



Fully Bio-based Polybenzoxazines Derived from Thymol: Thermal Stability, Hydrophobicity and Corrosion Resistant Properties

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Accepted: 8 September 2022 / Published online: 15 October 2022

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Abstract

In the present work, three types of bio-benzoxazines were synthesized from thymol using three structurally different amines viz. octadecylamine, dodecylamine and furfurylamine through Mannich condensation. The molecular structure of bio-based benzoxazines namely, TH-dda (thymol, dodecylamine), TH-oda (thymol, octadecylamine) and TH-ffa (thymol, furfurylamine) were characterized by Fourier transform infrared (FTIR) and ¹H-NMR spectroscopic techniques. The curing behaviour of synthesized benzoxazines was studied using differential scanning calorimetry (DSC). The occurrence of ring-opening and cross-linking polymerization of TH-dda, TH-oda and TH-ffa bio-based benzoxazines were studied by FTIR spectroscopy. The thermal stability of thermally cross-linked polybenzoxazines, poly(TH-dda), poly(TH-oda) and poly(TH-ffa) were studied by thermogravimetric analysis (TGA). The results obtained from TGA indicate that among the polybenzoxazines studied, poly(TH-oda) possesses the higher thermal stability than that of other polybenzoxazine samples viz., [poly(TH-dda) and poly(TH-ffa)]. The value of limiting oxygen index (LOI) for polybenzoxazine samples was calculated using char yield obtained from TGA indicate that these benzoxazines exhibit good flame retardant characteristics. Data from water contact angle studies infer that these samples possess good hydrophobic properties in the range of 134–139°. Results from corrosion studies infer that mild steel specimens coated with these benzoxazines were found to be more stable towards corrosion.

Keywords Bio-benzoxazine · Thymol · Thermal stability · Flame retardance · Hydrophobicity · Corrosion resistance

Introduction

Polybenzoxazines, a relatively new phenolic-type thermosets with excellent physio-chemical, thermal and mechanical properties, has attracted enormous interest from both

academia and industry [1, 2]. It is well known that the most outstanding properties of polybenzoxazines are due to the presence of Mannich bridges and intra-molecular hydrogen bonds in their molecular structure [3]. However, the existence of strong hydrogen bonding restricts the movement of molecular chains, which in turn results relatively lower cross-linking density and high brittleness [4]. Further, synthesis of polymers from renewable feedstock has received extensive attention because of the increasing concern on petroleum resources depletion and environmental issues [5, 6], hence, researchers around the world have turned their focus and efforts towards the replacement of petroleum-based phenols and amines by possible sustainable bio-based raw materials [7–10]. It is ascertained from literature, till now, variety of benzoxazine monomers have already been synthesized from the renewable resources by different research teams including our group [11, 12].

Recently, several naturally available phenolic compounds have been used for the synthesis of bio-benzoxazines including cardanol, guaiacol, urushiol, eugenol, vanillin, resorcinol,

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lignin, chavicol, coumarin, rosin, chalcone, etc. [13–16]. These types of phenolic compounds are plant-derived and are widely found in variety of plants. Zijian Feng et al. studied a novel bio-based benzoxazine resin with outstanding thermal and dielectric properties [17]. Alexandra et al. developed a bio-based polybenzoxazines by incorporating natural phenolic structures to produce polymers with near-zero shrinkage high char yield, and high chemical resistance and thermal stability, as sustainable high-performance polymers [18]. María Laura Salum et al. utilized naturally available and sustainable sesamol and furfurylamine to develop greener benzoxazine monomers with good thermal stability thermoset for fire-resistant applications [19].

Although several plant-derived phenolic compounds were utilized, to the best of our knowledge, thymol has not been extensively studied for the synthesis of benzoxazine resins to assess their utility towards thermal, hydrophobic and resistance to corrosion applications [20–23]. The prime objective of the present work is to develop a fully bio-based thermally stable, hydrophobic benzoxazine using thymol as a bio-phenol and furfurylamine, octadecylamine and dodecylamine as bio-amines. The molecular structure of the synthesized benzoxazine resins were characterised using FTIR and $^1\text{H-NMR}$ spectroscopic techniques. The curing behaviour bio-benzoxazine was ascertained from DSC analysis. Thermal stability and hydrophobic behaviour of polybenzoxazines were studied using TGA and goniometer respectively. Corrosion resistant behaviour towards mild steel specimen was studied using electrochemical workstation. The present work gives some insight into the effects on the curing behavior, cross-linking structure, and thermal and hydrophobic properties of benzoxazines. Data from different studies indicate that the bio-benzoxazines developed in the present work can be utilized in the form adhesives, coatings and matrices where application demands under harsh environments.

Experimental

Materials

The materials required for the synthesis of benzoxazines are procured from respective agencies, viz., thymol (Nice Chemicals, India), paraformaldehyde (Sigma-Aldrich, India), 1,4-dioxane (Merck, India), dodecylamine (SRL Chemicals, India), octadecylamine (SRL Chemicals, India), furfurylamine (SRL Chemicals, India) and ethyl acetate (Nice Chemicals, India).

Measurements

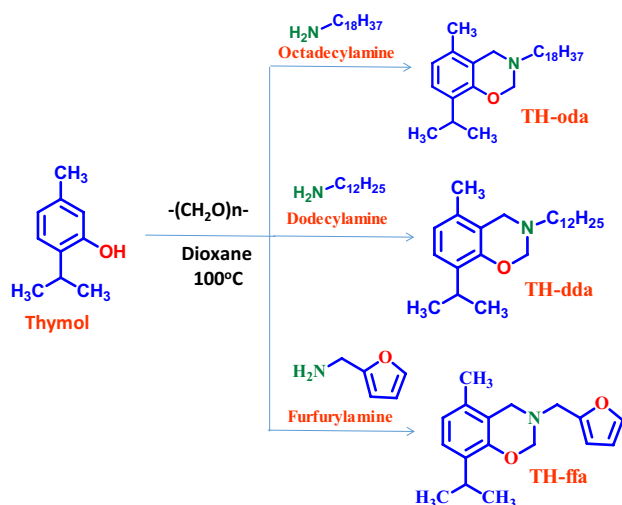
FTIR spectra measurements were carried out on a Shimadzu FTIR Spectrophotometer IRSpirit Single Reflectance

Attenuated Total Reflection (ATR) Accessory. The internal reflection element QATR-S Single bounce ATR - Diamond Prism Disc. FTIR-spectra was recorded with 4 cm^{-1} resolution and 45 scans were averaged in order to obtain a good signal-to-noise ratio. The ATR measurement area was circular spot of approximately 1.5 mm diameter. The spectrum was recorded in the wavenumber range of $400\text{--}4000\text{ cm}^{-1}$. NMR spectra were obtained with Bruker (400 MHz) using deuterated chloroform (CDCl_3) as a solvent and tetramethylsilane (TMS) as an internal standard. The DSC analysis was carried out on NETZSCH STA 449F3 with heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen atmosphere. The benzoxazines coated mild steel plates were tested for their corrosion protection behaviour in 3.5% sodium chloride solution. The corrosion experiments on low carbon mixed (0.25%) mild steel specimen and $30\text{ }\mu\text{m}$ polymer coated mild steel specimens were carried out using open-circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation. Thermogravimetric analysis (TGA) was obtained using NETZSCH STA 449F3, taking 5 mg of sample under N_2 flow (260 mL min^{-1}) and controlling the heating rate at $20^\circ\text{C min}^{-1}$. Water contact angle measurements were obtained using a Kyowa goniometer at 30°C (RH 69%) with $5\text{ }\mu\text{L}$ of water as the probe liquid and 10 numbers of water droplets were tested over the each sample and averaged for each value.

Syntheses of Benzoxazine Monomers

Synthesis of Thymol Based Benzoxazines Using Dodecylamine (TH-dda)/octadecylamine (TH-oda)/furfurylamine (TH-ffa)

3 g (0.0199 mol) of thymol and 4.56 mL (0.0199 mol) of dodecylamine was dissolved in 1,4-dioxane then 1.198 g (0.0399 mol) of paraformaldehyde was added in portion into a 100 mL double necked round bottomed flask equipped with a condenser and a magnetic stirrer. This was kept under constant stirring. Then the temperature was raised to 100°C and maintained for more than 4 h. The progress of the reaction was monitored with thin layer chromatography (TLC) (7:3 hexane: ethyl acetate solvent). After the completion of the reaction, the resinous crude product obtained was dissolved in 50 ml of ethyl acetate and washed twice with 2 N NaOH for removal of unreacted phenolic compounds, if any present. Furthermore, organic layer was washed twice with 100 ml of distilled water. Then, the organic phase was dried over anhydrous Na_2SO_4 and ethyl acetate was removed using the rotary evaporator and the product was recovered. The final product of thymol-dodecylamine based benzoxazine was labelled as TH-dda. In similar way, other two thymol based benzoxazine monomers viz. TH-oda and TH-ffa were



Scheme 1 Synthesis of thymol based benzoxazine monomers (TH-dda, TH-oda and TH-ffa)

synthesised using different amines like octadecylamine and furfurylamine respectively (Scheme 1).

TH-dda ATR-FTIR (cm⁻¹): 2964 – 2867 (ν_{CH}), 1626 ($\nu_{\text{C=C}}$), 1249 ($\nu_{\text{C-O}}$), 1347 ($\nu_{\text{C-N}}$), 961 ($\nu_{\text{O-C-N}}$) cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz, ppm): 0.5–3.5 (35 H, m), 3.9 (2 H, s, a), 4.9 (2 H, s, b) 6.7(1 H, d, c), 7.0 (1 H, d, d) ppm.

TH-oda ATR-FTIR (cm⁻¹): 2957 – 2842 (ν_{CH}), 1626 ($\nu_{\text{C=C}}$), 1245 ($\nu_{\text{C-O}}$), 1348 ($\nu_{\text{C-N}}$), 962 ($\nu_{\text{O-C-N}}$) cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz, ppm): 0.5–3.5 (47 H, m), 3.9 (2 H, s, a), 4.8 (2 H, s, b) 6.8(1 H, d, c), 7.0 (1 H, d, d) ppm.

TH-ffa ATR-FTIR (cm⁻¹): 2968 – 2865 (ν_{CH}), 1627 ($\nu_{\text{C=C}}$), 1248 ($\nu_{\text{C-O}}$), 1347($\nu_{\text{C-N}}$), 961 ($\nu_{\text{O-C-N}}$) cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz, ppm): 1.1 (6 H, d, a), 2.0 (2 H, s, b), 2.1(1 H, m, c), 3.2 (2 H, s, d), 3.9 (2 H, s, e), 4.9 (2 H, s, f) 6.1(1 H, t, g), 6.2 (1 H, d, h), 6.5 (1 H, d, i), 7.0 (1 H, d, j), 7.3 (1 H, d, k) ppm.

Preparation of Polybenzoxazines

Thymol based polybenzoxazines [poly(TH-dda), poly(TH-oda) and poly(TH-ffa)] were obtained from ring opening of corresponding benzoxazine (TH-dda, TH-oda and TH-ffa) monomers by thermal curing. The respective amine based homogeneous benzoxazine monomer was placed in the oven at 80 °C for 8 h to stabilize and to remove moisture and trace of solvents, if any. After stabilization, the temperature was raised to 220 °C at a heating rate of 20 °C/h. The heating was continued for another 3 h at 270 °C for the completion of the curing process. At this temperature, the monomer undergoes ring opening polymerization to form polybenzoxazine with cross-linked network structure. The process of polymerization was confirmed by FTIR spectroscopic results. Upon thermal curing, the bond between oxymethylene and

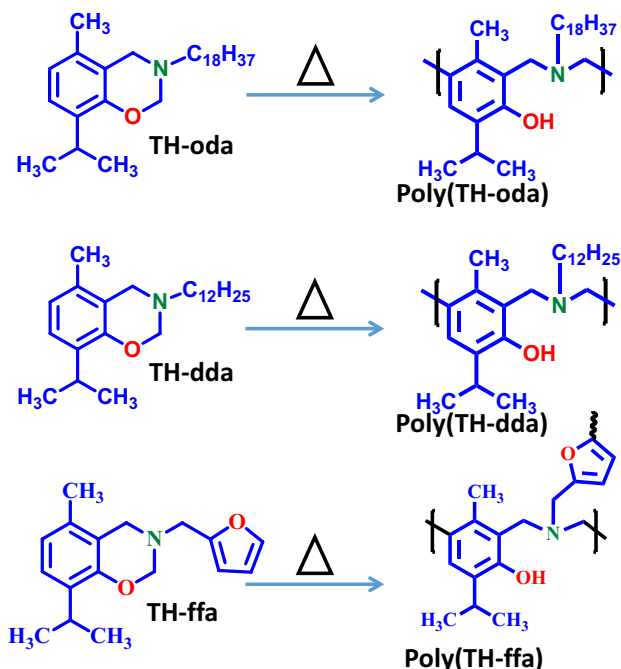
nitrogen gets cleaved followed by the rearrangement with ortho hydrogen present in the neighbouring oxazine ring by the reactive methylene group and thus polymerization occurs. The schematic representation for the synthesis of polybenzoxazines is shown in Scheme 2.

Results and Discussion

The new type of sustainable thymol based benzoxazine monomers were synthesized via one-step Mannich condensation reaction of thymol separately with dodecylamine, octadecylamine and furfurylamine using paraformaldehyde under appropriate experimental conditions. The molecular structure of the synthesized benzoxazine monomers namely TH-dda, TH-oda and TH-ffa and their respective polybenzoxazines, poly(TH-dda), poly(TH-ffa) and poly(TH-oda) were confirmed from spectra analysis.

FTIR Spectra Analysis

The FTIR spectra of thymol based benzoxazines are presented in Fig. 1. The appearance of bands at around 1240 and 1490 cm⁻¹ were attributed to the asymmetric and symmetric stretching vibrations of C–O–C bond present in the benzoxazines respectively. The peak at 1347 cm⁻¹ obtained due to the asymmetric stretching of C–N–C. Similarly, the appearance of bands at around 958 and 1446 cm⁻¹ are



Scheme 2 Ring opening polymerisation of TH-dda, TH-oda and TH-ffa

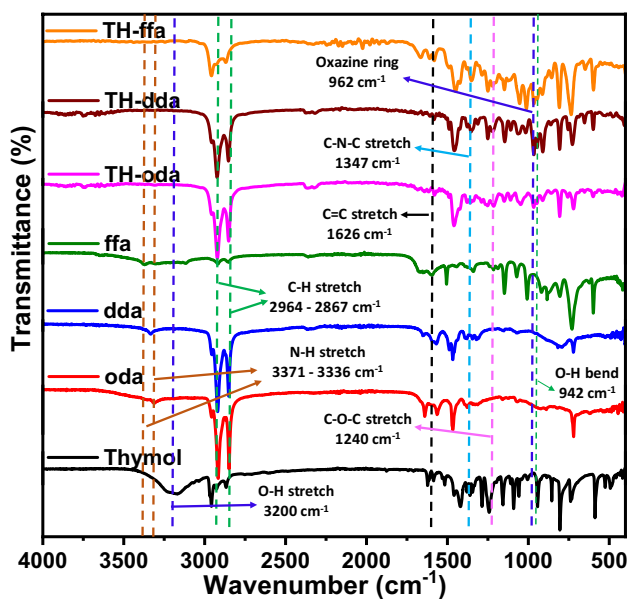


Fig. 1 FTIR spectra of thymol, oda, dda, ffa and its benzoxazine monomers (TH-dda, TH-oda and TH-ffa)

corresponds to a tri-substituted benzene ring which confirm the formation of benzoxazine ring. The characteristic absorption peak at around 962 cm^{-1} represents the stretching vibration of CH_2 of oxazine ring in all the benzoxazine monomers and absence of respective peak in corresponding amines and thymol which clearly indicated the oxazine ring formation. Further, the presence of phenolic $-\text{OH}$ stretching frequency at 3200 cm^{-1} in thymol and disappearance of peak at similar wavelength for TH-dda, TH-oda and TH-ffa showed the successful formation of corresponding benzoxazine monomers.

$^1\text{H-NMR}$ Spectra Analysis

The molecular structure of TH-dda, TH-oda and TH-ffa benzoxazine monomers was confirmed by $^1\text{H-NMR}$ spectra analysis and also on comparison with thymol and respective amines (oda, dda, ffa). The $^1\text{H-NMR}$ spectra of thymol, TH-dda, TH-oda and TH-ffa based benzoxazines and its corresponding amines (dda, oda, ffa) are given in Fig. 2. In the $^1\text{H-NMR}$ spectra, benzoxazine monomers (TH-dda), (TH-oda) and (TH-ffa) exhibit two characteristic resonance signals at around 3.9 ppm (S, 2 H) and 4.9 ppm (S, 2 H) for alkyl substituted methylene group of oxazine ring $-\text{N}-\text{CH}_2-\text{C}$ and oxygen and nitrogen bonded methylene group of benzoxazine molecule $-\text{N}-\text{CH}_2-\text{O}-$ respectively and the absence similar peaks in thymol and corresponding amines indicated the successful formation of targeted benzoxazine monomers.

Curing Behaviour

The curing behaviour of thymol based benzoxazines was studied by DSC analysis at the heating rate of $10\text{ }^\circ\text{C per/min}$ under nitrogen atmosphere and the results obtained are given in Table 1. The exothermic peak maximum of benzoxazine monomers (TH-oda, TH-dda, TH-ffa) was observed at 251, 257 and $261\text{ }^\circ\text{C}$ respectively (Fig. 3). The appearance of exothermic peak with regard to the benzoxazine confirms the occurrence of polymerization through thermal ring-opening (Scheme 2). On comparing the curing temperatures (T_p) of benzoxazines monomers TH-ffa exhibits higher curing temperature ($261\text{ }^\circ\text{C}$) than rest of the monomers due to the presence of heterocyclic ring structure. Among the other two benzoxazine monomers TH-dda exhibits slightly higher curing temperature than TH-oda this may be due to less number of carbon atoms in TH-dda skeleton.

FTIR Analyses of Polybenzoxazines

After the thermal treatment, the chemical structure of thymol based polybenzoxazines viz. poly(TH-oda), poly(TH-dda) and poly(TH-ffa) was confirmed by FTIR spectra analysis (Fig. 4). The absorption band at 930 cm^{-1} represent for oxazine ring was disappeared after thermal curing at $250\text{ }^\circ\text{C}$ for 3 h which confirms the occurrence of complete ring opening and the formation of cross-linking during polymerization of benzoxazines. Further, the appearance of new peak at 1472 cm^{-1} confirms the formation of tetrasubstituted benzene structure.

Thermogravimetric Analysis

The thermal stability of the cured poly(TH-dda), poly(TH-oda) and poly(TH-ffa) benzoxazines was studied using thermo-gravimetric analysis (TGA) at the heating rate of $20\text{ }^\circ\text{C/min}$ under nitrogen atmosphere and the results obtained are presented in Fig. 5. The data obtained from TGA studies are given in Table 2. There is no weight loss below $150\text{ }^\circ\text{C}$ which infers the complete removal of volatile molecules like solvents or water. The occurrence of 5% weight loss of all cured polybenzoxazines is noticed at above $300\text{ }^\circ\text{C}$ and the values of the 10% weight loss of TH-dda, TH-oda, TH-ffa are observed at 342, 376 and $333\text{ }^\circ\text{C}$ respectively. The values of maximum degradation temperature (T_{max}) is noticed at $447\text{ }^\circ\text{C}$, 436 and $401\text{ }^\circ\text{C}$ for poly(TH-dda), poly(TH-oda) and poly(TH-ffa) respectively. The maximum degradation was occurred due to the bond cleavage of tertiary amine group, which is expected to take more energy to undergo the complete decomposition of benzoxazine samples. The value of char yield observed for poly(TH-dda), poly(TH-oda) and poly(TH-ffa) at $850\text{ }^\circ\text{C}$ is 28, 32 and 28%, respectively. Among the synthesised polybenzoxazines,

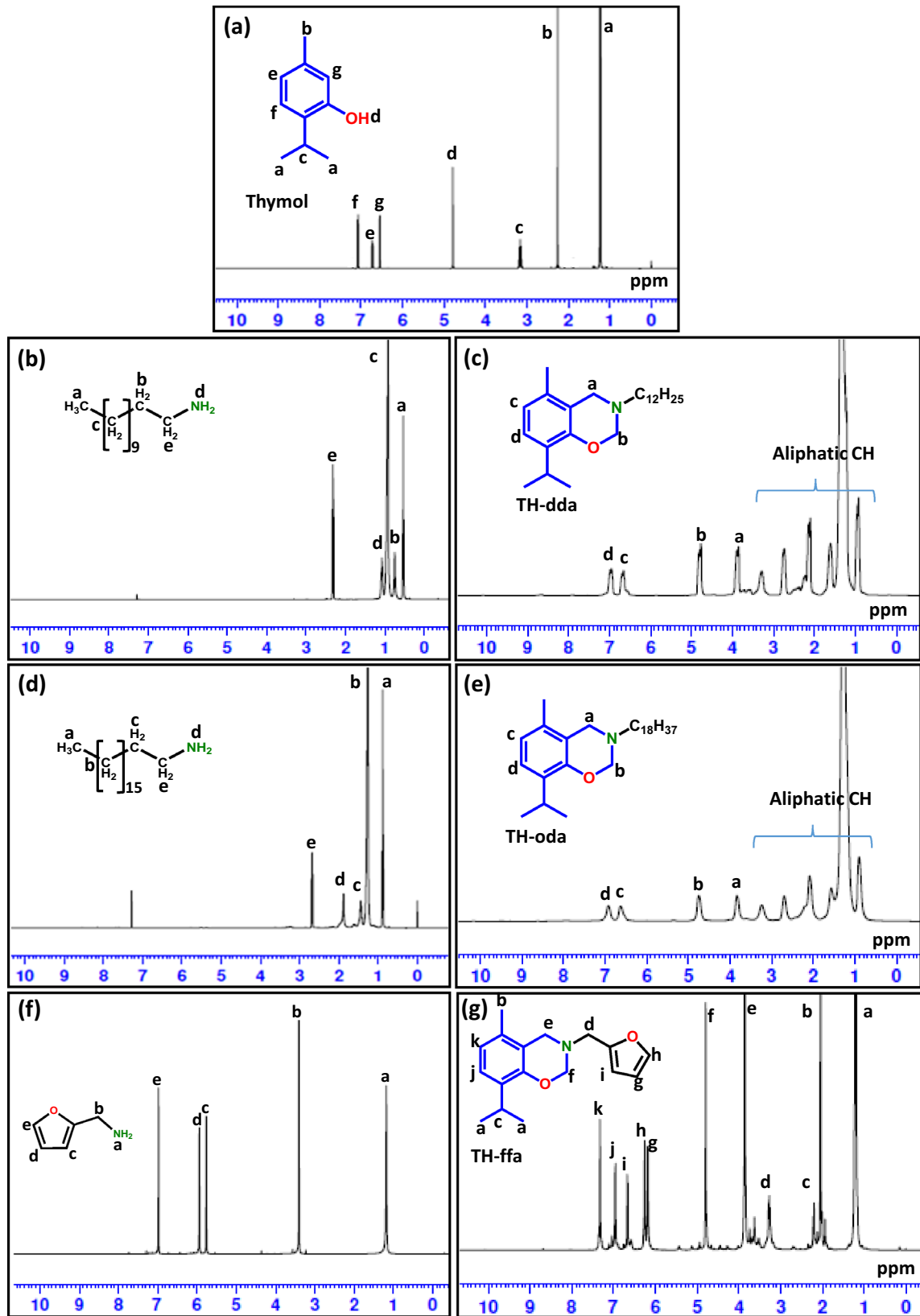
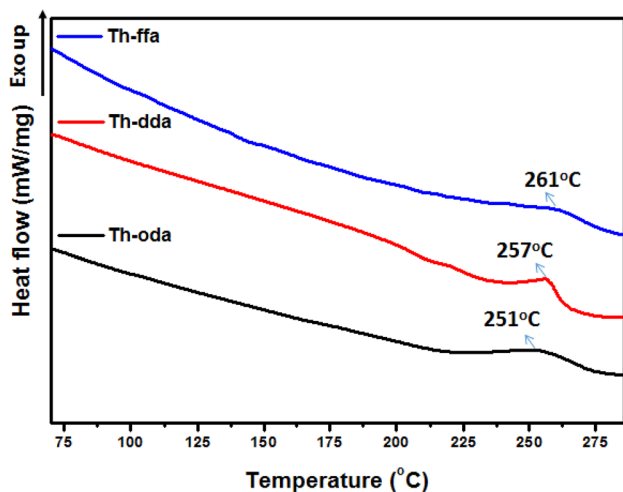
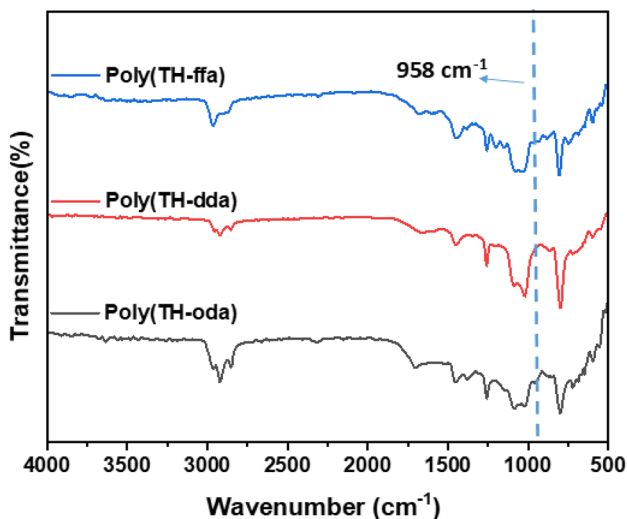


Fig. 2 $^1\text{H-NMR}$ spectrum of a Thymol b dodecylamine c TH-dda d octadecylamine e TH-oda f furfurylamine g TH-ffa

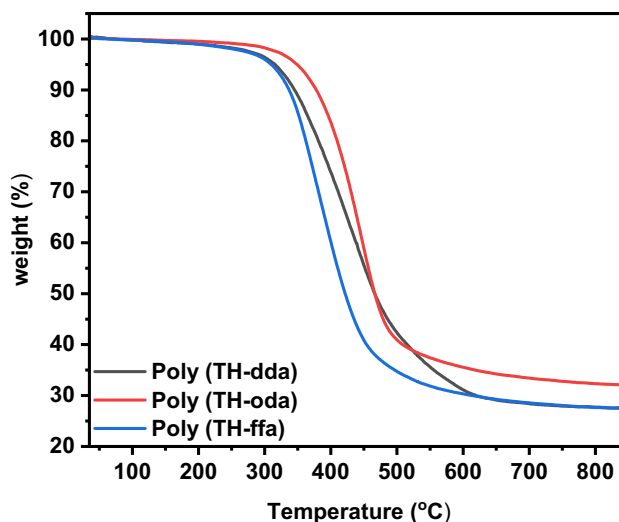
Table 1 Curing behaviour of thymol based benzoxazine monomers

Thymol based benzoxazine monomers	Curing behaviour at 10°C/min		
	T _i	T _p	T _f
TH-oda	231	251	263
TH-dda	238	257	279
TH-ffa	238	261	283

T_i, initial curing temperature; T_p, curing peak maximum temperature; T_f, final curing temperature

**Fig. 3** DSC traces of thymol based benzoxazine monomers**Fig. 4** FTIR spectra of polybenzoxazines

poly(TH-oda) possesses marginally higher thermal stability than that of the rest of the polybenzoxazines (TH-dda and TH-ffa) due to the extended cross-linked polymer network structure.

**Fig. 5** TGA traces of polybenzoxazines**Table 2** Thermal stability of thymol based polybenzoxazines

Thymol based polybenzoxazines	Thermal stability				
	5%wt loss (°C)	10%wt loss (°C)	T _{max} (°C)	Char yield % at 850 °C	LOI
Poly(TH-dda)	313	342	447	28	29
Poly(TH-oda)	345	376	436	32	30
Poly(TH-ffa)	306	333	401	28	29

T_{max} maximum degradation temperature; LOI limiting oxygen index

Flame Retardant Behaviour

The flame retardant behavior of the cured polybenzoxazines was also ascertained by calculating limiting oxygen index (LOI) value based on the obtained residual char yield at 850 °C from TGA analysis. The value of limiting oxygen index (LOI) is calculated from van Krevelen's and Hoftyzer equation [Eq. 1] [24, 25] and the results obtained are presented in Table 2.

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

where θ is the percentage char yield of materials remains at 850 °C.

The char yield value of the polybenzoxazines, poly(TH-dda), poly(TH-oda) and poly(TH-ffa) was found to be 29, 30 and 29% respectively. The LOI values of the polymers should be above the threshold value of 26, in order to possess good flame resistance. It is generally observed that the LOI increases with increase in char yield.

All the synthesized polybenzoxazine possesses the value of LOI above the threshold value and infer that these benzoxazines can be considered as a self-extinguishing flame

retardant material [26]. The good flame retardant behaviour arises due to the presence of three dimensional cross-linked network structure with inherent heterocyclic moiety of benzoxazine [27].

Water Contact Angle Studies

The values of water contact angle and images of poly(TH-oda), poly(TH-dda), poly(TH-ffa) are presented in Fig. 6. The value of water contact angle of the above mentioned polybenzoxazines is observed in the range of 134 to 139°. The lower water affinity of the developed polybenzoxazine towards water indicates that the inherent chemical nature associated with intramolecular hydrogen bonding exist in the polybenzoxazines. All the synthesised polybenzoxazines samples possess an excellent hydrophobicity and comparable with that of existing conventional organic matrices. In addition, the intra-molecular hydrogen bonding developed in the benzoxazine molecules enhanced values of water contact angle which in turn contributes to lower surface free energy and consequently enhanced hydrophobic behavior. The values of water contact angle suggest that these materials can be used as an effective insulation material under humid environmental conditions.

Corrosion Resistant Studies

In the present work, in addition to synthesis and characterization of physico-chemical, thermal behaviour and hydrophobic properties their anti-corrosion behaviour was also studied in 3.5% NaCl solution in order to predict their utility for the protection of mild steel surfaces. The adhesive property of the polybenzoxazines coated MS specimen was analysed by crosscut test. A cross cut can be used to assess the resistance of a coating to separate from the surface below after a cross cut has been applied down to the level of that surface. The edges of the cuts are completely smooth; none of the squares in the grid have detached. If a coating is easily removed from a surface, this can no longer protect the surface from environmental influences. In this context,

the corrosion protection efficiency of the thymol derived benzoxazines were coated on mild steel and immersed in 3.5% sodium chloride solution and studied their corrosion inhibition efficiency. The corrosion studies of the specimens were carried out using open-circuit potential (OCP), electrochemical impedance spectroscopy and potentiodynamic polarisation. Thymol based polybenzoxazines were used in the form coatings for corrosion protection applications [28, 29]. It was noticed that the TH-dda coating exhibits better resistance towards corrosion on mild steel than that of the TH-oda and TH-ffa benzoxazines coated on mild steel specimens.

Electrochemical impedance spectroscopy was used to assess the corrosion resistance property of the polybenzoxazines coatings on mild steel. Impedance analysis was performed using mild steel plate having 1 cm² area. The specimens after coating were immersed in 3.5% NaCl solution for different time periods. The OCP values were measured. It can be understood that OCP values of the coated specimens shifted significantly to the anodic direction when compared with that of the bare mild steel specimen. It can also be seen that OCP values of neat polybenzoxazines coated specimens decreased much slower rate when compared to that of bare mild steel specimen. The OCP shift progressively increasing towards positive values indicated that the high corrosion resistance offered by the coatings. The poly(TH-dda) coated specimen exhibits more anodic shift of OCP values which indicated that less porous, non-penetrable adherent film formed on the surface which in turn reduced the permeability of the corrosion medium into the film [30, 31].

Nyquist plots derived from the EIS measurements (Fig. 7) for three different benzoxazine coatings and uncoated mild steel specimens after immersing in 3.5% NaCl solution for 5 days. For uncoated mild steel specimen exhibits a small capacitive loop indicating that the poor corrosion resistance. The uncoated mild steel specimen has a single capacitive loop. Hence, fitting of EIS data is done using the equivalent circuit model (Fig. 8a and b). Benzoxazines coated steel specimens exhibited two capacitive loops, hence, fitting of EIS data is done using the equivalent circuit model (Fig. 10b). Out of the two constants the first one is related to the coated polybenzoxazine

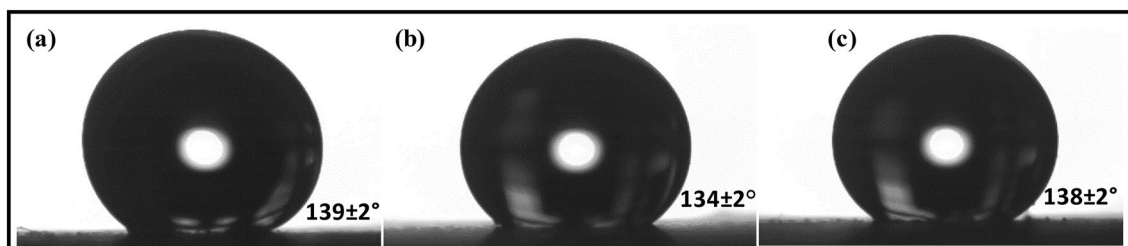


Fig. 6 Water contact angle images of **a** Poly(TH-oda), **b** Poly(TH-dda), **c** Poly(TH-ffa)

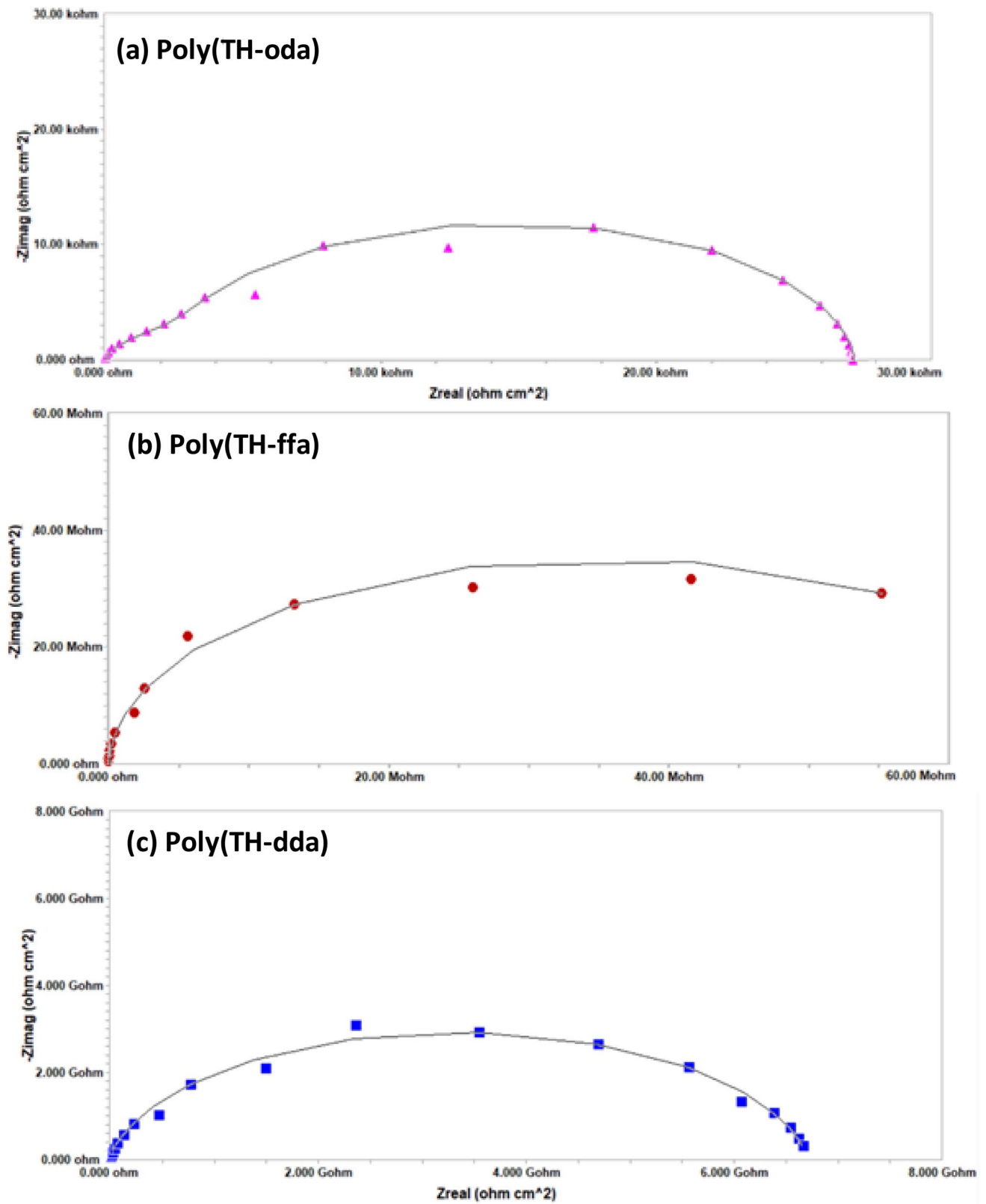


Fig. 7 EIS response of polybenzoxazine coated specimens in 3.5% NaCl solution

films, while the second time constant may be related to the corrosion taking place beneath the coatings, i.e. the polymer -steel specimen interface.

The phase angle modulation with frequency and impedance for corrosion of mild steel in 3.5% NaCl is represented by the Bode plots (Fig. 9). Bode plots provides vital information about the inductive, capacitive and resistive behaviours of the system at different frequencies [32]. The impedance spectra were analysed using the electrical equivalent circuit

represented in Fig. 8a and b, and a perfect fit for experimental data obtained was presented in Table 3.

The two equivalent circuits, Fig. 8a and b are used to evaluate the data, R_{ct} is the charge transfer resistance, which are used to measure the resistance of the electron transfer across the metal-solution interface, which is inversely proportional to the corrosion rate of the metal. Q_Y is the double layer capacitance, with constant phase element due to non-ideal behaviour of the polymer-NaCl solution interface R_7

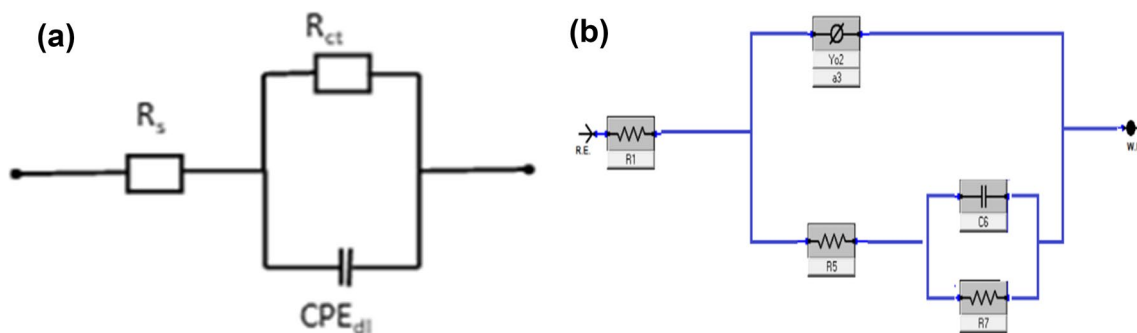


Fig. 8 Electrical circuit model used to fit EIS results with a one and b two time constants

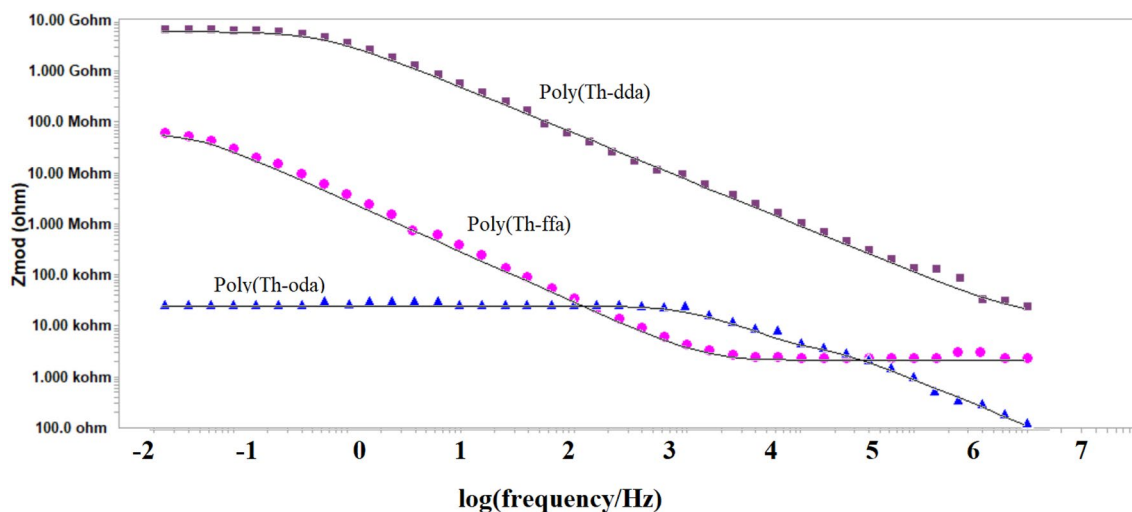


Fig. 9 Bode plot of polybenzoxazines coated mild steel specimen in 3.5% NaCl solution

Table 3 Calculated values of corrosion parameters of the polybenzoxazine coated and bare mild steel specimens in 3.5% NaCl solution from potentiodynamic polarisation studies

Material	$R_s(\Omega\text{cm}^2)$	$Y_{0,dl}(\mu\text{s}^n\Omega^{-1}\text{cm}^{-2})$	n_{dl}	$C_6(\mu\text{F cm}^{-2})$	$R_7(\Omega\text{cm}^2)$
Bare	–	908×10^{-6}	0.873	–	934
Poly(TH-dda)	6.731×10^9	39.69×10^{-12}	0.911	8.422×10^{-12}	1.527×10^9
Poly(TH-oda)	6.70×10^6	828×10^{-9}	0.995	3.796×10^{-12}	65.78×10^6
Poly(TH-ffa)	6.17×10^3	3.450×10^{-9}	0.937	3.66×10^{-9}	20.98×10^3

R_s , R_7 , are the charge transfer resistance values for the heterogeneous interfaces formed at the polymer coating and electrolytic solution interfaces respectively. Y_0 , Admittance of polymer coating and electrolytic solution interface. n , constant phase element. C , capacitance of polymer coating and electrolytic solution interface

is the diffusion resistance of coating and C_6 is the diffusion capacitance of the coating. The calculated values of the corrosion parameters from EIS measurements are presented in Table 3.

R_{ct} values of the polybenzoxazines coated specimens are higher than that of the bare mild steel specimen. Corrosion resisting behaviour was increased according to the nature of the polybenzoxazine matrix coated on mild steel specimen. The maximum R_{ct} and R_f values are obtained for poly(TH-dda) coated mild steel specimens (Table 3). The improved corrosion resistant behaviour offered by the benzoxazine coatings may be due to the presence of cross-linkages in the coating. The roughness factor values (n) are lower for poly(TH-dda) matrix which also corroborates the reduction of pores/cavities on the steel surface, however, all the values are close to unity indicating enhanced corrosion resting behaviour. Generally, all the organic coatings are not completely impenetrable for long time, their barrier properties could decrease when immersion time increases because of the water/corrosion medium penetration into the coatings. In the case of bare mild steel specimen, the corrosion medium had a direct contact with the metal surface which led to the generation of many electroactive sites and corrosion will take place freely, whereas polybenzoxazine coatings prevent the diffusion of oxygen and aggressive medium into the polymer matrix due to the complex crosslinking network structure of polymer coatings. From the values of water contact angle, it can also be understood that, all the polybenzoxazine samples are close to super hydrophobic nature, which could effectively reduce the surface wettability of polymer coating, which in turn ultimately reduces the sorption of water molecules on the surface of coatings. Among the three different polybenzoxazines studied in the present work, poly(TH-dda) offers a better corrosion resistance behaviour due to the enhanced cross-linked with efficient adherence over the metal surface which forms a strong binding film [33].

Figure 10, show the Tafel plots of poly(TH-oda), poly(TH-dda) and poly(TH-ffa) coated MS specimens. The corrosion rate (CR, in millimetres per year, mm year^{-1}) was calculated using I_{corr} values using the Eq. 2,

$$\text{CR} = M I_{\text{corr}} / \rho n F \quad (2)$$

where M is the molecular mass of copper (58.69 g mol^{-1}), I_{corr} is the corrosion current density (Acm^{-2}), F is the Faradays constant ($96,500 \text{ A s mol}^{-1}$), ρ is the density of the mild steel specimen (7.85 g cm^{-3}) and the number of electrons transferred during corrosion reaction is assumed to be 2.

The E_{corr} values of all the benzoxazine samples coated specimens shifted anodically. Maximum anodic shift was observed for poly(TH-dda) coated mild steel specimen. I_{corr} values the polybenzoxazine coated specimens are also reduced indicating that the corrosion resistance of the coated

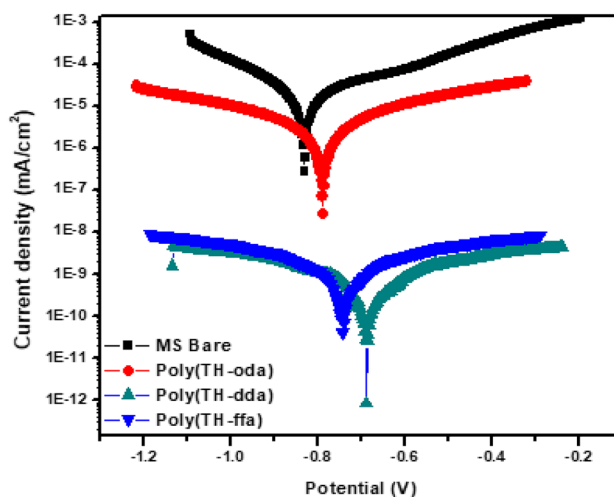


Fig. 10 Tafel plots of bare MS, polybenzoxazine coated specimens in 3.5% NaCl solution

specimens were improved after coating (Table 4). Furthermore, poly(TH-dda) possesses the better corrosion resistance behaviour than that of the other two benzoxazines coated MS samples. The result observed coincides with that of the data observed in the EIS. The significantly enhanced corrosion resistance again reiterates the presence of cross-linkages, which suppressed the anodic corrosion reactions (Fig. 9). The poly(TH-dda) coating offers better corrosion resistance when compared with that of similar types of benzoxazines studied and reported earlier [34].

Conclusion

Three types of bio-benzoxazine resins were synthesized from naturally occurring phenolic compound thymol with three structurally different amines and paraformaldehyde through Mannich reaction. Structural characterizations of the thymol based benzoxazines were performed by FTIR and $^1\text{H-NMR}$ spectroscopy and confirms the successful synthesis of targeted compounds. From the curing studies of thymol based benzoxazines namely TH-oda, TH-dda and TH-ffa, it was ascertained that thermal polymerization occurs at 251, 257 and 261 °C respectively. Ring opening and crosslinking of the oxazine ring were confirmed with FTIR spectra of thymol based benzoxazines. All the synthesized polybenzoxazines exhibit thermal stability up to 300 °C and degrade thereafter. There was no significant difference observed on thermal stability of thymol based polybenzoxazines (TH-oda, TH-dda and TH-ffa) prepared from different amines. The values of LOI also indicated that all the polybenzoxazines may possess self-extinguishing property, which will be suitably exploited for flame retardant applications in future. Poly(TH-dda) and poly(TH-ffa) have

Table 4 Calculated values of the corrosion parameters of the coated and uncoated mild steel specimens in 3.5% NaCl solution from Tafel studies

Samples	E_{corr} (mV)	I_{corr} (mA)	Efficiency (%)	β_b (mV dec ⁻¹)	β_a (mV dec ⁻¹)	R_p (M Ω × cm ²)
Bare MS	− 830	7.94×10^{-6}	0	23.8	25.3	3.6
(TH-oda)	− 792	9.58×10^{-7}	88	90.6	97.3	36.1
(TH-dda)	− 689	1.44×10^{-10}	100	102	79.8	89.6
(TH-ffa)	− 735	3.54×10^{-10}	100	66.5	89.3	182.0

E_{corr} , Corrosion potential; I_{corr} , Corrosion current density; R_p , polarization resistance; β_a and β_b are tafel constants for anodic and cathodic polarization regions respectively

better corrosion inhibition efficiency than that of poly(oda). Data obtained from different studies suggest that these benzoxazine materials can be used as an effective coating materials for different industrial applications under humid environments.

Acknowledgements The authors thank the PSG Management, Secretary, Principal, PSG Institute of Technology and Applied Research, Coimbatore-641062, India for their moral and financial support.

Author Contributions MMK and PKJ: Synthesis. AH: Conceptualization, Methodology, Investigation. KB: Methodology, writing—original draft, review & editing. SR: Characterization, validation. RG: Supervision. MA: Resources, Validation, Supervision.

Funding The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

Declarations

Conflict of interest The authors declare no conflict of interest.

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