

Synthesis and Characterization Bio-based Benzoxazine Oligomer from Cardanol for Corrosion Resistance Application

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ABSTRACT

The Mannich-like condensation of a cardanol, paraformaldehyde and N,N'-Bis(2- aminoethyl)ethane 1,2-diamine were carried out to synthesized the amine functional benzoxazine(Bnz) resin. The amine functionality of Bnz resin was evaluated by physiochemical method and structure was characterized using Fourier Transform Infrared (FTIR) and ¹H- Nuclear Magnetic Resonance (¹H-NMR) spectroscopy. The added functionality into the Bnz resin backbone was utilized to modify the Bnz resin structure by glycidoxypyltrimethoxy silane (GPTMS) in various proportions. The results revealed that the silane modified Bnz coatings have improved mechanical, chemical, and solvent resistance properties as compared to the neat Bnz coating. The gel and water absorption of polyamidecured coatings has been also evaluated. Furthermore, the cured films have been evaluated for glass transition temperature (T_g) by differential scanning calorimeter (DSC). The corrosion resistance properties were studied by salt spray and electrochemical analysis. It was observed that highly cross-linked structure of the GPTMS modified Bnz coatings enhanced the barrier protection to corrosive species.

Keywords: Cardanol; Benzoxazine resin; Silane Modification; Corrosion resistance.

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INTRODUCTION

Benzoxazine (Bnz) resin is nitrogen containing heterocyclic ring and good substitute to high-performance phenolic resin for high temperature coating applications. Bnz resin is distinguished by the presence of a Mannich base bridge and it is synthesized by Mannich-like condensation reaction between a phenolic compound, formaldehyde and amines. The Bnz resin may be viscous or thin liquid product and polymerization takes place at high temperature by the cationic ring-opening polymerization. Bnz resin during the polymerization does not generate any byproduct or volatile gas. Bnz resin has found application opportunities in the high performance matrices in aerospace, automotive, flame-retardants coating and electronic industries etc.¹

The Bnz resin is well known for excellent mechanical, electrical, and thermal properties as well as less water absorption. Even though, Bnz resin is not favorable for the coating application due to the high curing temperature and brittleness of the film. To overcome the negative aspect, the additional functional group in Bnz resin structure such as amino, amine, cyano and hydroxyl can be incorporated. The extra functionality incorporated into the Bnz resin may be achieved through the utilizing the multifunctional phenolic molecule with a monoamine, or with a multifunctional amine paired with a mono-phenol. This functionality is used for the synthesis of Bnz-based composites and alloys or copolymer with more flexible resin to enhance the coating properties. The most of the Bnz resin is synthesized from organic based raw materials and they have number of health related issues. Comparatively, renewable materials are easy to handle with no or less toxicity and health-related issues. Numbers of authors have published paper on Bnz resin synthesized from the bio based materials such as diphenolic acids, cardanol, vanillin, guaiacol and eugenol.²

The corrosion is the most critical issue in front of human being and annual cost of corrosion worldwide is estimated approximately US\$ 1.8 trillion.³ Generally, organic coatings have been employed to protect metal substrates from the versatile corrosion environments during their service life. The hydrophobicity, water uptake and mechanical properties of the organic coatings influence its ability by isolating the metal surface from corrosive electrolyte. Bnz coating is known for low water absorption, low surface free energy and excellent dielectric properties.⁴ The low surface free energy of Bnz coatings plays a vital part in the corrosion resistant performance of coatings. The main purpose of this work is to improve corrosion resistance properties of Bnz coating by synthesis of Bnz resin with added functionality. This functionality is used for modification of the resin backbone with silane in various percentages from 10, 20, 30 and 40 % with respect to the amine value. The silane modified Bnz coatings showed the dual cross-linking network of Bnz and Si–O–Si linkage. The changes in surface properties of coatings were characterized for mechanical, chemical, water absorption, gel content and solvent resistance properties. Corrosion resistance of coatings was studied by salt spray and electrochemical techniques.

EXPERIMENTAL PROCEDURE

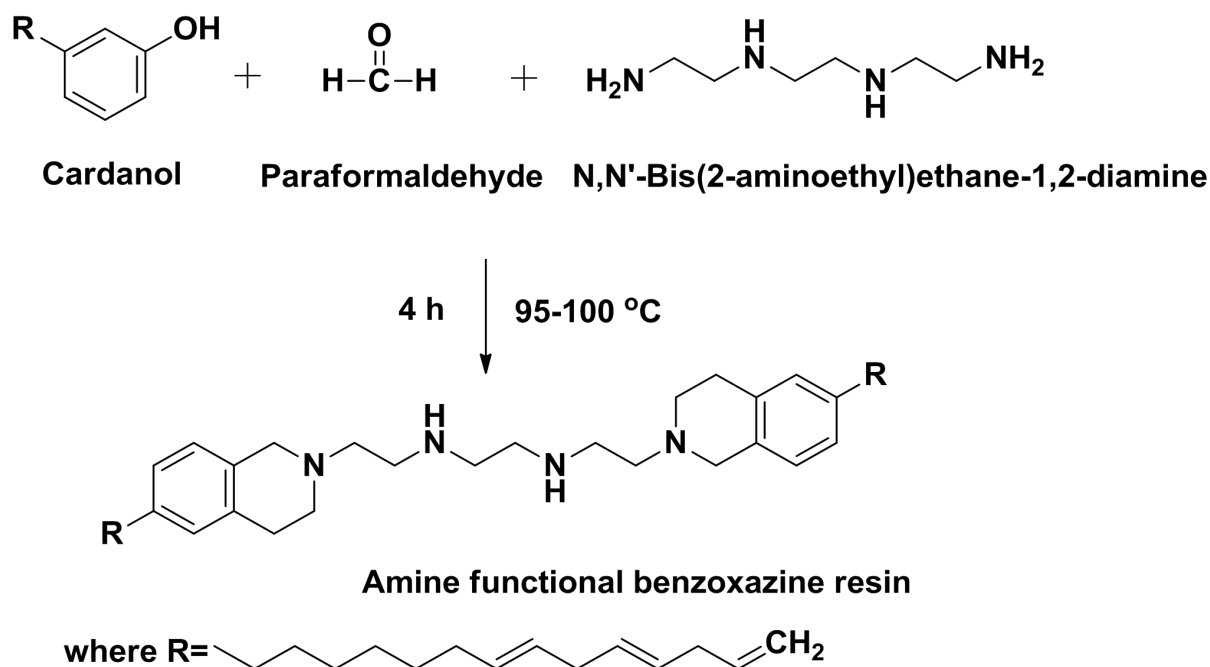
SYNTHESIS OF BNZ RESIN:

The solvent free synthesis reaction of amine functional Bnz resin from paraformaldehyde, *N,N'*-Bis(2-aminoethyl)ethane-1,2-diamine and cardolite NC-700 monomer is shown in scheme 1 and detailed procedure described below.

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A four-neck flask was charged with cardanol (0.114 mol, 34.73 gm) and paraformaldehyde (0.229 mol, 6.87 gm) at room temperature assembled with a thermometer, dean stark apparatus, nitrogen inlet and a mechanical stirrer. The reaction mixture mechanically stirred at 500 rpm and dropwise addition of *N,N'*-Bis(2-aminoethyl)ethane-1,2-diamine (0.057 mol, 8.38) over the period of 30 min done. Then reaction mixture was gradually heated up to 95-100 °C and continued at the same temperature for 4 h. During this period, the red color reaction mixture turned into dark maroon color. Then heating stopped and the reaction mixture temperature was brought down to room temperature. The maroon color liquid product dissolved in chloroform and repeatedly washed with water to remove the unreacted diamine and paraformaldehyde. The organic layer was dried over anhydrous sodium sulfate and filtered the product. Chloroform was removed by using a rotary evaporator.



Scheme 1. Synthesis reaction of amine functional Bnz resin.

SILANE MODIFICATION OF BNZ RESIN:

The modification of synthesized amine functional Bnz resin was done by using GPTMS coupling agent in various proportions as 10 to 40%. The calculated amount of amine functional Bnz resin and GPTMS added in four-neck flask assembled with a thermometer, water condenser, nitrogen inlet and a mechanical stirrer. Xylene used as the solvent and mixture heated at 60 °C for the three hours under constant stirring. FTIR spectroscopy was used to characterize the amine functional Bnz resin and modified amine functional Bnz resin.

RESULTS

The structure of amine functional Bnz resin characterized by FTIR analysis is as shown in Fig. 1. The FTIR spectrum of amine functional Bnz resin shows peaks at 1270, 1112 and 992 cm^{-1} which are attributed for asymmetric stretching of C-O-C, (trisubstituted benzene ring), symmetric stretching of C-O-C and trisubstituted benzene ring of benzoxazine ring respectively. The amine functional Bnz resin spectra display the peaks at 1154 cm^{-1} and 3287 cm^{-1} attributed for C-N and N-H stretching respectively. The peak at 1371 cm^{-1} is attributed for the C-H deformation vibration. Other band at 2851, 2923 and 3008 cm^{-1} are owing to the asymmetric and symmetric stretching vibrations of CH_2 of oxazine ring as well as alkyl side chain of cardanol. The characteristic absorption band of cardanol in the range 3300-3500 cm^{-1} due to the phenolic hydroxyl group was absent in amine functional Bnz resin spectra. The FTIR result showed that Bnz resin was successfully synthesized from cardanol and it may be conclude that cardanol based Bnz resin has amine functionality. Bnz resin backbone was modified by using GPTMS with various proportions to enhance the coating properties. The Fig. 2 showed the FTIR spectra of Bnz and GPTMS modified amine functional Bnz resins. The FTIR analysis GPTMS modified Bnz resin spectra shows the same absorption peak as Bnz resin spectra. However, GPTMS modified Bnz resins FTIR spectra show additional broad absorption band at 3350-3500 cm^{-1} for the hydroxyl group of GPTMS. Hence, it may be conclude that the Bnz resin backbone was successfully modified with GPTMS.

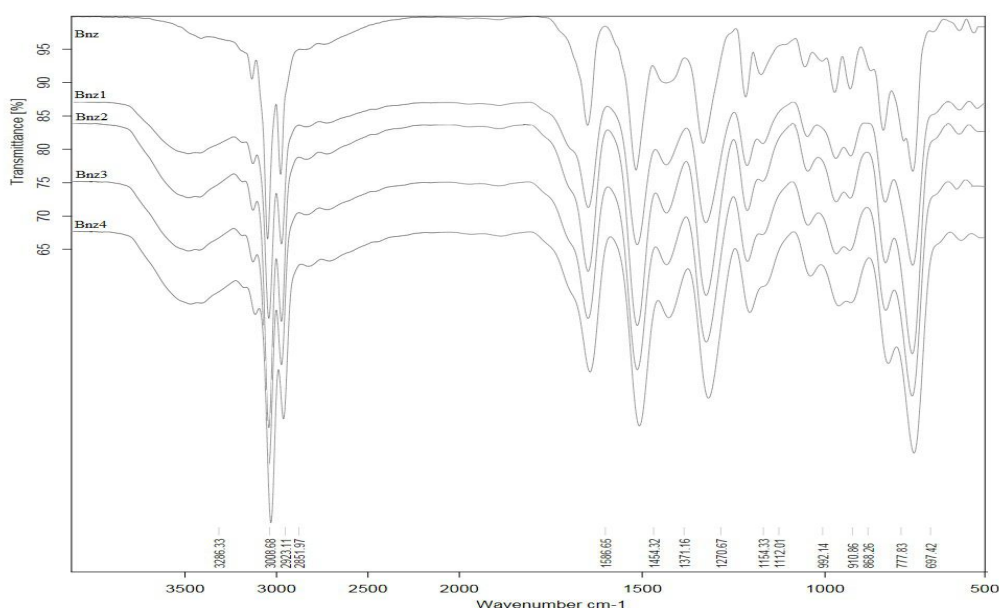


Figure 1: FTIR spectra of Bnz resin and silane modified Bnz resin at various proportions

The ^1H -NMR analysis of cardanol and cardanol based amine functional Bnz resin as shown in Fig. 2. The aromatic protons are observed at 7.1 ppm and 6.60 ppm for triplet and doublet respectively. The peak at 5.85 is due to vinyl double bond ($\text{C}=\text{CH}$) protons of long alkyl side chain originally present in cardanol. The other peaks at 2.1 and 2.85 ppm are assigned to the methylene protons attached to the vinyl double bond. The NMR spectrum of amine functional Bnz resin is shown singlet characteristic oxazine ring protons at 3.70 ppm and 4.80 ppm for $\text{Ar-CH}_2\text{-N}$ and $\text{Ar-O-CH}_2\text{-N}$

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respectively. The sharp peak is observed at 3.35 ppm for the amine proton. Thus from $^1\text{H-NMR}$ spectrum data, it can be concluded that Bnz resin with amine functionality was successfully synthesized. The T_g values for Bnz, Bnz1, Bnz2, Bnz3 and Bnz4 coatings as 80, 91, 92, 94 and 102 $^\circ\text{C}$ respectively. The silane acts as coupling agent and increases the cross-linking density of cured coating. Subsequently, T_g of coatings was improved due to the increased in cross-linking. In addition, high thermal stability of C-Si-O bond also enhances the thermal stability. Further, free hydroxyl groups present in the silane molecules create a hydrogen bonding in same or with other molecules; which can be considered as effective physical cross-linker. Due to this segmental and chain mobility of the polymer was reduced, thus increasing the T_g significantly.

Coating Preparation

The MS panel was cleaned by using solvent to remove oil, grease and scrub the metal surface by using sandpaper to enhance the adhesion. Bnz and silane modified Bnz resins were mixed with xylene to gain application viscosity. The mixed formulations were applied onto the MS panel by flow coating method and thermally cured at 200 $^\circ\text{C}$ for 3 h. The surface uniformity was checked by dry film thickness (DFT) gauge.

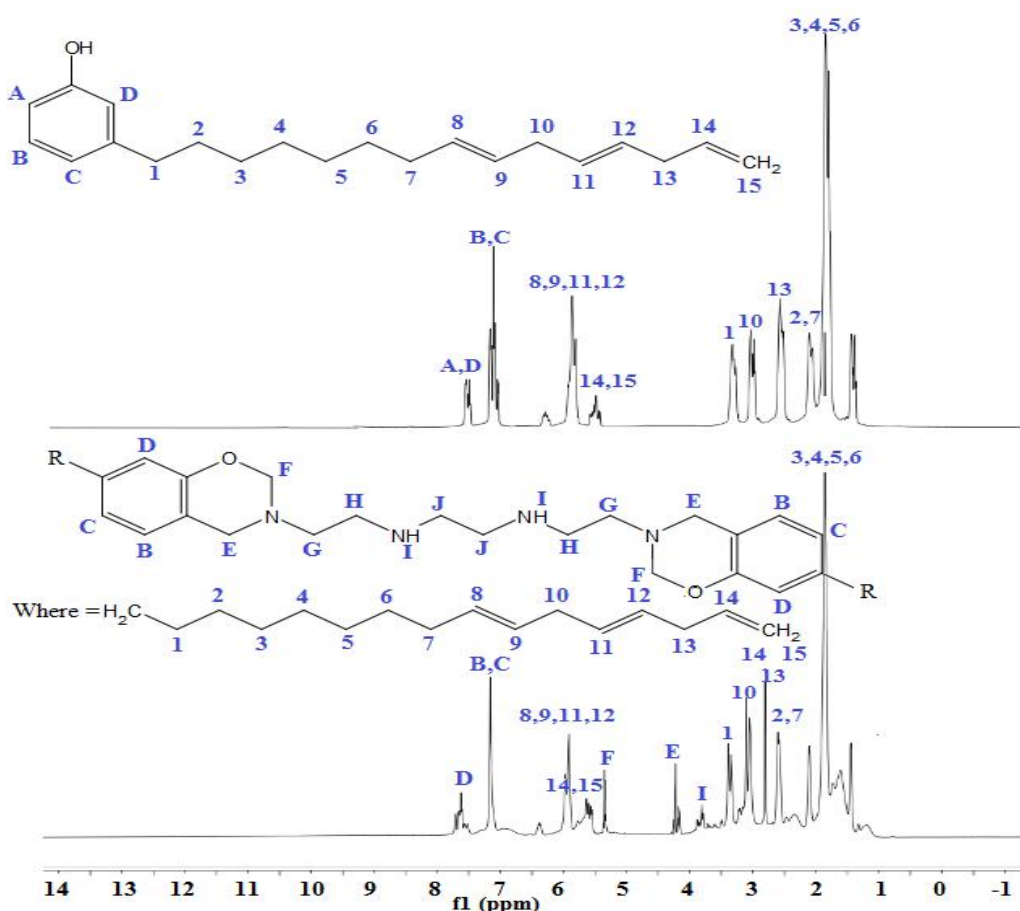


Figure 2: $^1\text{H-NMR}$ analysis of Cardanol and amine functional Bnz resin.

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Mechanical Properties

The thermally cured coatings were evaluated for various mechanical properties and results given in the table 1. The coating showed good cross-cut adhesion to the metal substrate and this is due to the long aliphatic chain of cardanol in Bnz coating. In addition, hydroxyl groups of silane also enhance the adhesion of coatings to the metal substrate via forming the hydrogen bond. The coatings were evaluated for flexibility using a conical mandrel and tests show improvement in flexibility with silane modification. Further, hardness properties of coating were evaluated by pencil and scratch resistance test. The results show that all Bnz coatings have good hardness properties due to the high cross-linking density. Coating hardness is increased with the silane modification; increased proportion of silane in Bnz coating increases the cross-linked networks. Impact resistance is a very important phenomenon in governing the life of a coating. Bnz3 and Bnz4 coatings show improved impact resistance as compared to the Bnz coating. This could be attributed due to silane modification and Bnz resin backbone carrying the free hydroxyl groups along the chain that form the hydrogen bonds with one another and increase the cohesive strength of coatings. The adhesive properties of the Bnz and silane modified coating on MS panel were also estimated by a pull off adhesion test. The silane modified coatings exhibit highest pull off strength as compared to Bnz coating. However, as the silane modification percentage increases in coating system the pull off strength improved and this could be attributed due to the free hydroxyl groups present along the chain that form hydrogen bonds with the metal substrate.

Table 1 Mechanical properties of Bnz and silane modified coatings

Coating Properties		Bnz	Bnz1	Bnz2	Bnz3	Bnz4
DFT (Micron)		55-65	60-70	55-65	55-70	50-60
Pencil Hardness		3H	4H	4H	5H	6H
Scratch Hardness (gm)		2200	2450	2350	2500	2650
Cross-cut adhesion		5B	5B	5B	5B	5B
Flexibility (mm)		3 mm	2 mm	0 mm	0 mm	0 mm
Impact Test (lb.cm)	Intrusion	96	106	104	108	112
	Extrusion	60	64	68	74	72
Pull of adhesion Test (MPa)		1.54	1.66	1.72	1.94	2.12

Chemical and Solvent resistance of coatings

Acid (5% HCl) and alkali (5% NaOH) resistance of Bnz and silane modified Bnz coatings were evaluated for 24 h. All coatings have good resistance to the chemical. This could be attributed due to the presence of aromatic ring structure in coating backbone has been greatly enhancing the chemical resistance. The GPTMS has ability to coupling the two Bnz molecules and increases the cross-linking density. The penetration of acid and alkali solution into the cured coating becomes difficult. Scrub resistance of coating was studied using xylene, methanol and acetone and change in coating property of film. The solvent scrub resistance properties improved with silane modification. This silane modified coatings have dual cross-linking networks of Bnz and Si-o-Si linkage. Hence, coating show the higher resistance to the penetration of solvents. Further, free hydroxyl groups of silane along the chain backbone create a hydrogen bonding in same or with other molecules; which can be considered as effective physical cross-linker that enhanced the solvent resistance properties with increasing the silane proportions.

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Corrosion resistance properties of coatings

The salt spray analysis of coating of each system has been carried to evaluate anticorrosive performance up to 750 hrs of exposure. Corrosion is deterioration of a metal by chemical or electrochemical reactions with its environment. The images of each panel before and after salt spray testing are shown in Figure 3. It is clearly seen from Figure; the corrosion spreading along the cross-cut was more in Bnz coating compared to silane modified Bnz coatings. The corrosion resistance property of coating improved as silane proportion increased. This could be due to the silane acts as coupling agent that combine the two Bnz molecules and increases the three-dimensional cross-linked structure via Si-O-Si linkage. The permeation of water molecules suppressed by the dense dual cross-linked network of cured coatings and hence barrier properties of coatings increase to the corrosion environments.⁵ Hence, we conclude that the silane modification of Bnz coatings prevented the penetration of corrosion species at surface and exhibited good corrosion resistance properties. The cured coatings were evaluated for the corrosion resistance properties using electrochemical analysis in 3.5 weight % NaCl electrolyte solution at room temperature. The exposed area of working electrode to the electrolyte was 1 X 2 cm² and electrochemical window was -1.5 to 0.5 V with 0.01 mV/s scan rate in all cases. In this experiment uncoated and coated mild steel panel strip are used as working electrode, while pt and Ag/AgCl were used as counter and reference electrodes respectively. The electrochemical analysis results are as shown in Figure 4. The E_{corr} and I_{corr} value was used to calculate the corrosion rate of coatings by using Eq. (1).

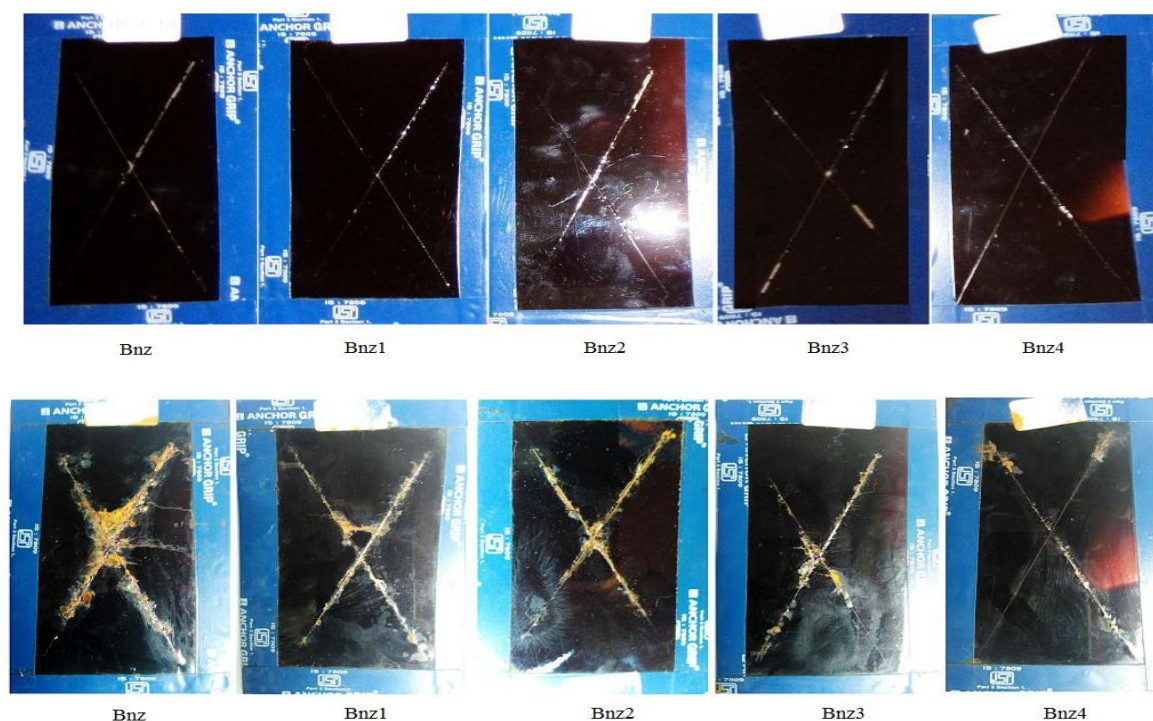


Figure 3: Coating surface before and after the salt spray immersion in 3.5% NaCl solution; (a) Bnz, (b) Bnz1, (c) Bnz2, (d) Bnz3, and (e) Bnz4

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The calculated corrosion rate value (table 5) of bare metal, Bnz, Bnz1, Bnz2, Bnz3 and Bnz4 coatings such as 4.988, 2.265, 1.577, 1.496, 1.053 and 0.876 mmpy respectively. It is due to the dual cross linked structure formed by homopolymerization of Bnz as well as the Si-O-Si linkage of GPTMS. The free hydroxyl groups in backbone of Bnz molecules chemically adsorbed onto the metal substrate and coating adhesion property with metal enhanced. Therefore, transport rate of corrosive species into the coating become difficult. Hence, Bnz4 coating has shown the highest barrier resistance properties towards the corrosion.

Where I_{corr} = corrosion current (A), K = constant, EW = equivalent weight (in g/equivalent), D = density (g/cm^3), A = Exposed sample area to electrolyte (cm^2), CR is in millimeter per year (mmpy).

Table 2 Tafel plot analysis of Bnz and silane modified coatings

Coating	E _{corr} (mV)	I _{corr} (μA)	Corrosion rate (mmpy)
Bare Metal	-1 111.887	874.32	4.988 02
Bnz	-1 109.182	397.091	2.265 41
Bnz1	-1106.625	276.483	1.577 34
Bnz2	-1100.205	262.381	1.496 89
Bnz3	-1134.863	184.741	1.053 95
Bnz4	-1 121.256	153.565	0.876 092

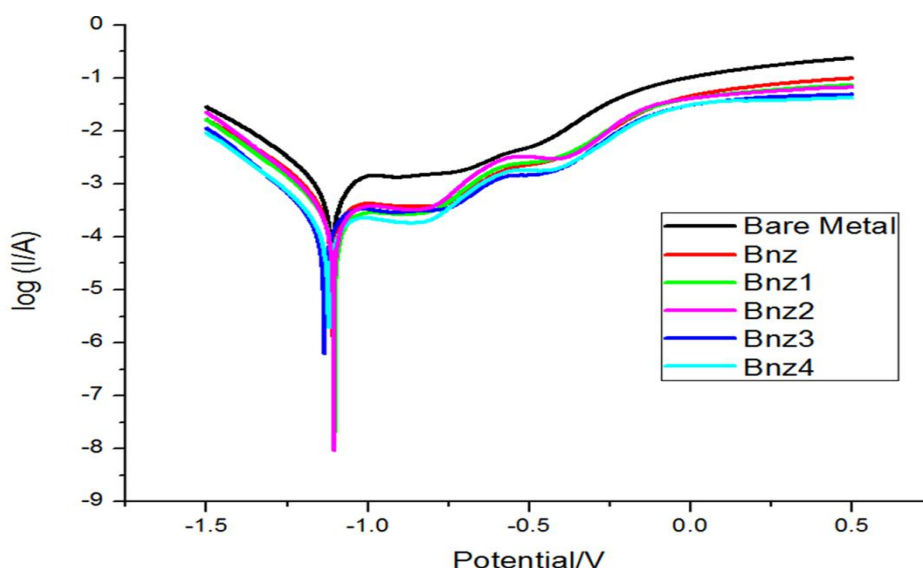


Figure 4: Tafel plot analysis of Bnz Coatings at various silane modified proportion

CONCLUSION:

Cardanol was successfully utilized to synthesize the amine functional benzoxazine resin via Mannich-like condensation of a cardanol, paraformaldehyde and N,N'-Bis(2-aminoethyl)ethane-1,2-diamine. The amine groups present in the final resin structure was confirmed by amine value, FTIR and ¹H-NMR analysis. The silane modification of Bnz resin was carried out successfully in various proportions to effectively enhancing the mechanical properties of coating such as adhesion, hardness, flexibility and impact resistance. DSC analysis of coatings showed that the thermal stability of coating was improved with the silane modification proportions. The electrochemical analysis test shows the Bnz4 coating corrosion rate decreased approximately six times than Bnz coating. The excellent chemical resistance and anticorrosive performance of silane-modified coatings confirmed that the coating could be suitably applied on metal substrates for high performance applications.

ACKNOWLEDGMENT:

We wish to thank Cardolite Specialty Chemicals Ltd., Manglore, India for providing NC-700 sample.

REFERENCES:

- Jin, L, Agag, T, Ishida, H, "Bis(benzoxazine-maleimide)s as a novel class of high performance resin: Synthesis and properties", *Eur Polym J.*, 46 (2010)
- Wang, C, Zhao, C, Sun, J, Huang, S, Liu, X, Endo, T, "Synthesis and thermal properties of a bio-based polybenzoxazine with curing promoter", *Polym Sci Part A: Polym Chem.*, 51 (2013)
- Grundmeier, G, Schmidt, W, Stratmann, M, "Corrosion protection by organic coatings: electrochemical mechanism and novel methods of investigation", *Electrochimica Acta.*, 45 2515–2533 (2000)
- Zhou, C, Lu, X, Xin, Z, Liu, J, Zhang, Y, "Hydrophobic benzoxazine-cured epoxy coatings for corrosion protection", *Prog Org Coat.*, 76 1178–1183 (2013)
- Zhou, C, Lu, X, Xin, Z, Liu, J, "Corrosion resistance of novel silane-functional polybenzoxazine coating on steel", *Corros Sci.*, 70 145–151 (2013)