

Bio-based polybenzoxazines as an efficient coating to protect mild steel surfaces from corrosion

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Abstract

New types of mono and bi-functional benzoxazine monomers were synthesized using cardanol (C) and 4-aminobenzonitrile (abn), *p*-phenylenediamine (*ppda*) along with paraformaldehyde. The synthesized benzoxazine monomers structure was elucidated by ¹H, ¹³C-NMR and FTIR spectroscopic techniques. The polymerisation temperature (T_p) of C-abn and C-*ppda* are noticed at 280°C and 237°C respectively. It was also noticed that bi-functional benzoxazine (C-*ppda*) possesses lower curing temperature than mono-functional benzoxazine (C-abn). The ring opening polymerization of benzoxazine was confirmed by FTIR spectroscopy. Thermal analyses indicate that, benzoxazine [poly(C-*ppda*)] possesses higher thermal stability than poly(C-abn). The surface roughness of the benzoxazine coated MS specimen was analysed by atomic force microscope. The values of water contact angles obtained for poly(C-abn) and poly(C-*ppda*) are 145° and 148° respectively. It was noticed that the mild steel specimen coated with bio-based benzoxazine C-abn exhibit excellent resistance to corrosion.

Key words: Bio-benzoxazine, cardanol, thermal stability, hydrophobicity.

Introduction

Polybenzoxazines are one of the most important and versatile classes of thermosetting polymeric materials with excellent mechanical and thermal properties, low moisture uptake, high carbon residue, flame retardant, low surface free energy and excellent dielectric properties suitable for wide range of high performance industrial and engineering applications¹⁻⁵. Though the benzoxazines (bisphenol-A, bisphenol-F, etc.) prepared from petroleum products, possess excellent properties, their brittle behaviour and higher polymerization temperature restrict their utility when they are interfaced with low melting substrates, to overcome these drawbacks and to replace the petroleum based precursors, it is warranted to develop the benzoxazines using sustainable bio-mass based precursors with varying skeletons capable of contributing high performance properties.⁶⁻¹¹

In this context, a class of bio-based benzoxazines have been developed in the recent past¹² using varied nature of bio-phenols with different molecular structure by researchers around the world. Among them, cardanol based benzoxazines⁹⁻¹² are considered to be most useful since they possess good storage stability at room temperature, low heat release, near-zero shrinkage during curing and low water uptake make them suitable materials for different industrial applications. In addition, when these bio-based benzoxazines are reinforced with silica and carbon derived from rice-husk ash and palm flower respectively improved the thermal, mechanical and electrical properties to a significant extent.^{13,14} Our research group have developed a number of bio-based benzoxazine matrices and composites and studied their thermal properties, dielectric behavior, oil-water separation efficiency, sound absorption behavior and resistance to corrosion to assess their suitability for some of the industrial applications.¹⁵⁻¹⁸ Also, Deepak et al. reported the enhancement of anti-corrosive performances of cardanol based amine functional benzoxazine resin by copolymerizing with epoxy resins.²³

The present work focuses on the development of cardanol based polybenzoxazine matrices and to assess their hydrophobic behaviour and protection of mild steel surfaces from corrosion. The cardanol based mono and bi-functional benzoxazines were developed and their molecular structures were characterised using FTIR and $^1\text{H-NMR}$ spectroscopic techniques. The curing behaviour bio-benzoxazine was ascertained from DSC analysis. Further, the cardanol based mono and bi-functional benzoxazines cured by thermal ring opening polymerisation method. Thermal stability and hydrophobic behaviour of polybenzoxazines were studied using TGA and goniometer analysis. Corrosion resistant behaviour towards mild steel specimen was checked using electrochemical workstation. Data from different studies indicate that the bio-benzoxazines developed in the present work are analysed to utilize them in the form insulators, sealants, adhesives, coatings and matrices where application demands under harsh environments.

Experimental

Materials

Cardanol was obtained from Sathya cashew products, Chennai. Analytical grade of chemicals, 4-amino benzonitrile and paraformaldehyde were purchased from Sigma-Aldrich (India) and *p*-phenylene diamine was purchased from Alfa Aesar (UK). Ethyl acetate was purchased from Thomas Baker, sodium hydroxide and magnesium sulphate were purchased from Merck (Mumbai).

Characterization

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ (400 MHz) spectra for benzoxazine monomers were recorded on a Bruker instrument with TMS standard in CDCl_3 solvent. Fourier-transform infrared spectroscopy (FTIR) data were used to identify the functional groups of synthesized benzoxazines and were recorded in a Perkin Elmer instrument Spectrum Two FTIR spectrometer, L160000A using powdered KBr. About 3 mg of sample was grained well with

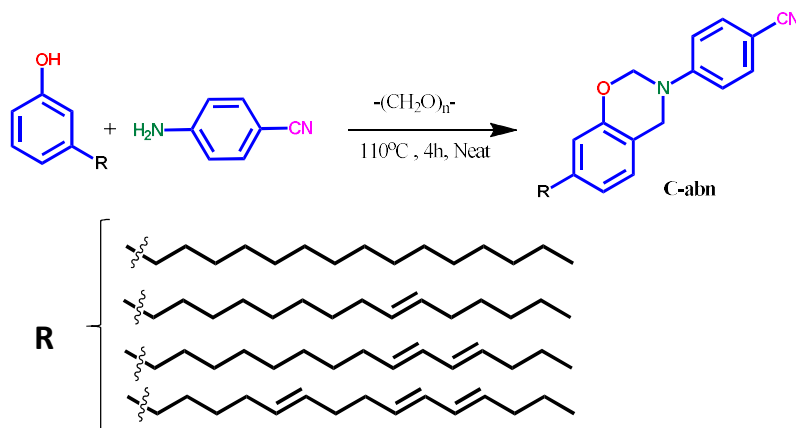
100 mg of KBr powder until the formation of homogeneous dispersion and then made a 10 mm diameter pellet with high-pressure pelletizer. Further, the pellet sample was utilized for FTIR analysis. Differential scanning calorimetry (DSC) measurements were recorded using NETZSCH STA 449F3 under N₂ purge (60 mL min⁻¹) at the scanning rate of 10°C min⁻¹. Thermogravimetric analysis (TGA) was carried out by NETZSCH STA 449F3 under N₂ purge (60 mL min⁻¹) at the scanning rate of 20°C min⁻¹. Contact angle of water droplet on the coated benzoxazine samples was measured using a Kyowa contact angle goniometer (model DMe-211 plus) with 5 µl of water as probe liquid. 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 30µm polymer coated mild steel specimens were carried out using open-circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation.

Synthesis of cardanol-based benzoxazine 4-(7-pentadecyl-2H-benzo[1,3]oxazin-3(4H)-yl)benzene (C-abn)

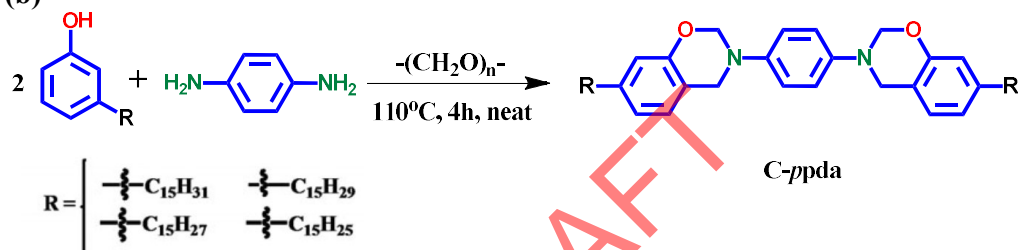
3 g (0.02 mol) of 4-aminobenzonitrile was mixed with 7.6 g (0.02 mol) of cardanol and 1.52 g (0.04 mol) of paraformaldehyde were added portion-wise into a 100 ml double necked round bottomed flask under constant stirring in the absence of solvents. Then the temperature was raised to 110°C and maintained for more than 4 h until the completion of benzoxazine formation. The progress of the reaction was monitored with TLC (8:2 hexane:ethylacetate solvent). After the completion of reaction, the resinous crude product obtained was dissolved in 50 ml of ethyl acetate and washed twice with 2N NaOH for the removal of traces of unreacted phenolic compounds, if present any. Further, organic layer was washed twice with 100 ml of distilled water. Then, the organic phase was dried over anhydrous Na₂SO₄ and ethyl acetate is removed using the rotary evaporator and the product was recovered and

preserved for further analysis. The yield of the benzoxazine is 93%. The synthesized cardanol-based benzoxazine was labelled as C-abn (Scheme 1a).

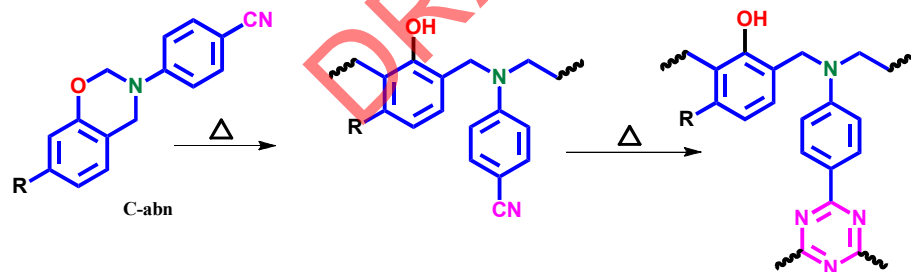
(a)



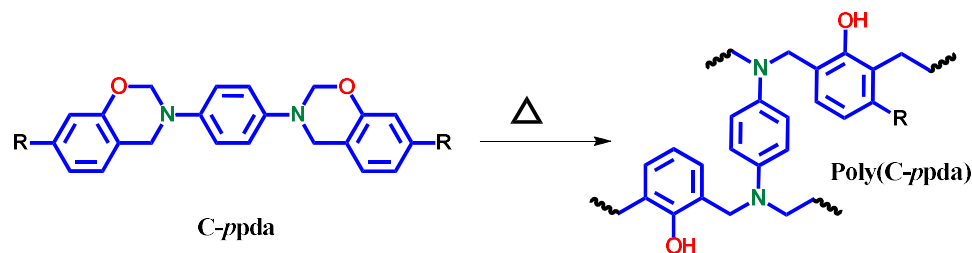
(b)



(c)



(d)



Scheme 1. (a) Synthesis of 4-(7-pentadecyl-2H-benzo[1,3]oxazin-3(4H)-yl)benzene (C-abn), (b) 1,4-bis(7-pentadecyl-2H-benzo[1,3]oxazin-3(4H)-yl)benzene (C-ppda) (c) Ring opening polymerisation and triazine ring formation of C-abn and (d) Ring opening polymerization of C-ppda.

Synthesis of cardanol-based benzoxazine 1,4-bis(7-pentadecyl-2H-benzo[1,3] oxazin-3(4H)yl)benzene (C-ppda)

5 g (0.04 mol) of *p*-phenylene diamine was mixed with 27.6 g (0.08 mol) of cardanol and 5.5 g (0.16 mol) of paraformaldehyde were added portion-wise into a 100 ml double necked round bottomed flask under constant stirring in the absence of solvents. Then, the temperature was raised to 110°C and maintained for more than 4h until the completion of benzoxazine formation. Rest of the steps had been followed according to the synthesis procedure adopted for C-abn. The yield of the benzoxazine resin is 85%. The synthesized cardanol-based benzoxazine was labelled as C-ppda (Scheme 1b).

Preparation of polybenzoxazines

The thermal ring opening polymerization of cardanol based benzoxazine was carried out according to the reported procedure (Schemes 1c and 1d). A typical procedure for polymerization is as follows: the respective amine based homogeneous benzoxazine monomer was placed in the oven at 80°C for 8 h to stabilize and to remove the impurities (moisture and trace of solvent). After stabilization, the temperature was raised gradually to 280°C at a heating rate of 20°C/h. The heating is continued for another 3 h at 280°C for the completion of the curing process. At this temperature, the monomer undergoes ring opening polymerization to form polybenzoxazine with three dimensional cross-linked network structure. The process of polymerization was confirmed by FTIR spectroscopy.

Results and discussion

The cardanol-based benzoxazines (C-abn and C-ppda) were prepared through Mannich condensation reaction using cardanol with two different amino compounds and paraformaldehyde at an appropriate experimental conditions as shown in Schemes 1a and 1b.

Cardanol is a naturally available compound from cashew nut shell liquid with C₁₅ aliphatic chain, which is substituted in meta position of phenolic ring. Further, aliphatic

chain is consist of four types of units with the composition namely, saturated chains (8.4%), monoolefinic (48.5%), diolefinic (16.8%) and triolefinic (29.33%) chains. Due to the presence of meta-substituted long alkenes/alkyl (15 carbon) chain groups, the benzoxazines obtained from cardanol will exist in the liquid form. Consequently, cardanol based benzoxazines possess an improved flexibility and good water repellent behaviour. The molecular structure of cardanol based benzoxazine monomers was confirmed from FTIR and ¹H-NMR spectral analyses. Curing behaviour and thermal stability of benzoxazines were studied using DSC and TGA techniques.

FTIR spectral analyses of monomers

The FTIR spectra of cardanol based benzoxazines are presented in Figure S1. The absorption bands appeared at around 1238 cm⁻¹ and 1096 cm⁻¹ were attributed to the asymmetric and symmetric stretching vibrations of C-O-C bond present in the benzoxazines respectively. The peak at 1189 cm⁻¹ obtained due to the presence of asymmetric stretching of C-N-C. Similarly, the appearance of bands at around 918 cm⁻¹ and 1496 cm⁻¹ correspond to a tri-substituted benzene ring which confirms the formation of benzoxazine ring. Further, the band appeared at around 3009 cm⁻¹ corresponds to C-H stretching vibrations of the benzene ring. The characteristic absorption peaks appeared at around 2925 cm⁻¹ and 2853 cm⁻¹ represent the asymmetric and symmetric stretching respectively for vibrations of CH₂ of oxazine ring as well as alkyl side chain of cardanol moiety.

NMR spectral analyses

The structure of benzoxazines was also confirmed using the data derived from ¹H-NMR spectral analyses. The benzoxazine rings present in both cases of C-abn and C-ppda samples was confirmed from the appearance of resonance peaks at around 4.5 ppm (singlet, 2H, **a** type signal in Figures 1a and 1b) for methylene group of Ar-CH₂-N and around 5.5 ppm (singlet, 2H, **b** type signal in Figures 1a and 1b) for (O-CH₂-N) from ¹H-NMR spectra.

Additionally, alkyl chain of cardanol core contains $-\text{CH}_2-$ and $-\text{CH}_3$, which corresponding peaks are appeared at 0.8-3 ppm. Aromatic protons peaks were observed at 6.5-7.5 ppm. The ^{13}C -NMR spectra shown in Figures 2a and 2b, also confirm the structures of C-abn and C-ppda benzoxazine monomers. The characteristic carbon resonance of the oxazine ring is found at around 50 and 80 ppm for $\text{Ph}-\text{CH}_2-\text{N}$ and $\text{O}-\text{CH}_2-\text{N}$, respectively.^{24,25}

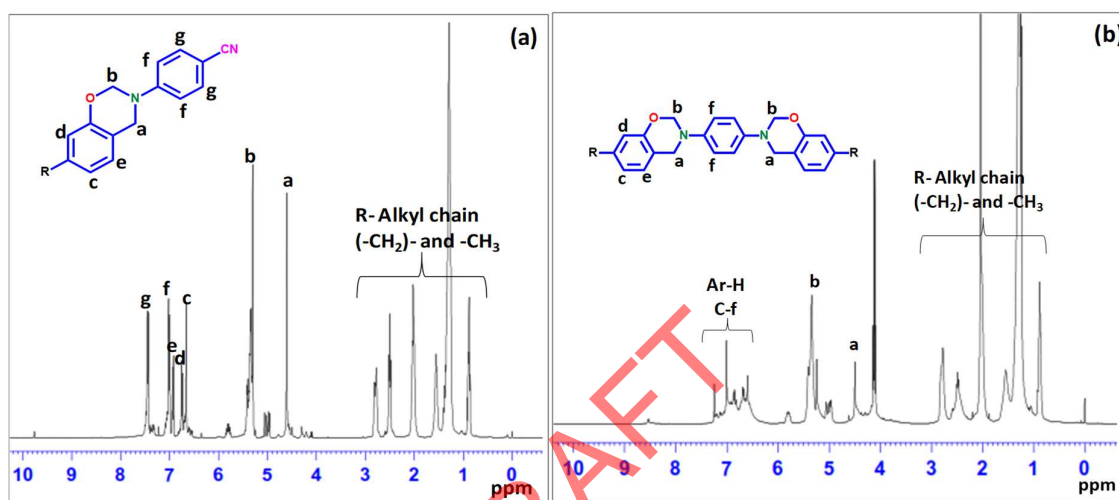


Figure 1. ^1H -NMR spectra of (a) C-abn benzoxazine, (b) C-ppda benzoxazine.

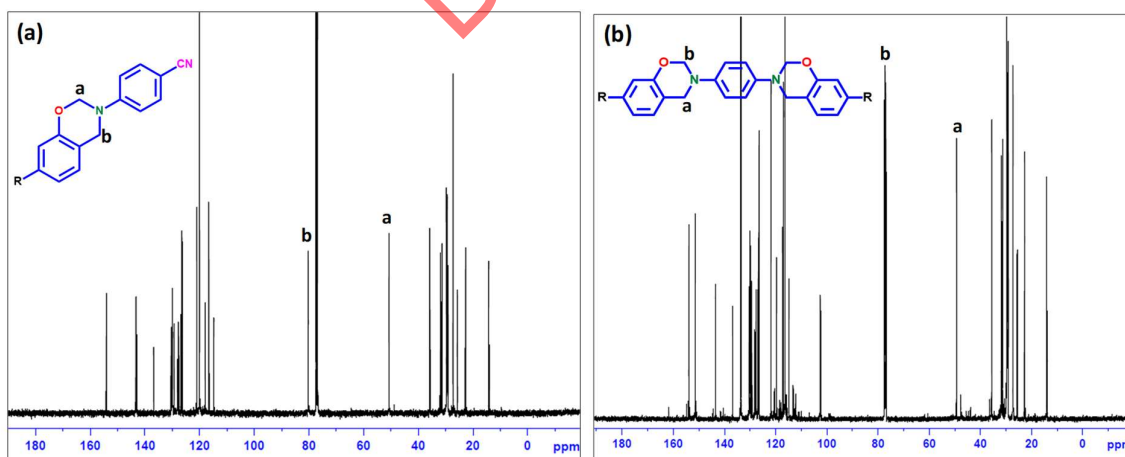


Figure 2. ^{13}C -NMR spectra of (a) C-abn benzoxazine, (b) C-ppda benzoxazine.

Curing behaviour of benzoxazines

The curing behaviour of synthesized benzoxazine monomers was studied by DSC analysis at heating rates of $10^\circ\text{C}/\text{min}$ and $20^\circ\text{C}/\text{min}$. Figures 3 and S2, shows the DSC thermograms of

cardanol based benzoxazines with different amino compounds, viz., 4-aminobenzonitrile and p-phenylene diamine. The appearance of exothermic peaks of benzoxazines viz, C-abn and C-ppda confirms the polymerization proceeds through thermal ring-opening mechanism (Scheme S1 and Figure 3). C-abn exhibits two exothermic peaks, the first peak is corresponds to benzoxazine polymerization and second peak is corresponds to nitrile group crosslink to form triazine ring. Initially the polymerization process started with ring opening polymerization of benzoxazine ring at 230°C, followed by crosslinking (trimerization) of nitrile group and formation of triazine ring at 280°C. Whereas, the values of curing temperature (T_p) observed for the same benzoxazine samples with a heating rate of 20°C/min are 294°C and 267°C respectively (Figure S2). The curing temperature of the benzoxazine is increased with increase in the rate of the heating.²⁶⁻²⁸ The value of curing temperature reported in the literature for cardanol-aniline benzoxazine is also included in Table S1 for comparison.^{14,20}

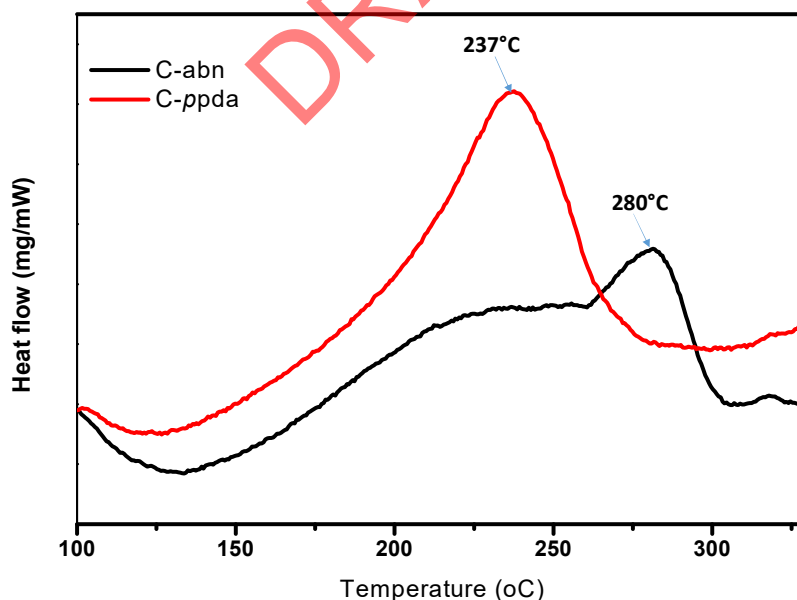


Figure 3. DSC thermogram of benzoxazine monomers at the rate of 10°C per min.

It was observed that the benzoxazines prepared using amino derivatives with electron withdrawing (-CN) group as well as difunctional benzoxazines (C-ppda) possess lower curing

temperature than that of cardanol-aniline (C-a) based benzoxazines. The lowering of cure temperature may be explained due to the formation of Zwitterion intermediate followed by the proton exchange in the case of benzoxazines moiety (Scheme S1). Consequently, the formation of Zwitterion intermediate reduces the polymerization temperature when compared to that of aniline based cardanol benzoxazine.

FTIR spectral analyses for polybenzoxazines

After the thermal treatment, the chemical structure of cardanol based polybenzoxazines viz., poly(C-abn) and poly(C-ppda) was re-analysed and ascertained using FTIR spectral analyses. The absorption band appeared at 918 cm^{-1} for oxazine ring was disappeared after thermal curing at 280°C for 3 h which confirms the occurrence of opening of oxazine ring followed by the formation of polybenzoxazine with three dimensional cross-linked network structure (Figure S3). **Also, a formation new peak at 1470 cm^{-1} confirms the formation of tetrasubstituted benzene. The formation of triazine structure was also confirmed through a new peak appeared at 1665 cm^{-1} .**

Thermal stability of polybenzoxazines

The thermal stability of cardanol based benzoxazines was studied by thermogravimetric analysis (Figure 4 and S4) and the results obtained are presented in Table 1. Thermal stability of polybenzoxazine matrix is one of the important factors to be considered when used in the form of sealants, encapsulants and impregnants during the fabrication of electronic devices and components. TGA provides a valuable data with regard to the thermal stability of materials, the types of impurities or solvents present and the nature of degradation occurs by measuring the weight loss at each instant. For the cardanol based benzoxazines with three different amines viz., (poly(C-a), poly(C-abn) and poly(C-ppda)), 5% weight loss was noticed at 381 , 359 and 368°C respectively. The maximum degradation (T_d) takes place at 461 , 481 and 468°C , respectively. The char yield of benzoxazine samples obtained at 850°C

from TGA (Figure 4 and S4) is presented in Table 1. The residual char yields obtained for poly(C-a), poly(C-abn) and poly(C-ppda) based benzoxazines are 8, 19 and 20% respectively. The poly(C-ppda) and poly(abn) possess the higher char yield than that of poly(C-a) due to the presence of highly complexed cross-linked network structure imparted by multifunctional benzoxazine moiety. The **total organic content (TOC) of the samples varying between 80% and 92% based on the data derived from TGA analysis.**

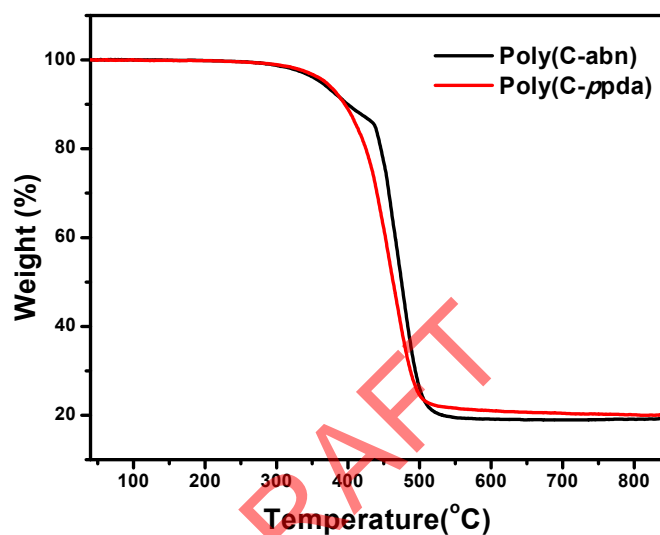


Figure 4. TGA thermograms of polybenzoxazines

Table 1. Thermal behavior of cardanol based polybenzoxazines

Cardanol based benzoxazines	T_p	5% weight loss (°C)	10% weight loss (°C)	T_{max} (°C)	Char yield % at 850°C	LOI
Poly(C-a)	285	381	419	461	8	21
Poly(C-abn)	237	359	393	481	18	25
Poly(C-ppda)	280	368	393	468	20	25

Flame retardant behaviour

The flame retardant behaviour 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^{29,30} [eq. 1] and the results are obtained presented in Table 1.

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

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

The char yield of polybenzoxazines viz., poly(C-abn) and poly(C-ppda) was found to be 18 and 20% respectively. The threshold LOI value of 26 is tentatively considered for polymeric materials become self-extinguishing and for their qualification for many applications requiring good flame resistance. The synthesized polybenzoxazines shows values of LOI are close to 26 confirming their good flame retardant property. The value of LOI obtained for both poly(C-abn) and poly(C-ppda) possess about 25. This indicates that poly(C-ppda) and poly(C-abn) have higher LOI value than that of poly(C-a), due to the formation of complex cross linked network structure.

Contact angle studies

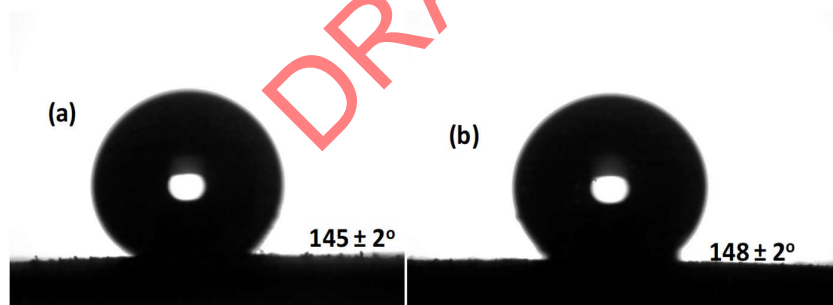


Figure 5. The water contact angle of (a) poly(C-abn) (b) poly(C-ppda)

Polymer coated mild steel specimen was used for WCA measurement. The value of water contact angle and images of poly(C-abn) and poly(C-ppda) obtained are presented in Figure 5. It can be observed that the poly(C-ppda) possesses the higher value of contact angle when compared to that of poly(C-abn) due to its bifunctional complex molecular structure. The values of contact angle obtained for poly(C-abn) and poly(C-ppda) are 145° and 148 ± 2° respectively. The lower affinity of the developed polybenzoxazine matrix indicates the

improvement of the hydrophobic behaviour. This may be due to the presence of long aliphatic chain of cardanol moiety. In addition, the existence of an intra-molecular hydrogen bonding in the benzoxazine molecular system contributes to enhanced values of water contact angle and also, compared with the previously reported literature. Generally, the value of water contact angle of conventional benzoxazine (bisphenol A based polybenzoxazines) are less than 120° .^{31,32} However, the water contact angle of cardanol based benzoxazines and other specialty benzoxazines are above 150° .^{33,34}

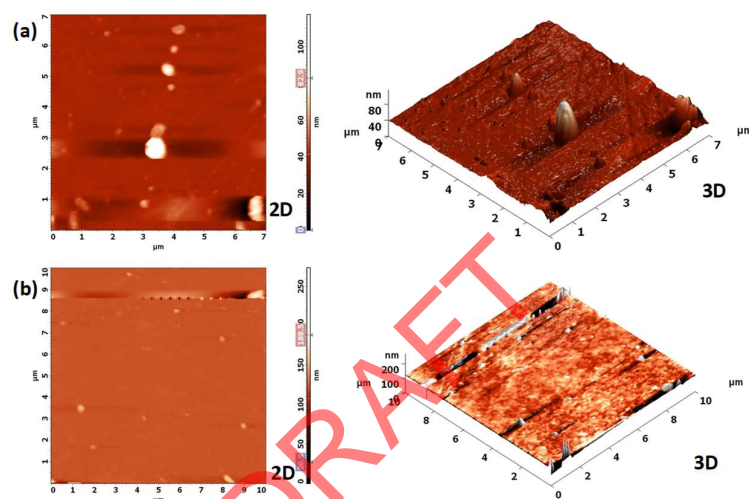


Figure 6. Atomic force microscopy (AFM) images of 2D and 3D surface (a) poly(C-abn) and (b) poly(C-ppda) coatings.

WCA results may be caused by the roughness of the sample surface. In addition, AFM analysis was also performed for the characterization of surface roughness of the poly(C-abn) and poly(C-ppda) coating on MS plate. In Figure 6, a two dimensional (2D) and three dimensional (3D) profile in three different regions of the surface are presented. The roughness of the coatings is checked by AFM analysis. 2D and 3D image of coated substrate was subjected to AFM analysis. The roughness of the coating is less than 2 nm.

Corrosion resistant studies

In the present work, in addition to synthesis and characterization of physico-chemical, thermal behaviour and hydrophobic properties of some of the new cardanol based

benzoxazines, their corrosion resistance behaviour was also studied in order to utilize them for protection of mild steel surfaces. **The adhesive property of the polybenzoxazines coated MS specimen was analyzed by crosscut test. A cross cut can be used to assess the resistance of a coating to separation 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 cardanol derived bio-benzoxazines were coated on mild steel and immersed in 3.5% sodium chloride solution and predicted their corrosion protection efficiency. The corrosion studies of the specimens were carried out using open-circuit potential (OCP), electrochemical impedance spectroscopy and potentiodynamic polarisation. Cardanol based polybenzoxazines viz., poly(C-abn) and poly(C-ppda) were used in the form coatings for corrosion protection applications. It was noticed that the poly(C-abn) coatings exhibit better resistance towards corrosion on mild steel than that of similar types of benzoxazines coated on mild steel specimens studied earlier.

Electrochemical impedance spectroscopy was used to assess the corrosion resistance property of the polybenzoxazines (poly(C-abn and poly(C-ppda)) coated 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, (poly(C-abn and poly(C-ppda)) 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(C-abn) coated

specimen exhibits more anodic shift of OCP values which indicated that less porous and adherent film formed on the surface which in turn reduced the permeability of the corrosion medium into the film.

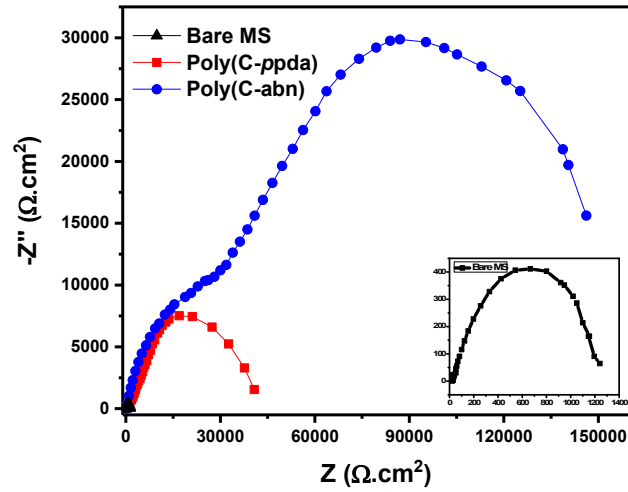


Figure 7. EIS response of bare MS and polybenzoxazine coated specimens in 3.5% NaCl solution

Nyquist plots derived from the EIS measurements (Figure 7) for two different benzoxazine coatings and uncoated mild steel specimens after immersing in 3.5% NaCl solution for 5 days. For uncoated mild steel specimens exhibits a small capacitive loop indicating that the poor corrosion resistance. The uncoated mild steel specimen and poly(C-ppda) coated specimens have a single capacitive loop. Hence, fitting of EIS data is done using the equivalent circuit model (Figure 8a and 8b). Poly(C-abn) shows two capacitive loop so, fitting of EIS data is done using the equivalent circuit model (Figure 8b). Out of the two constants the first one is related to the coated polymer film, while the second time constant may be related to the corrosion taking place beneath the coating.³⁵

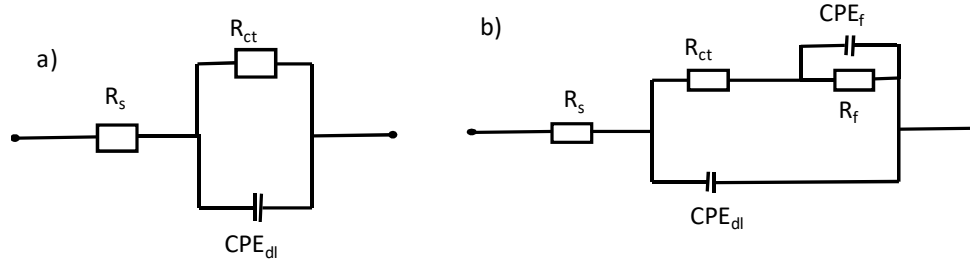


Figure 8. Electrical circuit model used to fit EIS results with a) one and b) two time constants

Table 2. 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 (Ωcm^2)	R_{ct} (Ωcm^2)	$Y_{0,dl}$ ($\mu\text{s}^n\Omega^{-1}\text{cm}^{-2}$)	n_{dl}	CPE _{dl} ($\mu\text{F cm}^{-2}$)	R_f (Ωcm^2)	$Y_{0,dl}$ ($\mu\text{s}^n\Omega^{-1}\text{cm}^{-2}$)	n_f	CPE _f ($\mu\text{F cm}^{-2}$)
Bare	12	1239	87.8	0.87	59.8	-	-	-	-
Poly(C- ppda)	141	1.55×10^5	3.84	0.74	0.04	-	-	-	-
Poly(C- abn)	71.5	2.741×10^5	1.14	0.61	0.02	8.28×10^2	3.48	0.74	4.7

These two equivalent circuits, Figure 8a and 8b are used to evaluate the data, where R_s is the solution resistance of the solution between the working electrode and the counter electrode. R_s values are not only depending on the ionic conductivity of the solution but also depending on the geometrical area of the electrode. R_s values are not an important data while studying the corrosion resistance behaviour of the film because it does not yield any information about the coatings.³⁶ 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. CPE_{dl} is the double layer capacitance, R_f is the diffusion resistance of coating and CPE_f is the diffusion capacitance of

the coating. The calculated values of the corrosion parameters from EIS measurements are presented in Table 2.

R_{ct} values of the polybenzoxazines coated specimens are higher than that of the bare MS. Coating resisting behaviour was increased according to the nature of the polymer matrix coated on mild steel specimen. The maximum R_{ct} and R_f values are obtained for the poly(C-abn) coated mild steel specimens are given in Table 2. The improved corrosion resistance behaviour offered by the benzoxazine coatings may be due to the presence of triazine cross-linkages in the polymer coating. The improved corrosion resistance property may be due to the triazine cross-linkage present in the polymer coating. The roughness factor values (n) are lower for poly(C-abn) matrix which also corroborates the reduction of pores/cavities on the steel surface.³⁷ 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.³⁸ For bare MS, 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. Triazine containing 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 contact angle measurement, it can also be understood that, all the polymers are close to super hydrophobic nature, which could effectively reduce the wettability of polymer which in turn ultimately reduces the sorption of water molecules on the surface of coatings. Among the two different polybenzoxazines studied in the present work, poly(C-abn) 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.

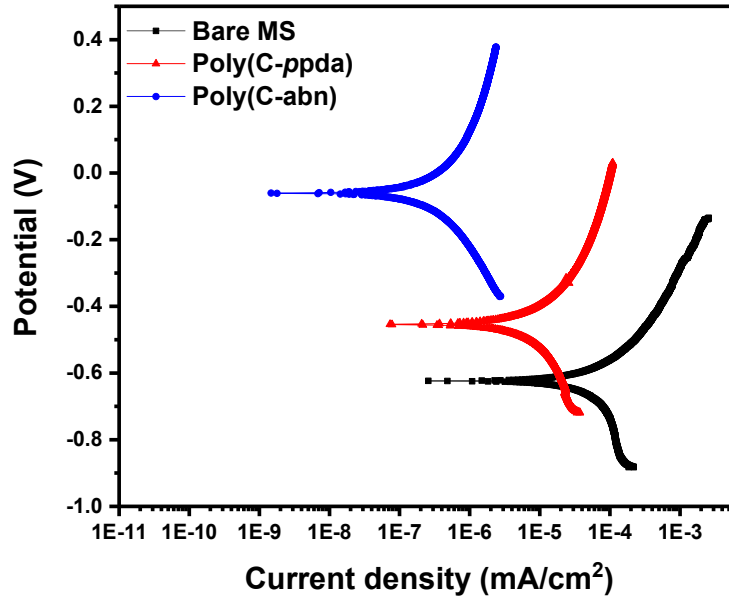


Figure 9. Tafel plots of bare MS, polybenzoxazine coated specimens in 3.5% NaCl solution

Figure 9, show the Tafel plots of poly(C-abn) and poly(C-ppda) coated MS specimens. The corrosion rate (CR, in millimetres per year, mm year⁻¹) was calculated using I_{corr} values with the help of the following equation 2,

$$CR = MI_{\text{corr}} / \rho nF \text{ -----(2)}$$

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 (96500 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 2.³⁹

The E_{corr} values of poly(C-abn) and poly(C-ppda) coated specimens shifted anodically. The significant anodic shift was observed for coated specimens. Maximum anodic shift was observed poly(C-abn) coated mild steel specimen. I_{corr} values the polybenzoxazine coated specimens are also reduced indicating that the corrosion resistance of the coated specimens were improved after coating (Table 3). Further, poly(C-abn) possesses the better corrosion resistance behaviour than that of poly(ppda). The results observed coincides with

that of the data observed in the EIS. The significantly enhanced corrosion resistance again reiterates the presence of triazine cross-linkages, which suppressed the anodic corrosion reactions (Figure 10). The poly(C-abn) coating offers better corrosion resistance when compared with similar types of benzoxazines studied and reported earlier.

Table 3. Calculated values of the corrosion parameters of the coated and uncoated mild steel specimens in 3.5 % NaCl solution from Tafel studies

Name of the sample	E_{corr} (mV)	I_{corr} (mA)	β_c (mV dec ⁻¹)	β_a (mV dec ⁻¹)	Corrosion rate mils year ⁻¹ (mpy)	Efficiency (%)
Bare MS	-618.48	4.012×10^{-5}	148.38	94.41	1.5542×10^{-4}	0
Poly(C-ppda)	-455.11	4.545×10^{-6}	169.96	105.26	1.7606×10^{-5}	88.93
Poly(C-abn)	-57.85	1.460×10^{-7}	97.13	98.43	9.6367×10^{-9}	99.63

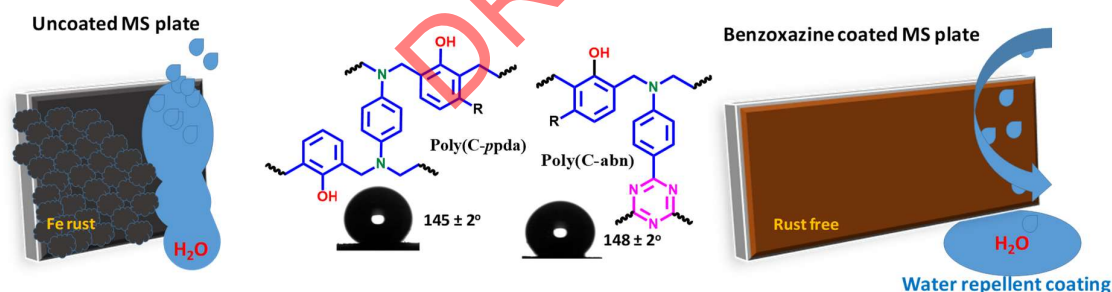


Figure 10. Illustration of water resistant benzoxazine coated MS specimen for corrosion protection.

Conclusion

The mono-functional benzoxazine was prepared using cardanol, 4-aminobenzonitrile and paraformaldehyde. The bi-functional benzoxazine was synthesised using cardanol, p-phenylenediamine and paraformaldehyde through solventless process. The molecular structure of synthesized monomers was confirmed by FTIR and ¹H-NMR spectral analyses.

The DSC traces confirmed the exothermic ring-opening polymerization reaction of oxazine moieties. The polymerisation temperature (T_p) of C-abn was found to be 280°C and that of C-ppda was about 237°C. It was observed that the bi-functional benzoxazine possesses the lower curing temperature than that of mono-functional benzoxazine. The formation of polybenzoxazine structure was confirmed by FTIR analysis after the thermal curing which ascertains the benzoxazine ring opening polymerisation. The thermal stability of cured poly(C-abn) and poly(C-ppda) were studied by TGA analysis. The char yield of poly(C-abn) and poly(C-ppda) at 850°C are noticed at 18 and 20%, respectively. The LOI value of poly(C-abn) and poly(C-ppda) calculated from char yield value at 850°C and were found to be 25 and 26 respectively. The value of water contact angle of poly(C-abn) and poly(C-ppda) are observed at 145° and 148° respectively. Data resulted from corrosion studies, it was noticed that the mild steel specimen coated with bio-based benzoxazine poly(C-abn) matrices exhibit an excellent resistance towards corrosion. The data obtained from the different studies, it is concluded that the cardanol based benzoxazines can be used in the form of sealants, encapsulants, adhesives, coatings and matrices in the fields of microelectronics and automobile applications for better performance.

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Conflict of interest

The authors declare no conflict of interest.

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