Vanillin derived partially bio-based benzoxazine resins for hydrophobic coating and anticorrosion applications: Studies on syntheses and thermal behavior.

Abstract

This study mainly concentrates on the synthesis, thermal, hydrophobic and anti-corrosion properties of sustainable vanillic acid based polybenzoxazines for water repellent coatings and anticorrosion applications. Structurally different benzoxazines were synthesized by reacting vanillic acid (VA) separately with different amines viz., cyclohexylamine (cha), dodecylamine (dda), furfurylamine (ffa), and 3-trifluoromethylaniline (tfma). The molecular structure of the synthesized monomers was characterized by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy and proton nuclear magnetic resonance spectroscopy (^{H}NMR). Thermal properties were also characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). From DSC analysis, polymerization temperature (T_p) of benzoxazines were found to be in the range of 203-245^{o}C. VA-ffa shows the lower polymerization temperature of 203^{o}C than that of other benzoxazine monomers. Typically, all the developed polybenzoxazines showed excellent thermal stability with initial decomposition temperatures over 250°C. Among the polybenzoxazines, poly(VA-tfma) exhibit a char yield of 43% at 850°C. The value of water interface angle noticed for polybenzoxazine ranges from 142° to 145°. Among the synthesized polybenzoxazines, poly(VA-tfma) showed excellent hydrophobicity with highest value of 145^{0}. In addition, hydrophobicity of the cured benzoxazine coated cotton fabric was tested for its durability at various time intervals. Further, from electrochemical impedance studies, poly(VA-tfma) exhibits better corrosion resistance behavior than that of poly(VA-cha), poly(VA-dda), and poly(VA-ffa). Data obtained from various studies suggested that vanillic acid based benzoxazine can be utilized for water resistant and corrosion prevention applications.

Keywords: Vanillic acid, curing behavior, water interface angle, hydrophobic cotton fabric, anticorrosion behavior.

Introduction

Mild steel (MS) is one of the most important materials used for domestic and industrial applications and is widely used in construction, petroleum processing, wastewater systems, etc. MS has tendency to undergo structural deterioration due to corrosion process. Hence, it needs surface protection to avoid deterioration, loss of strength and to improve its lifespan. Many approaches have been made to reduce and prevent the corrosion of metals and their alloys, such as organic and inorganic coatings. Although coatings are commonly used for corrosion protection, they may cause some environmental problems as they could contain number of

hazardous constituents, inhibitors, etc. It is well known that, the organic coatings have been applied to protect metal substrates from the severe corrosion environments. The hydrophobicity, water uptake, and mechanical properties of the organic coatings significantly influence their surface protection ability by extracting the metal surface from the corrosive electrolyte. Several organic polymers can be used to protect metals from corrosion, such as epoxy, polyacrylates, polybenzoxazine, etc. Many researchers in the recent years are focused their attention towards benzoxazine based coating materials, due to their excellent properties suitable for different industrial coating applications.

As an appealing replacement for conventional thermoset resins, polybenzoxazines have been evolved. The design of polybenzoxazines frequently targets bisphenols due to their availability. The development of bio-based polymers from phenolic monomers derived from lignin, such as vanillin, syringaldehyde, eugenol, vanillyl alcohol, vanillic acid, ferulic acid, etc., has received a lot of interest. It also successfully replaces and minimizes the use of fossil-based petroleum precursors and expected to significantly reduces the environmental pollution.

In recent years, lignin and its derivatives have shown potential as prospective source material for the development of wide range of bio-based products including antimicrobials, stabilizers, flame retardants and polymeric coatings. Among them, ortho-methoxy substituted phenolic compounds are an attractive source which includes phenolic compounds of vanillin family, i.e, vanillyl alcohol and vanillic acid. Vanillic acid, also named 4-hydroxy-3-methoxybenzoic acid, is a lignin-derived aromatic acid that can be oxidized from vanillin under strong oxidizing environment. Some researchers focused on vanillic acid derived polymeric materials including polybenzoxazines. Only few research has been made on vanillic acid based polybenzoxazines. The acidic functionality in vanillic acid is known to have an impact on the ring opening of benzoxazine and to significantly alter curing temperature.

In the current work, monofunctional benzoxazines from vanillic acid utilizing four distinct amines (cyclohexylamine, dodecylamine, furfurylamine, and 3-trifluoromethylaniline) and paraformaldehyde have been synthesized through Mannich condensation. The characterization of vanillic acid based polybenzoxazines, namely VA-cha, VA-dda, VA-ffa and VA-tfma were studied using modern analytical instruments. Thermal stability and cure behavior, hydrophobic behavior, and corrosion resistive behavior were studied and the data obtained are discussed and reported.

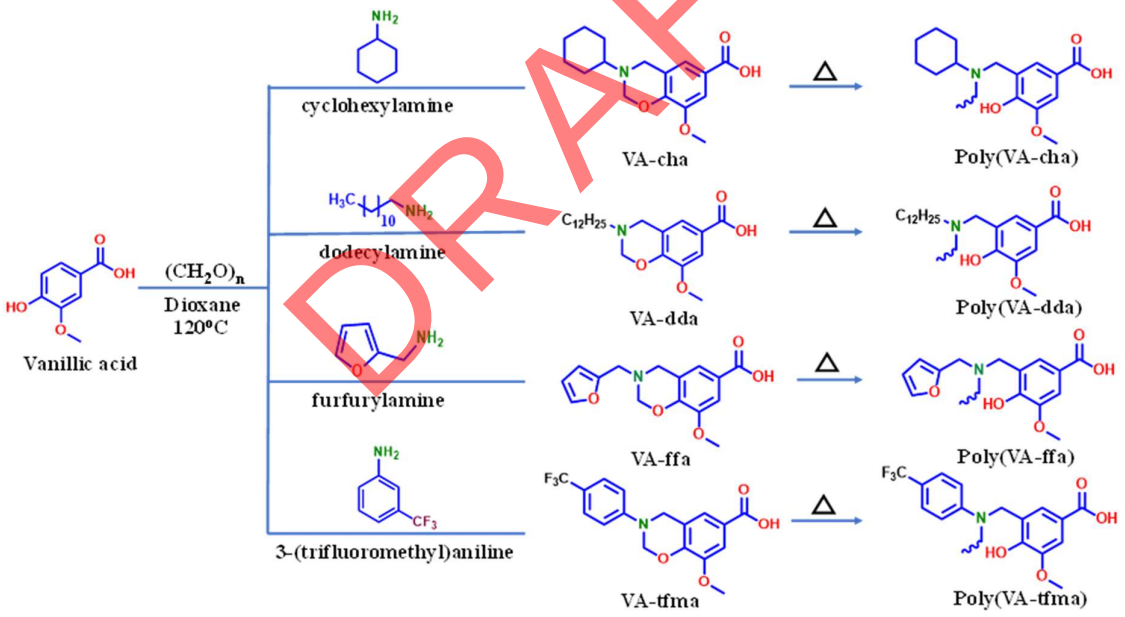
Experimental

Materials

Vanillic acid (Avra), furfurylamine (SRL, Mumbai), cyclohexylamine (SRL, Mumbai), dodecyl amine (TCI, India), trifluoromethyl aniline (Sigma-Aldrich, India) were purchased and utilized without any further purification. 1,4-Dioxane and ethyl acetate were obtained from SRL, Mumbai.

Syntheses of vanillic acid based benzoxazines

A mixture of vanillic acid, cyclohexylamine, paraformaldehyde was taken in a 100 mL round bottomed flask in a stoichiometric ratio of 1:2:1 in the presence of dioxane solvent. The content was gradually heated to 110°C under constant stirring. The progress of the reaction was monitored through TLC (Thin layer Chromatography). After the completion of the reaction, the reaction mixture was processed as per the reported procedure and referred to as VA-cha. The same procedure was repeated to synthesize other three amines namely furfurylamine, dodecylamine, trifluoromethylaniline based benzoxazines and are referred to as VA-ffa, VA-dda and VA-tfma (Scheme 1).



Scheme 1. Syntheses of vanillic acid (VA) based benzoxazines and polybenzoxazines.

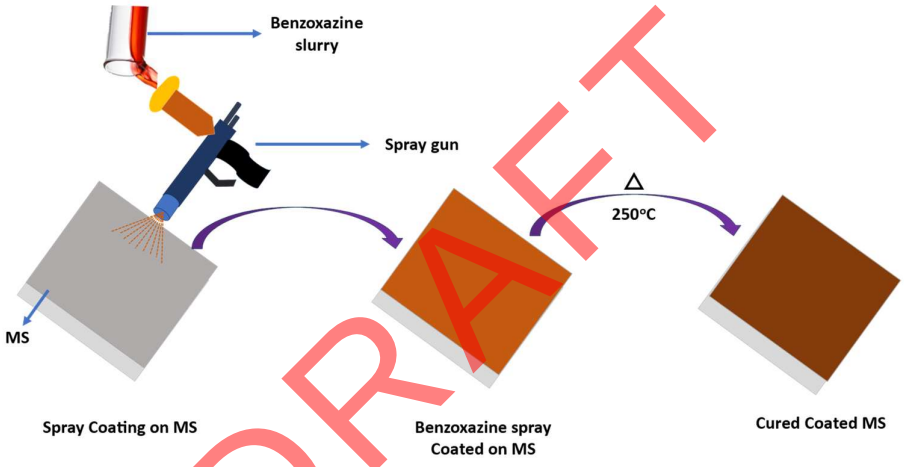
Polymerization of benzoxazine monomers to polybenzoxazines

Polybenzoxazines were prepared by thermal curing of the resulted benzoxazine monomers. The stepwise curing procedure was adopted for all benzoxazine monomers up to the bench mark of 250°C as per the standard report. At this temperature all the benzoxazine monomers

are expected to undergo ring opening reaction and leads to form corresponding polybenzoxazines (Scheme 1).

Preparation of benzoxazine coated mild steel

The mild steel plates(specimens) were first polished with emery paper and rinsed with ethanol to remove the surface impurities. The treated plates were then allowed to dry before being used for coating with benzoxazines. To coat the mild steel specimen, a slurry of the benzoxazine monomer was made with THF solvent and placed into a spray coater. The benzoxazine monomer VA-cha was sprayed onto the mild steel plate, then cured for one hour at 60°C. The stepwise curing procedure was adopted for the coated plates to undergo polymerization (Scheme 2). Similar process was followed for coating with other three benzoxazine monomers,namely VA-dda, VA-ffa and VA-tfma.



Scheme 2. Preparation of VA-benzoxazines coated MS.

Measurements

All the details about the instruments and measurements were given in the supporting information.

Results and discussion

ATR-FTIR studies of vanillic acid based benzoxazines

ATR-FTIR spectra recorded for the benzoxazine monomers are presented in Figure 1. The absence of a broad peak in the range of 3000-3500 cm^{-1} corresponding to -OH group indicates that the -OH has been involved in the formation of benzoxazines. The formation of oxazine ring is supported by the formation of new peak at 933 cm^{-1}. Appearance of peak at 1710 cm^{-1} indicates the presence of carbonyl stretching of carboxylic acid group present in the vanillic acid. The similarly the peaks observed in all the monomers between 2850 cm^{-1} and 2970 cm^{-1}

are responsible for the asymmetric and symmetric stretching vibration of methylene units present in aromatic and aliphatic groups.

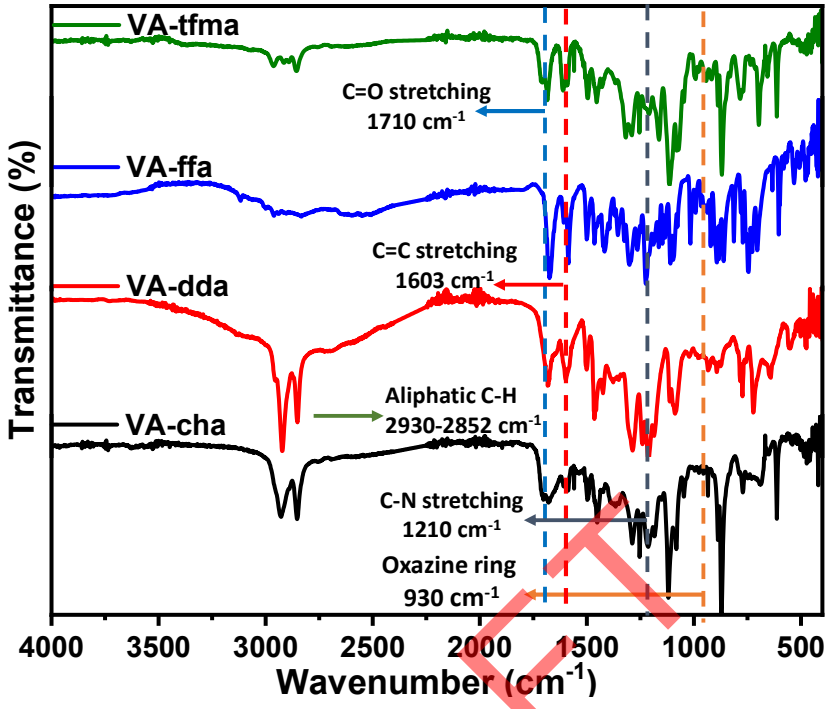


Figure 1. FTIR spectra of vanillic acid (VA) based benzoxazine monomers.

^{1}H-NMR spectral analysis

Figure 2, shows the proton ^{1}H-NMR spectra of all the synthesized benzoxazines. In common the methoxy group (-OCH_3) and the solvent peak corresponding to DMSO in all benzoxazines are observed at 3.6 ppm and 2.5 ppm respectively. The aromatic protons are appeared in the range between 6.8 and 8.0 ppm. The proton peaks attributed to methylene group (-N-CH_2-Ar) and O-CH_2-N group of oxazine ring are appeared at 4.0 ppm and 5.0 ppm respectively except for dodecylamine based benzoxazines, which appeared between 4.6 and 5.6 ppm. The acidic proton in the chemical structure of vanillic acid seems to be appeared at 12.5 ppm. The aliphatic protons present in the aliphatic amine based benzoxazines appeared in between 0.9 and 2.0 ppm. These results supports the syntheses of targeted benzoxazine monomers.

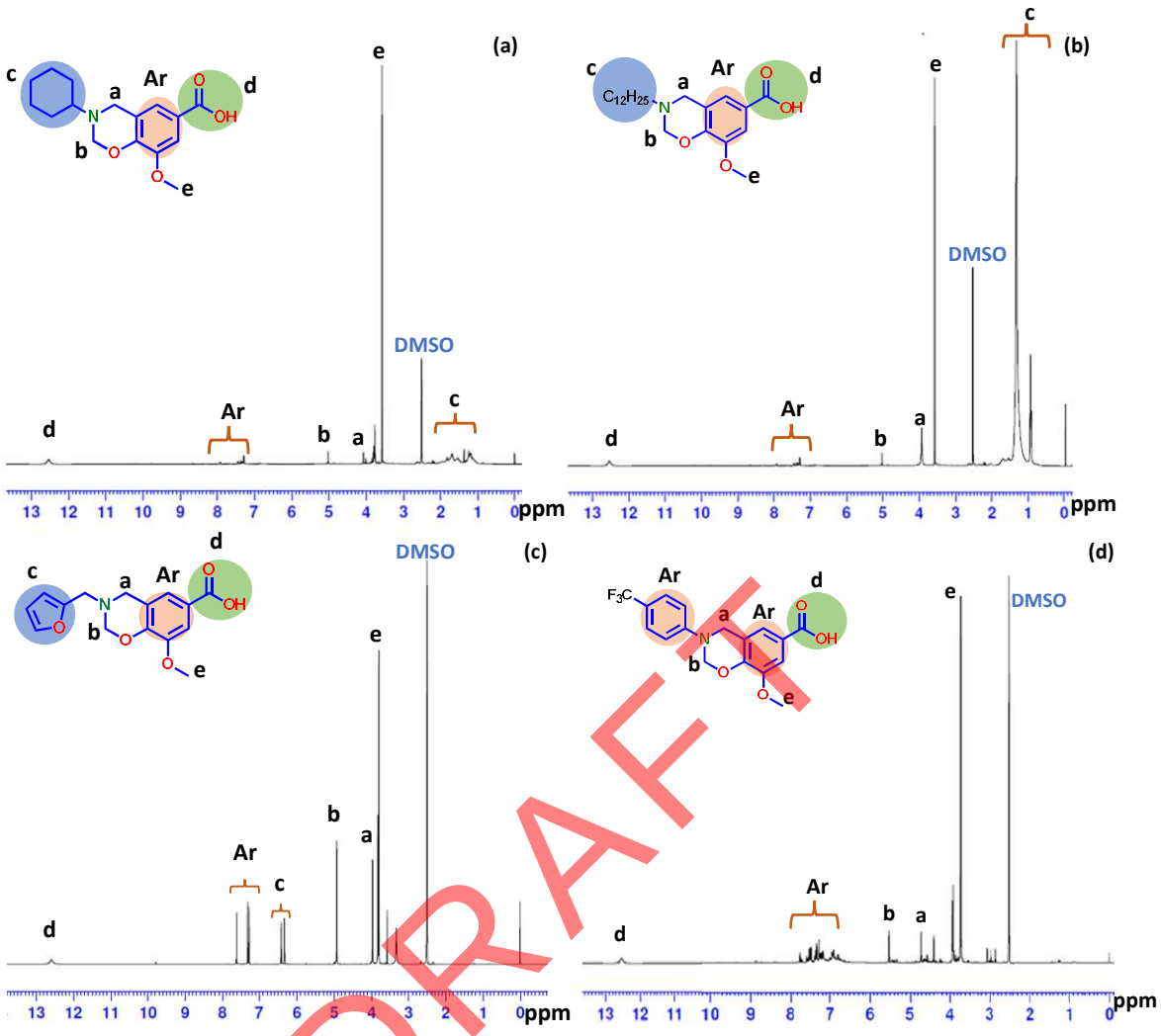


Figure 2. ^{1}H-NMR spectra of VA-benzoxazine monomers (a)VA-cha, (b)VA-dda, (c)VA-ffa and (d)VA-tfma.

Curing of VA-benzoxazines

The curing behaviour of the VA benzoxazines is presented in Figure 3. Curing parameters such as melting point, onset temperature (T_{onset}), offset temperature (T_{offset}), and polymerisation temperature (T_p) are presented in Table 1. The presence of electron withdrawing carboxyl substituent in vanillic acid triggers the ring opening reaction. The acidic functionality preferably interacts with oxygen atom in the O-CH_2-NH_2 monomer which leads to ring opening of benzoxazine monomers. Among the VA based benzoxazines, VA-ffa shows lower curing temperature of 203^{o}C than the rest of the benzoxazine monomers, this is due the presence of furan ring in its backbone with involves in the crosslinking of benzoxazines.

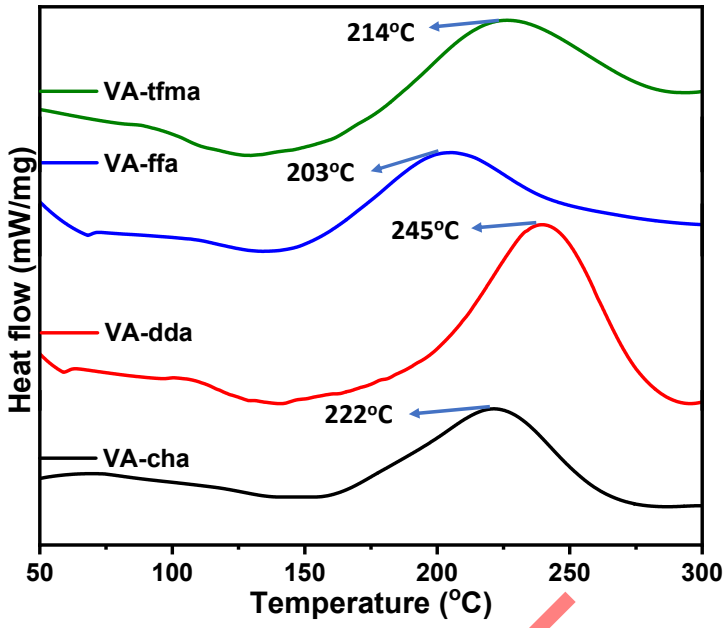


Figure 3. DSC thermograms of VA-benzoxazine monomers.

Table 1. Curing behavior of vanillic acid (VA) based benzoxazines

VA-benzoxazines	Curing characteristics at the rate of 10°C min^{-1}		
	T_{onset}	T_p	T_{offset}
VA-cha	158	222	272
VA-dda	186	245	289
VA-ffa	153	203	244
VA-tfma	162	218	269

Thermal properties of VA-benzoxazines

The thermal properties of the VA based polybenzoxazines were assessed using the data obtained from TGA. According to thermogravimetric analysis (TGA), the polybenzoxazines degrade in a single step, as represented in Figure 4 and results are presented in Table 2, which provides an overview of the thermal stability of polybenzoxazines. Thermal behavior results on comparison infers that poly(VA-tfma) is better thermally stable ($T_{5\%}$-266 ^{0}Cand $T_{10\%}$-288^{0}C) than that of other polybenzoxazines (Tablbe2). This may be explained due to the influencing effect of occurrence of hydrogen bonding interaction with in the poly(VA-tfma) molecules, the post-curing reaction, expected to enhance crosslinking density and the presence of three fluorine atoms in 3-trifluoromethylaniline may also responsible for the increasing the residual char yield ie., 43% in the case of poly(VA-tfma) (Table 2).

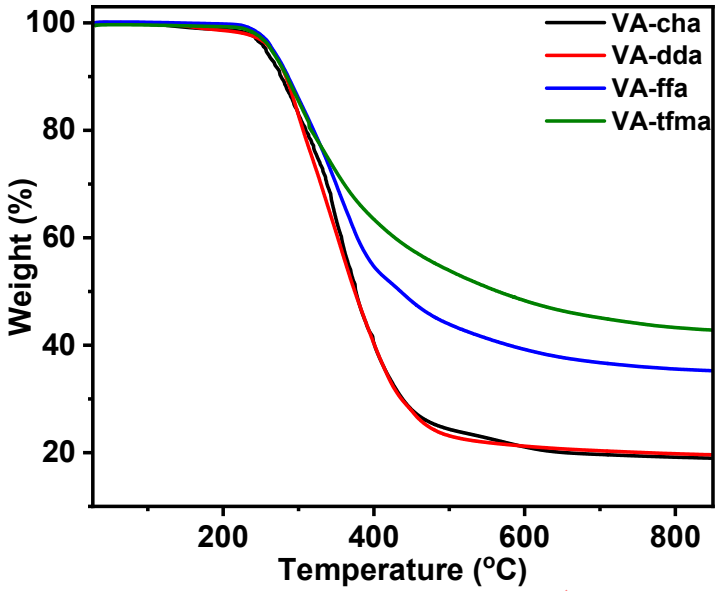


Figure 4. TGA thermograms of VA-polybenzoxazines.

Table 2. Thermal stability parameters of polybenzoxazines.

VA-Polybenzoxazine	5 wt% loss (°C)	10 wt% loss (°C)	T_{max} (°C)	CY % at 850°C	LOI	WIA
Poly(VA-cha)	257	276	355	19	25	142
Poly(VA-dda)	262	282	347	20	26	144
Poly(VA-ffa)	263	285	331	35	32	143
Poly(VA-tfma)	266	288	313	43	39	145

FTIR analysis of VA based polybenzoxazines and VA-tfma coated cotton fabric.

Figures 5(a) and (b), present the FTIR spectra of VA polybenzoxazines and VA-tfma coated cotton fabric respectively. Upon polymerization of benzoxazine to polybenzoxazine, the ring opening of benzoxazine occurs and is evidenced from the appearance of broad peak which is obvious at 3000 cm^{-1} corresponds to -OH group of phenol and the absence of peak at 930 cm^{-1} infers the complete ring opening of oxazine ring led to the formation of polybenzoxazine. The FTIR spectra of uncoated and coated cotton fabric are presented in Figure 5(b). To confirm the adherence of coating, the VA-tfma coated cotton cloth was examined using FTIR, and it was ascertained that the peak appeared at 930 cm^{-1} corresponds to benzoxazine. The disappearance

of the benzoxazine peak in the cured VA-tfma coated cotton fabric indicates that it was fully cured.

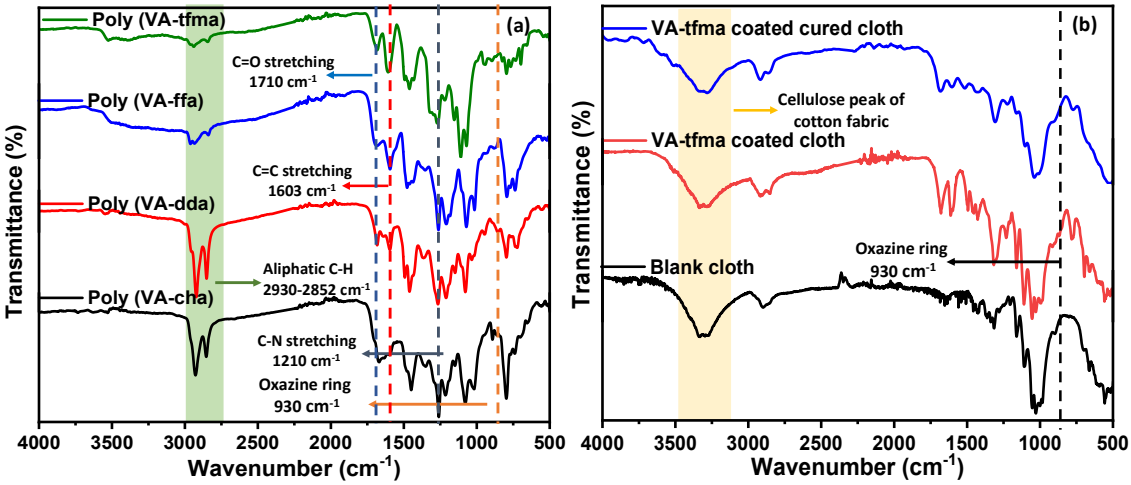


Figure 5. (a) FTIR spectra of VA-polybenzoxazines and (b) VA-tfma coated cotton fabric.

Water interface angle (WIA) studies on VA based polybenzoxazines

Contact angle provides whether the material has tendency to absorb (wetting) water (hydrophilic) or it repels (beading) water (hydrophobic), this behavior was assessed from sessile-drop goniometric method. The synthesized polybenzoxazines were exposed to the water droplets where its edge comes in contact with surface of polybenzoxazines. Water droplets formed sphere on all polybenzoxazines which barely touched the surface hence all polybenzoxazines studied in the present work are hydrophobic in nature. The water interface angle images and the values obtained are presented in Figure 6 and Table 2 respectively. Among the polybenzoxazines studied, poly(VA-tfma) exhibits the highest value of water contact angle of 145°. The increasing order of hydrophobicity is as follows: poly(VA-tfma) > poly(VA-dda) > poly(VA-ffa) > poly(VA-cha).

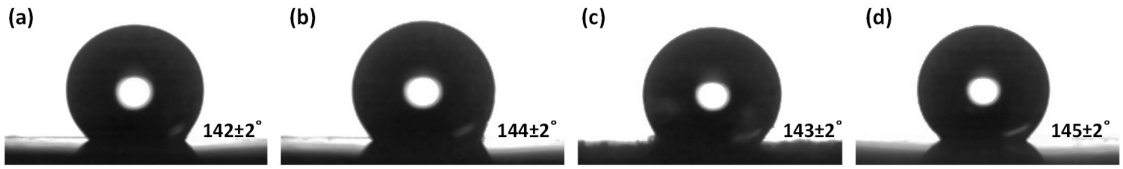


Figure 6. Water interface angle images of (a) poly(VA-cha), (b) poly(VA-dda), (c) poly(VA-ffa) and (d) poly(VA-tfma).

Contact angle durability test for benzoxazine coated cured cotton fabric

To study the coating's hydrophobic behavior, the best-performing benzoxazine sample based on water interface angle measurement, VA-tfma, was chosen. The benzoxazine monomer (VA-tfma) was dissolved in THF and sprayed to the alkaline-treated cotton fabric. The coated cotton fabric was dried at 60°C to remove moisture before being subjected to 230°C for 3 minutes to undergo crosslinking and curing. The completion of curing was confirmed by FTIR spectroscopy, as shown in Figure 5(b). The hydrophobicity of the cured coated fabric was tested using a goniometer, and the durability of the cured coated cloth was examined at various time intervals. The water interface angle value was retained even after 3 washings of coated fabric with n-hexane solvent. After that, it gradually decreased with a difference of 6-points from the initial contact angle as shown in Figure 7.

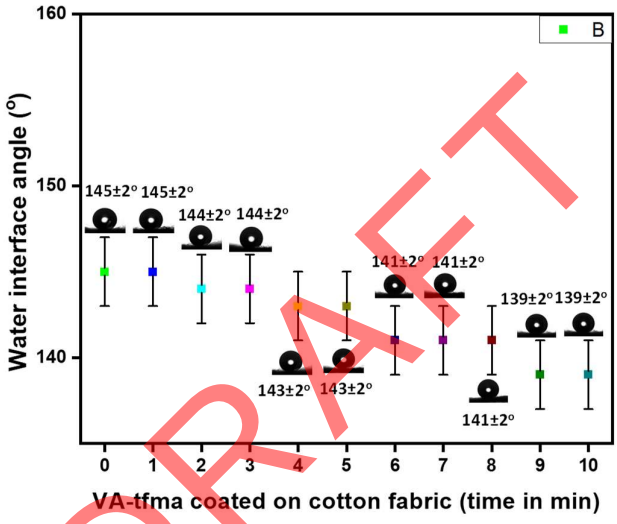


Figure 7. Images and values of durability test on VA-tfma coated cotton fabric.

Corrosion resistance of VA based benzoxazines coated and uncoated MS

Electrochemical impedance spectroscopy (EIS) measurements were used to assess the corrosion resistance of uncoated and VA based benzoxazines coated mild steel specimens. The coated specimens, poly(VA-cha), poly(VA-dda), poly(VA-ffa), and poly(VA-tfma), which were cured at 250°C. The cured MS specimens were immersed in a 3.5% NaCl solution and tested for corrosion protection efficiency. Poly(VA-tfma) coated MS specimen exhibit exceptional corrosion resistance on mild steel than that of other benzoxazines. The OCP values of coated specimens with polybenzoxazines, poly(VA-cha), poly(VA-dda), poly(VA-ffa), and poly(VA-tfma) decreased significantly as compared to that of bare MS specimen.

The OCP shift, which steadily increased demonstrated the coatings' excellent resistance towards corrosion. This behavior arises from the formation of impervious and adherent coating

on the surface and reducing the permeability of the corrosive medium into the film, poly(VA-tfma) coated specimen possesses a higher anodic shift of OCP values. Figure 8(a) presents the Nyquist plots for four different polybenzoxazines coated mild steel specimens including uncoated mild steel specimen. The plots were drawn using the data obtained from the EIS. Figure 9, shows an equivalent circuit model that is used to fit the EIS data.

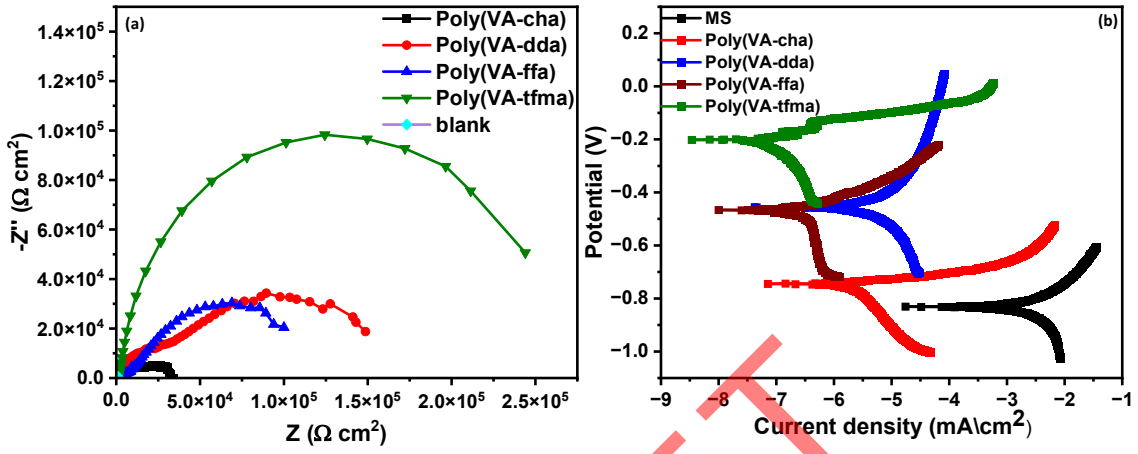


Figure 8. (a) Nyquist plots and (b) Tafel plots of MS bare, polybenzoxazine coated specimens in 3.5% NaCl solution.

The solution resistance (R_s), charge transfer resistance (R_{ct}), and constant phase element (CPE), which is coupled in parallel with the charge transfer resistance element, were used in a similar circuit. Therefore, pure double layer capacitance (C_{dl}) in this case is best described by a transfer function equation 1.

$$Z_{CPE} = Y_0^{-1}(j\omega)^{-n} \quad \text{.....(1)}$$

When, n = 0, the CPE is a pure resistor, when n = +1, it is a pure capacitor, and when n = -1, it is an inductor. Y_0 is the admittance of the corroded system at 1 rad s^{-1}. The value of angular frequency can be determined using the equation 2.

$$\omega = \left(\frac{1}{R_{ct}Y_0}\right)^{1/n} \quad \text{.....(2)}$$

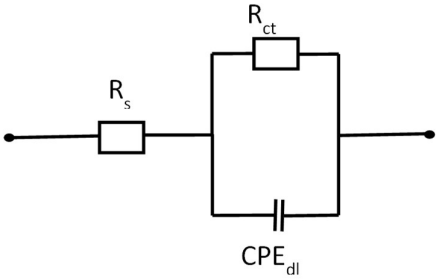


Figure 9. Electrical circuit model used to fit EIS results.

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 (Ω cm^2)	R_{ct}(Ωcm^2)	$Y_{0,dl}$ ($\mu s^n \Omega^{-1}$ cm^{-2})	n_{dl}	CPEdl (μF cm^{-2})
Bare	18	1365	82.90	0.88	69.8
Poly(VA-cha)	54	1.1 x 10^5	23.60	0.87	15.6
Poly(VA-dda)	84	1.5 x 10^5	18.60	0.89	15.3
Poly(VA-ffa)	25	2.4 x 10^5	4.58	0.84	10.5
Poly(VA-tfma)	22	3.2 x 10^4	61.40	0.91	41.2

In comparison to the bare MS, the polybenzoxazines coated MS specimens possess the higher values of R_{ct}. Corrosion protection activity has been improved for the polymeric matrix coated on the mild-steel specimen. The maximum values of R_{ct} and R_f that obtained for mild steel specimens coated with poly(VA-tfma) are presented in Table 3. Benzoxazine coatings may exhibit better corrosion resistance due to cross-linking in the polymer coating.

The Tafel plots of the MS specimen coated with poly (VA-cha), poly (VA-dda), poly (VA-ffa), and poly (VA-tfma) are shown in Figure 8(b). Using the I_{corr} results, the corrosion rate (CR, measured in millimetres per year, mm $year^{-1}$) has computed. The E_{corr} values have been shifted anodically for the specimens coated with poly (VA-cha), poly (VA-dda), poly (VA-ffa), and poly (VA-tfma). A mild steel specimen coated with poly(VA-tfma) showed the highest anodic shift than that of other three specimens. I_{corr} values of the polybenzoxazine-coated specimens are decreased from the bare MS specimen, indicating an improvement in the coated specimens' corrosion resistance (Table 4). Further, poly(VA-tfma) has a better corrosion resistant behavior than that of poly(VA-cha), poly(VA-dda), and poly(VA-ffa). The results obtained are fall in-line with the data obtained from EIS studies.

Table 4. 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 (mpy)	Efficiency (%)
Bare MS	-624.62	7.214×10^{-3}	155.8	96.32	2.662×10^{-1}	0
Poly(VA-cha)	-741.25	5.547×10^{-4}	145.6	84.11	8.654×10^{-2}	92
Poly(VA-dda)	-451.57	6.492×10^{-4}	135.7	102.5	7.584×10^{-3}	91
Poly(VA-ffa)	-466.21	4.551×10^{-4}	141.2	132.4	3.221×10^{-3}	93
Poly(VA-tfma)	-205.41	1.441×10^{-4}	121.5	74.21	8.224×10^{-4}	98

Conclusion

Vanillic acid based benzoxazine monomers were synthesized using four structurally different amines, namely cyclohexylamine, dodecylamine, furfurylamine and 3-trifluoromethylaniline with paraformaldehyde through Mannich condensation. Among the benzoxazines synthesized poly(VA-tfma) possesses the higher char yield of 43% and LOI value of 39, than those of other polybenzoxazines and also satisfy the criterion for flame retardancy, therefore they can be employed as a self-extinguishing material. The hydrophobic and the anti-corrosion studies infer that poly(VA-tfma) exhibits the highest value of water contact angle and better corrosion resistance than those of other benzoxazines. The VA-tfma benzoxazine coated cotton fabric has found to be a better hydrophobic material. It is concluded that, the vanillic acid based polybenzoxazines can be used as potential class of materials considered for water repellent, and corrosion-resistant applications.

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