

## Studies on Syntheses, Spectral, Thermal and Hydrophobic Behaviour of Cardanol based Tetra Functional Benzoxazines

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### Abstract

In the present work, the tetra-functional benzoxazine was prepared using the calculated stoichiometric quantities of cardanol (C), 4-aminophenol (ap), paraformaldehyde, isophoronediamine (ipda) and diaminodiphenylmethane (ddm) under an appropriate experimental conditions. The molecular structure of benzoxazines synthesized namely cardanol-aminophenol-isophoronediamine (C-ap-ipda) and cardanol-aminophenol-diaminodiphenylmethane (C-ap-ddm) was ascertained from FTIR and <sup>1</sup>H-NMR spectral analyses. The curing behaviour of C-ap-ipda and C-ap-ddm benzoxazines was studied using differential scanning calorimetry (DSC). From DSC thermograms, the polymerization temperatures (T<sub>p</sub>) observed for C-ap-ipda and C-ap-ddm are 246°C and 254°C respectively. It was noticed that the benzoxazine with cycloaliphatic ring (C-ap-ipda) possesses the lower curing temperature than that of aromatic substituted (C-ap-ddm) benzoxazine. The cleavage of benzoxazine ring and the occurrence of ring-opening polymerization were confirmed by FTIR analysis after the thermal curing. The thermal stability of cured poly(C-ap-ipda) and poly(C-ap-ddm) benzoxazines was studied by TGA analysis. The values of char yield observed for poly(C-ap-ipda) and poly(C-ap-ddm) at 850°C are 27% and 30%, respectively. Further, the values of LOI calculated for poly(C-ap-ipda) and poly(C-ap-ddm) are 28.3 and 29.5 respectively and these values suggest that both poly(C-ap-ipda) and poly(C-ap-ddm) possess good flame retardant characteristics. The values of water contact angle obtained for poly(C-ap-ipda) and poly(C-ap-ddm) are 128° and 137° respectively and these values infer that both the polybenzoxazine matrices exhibit very good hydrophobic behaviour. Among the synthesized polybenzoxazines, poly(C-ap-ddm) possesses better thermal and hydrophobic character than those of poly(C-ap-ipda), however both the samples qualify for high performance thermal and moisture resistant applications.

**Keywords:** Cardanol terminated benzoxazine, polymerization temperature, thermal stability, flame retardant behaviour, water contact angle, hydrophobic nature.

## Introduction

Polybenzoxazines emerged as a preferred resin over traditional phenolic resins as the former offers molecular design flexibility and ability to undergo thermal polymerization in the absence of any catalysts or curatives [1][2]. In addition, polybenzoxazines exhibits good flame retardancy with enhanced thermal and mechanical properties and also cure almost near zero shrinkage [3][4]. Polybenzoxazines offer wide range of applications, viz., composite materials for aerospace, construction, printed circuit boards, insulation and packaging in the microelectronics industry, brake pad adhesives, fire retardants and co-curing agents, etc., [5][6]. Cardanol based benzoxazines overcome many of the short-comings associated with conventional phenolic resins with versatility in polymerization in the absence of any solvents and offer facile processability [7][8]. Further, the cardanol based benzoxazine resins offers benefit of very good water repellence with improved flexibility [9][10]. Polymers have become a material of choice surpassing many other man-made materials as they offer synthetic control to tune the structure–property relationships to suit specific use and also widen their applications [11].

Cardanol based benzoxazine resins are in liquid form due to the presence of long aliphatic chain in the meta-position of phenol moiety. Cardanol based benzoxazine also exhibits good storage stability at room temperature, low heat release, near-zero shrinkage during curing and low water uptake which make these polybenzoxazines become more suitable materials for commercial applications [12][13]. Cardanol based mono and bifunctional benzoxazines possess the higher curing temperature [14]. Hence, researchers around the world including our research team made number of attempts to reduce the curing temperature through various designs of molecular skeleton and other methods [15][16]. Recently, our research group have adopted different routes to reduce cure temperature of benzoxazines through various modified synthetic avenues, such as external catalytic approaches, in-built catalytic and reactive group substitution approaches. A. Hariharan *et. al.* [17] studied cardanol and three different amines (aniline, N, N-dimethylaminopropylamine, and caprolactam modified N, N-dimethylaminopropylamine) based benzoxazines and their curing behaviour. The lower curing temperature of 251 °C was observed than those of 280 °C reported for cardanol–aniline benzoxazine. Recently, heterocyclic (imidazole and pyridine core) amines based cardanol-benzoxazines with cure temperature of 206 °C was developed and reported [18]. Other research team have also reported the low temperature cure

benzoxazines obtained through utilizing multifunctional benzoxazine moieties of triaminio triphenylmethane, tetraamine tetraphenylmethane and cardanol [2].

In the present work deals with the synthesis of two different molecular structured bio-based tetra functional benzoxazines (C-ap-ipda and C-ap-ddm) through Mannich condensation reaction. The tetra-functional benzoxazines were prepared using calculated stoichiometric ratios of cardanol, 4-aminophenol, paraformaldehyde, isophorondiamine and diaminodiphenylmethane (ddm) under an appropriate experimental condition in the absence of any solvents. The benzoxazines synthesized in the present study were characterized for their molecular structure, curing behaviour, thermal stability and hydrophobic behaviour using an appropriate modern analytical techniques. Data obtained from different studies were discussed and reported.

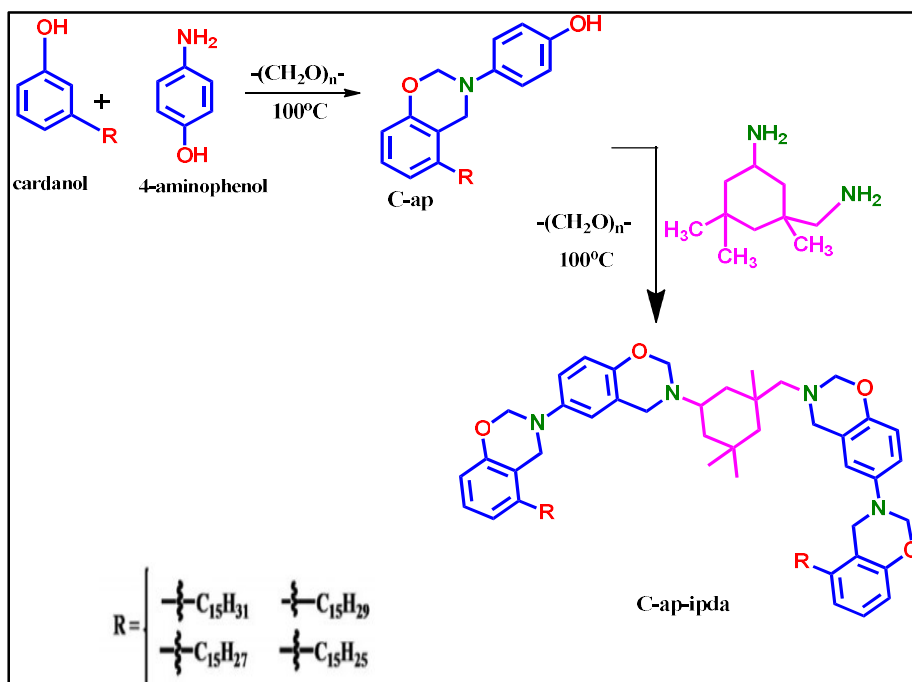
## **Experimental**

### **Materials**

The analytical grade chemicals required for the synthesis of benzoxazines namely cardanol paraformaldehyde, 4-aminophenol, isophoronediamine (ipda) and diaminodiphenylmethane (ddm) were procured from the respective sources. Cardanol was received from Sathya cashew products, Chennai. 4-aminophenol was obtained from Alfa-Aesar (Britain), paraformaldehyde was purchased from Sigma-Aldrich (India) and isophoronediamine from TCI (Japan) and DDM was purchased from Sigma-Aldrich (India).

### **Synthesis of cardanol -aminophenol-isophoronediamine based benzoxazine**

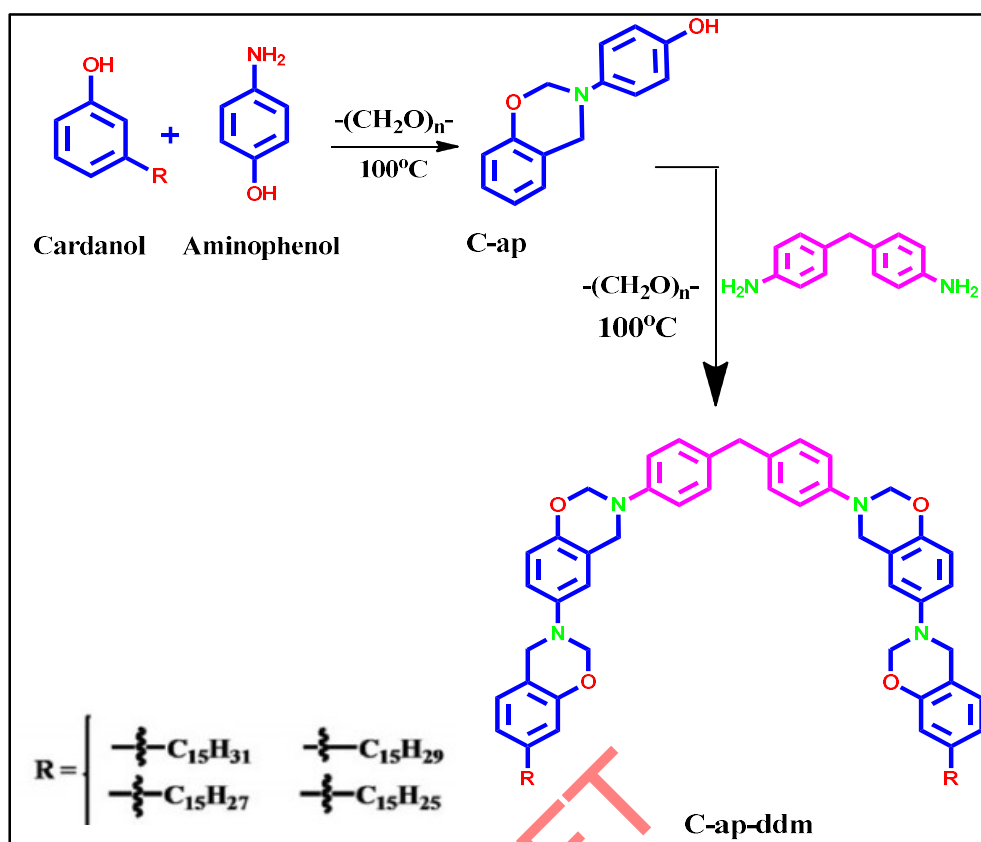
10 g (0.034 mol) of cardanol was mixed with 3.6 g (0.034 mol) of 4-aminophenol and 2.0 g (0.067 mol) of paraformaldehyde were added portion-wise into a 100 ml double necked round bottomed flask under constant stirring in the absence of any solvents. Then, the temperature was raised to 110°C and maintained for more than 3h. After that, 2.85 g (0.0167 mol) of isophoronediamine and add 2.0 g (0.067 mol) of paraformaldehyde were added and again left for 2 h until completion of benzoxazine formation. The progress of the reaction was monitored with thin layer chromatography (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 unreacted phenolic compounds. Further, organic layer was washed twice with 100 ml of distilled water. Then, the organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and ethyl acetate was removed using the rotary evaporator to obtain the final product. The synthesized cardanol-based benzoxazine is labelled as C-ap-ipda (Scheme 1).



**Scheme 1. Synthesis of C-ap-ipda**

### Synthesis of cardanol-aminophenol-ddm based benzoxazine

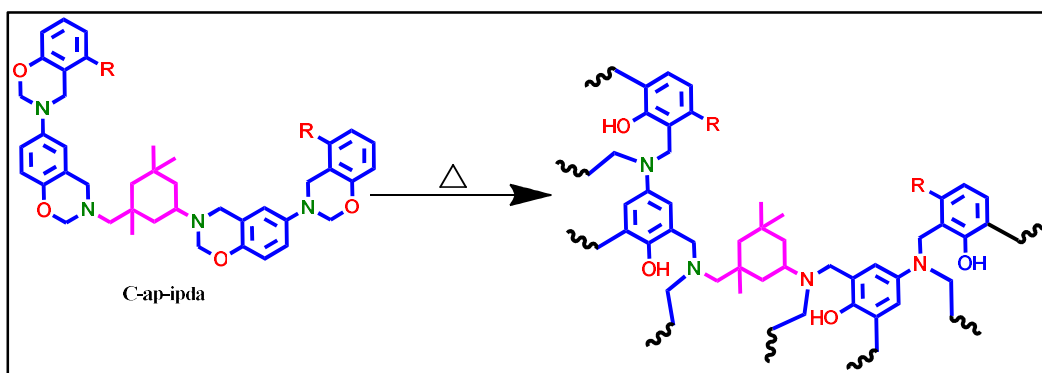
10 g (0.0335 mol) of cardanol was mixed with 3.65 g (0.0335 mol) of 4-aminophenol and 2.01 g (0.067 mol) of paraformaldehyde were added portion-wise into a 100 ml double necked round bottomed flask under constant stirring in the absence of any solvents. Then, the temperature was raised to 110°C and maintained for more than 3 h and added 3.318 g (0.0167 mol) of ddm and paraformaldehyde 2.0 g (0.067 mol) and again left for 2 h until completion of benzoxazine formation. Rest of the steps had been followed according to the synthesis procedure adopted for (C-ap-ipda). The synthesized cardanol-based benzoxazine is labelled as C-ap-ddm (Scheme 2).



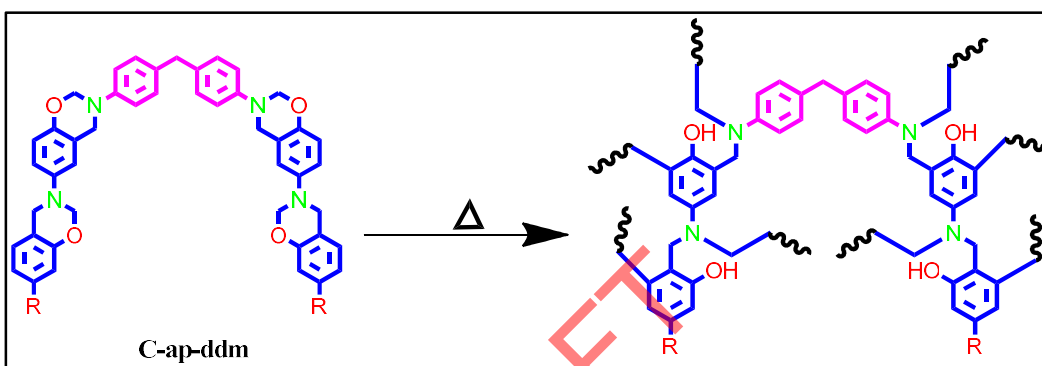
Scheme2. Synthesis of C-ap-ddm

### Preparation of polybenzoxazines

The thermal ring opening polymerization of cardanol based benzoxazines C-ap-ipda and C-ap-ddm were carried out according to the reported procedure [2] (Schemes 3 and 4). A typical procedure for polymerization is as follows: the respective amine based homogeneous benzoxazine monomers were placed in an 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 to 250°C at a heating rate of 20°C/h. The heating is continued for another 3 h at 250°C for the completion of the curing process. At this temperature, the monomer undergoes the ring opening polymerization to form polybenzoxazine with three dimensional cross-linked network structure. The process of polymerization was ascertained from FTIR spectroscopy.



**Scheme 3. Preparation of poly(C-ap-ipda)**



**Scheme 4. Preparation of poly(C-ap-ddm)**

### Measurements

$^1\text{H-NMR}$  (400 MHz) spectrum of monomers were recorded on a Bruker instrument and TMS standard contain  $\text{CDCl}_3$  is a solvent medium. 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 equipment. Further, the pellet sample was utilized for FTIR analysis. Differential scanning calorimetry (DSC) measurements were recorded using NETZSCH STA 449F3 under  $\text{N}_2$  purge ( $60 \text{ mL min}^{-1}$ ) at the scanning rate of  $10^\circ\text{C min}^{-1}$ . Thermogravimetric analysis (TGA) was carried out by NETZSCH STA 449F3 under  $\text{N}_2$  purge ( $60 \text{ mL min}^{-1}$ ) at the scanning rate of  $20^\circ\text{C min}^{-1}$ . Contact angle of water droplet on the coated benzoxazine samples was measured using a Kyowa contact angle Goniometer (model DMe-211 plus) with  $5 \mu\text{l}$  of water as probe liquid.

## Results and discussion

The cardanol-based benzoxazines (C-ap-ipda and (C-ap-ddm) were prepared by the Mannich based condensation reaction of cardanol with different amino compounds and paraformaldehyde at an appropriate reaction conditions as shown in Schemes 1 and 2. Due to the presence of meta-substituted long alkenes/alkyl (15 carbon) chain groups, the cardanol derived benzoxazines will exist in the liquid form. The benzoxazines obtained were characterized using different modern analytical techniques in order to predict their utility towards different industrial applications.

### FTIR spectral analyses of benzoxazine monomers

The FTIR spectra of cardanol based benzoxazines are presented in Figure 1. The bands appeared at around  $1228\text{ cm}^{-1}$  and  $1498\text{ cm}^{-1}$  were attributed to asymmetric and symmetric stretching vibrations of C-O-C bond present in the benzoxazine respectively. The peak appeared at  $1105\text{ cm}^{-1}$  is due to an asymmetric stretching of C-N-C. Similarly, the formation of bands at around  $936\text{ cm}^{-1}$  and  $1496\text{ cm}^{-1}$  are correspond to a tri-substituted benzene ring which confirms the formation of benzoxazine ring. Further, the band appeared at around  $3109\text{ cm}^{-1}$  corresponds to C-H stretching vibrations of the benzene ring. The characteristic absorption peaks appeared at around  $2925$  and  $2841\text{ cm}^{-1}$  represent an asymmetric and symmetric vibrations of  $\text{CH}_2$  of oxazine ring as well alkyl side chain of cardanol moiety respectively.

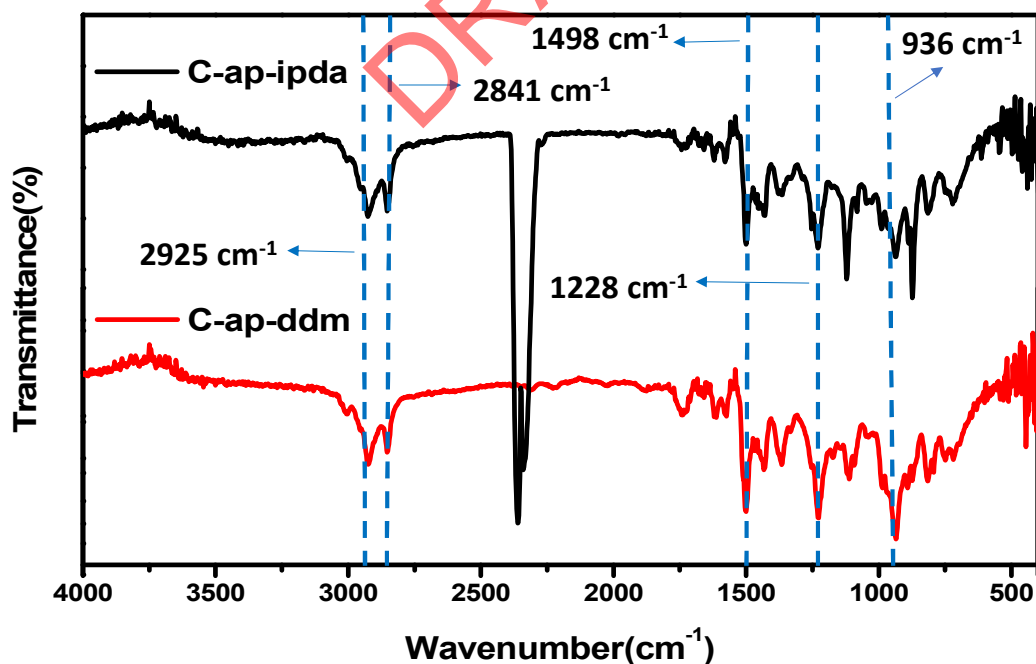
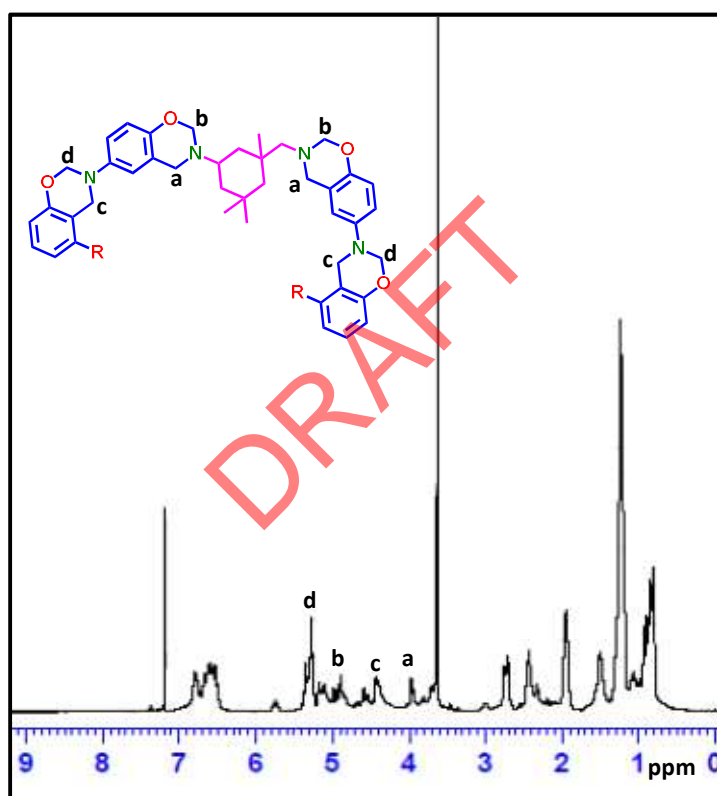


Figure 1. FTIR spectra of benzoxazine monomers

## **<sup>1</sup>H-NMR spectral analyses of benzoxazine monomers**

The structure of benzoxazines viz., C-ap-ipda and C-ap-ddm, has been confirmed by <sup>1</sup>H-NMR spectral analyses. The formation of benzoxazine ring in C-ap-ipda and C-ap-ddm was confirmed with the appearance of different environment resonance peaks. For the ipda (aliphatic amine) attached benzoxazine the resonance peaks appeared at around 4.0 ppm (singlet, 2H a type signal in Figures 2 and 3) and for methylene group of Ar-CH<sub>2</sub>-N around 5.0 ppm (singlet, 2H b type signal) for (O-CH<sub>2</sub>-N) from <sup>1</sup>H-NMR spectroscopy. In the case of aryl amine (DDM) and cardanol based benzoxazine resonance peaks appeared at around 4.5 ppm (singlet, 2H c type signal in Figures 2 and 3) and for methylene group of Ar-CH<sub>2</sub>-N around 5.5 ppm (singlet, 2H d type signal) for (O-CH<sub>2</sub>-N) from <sup>1</sup>H-NMR spectroscopy.



**Figure 2.** <sup>1</sup>H-NMR spectrum of C-ap-ipda benzoxazine



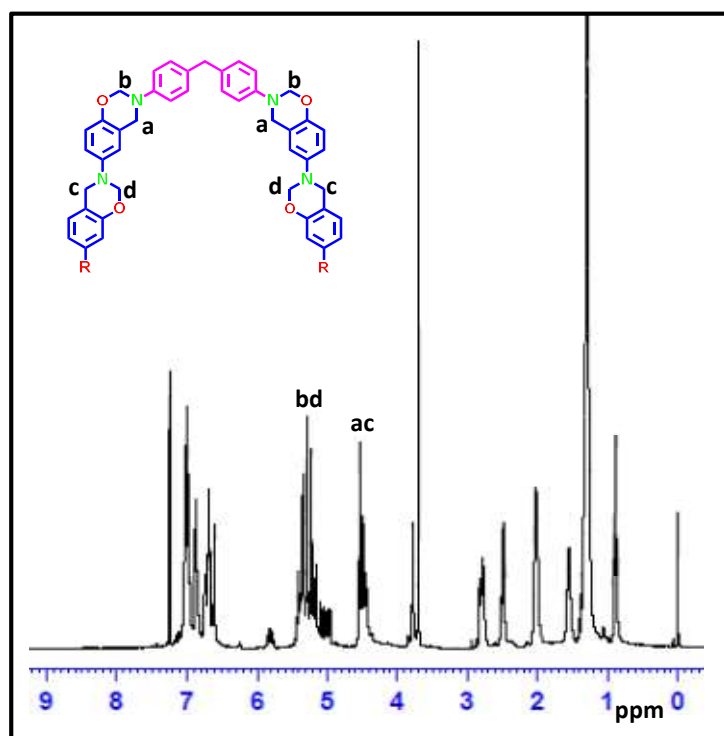


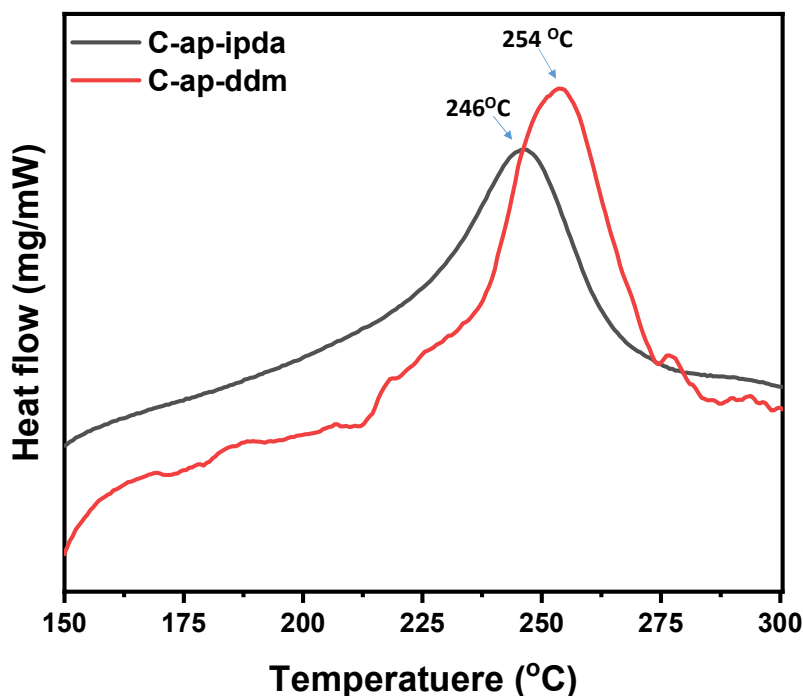
Figure 3.  $^1\text{H-NMR}$  spectrum of C-ap-ddm benzoxazine

### Curing behaviour of benzoxazine

The curing behaviour of all the synthesized benzoxazine monomers was studied by DSC analysis at the heating rate of  $10^\circ\text{C}/\text{min}$ . Figure 4, shows the DSC thermograms of cardanol based benzoxazines with different amino derivatives (ipda and ddm). The appearance of exothermic peaks with regard to the benzoxazines viz., C-ap-ipda and C-ap-ddm confirm the polymerization proceeds through thermal ring-opening mechanism (Schemes 3 and 4). The curing study carried out at the heating rate of  $10^\circ\text{C}/\text{min}$ , the curing temperatures (exotherm maxima  $-T_p$ ) of C-ap-ipda and C-ap-ddm benzoxazines were observed at  $246^\circ\text{C}$  and  $254^\circ\text{C}$  (Table 1) respectively.

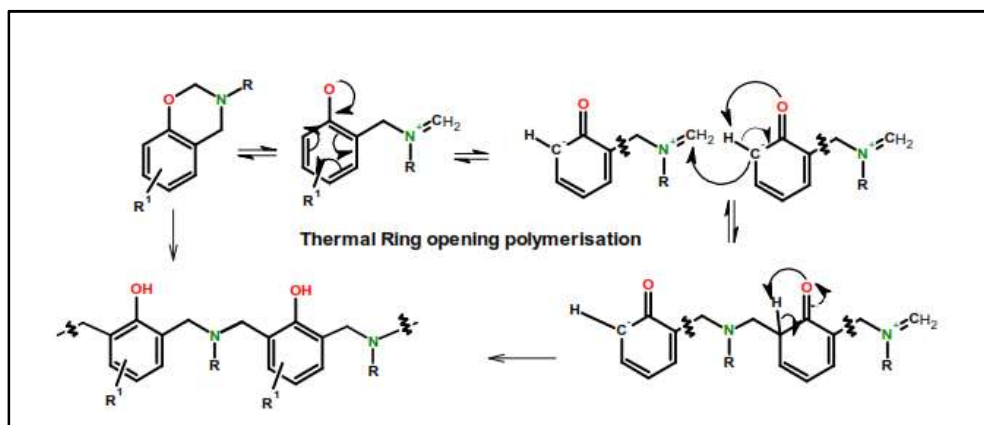
Table 1 The curing behaviour of cardanol based benzoxazines

Cardanol based benzoxazines	Curing behaviour at the rate of $10^\circ\text{C}/\text{min}$		
	$T_i(^{\circ}\text{C})$	$T_p(^{\circ}\text{C})$	$T_f(^{\circ}\text{C})$
C-a (cardanol-aniline)	243	285	297
C-ap-ipda	228	246	264
C-ap-ddm	237	254	270



**Figure 4. DSC thermograms of benzoxazine monomers at the heating rate of 10°C/min**

In general, the curing temperature of tetra-functional C-ap-ipda and C-ap-ddm is lower than that of cardanol-aniline (280°C) based benzoxazine. The lowering of cure temperature obtained may be explained due to the formation of Zwitterion intermediate followed by the proton exchange in the case of benzoxazines moiety [2]. Consequently, the formation of Zwitterion intermediate reduces the polymerization temperature, when compared to that of aniline based benzoxazines (Scheme 5).

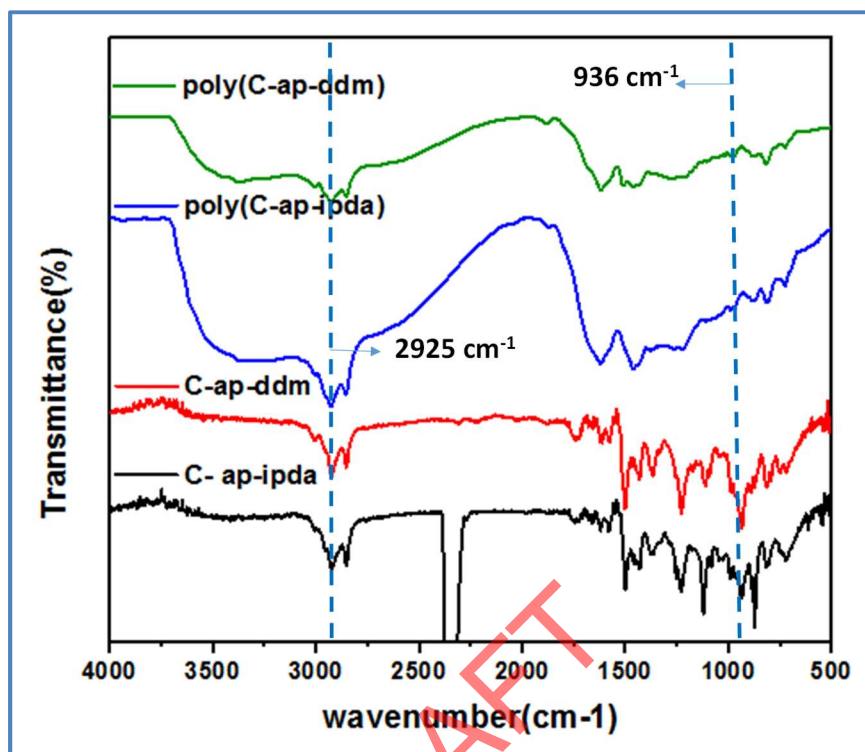


**Scheme 5. Curing mechanism of benzoxazine**

### FTIR spectral analyses of polybenzoxazines

After the thermal treatment, the chemical structure of cardanol based polybenzoxazines poly(C-ap-ipda) and poly(C-ap-ddm) were confirmed by FTIR spectral analyses (Figure 5). The

absorption band appeared at  $936\text{ cm}^{-1}$  for oxazine ring disappeared after thermal curing at  $250^\circ\text{C}$  for 3 h which in turn confirms the occurrence of complete ring opening and cross-linking polymerization of benzoxazines.



**Figure 5. FTIR spectra of benzoxazine monomers and its respective polybenzoxazines**

#### **Thermal stability of polybenzoxazines**

The thermal stability of cardanol based polybenzoxazines was studied by thermogravimetric analysis (TGA) (Figure 6) and the results obtained are presented in Table 2. Thermal stability of polybenzoxazine matrix is one of the important factors to be considered in device fabrication for thermally sensitive applications [2]. TGA provides a valuable data with regard to the thermal stability of materials, the number of impurities or solvents present and the nature of degradation by measuring the weight loss at each instant. For the cardanol based polybenzoxazine poly(C-ap-ipda) and poly(Cap-ddm), the 5% weight loss is noticed at  $344^\circ\text{C}$  and  $369^\circ\text{C}$  respectively. The maximum degradation takes place at  $437^\circ\text{C}$  and  $448^\circ\text{C}$  for poly(C-ap-ipda) and poly(Cap-ddm) respectively. The char yield of poly(C-ap-ipda) and poly(Cap-ddm) derived from TGA curves at  $850^\circ\text{C}$  from (Figure 6) the values of residual char yield obtained for poly(C-ap-ipda) and poly(C-ap-ddm) benzoxazines are 27% and 30% respectively. Among the polybenzoxazines studied, poly(C-ap-ipda) and poly(C-ap-ddm) have higher char yield than that of poly(C-a) due to the presence of complex cross-linked network structure. A polymer possesses high char yield in TGA analysis under nitrogen atmosphere indicates that the polymer can be considered as a good flame

retardant material. Thick char becomes a better thermal insulating layer and undergoes slow oxidative degradation, protecting the remaining polymer from heat radiation [2].

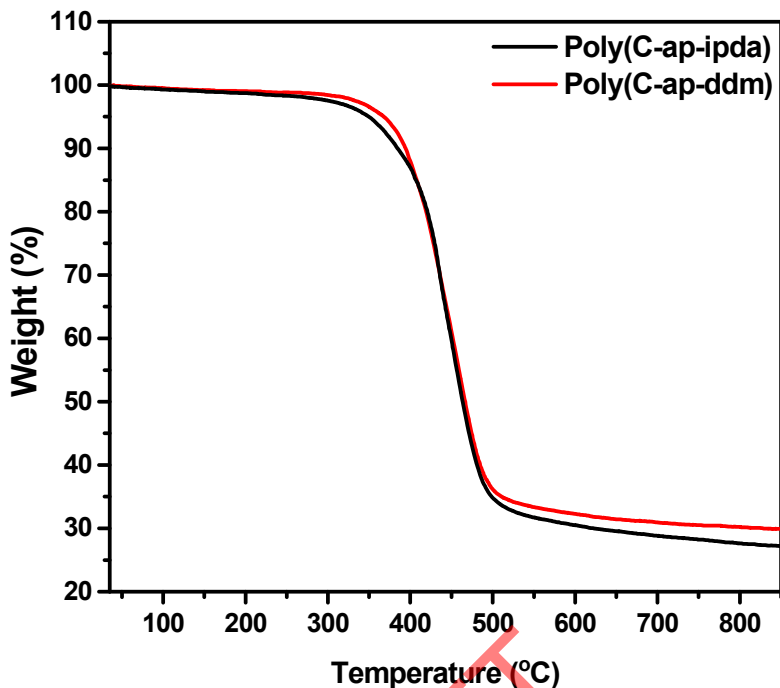


Figure 6. TGA thermograms of polybenzoxazines

Table 2. Thermal behaviour of polybenzoxazines

Cardanol based benzoxazines	Curing temperature (°C)	5% weight loss (°C)	10% weight loss (°C)	T <sub>max</sub> (°C)	Char yield (%) at 850°C	LOI
Poly(C-ap-ipda)	246	344	384	437	27	28.3
Poly(C-ap-ddm)	254	369	396	448	30	29.5

### Flame retardant studies

The flame retardant study of the polybenzoxazines is also ascertained by using the value of residual char yield obtained from TGA analysis. The values of limiting oxygen index (LOI) value are theoretically calculated from van Krevelen [19] and Hoftzyer equation [20] [equation 1] and the results obtained are presented in Table 2.

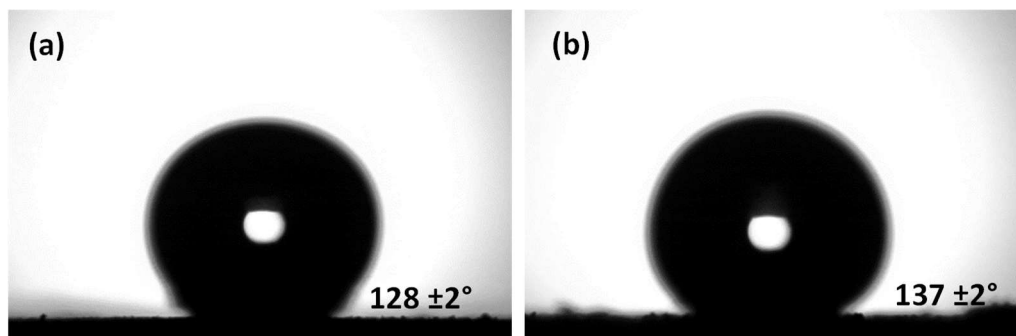
$$LOI = 17.5 + 0.4(\theta) \text{ ----- (1)}$$

Where,  $\theta$  is the percentage char yield of polybenzoxazines remains at 850°C.

The char yield of the polybenzoxazines [poly(C-ap-ipda) and poly(C-ap-ddm)] is found to be 27% and 30% respectively. It is generally accepted that the polymers possessing LOI values

above the threshold value of 26 to render them self-extinguishing and utilized for flame retardant applications. The polybenzoxazines synthesized in the present work possess the values of LOI higher than 26 indicate their good flame retardant property. The obtained LOI value of poly(C-ap-ipda) and poly(C-ap-ddm) are 28.3 and 29.5 respectively (Table 2). This indicates that poly(C-ap-ddm) has higher LOI value than poly(C-ap-ipda), due to the formation of higher cross-linked network structure.

### Water contact angle studies



**Figure 7. Water contact angle of (a) poly(C-ap-ipda) and (b) poly(C-ap-ddm) benzoxazines**

The water contact angle images of poly(C-ap-ipda) and poly(C-ap-ddm) are presented in Figure 7. It can be observed that the poly(C-ap-ddm) possesses the higher values of contact angle when compared to that of poly(C-ap-ipda). The values of contact angle of poly(C-ap-ipda) and poly(C-ap-ddm) are  $128^{\circ} \pm 2^{\circ}$  and  $137^{\circ} \pm 2^{\circ}$  respectively. The lower affinity of the developed polybenzoxazine matrix indicates the improvement in the hydrophobic behaviour. This may be due to the presence of long aliphatic chain of cardanol moiety. In addition, the intra-molecular hydrogen bonding exists in the benzoxazine molecular system also contributes to the enhanced values of water contact angle. The developed polybenzoxazine matrices in the present work possess the reduced surface free energy with enhanced hydrophobic behaviour indicate that these can be used as an efficient moisture resistant materials under humid environmental conditions.

### Conclusion

Tetra functional benzoxazines (C-ap-ipda and C-ap-ddm) were synthesized using cardanol, 4-aminophenol, paraformaldehyde, isophoronediamine (ipda) and diaminodiphenylmethane (ddm) through Mannich condensation under suitable experimental conditions. The molecular structure of synthesized benzoxazine monomers was confirmed by FTIR and  $^1\text{H-NMR}$  spectral analyses. Data from DSC analysis confirm that the curing temperature of tetra-functional C-ap-ipda and C-ap-ddm is lower than that of cardanol-aniline based benzoxazine due to the formation of Zwitterion intermediate followed by the proton exchange. Results from TGA studies infer that both the polybenzoxazines possess the higher values of char yield than that of

poly(C-a) due to the complex network structure formation. The values of char yield obtained for both poly(C-ap-ipda) and poly(C-ap-ddm) indicate their better flame retardant behaviour. From the water contact angle studies both poly(C-ap-ipda) and poly(C-ap-ddm) exhibit good hydrophobic behaviour. Results obtained from different studies, it is concluded that both the polybenzoxazines possess an enhanced thermal stability, good flame retardant behaviour and better moisture resistance indicate these materials can be used in the form of sealants, coatings and matrices for high performance insulation and coating applications.

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### **Conflict of interest**

The authors declare no conflict of interest.

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