

shortcomings, such as brittle behaviour<sup>[6]</sup> and requiring high polymerization temperature, to overcome these drawbacks, the development of polybenzoxazine matrices with varying skeletons capable of contributing high performance characters are warranted. The improvement of polybenzoxazines with excellent thermo-mechanical and electrical properties are the major challenges to expand their electrical and engineering applications in harsh environments. Different approaches have been made to enhance their physico-chemical properties; 1) curing benzoxazine resins at low temperature<sup>[6]</sup> 2) enhancing thermal stability of polybenzoxazine<sup>[7]</sup>, 3) achieving desirable hydrophobic behaviour by the skeletal modifications of polybenzoxazine matrices<sup>[8]</sup>.

The conventional polybenzoxazine<sup>[9,10]</sup> (bisphenol-A, bisphenol-F, etc.) are prepared from petroleum products, which possesses some shortcomings, such as brittleness and high polymerization temperature, to overcome these drawbacks and reduce the petroleum products, the development of bio-polybenzoxazine composites with varying skeletons capable of contributing high performance characters are warranted. The most used bio-phenols are cardanol, eugenol, guaiacol, vanillin etc., and bio-amines are stearyl amine, furfuryl amine etc. The improvement of polybenzoxazines and composites with excellent thermo-mechanical and electrical properties are the major challenges to expand their electrical and engineering applications in harsh environments. Recently our research group reported the bio-based polybenzoxazine composites for, low dielectric<sup>[6]</sup>, oil-water separation<sup>[11]</sup>, sound absorption<sup>[12]</sup> and corrosion resistance applications<sup>[13]</sup>.

The novelty and importance of the present work is to develop bio-based benzoxazine with improved thermal stability and enhanced water contact angle to utilize them in the form of adhesive and sealants for micro-electronics applications demands high thermal stability and moisture resistance. In this context new types of eugenol based mono and bi-functional polybenzoxazine matrices with improved thermal stability and desirable hydrophobic

behaviour have been developed using an appropriate amino derivatives. The mono-functional benzoxazine monomer was synthesized using eugenol (bio-phenol) with allyl moiety, 4-aminobenzonitrile having nitrile moiety and paraformaldehyde through Mannich condensation reaction. Similarly, di-functional benzoxazine monomer was synthesized using eugenol with isophoronediamine having cycloaliphatic moiety and paraformaldehyde through Mannich condensation reaction. The molecular structure of synthesised benzoxazines was ascertained from FTIR and <sup>1</sup>H-NMR analyses. The curing behaviour of E-abn and E-ipda benzoxazine monomers was studied using DSC technique and followed by the occurrence of ring opening polymerisation of benzoxazine monomers was confirmed from FTIR spectroscopy. Thermal stability of polybenzoxazines was studied using TGA technique. LOI value of polybenzoxazines was calculated from the residual char yield value obtained from TGA analysis. The hydrophobic nature of synthesised polybenzoxazines was ascertained from the value of water contact angle obtained from goniometer technique using water as probe liquid. Data obtained from different studies were correlated, discussed and presented with possible uses of these materials in the form of insulators, sealants, adhesives, and matrices where application demands at different engineering applications.

### ***Materials***

In this work, the materials that required for the synthesis of benzoxazines were eugenol, para formaldehyde, 4-aminobenzonitrile (abn) and isophoronediamine (ipda). Eugenol was purchased from Loba chemicals (Mumbai, India), paraformaldehyde and 4-aminobenzonitrile were obtained from Sigma-Aldrich (India) and isophoronediamine was obtained from TCI (Japan). Ethyl acetate was purchased from Thomas Baker (Mumbai) and sodium hydroxide and sodium sulphate were procured from Merck (Mumbai).

### ***Methods***

FTIR spectra measurements were carried out with Agilent Cary 630 FTIR Spectrometer. NMR spectra were obtained with Bruker (400 MHz) using deuterated chloroform ( $\text{CDCl}_3$ ) as a solvent and tetramethylsilane (TMS) as an internal standard. DSC measurements were recorded using NETZSCH STA 449F3 under  $\text{N}_2$  purge ( $60 \text{ mL min}^{-1}$ ) at scanning rate of  $10 \text{ }^\circ\text{C min}^{-1}$ . Thermogravimetric analysis (TGA) was obtained using NETZSCH STA 449F3 taking 5 mg of sample under  $\text{N}_2$  flow ( $260 \text{ mL min}^{-1}$ ) and controlling the heating rate at  $20 \text{ }^\circ\text{C min}^{-1}$ . Contact angle measurements were obtained using a Kwoya goniometer with  $5\mu\text{l}$  of water as probe liquid.

***Synthesis of eugenol-based benzoxazine 4-(6-allyl-8-methoxy-2H-benzo[1,3]oxazin-3-(4H)-yl)benzotrile (E-abn)***

2.15 g (0.01 mol) of 4-aminobenzotrile was mixed with 3.0 g (0.01 mol) of eugenol and 1.09 g (0.02 mol) of paraformaldehyde were added portion-wise into a 100 ml double necked round bottomed flask under constant stirring in the absence of any solvents. Then, the temperature was raised to  $110^\circ\text{C}$  and maintained for about 4 h until the completion of formation of benzoxazine. The progress of the reaction was monitored with thin layer chromatography (TLC) (8:2 hexane:ethylacetate solvent). After completion of the reaction, the resinous crude product obtained was dissolved in 50 ml of ethyl acetate and washed twice with 2N NaOH for removal of unreacted phenolic compounds. Further, the organic layer was washed twice with 100 ml of distilled water. Then, the organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and ethyl acetate was removed using the rotary evaporator and the product resulted was recovered. The synthesized eugenol-based benzoxazine was labelled as E-abn (Scheme 1).

***Synthesis of eugenol-based benzoxazine 6-allyl-3-((5-(6-allyl-8-methoxy-2H-benzo[1,3]oxazin-3-(4H)-yl)-1,3,3-trimethylcyclohexyl)methyl)-8-methoxy-3,4-hydro-2H-benzo[1,3]oxazine(E-ipda)***

12.96 g (0.07 mol) of isophoronediamine was mixed with 25 g (0.14 mol) of eugenol and 9.14 g (0.28 mol) of paraformaldehyde were added portion-wise in a 100 ml double necked round bottomed flask under constant stirring in the absence of any solvents. Rest of the steps had been followed according to the synthesis procedure adopted for (E-abn). The synthesized eugenol-based benzoxazine was labelled as E-ipda (Scheme 2).

### ***Ring-opening polymerization of eugenol-based benzoxazines***

The eugenol-based polybenzoxazines (E-abn and E-ipda) were prepared through thermal cationic ring opening polymerization<sup>[14]</sup>. In brief, the respective benzoxazine monomer was separately dissolved in 1,4-dioxane and sonicated to obtain the homogenous products. The resultant products obtained were separately heated at 80°C for 8 h to remove the solvent. After the removal of solvent, temperature was gradually raised to 200°C at a heating rate of 10°C/h. The heating was further continued for another 3 h at 210°C for the completion of curing reaction. The polymerization of benzoxazine samples were confirmed from infrared spectroscopic analysis. At this temperature, the benzoxazine monomers undergo ring-opening polymerization to form polybenzoxazines with three dimensional crosslinked network structure<sup>[15]</sup> (Schemes 3 and 4).

### **Results and discussion**

The eugenol-based benzoxazines (E-abn and E-ipda) were prepared by the Mannich condensation reaction of eugenol with different amino derivatives and paraformaldehyde at appropriate reaction conditions as shown in Schemes 1 and 2. The E-abn mono-benzoxazine is a reactive functional monomer resin. E-abn possesses a cyano group and a allyl group which helps to improve the cross-link of polymer through cyano to triazine<sup>[16]</sup> and allyl cross-link<sup>[17]</sup>. Consequently, the thermal behaviour and hydrophobicity of benzoxazine were improved. E-ipda is a bi-functional benzoxazine which possesses a alicyclic core and a allylic substitution group. Consequently, resulted benzoxazines possess an improved flexibility,

weather resistant and good water repellence. The molecular structure of prepared cardanol based benzoxazine monomers was confirmed by FTIR and  $^1\text{H-NMR}$  spectral analyses. Curing behaviour of benzoxazines was studied by DSC technique. The thermal stability of the synthesized polybenzoxazines was studied by TGA technique.

### ***FTIR spectral analysis***

The FTIR spectra of benzoxazine monomers (E-abn and E-ipda) are presented in Figure 1. The FTIR spectrum of eugenol-based benzoxazines shows the characteristic absorption bands at  $1215\text{ cm}^{-1}$  (asymmetric stretching of C–O–C),  $1088\text{ cm}^{-1}$  (symmetric stretching of C–O–C) and  $921\text{ cm}^{-1}$  which is typical of benzoxazine ring structure (N–C–O). The spectrum also shows a band at  $1349\text{ cm}^{-1}$  due to the tetra substituted benzene ring. Other aromatic vibration peaks are observed at  $1595\text{ cm}^{-1}$  and C–H stretching vibration of benzene ring appears at  $3013\text{ cm}^{-1}$ . The peaks appeared at  $2940$  and  $2819\text{ cm}^{-1}$  are owing to the asymmetric and symmetric stretching vibrations of the methylene group of the oxazine ring as well as alkyl side chain of eugenol<sup>[18]</sup>.

### ***$^1\text{H-NMR}$ spectral analysis***

The molecular structure of E-abn and E-ipda benzoxazines was confirmed by  $^1\text{H-NMR}$  spectral analysis. The  $^1\text{H-NMR}$  spectra of E-abn and E-ipda benzoxazines are presented in Figures 2 and 3. In the  $^1\text{H-NMR}$  spectrum, the aryl-substituted benzoxazine monomer (E-abn) exhibits two characteristic resonance signals at around 4.5 ppm (singlet, 2H) for aryl substituted methylene group of oxazine ring -N-CH<sub>2</sub>-Ar and 5.5 ppm (singlet, 2H) for oxygen and nitrogen bonded methylene group<sup>[19]</sup> of benzoxazine molecule -N-CH<sub>2</sub>-O-.

Similarly, eugenol-isophoronediamine benzoxazine monomer (E-ipda) also exhibited two resonance peaks at 4 ppm (singlet, 2H) for aryl substituted methylene group of oxazine ring -N-CH<sub>2</sub>-Ar and around 5 ppm (singlet, 2H) for oxygen and nitrogen bonded methylene group

of benzoxazine molecule -N-CH<sub>2</sub>-O-. These signals confirm the formation of targeted benzoxazine moiety.

### ***Curing behavior of benzoxazine monomers***

The curing behavior of E-abn and E-ipda benzoxazines were examined by DSC analysis at two different heating rate viz., 10°C/min and 20°C/min under a nitrogen atmosphere. Figures 4 and 5 shows the DSC thermogram of E-abn and E-ipda at heating rates of 10 and 20°C/min, respectively. The thermograms of E-abn and E-ipda show that the endothermic peaks and exothermic peaks shifted to higher temperatures with an increase of heating rate. From Figure 4 (10°C/min), an exothermic peak maxima observed for benzoxazine ring opening polymerisation<sup>[20]</sup> viz., E-ipda and E-abn are 212°C and 225°C, respectively (Figure 4). Similarly, an exothermic peak observed at 259°C and 272°C for E-ipda and E-abn monomers, which may be the allylic cross-link of eugenol core<sup>[21]</sup>. For E-abn, an overlapped exothermic peak observed at 282°C, which may be the triazine ring (cyano to triazine) cross-link formation<sup>[22, 23]</sup>.

### ***FTIR analysis of polybenzoxazine***

The molecular structure of eugenol based polybenzoxazines poly(E-abn) and poly(E-ipda) were confirmed using FTIR analysis. The schematic representation for the synthesis of eugenol-based polybenzoxazines is presented in Schemes 3 and 4. Thermally cured samples of poly(E-abn) and poly(E-ipda) were subject to FTIR analysis. The results indicate that the absorption bands of N-C-O band appeared at 916 cm<sup>-1</sup> (oxazine ring) was disappeared after thermal curing at 280°C for 2 h which infers the cleavage of benzoxazine ring and the formation of polybenzoxazine (Figure 6). An overlapped peak observed at 1578 cm<sup>-1</sup> indicates the formation triazine cross-link. The trace of unreacted -CN confirms through stretching vibrations at 1220 cm<sup>-1</sup> [16].

A recent report has demonstrated a competitive pathway through phenoxy structures that finally converted into the phenolic polymers upon thermal treatment. Upon thermal curing, the chemical bond present between oxymethylene and nitrogen gets cleaved and the reactive methylene group abstracts the ortho hydrogen present in the neighbouring oxazine ring and thus polymerization occurs<sup>[14]</sup>.

### ***Thermal stability of polybenzoxazine***

The thermal stability of poly(E-ipda) and poly(E-abn) were studied by TGA at the rate of 20°C/min under a nitrogen atmosphere and the results obtained are presented in Figure 7a. The 5% weight loss, 10% weight loss,  $T_{\max}$  and char yield values are presented in Table 2. It was noticed that, there was no weight loss below 150°C which infers the complete removal of solvents/water. The 5% weight loss of cured polybenzoxazines namely poly(E-ipda) and poly(E-abn) was noticed at about 300°C, and the 10% weight loss value of poly(E-ipda) and poly(E-abn) was observed are 323 and 330°C, respectively. The initial degradation of (E-ipda) and poly(E-abn) were noticed at 248°C and 264°C. There were two types of degradations observed in TGA (Figure 7a) and DTA (Figure 7b) analysis; first degradation maxima ( $1T_{\max}$ ) of poly(E-ipda) and poly(E-abn) were observed at 337°C and 345°C, which may be the cleavage of the phenolic Mannich bridge (tertiary amine), allylic group cross-linkages. The values of second maxima degradation temperature ( $2T_{\max}$ ) observed are 412 and 423°C for poly(E-ipda) and poly(E-abn), which may be the breakup of the phenolic backbones. Finally, the last degradation stage of both polymers at 551°C is attributed to the pyrolysis of the char. The residual char yield obtained at 850°C for poly(E-abn) and poly(E-ipda) are 36% and 32%, respectively<sup>[24]</sup>. Among the polybenzoxazine samples studied, poly(E-abn) has better thermal stability than that of poly(E-ipda), due to the presence triazine cross-linkages in the matrix system.

### ***Flame retardant behavior***



The flame retardant behavior of the cured benzoxazines is also ascertained by using the value of residual char yield. Limiting oxygen index (LOI) value is calculated from van Krevelen and Hoftyzer equation<sup>[25,26]</sup>[eq. 1] and the results are presented in Table 2.

$$\text{LOI}=17.5+0.4(\theta) \text{ ----- (1)}$$

where  $\theta$  is the percentage char yield of materials remains at 850°C.

The char yield of the polybenzoxazines, poly(E-abn) and poly(E-ipda) is found to be 36% and 32% respectively. The LOI values of the polymers should be above the threshold value of 26 to render them self-extinguishing and for their qualification for many applications requiring good flame resistance. The synthesized polybenzoxazines show LOI value greater than 26 confirming their good flame retardant property<sup>[27]</sup>. The obtained LOI value of poly(E-abn) and poly(ipda) are 32 and 30 respectively, this indicates that poly(E-abn) has higher LOI value than poly(E-ipda), due to the presence of hetrocyclic triazine cross linkages<sup>[28]</sup>.

#### ***Water contact angle studies***

The water contact angle images of poly(E-abn) and poly(E-ipda) obtained from goniometer are given in Figure 8. The values of water contact angle obtained for poly(E-abn) and poly(E-ipda) are 135° and 139°, respectively. The lower moisture affinity of the developed polybenzoxazines indicates their covalent nature. The values of water contact angle obtained infer that the benzoxazine samples developed in the present work possess an excellent hydrophobic behaviour than that of existing conventional organic matrices. Among the synthesized benzoxazines, poly(E-ipda) possesses better hydrophobic character than that of poly(E-abn), due to the presence of isophorone (alicyclic) group and allyl substitution.

#### **Conclusion**

Bio-based benzoxazines (E-abn and E-ipda) were synthesised based on Mannich condensation reaction. The mono-functional and bi-functional benzoxazines were synthesised

using eugenol, aminobenzonitrile /isophronediammine and paraformaldehyde through solvent-less process. The molecular structure of synthesized benzoxazine monomers was confirmed by FTIR and <sup>1</sup>H-NMR spectral analyses. The curing behavior of E-abn and E-ipdabenzoxazines were studied at two different heating rates (10°C and 20°C per minute). The heating rate of 10°C per min provides lower curing temperature than that of 20°C per min. The DSC traces confirmed the exothermic ring-opening polymerization reaction of oxazine moieties. Bi-functional benzoxazine has lower curing temperature than that of mono-functional benzoxazine. Two types of degradation observed in TGA studies indicated the bond cleavage of allylic group cross-linkages and cleavage of tertiary amine group. The value of LOI was found to be 32 and 30 respectively, and this indicates that poly(E-abn) possesses higher LOI value than that of poly(E-ipda), due to the formation of hetrocyclic triazine cross linkages. This study indicated the synthesized polybenzoxazines may be suitably exploited for flame retardant applications. The value of water contact angle obtained for poly(E-abn) and poly(E-ipda) are 135° and 139°, respectively suggest their inherent hydrophobic behaviour . Data obtained from different studies indicate that polybenzoxazines developed in the present work can be conveniently used in the form of insulators, sealants, adhesives, and matrices where application demands for high thermal stability and resistant towards moisture absorption.

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### **Conflict of interest**

The authors declare no conflict of interest.

## References

1. Sethuraman, K.; Alagar, M. Thermo-mechanical and dielectric properties of graphene reinforced caprolactam cardanol based benzoxazine-epoxy nanocomposites. *RSC Adv.* 2015, 5, 9607–9617. <https://doi.org/10.1039/c4ra14383c>.
2. Zhu, C.; Gao, X.; Fan, W.; Fu, X. Synthesis, characterization, and properties of a novel aromatic ester-based polybenzoxazine. *RSC Adv.* 2020, 10, 6953–6959. <https://doi.org/10.1039/c9ra10191h>
3. Chen, J.; Zeng, M.; Feng, Z.; et al. Design and Preparation of Benzoxazine Resin with High-Frequency Low Dielectric Constants and Ultralow Dielectric Losses. *ACS Appl. Polym. Mater.* 2019, 1, 625–630. <https://doi.org/10.1021/acsapm.8b00083>
4. Feng, Z.; Zeng, M.; Meng, D.; et al. A novel bio-based benzoxazine resin with outstanding thermal and superhigh-frequency dielectric properties. *J. Mater. Sci. Mater. Electron.* 2020, 31, 4364–4376. <https://doi.org/10.1007/s10854-020-02995-7>
5. Peng, C.; Wu, Z.; Zhou, D.; Synthesis of a benzoxazine-type dispersant and its application on epoxy/benzoxazine/ZrO<sub>2</sub> composite: Dispersion performance and tensile behavior. *Compos. Part B Eng.* 2019, 167, 507–516. <https://doi.org/10.1016/j.compositesb.2019.02.068>
6. Selvaraj, V.; Raghavarshini, T. R.; Alagar, M. Evaluation of thermo-mechanical, dielectric and corrosion resistant properties of cardanol benzoxazine-epoxy based hybrid composites: A very low temperature curing pre-polymer for high performance paint related applications. *High. Perform. Polym.* 2020, 32, 524–539. <https://doi.org/10.1177/0954008319885006>
7. Sharma, P.; Dutta, P.; Nebhani, L. Sustainable approach towards enhancing thermal stability of bio-based polybenzoxazines. *Polymer* 2019, 184, 121905. <https://doi.org/10.1016/j.polymer.2019.121905>

8. Zhang, W.; Lu, X.; Xin, Z.; Zhou, C. Development of a superhydrophobic polybenzoxazine surface with self-cleaning and reversible water adhesion properties. *RSC Adv.* 2016, 6, 106054–106063. <https://doi.org/10.1039/C6RA22524A>
9. Hariharan, A.; Srinivasan, K.; Murthy, C.; Alagar, M. Synthesis and characterization of a novel class of low temperature cure Benzoxazines. *J. Polym. Res.* 2017, 25, <https://doi.org/10.1007/s10965-017-1423-0>
10. Sun, J.; Wei, W.; Xu, Y.; et al. A curing system of benzoxazine with amine: Reactivity, reaction mechanism and material properties. *RSC Adv.* 2015, 5, 19048–19057. <https://doi.org/10.1039/c4ra16582a>
11. Manickam, M.; Pichaimani, P.; Arumugam, H.; Muthukaruppan, A. Synthesis of Nontoxic Pyrazolidine-Based Benzoxazine-Coated Cotton Fabric for Oil-Water Separation. *Ind. Eng. Chem. Res.* 2019, 58, 21419–21430. <https://doi.org/10.1021/acs.iecr.9b03440>
12. Hariharan, A.; Prabunathan, P.; Kumaravel, A.; et al. Bio-based polybenzoxazine composites for oil-water separation, sound absorption and corrosion resistance applications. *Polym. Test.* 2020, 86, 106443. <https://doi.org/10.1016/j.polymertesting.2020.106443>
13. Gnanapragasam, S.; Krishnan, S.; Arumugam, H.; et al, Synthesis and characterization of a novel high-performance benzoxazine from benzaldehyde-based bisphenol. *Adv Polym Technol.* 2018, 37, 3056–3065. <https://doi.org/10.1002/adv.21976>
14. Arumugam, H.; Pichaimani, P.; Manickam, M.; Muthukaruppan, A. Studies on heterocyclic amines based cardanol-benzoxazine for oil-water separation. *Polym. Engg. Sci.* 2020, 60, 1494-1506. <https://doi.org/10.1002/pen.25396>
15. Arumugam, H.; Krishnan, S.; Chavali, M.; Muthukaruppan, A. Cardanol based benzoxazine blends and bio-silica reinforced composites: Thermal and dielectric

- properties. *New J. Chem.* 2018, 42, 4067–4080. <https://doi.org/10.1039/c7nj04506a>
16. Yan, H.; Wang, H.; Cheng, J.; et al, Effect of iron acetylacetonate on the crosslink structure, thermal and flammability properties of novel aromatic diamine-based benzoxazines containing cyano group. *RSC Adv.* 2015, 5, 18538–18545. <https://doi.org/10.1039/c4ra15035j>
17. Dumas, L.; Bonnaud, L.; Olivier, M.; et al. Chavicol benzoxazine: Ultrahigh Tg biobased thermoset with tunable extended network. *Eur. Polym. J.* 2016, 81:337–346. <https://doi.org/10.1016/j.eurpolymj.2016.06.018>
18. Hariharan, A.; Prabunathan, P.; Kumaravel, A.; Alagar, M. Bio-based polybenzoxazine composites for oil-water separation, sound absorption and corrosion resistance applications. *Polym. Test.* 2020, 86,106443. <https://doi.org/10.1016/j.polymertesting.2020.106443>
19. Hariharan, A.; Prabunathan, P.; Subramanian, S. S.; et al. Blends of Chalcone Benzoxazine and Bio-benzoxazines Coated Cotton Fabrics for Oil–Water Separation and Bio-silica Reinforced Nanocomposites for Low-k Applications. *J. Polym. Environ.* 2019, 28, 598–613. <https://doi.org/10.1007/s10924-019-01629-2>
20. Krishnan, S.; Arumugam, H.; Kuppan, C.; et al. Silane-functionalized polybenzoxazines: A superior corrosion resistant coating for steel plates. *Mater. Corros.* 2017, 68, 1343–1354. <https://doi.org/10.1002/maco.201709587>
21. Santhosh Kumar, K. S.; Reghunadhan, Nair C. P.; Radhakrishnan, T. S.; Ninan, K. N. Bis allyl benzoxazine: Synthesis, polymerisation and polymer properties. *Eur. Polym. J.* 2007, 43, 2504–2514. <https://doi.org/10.1016/j.eurpolymj.2007.03.028>
22. Zhang, K.; Liu, Y.; Han, L.; et al. Synthesis and thermally induced structural transformation of phthalimide and nitrile-functionalized benzoxazine: toward smart ortho-benzoxazine chemistry for low flammability thermosets. *RSC Adv.* 2019, 9,

- 1526–1535. <https://doi.org/10.1039/C8RA10009H>
23. Zhang, K.; Ishida, H. An anomalous trade-off effect on the properties of smart ortho-functional benzoxazines. *Polym. Chem.* 2015, 6, 2541–2550.  
<https://doi.org/10.1039/c5py00031a>
24. Ran, Q.; Gu, Y.; Ishida, H. Thermal Degradation Mechanism of Polybenzoxazines. 2017.
25. van Krevelen D. W. Some basic aspects of flame resistance of polymeric materials. *Polymer* 1975, 16, 615–620. [https://doi.org/10.1016/0032-3861\(75\)90157-3](https://doi.org/10.1016/0032-3861(75)90157-3)
26. Krishnasamy, B.; Shanmugaraj, B. P.; Murugavel, S. C.; et al. Investigation on dual functional epoxy resins containing photosensitive group in the main chain for photoresist applications. *Int. J. Polym. Anal. Charact.* 2020, 25, 1–18.  
<https://doi.org/10.1080/1023666X.2020.1780849>
27. Chen, T.; Wang, X.; Peng, C.; et al. Efficient Flame Retardancy, Smoke Suppression, and Mechanical Enhancement of  $\beta$ -FeOOH@Metallo-Supramolecular Polymer Core-Shell Nanorod Modified Epoxy Resin. *Macromol. Mater. Eng.* 2020, 305, 2000137.  
<https://doi.org/10.1002/mame.202000137>
28. Appavoo, D.; Amarnath, N.; Lochab, B. Cardanol and Eugenol Sourced Sustainable Non-halogen Flame Retardants for Enhanced Stability of Renewable Polybenzoxazines. *Front. Chem.* 2020, 8, 1–15.  
<https://doi.org/10.3389/fchem.2020.00711>

### **Scheme Captions**

Scheme 1. Synthesis of 4-(6-allyl-8-methoxy-2H-benzo[1,3]oxazin-3-(4H)-yl)benzotrile (E-abn)

Scheme 2. Synthesis of eugenol-based benzoxazine 6-allyl-3-((5-(6-allyl-8-methoxy-2H-benzo[1,3]oxazin-3-(4H)-yl)-1,3,3-trimethylcyclohexyl)methyl)-8-methoxy-3,4-hydro-2H-benzo[1,3]oxazine (E-ipda)

Scheme 3. Ring opening polymerization of eugenol based benzoxazine

Scheme 4. Ring opening polymerisation and triazine ring formation of E-abn

### **Figure Captions**

Figure 1. FTIR spectra of benzoxazine monomers

Figure 2. <sup>1</sup>H-NMR spectrum of E-abn

Figure 3. <sup>1</sup>H-NMR Spectrum of E-ipda

Figure 4. DSC thermograms of E-abn and E-ipda at the heating rate of 10°C/min

Figure 5. DSC thermograms of E-ipda at the heating rate of 20°C/min

Figure 6. FTIR spectra of poly(E-abn) and poly(E-ipda)

Figure 7. a) TGA traces of poly(E-abn) and poly(E-ipda) and b) DTG traces of poly(E-abn) and poly(E-ipda)

Figure 8. The water contact angle of (a) poly(E-abn) (b) poly(E-ipda)

### **Table Captions**

Table 1. The curing behaviour of eugenol based benzoxazines

Table 2. Thermal stability of eugenol based polybenzoxazine