

Effective low temperature cure cardanol based mono-functional benzoxazines: A comparison

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Abstract

An attempt has been made in the present work to assess the thermal and hydrophobic behavior of sustainable and renewable bio-based cardanol benzoxazines were synthesized by reacting different aryl amines with varied functionalities [viz., aniline (a), p-toluidine (pt), p-fluoroaniline (fa), p-aminophenol (ap), p-acetylaniline (aa), p-nitroaniline (na)] with cardanol (C) in presence of formaldehyde at an appropriate conditions. The varied molecular nature of benzoxazines obtained was characterized for their molecular structure, curing behavior, thermal stability and hydrophobic behaviour by analytical techniques. The structural elucidation of benzoxazines was carried out by FTIR and ¹H-NMR spectroscopic studies. Among the different benzoxazines studied, the p-aminophenol based benzoxazine possesses the lowest curing (191°C) temperature (C-a-282°C > C-pt-262°C > C-fa-258°C > C-aa-251°C > C-na-227°C > C-ap-191°C). The thermal stability of different cardanol based polybenzoxazines was studied by TGA technique. Among the different samples of cardanol benzoxazine systems studied, the benzoxazines viz., poly(C-fa) and poly(C-ap) possess the higher thermal stability and higher char yield than those of other polybenzoxazines [viz., poly(C-a) > poly(C-pt) > poly(C-na) > poly(C-aa) > poly(C-ap) > poly(C-fa)]. The limited oxygen index (LOI) value of polybenzoxazines has been calculated from char yield of polybenzoxazines. Poly(C-ap) and poly(C-fa) show the LOI value greater than 26, which ascertain their good flame retardant behaviour. The value of water contact angle obtained for cardanol based benzoxazines are in the following order, poly(C-a) 112° > poly(C-pt) 117° > poly(C-na) 124° > poly(C-aa) 124° > poly(C-ap) 131° > poly(C-fa) 134°. Cardanol based benzoxazines derived from varying nature of amines groups influence the both thermal and hydrophobic behavior according to their chemically interactive and molecular geometry.

Keywords: Cardanol, mono-functional benzoxazine, curing temperature, thermal stability, char yield, flame retardance, water contact angle, hydrophobic nature.

Introduction

The bio-based industrial polymeric materials are developed in order to substitute and replace fossil petroleum based environmentally hazardous synthetic chemicals applications wherever possible. Cashew nut shell liquid (CNSL), is one of the renewable and sustainable, versatile and valuable industrial raw materials for the production of polymeric materials in the form of coatings, paints, varnishes, adhesives, sealants, matrices and composites for high performance applications [1]. Recently researchers around the world have been tirelessly working to develop an alternate polymeric materials from bio-based sustainable raw materials with a view to utilize them for different industrial and engineering applications [2–9]. In this direction, in particular, number of cardanol based polymeric materials such as epoxy resins and its hardeners [10], polyols [11], benzoxazines [12], cyanate esters [13] have been developed for different applications. Cardanol is a meta substituted aliphatic chain (C₁₅) containing phenolic compound, which is a by-product of CNSL [14].

Cardanol based benzoxazine resins are in a liquid form due to the presence of long chain aliphatic meta substitutions. Cardanol based benzoxazines exhibits good storage stability at room temperature, low heat release, near-zero shrinkage during curing and low water uptake which make these cardanol based polybenzoxazines become more suitable materials for different industrial applications [15]. However, it is well known that the cardanol based benzoxazines require high thermal energy for curing, this behavior restricts and limits the applications of cardanol-based benzoxazines. In this content, number of researches have been carried out in order to reduce the cure temperature to utilize for different industrial and engineering applications [5],[16]. Recently, our research group have been actively involved to reduce the cure temperature of benzoxazines through various approaches, such as external catalytic approaches, in-built catalytic mechanism and reactive functional group substitution methodology [17],[18]. Hariharan *et al.* studied and reported cardanol based benzoxazines obtained by reacting cardanol separately with three different amines (aniline, N,N-dimethylaminopropylamine, and caprolactam modified N,N-dimethylaminopropylamine) and paraformaldehyde using an appropriate experimental conditions and the lowest curing temperature obtained was about 251°C [15]. Further, the same research group reported that the heterocyclic (imidazole and pyridine core) [19] amines based cardanol-benzoxazine developed possesses the lowest curing temperature of about at 206°C [20].

In the present work, an attempt has been made to develop a series of sustainable bio-phenolic cardanol based benzoxazines using cardanol and paraformaldehyde with different functional group substituted amines *viz.*, aniline, p-toluidine, p-fluoroaniline, p-aminophenol, p-acetylaniline, and p-nitroaniline at an appropriate experimental conditions. The prime objective of the present work is to reduce the cure temperature by utilizing different functional group substituted amines and to alleviate problems associated with interfacing of low melting substrates and to minimize energy required for processing. Among the cardanol based benzoxazines developed in the present study, cardanol based benzoxazine obtained from p-aminophenol possesses the lowest curing temperature than that of other cardanol based benzoxazines. Further, thermal stability and hydrophobic nature of different samples of cardanol based benzoxazines have also been studied. Data obtained from different studies are correlated, discussed and reported.

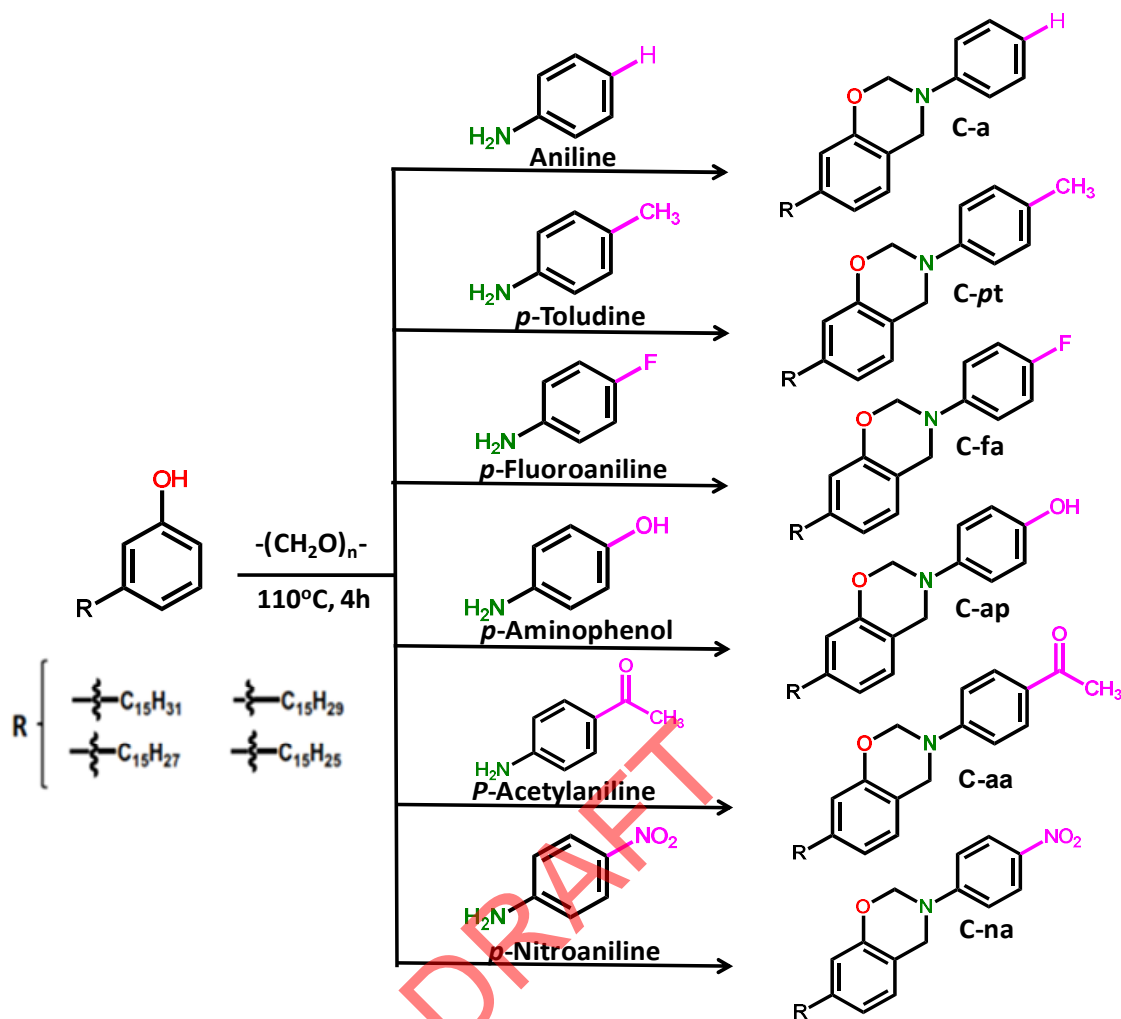
Experimental

Materials

Cardanol was obtained from Sathya Cashew Products Chennai. Analytical grades of aniline, p-nitroaniline, paraformaldehyde, chloroform, ethyl acetate, anhydrous Na₂SO₄ and sodium hydroxide were purchased from SRL and p-toluidine, p-fluoroaniline, p-aminophenol, p-acetylaniline were received from Sigma Aldrich, India.

General procedure for synthesis of cardanol based benzoxazines.

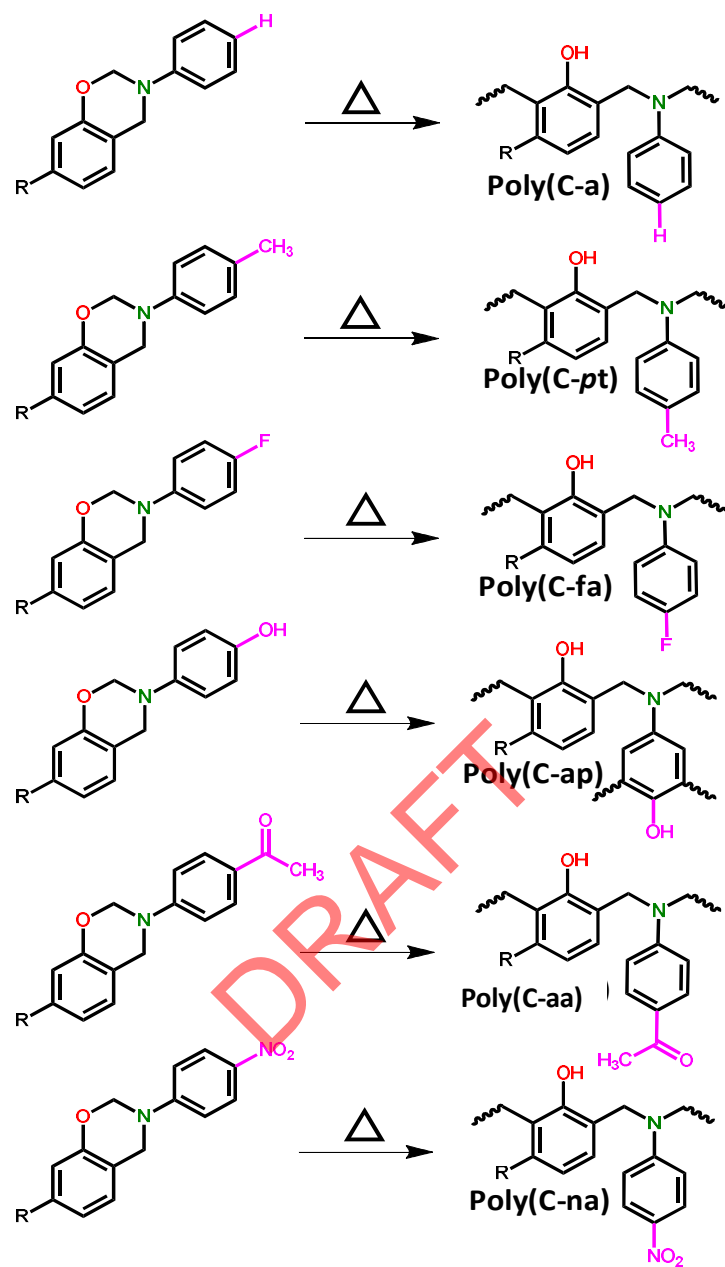
About 0.03 mole of substituted aryl amine (aniline, p-toluidine, p-fluoroaniline, p-aminophenol, p-acetylaniline, p-nitroaniline) was mixed with 0.03 mole of cardanol and 0.06 mol of paraformaldehyde were added portion-wise in a 100 ml double necked round bottomed flask under constant agitation in the absence of any solvents. Then, the temperature was raised to 110°C and maintained for more than 4 h until the completion of benzoxazine formation (Scheme 1). The progress of the reaction was monitored using thin layer chromatography (TLC). After completion of the reaction, the resinous crude product obtained was dissolved in 100 ml of ethyl acetate and washed twice with 2N NaOH for the removal of unreacted phenolic compounds. Further, the organic layer was washed twice with 100 ml of distilled water. Then, the organic phase was dried over anhydrous Na₂SO₄ and ethyl acetate was removed using the rotary evaporator, and the purified product was recovered and preserved for further use.



Scheme 1. Synthesis of cardanol based mono-functional benzoxazines

Preparation of polybenzoxazines

The thermal ring opening polymerization of cardanol based benzoxazine was carried out according to the reported procedure [15]. A typical procedure for polymerization is as follows (Scheme 2): 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 including moisture and the trace of solvent. After the stabilization, the temperature was raised to 260°C at a heating rate of $20^\circ\text{C}/\text{h}$. The heating was continued for another 3 h at 260°C for the completion of the curing process. At this temperature, the monomer undergoes ring opening polymerization to form corresponding polybenzoxazines with three dimensional cross-linked network structures. The process of polymerization was confirmed by FTIR spectroscopy.



Scheme 2. Ring opening polymerisation of cardanol based mono-functional benzoxazines

Measurements

FTIR spectra measurements were carried out with Agilent Cary 630 FTIR Spectrometer. NMR spectra were obtained with Bruker (400 MHz) using deuterated chloroform (CDCl_3) as a solvent and tetramethylsilane (TMS) as an internal standard. DSC measurements were recorded using NETZSCH STA 449F3 under N_2 purge (60 mL min^{-1}) at scanning rate of $10 \text{ }^\circ\text{C min}^{-1}$. Thermogravimetric analysis (TGA) was obtained using NETZSCH STA 449F3

taking 5 mg of sample under N₂ flow (260 mL min⁻¹) and controlling the heating rate at 20 °C min⁻¹. Contact angle measurements were obtained using a Kwoya goniometer with 5 μl of water as probe liquid.

Results and Discussion

The cardanol-based benzoxazines (C-a, C-pt, C-fa, C-ap, C-aa and C-na) were prepared by the condensation reaction of cardanol with different amino compounds with varied nature of functional substituents and formaldehyde at an appropriate reaction conditions as shown in Scheme 1. Due to the presence of meta-substituted long alkenes/alkyl (15 carbon) chain groups, the cardanol derived benzoxazines will exist in the liquid form. Consequently, benzoxazines obtained from the present study possess an improved flexibility, thermal stability, flame retardant behavior and good water repellent characteristics. The molecular structure of prepared cardanol based benzoxazine monomers was confirmed by FTIR and ¹H-NMR spectral analyses. Curing behavior and thermal stability of benzoxazines were studied using DSC and TGA techniques respectively.

FTIR spectral analyses of benzoxazine monomers

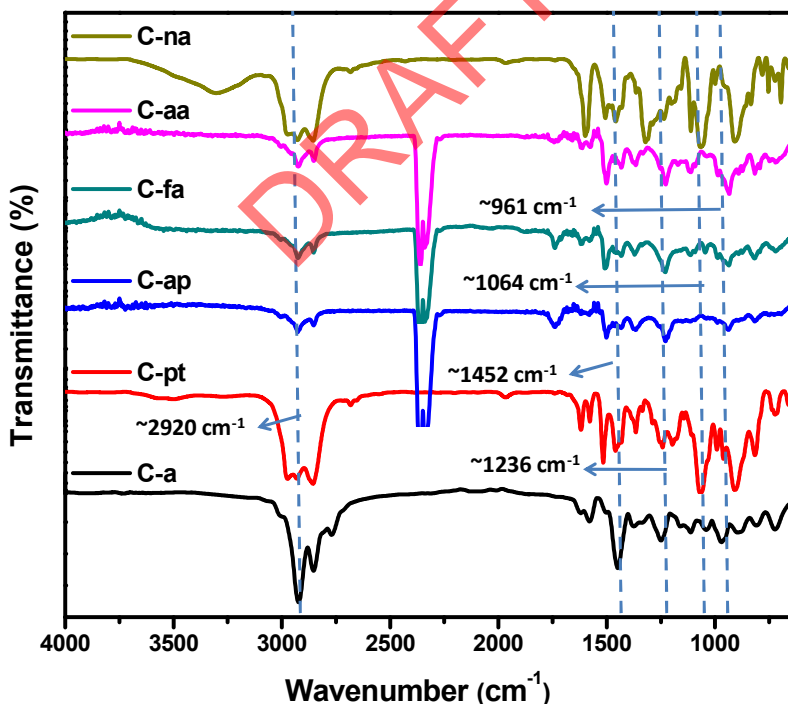


Figure 1. FTIR spectra of benzoxazine monomers

The FTIR spectra of cardanol based benzoxazines are presented in Figure 1. The bands appeared at around 1236 cm⁻¹ and 1064 cm⁻¹ were attributed to the asymmetric and symmetric stretching vibrations of C-O-C bond present in the respective benzoxazine

molecules. The peak appeared at 1189 cm^{-1} is due to the asymmetric stretching of C-N-C. Similarly, the appearance of bands at around 961 cm^{-1} and 1452 cm^{-1} are 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 2920 and 2853 cm^{-1} represent the asymmetric and symmetric stretching vibrations of CH_2 of oxazine ring as well as alkyl side chain of cardanol moiety respectively.

$^1\text{H-NMR}$ spectral analysis

Additionally, the structure of benzoxazine compounds was confirmed by $^1\text{H-NMR}$ spectral analysis. The formation of benzoxazine ring in C-a, C-pt, C-fa, C-ap, C-aa and C-na was confirmed by the appearance of resonance peaks at around 4.5 ppm (singlet, 2H, **a.** type signal in Figures 2 and 3) for methylene group of $\text{Ar-CH}_2\text{-N}$ and around 5.5 ppm (singlet, 2H, **b.** type signal in Figures 2 and 3) for $(\text{O-CH}_2\text{-N})$ from $^1\text{H-NMR}$ spectroscopy.

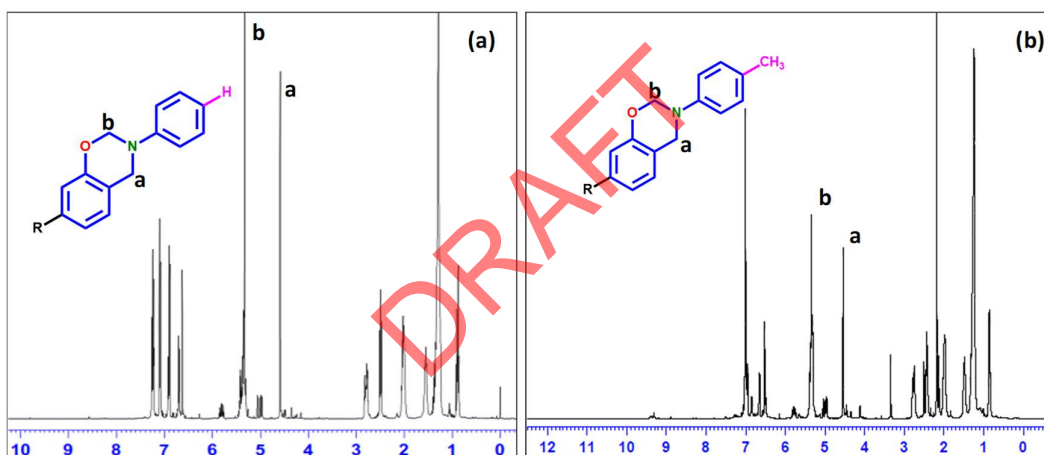


Figure 2. $^1\text{H-NMR}$ spectra of (a) C-a and (b) C-pt benzoxazines

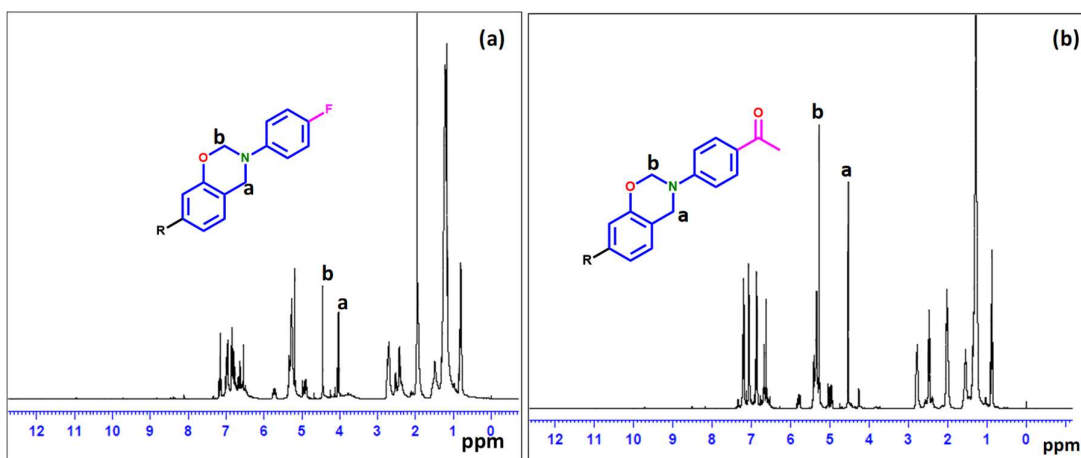


Figure 3. $^1\text{H-NMR}$ spectra of (a) C-fa and (b) C-aa benzoxazines

Curing behaviour of benzoxazines

The curing behavior of all the synthesized benzoxazine monomers was examined by DSC analysis at the heating rate of 10 °C/min. Figure 4, represents the DSC thermograms of cardanol based benzoxazines obtained with different amines, such as aniline (a), *p*-toluidine (pt), *p*-fluoroaniline (fa), *p*-aminophenol (ap), *p*-acetylaniline (aa) and *p*-nitroaniline (na). The appearance of exothermic peaks with regard to the benzoxazines *viz.*, C-a, C-pt, C-ap, C-fa, C-aa and C-na confirms the polymerization proceeds through thermal ring-opening mechanism (Scheme 2). The curing temperature (exotherm maxima- T_p) of C-a, C-pt, C-ap, C-fa, C-aa and C-na benzoxazines was observed at 282°C, 262°C, 191°C, 258°C, 251°C, 227°C (Table 1) respectively.

Table 1. The curing behaviour of cardanol based benzoxazines

Cardanol based benzoxazines	Curing behaviour at the rate of 10°C per min		
	$T_i(^{\circ}\text{C})$	$T_p(^{\circ}\text{C})$	$T_f(^{\circ}\text{C})$
C-a	260	282	297
C-pt	242	262	280
C-ap	151	191	236
C-fa	238	258	278
C-aa	221	251	271
C-na	201	227	252

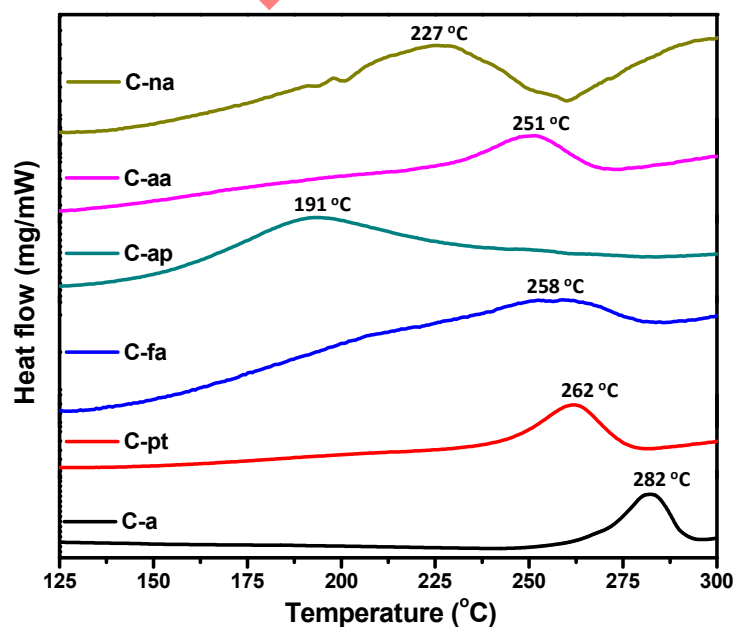
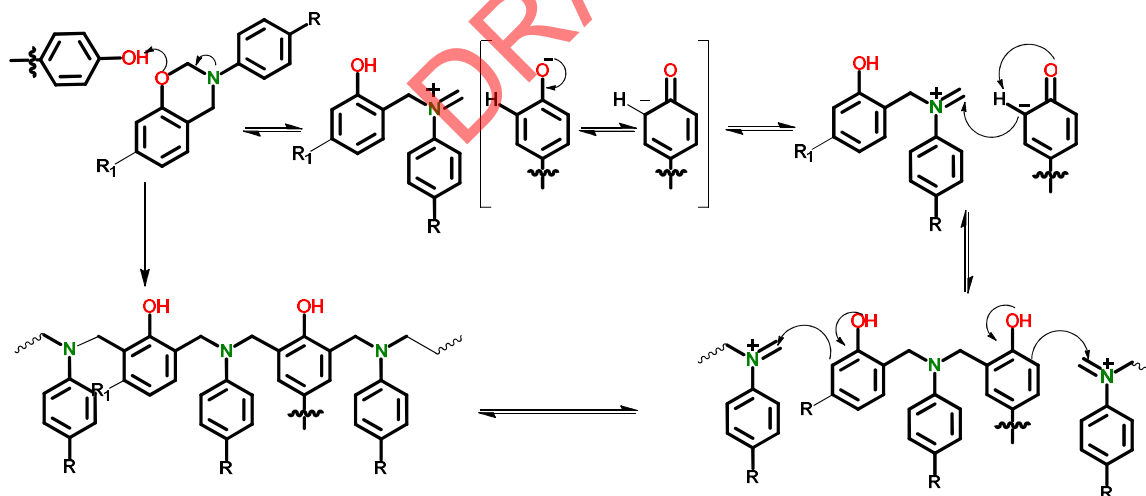


Figure 4. DSC thermograms of benzoxazine monomers at the rate of 10°C per min

In the present work, the different functional substituted amines have been used for the synthesis of benzoxazines are *p*-toluidine (methyl substituted), 4-fluoroaniline (fluoro substituted), 4-aminoacetophenone (carbonyl substituted). The amines with different substituent groups used in the present work are namely methyl group (electron donating group), -F and -OH groups (mid electron withdrawing groups), carbonyl and nitro groups (strong electron withdrawing groups) [-NO₂ > -CO- > -F > -OH > -CH₃ > -H]. It is already established that there is a possibility of reducing the curing temperature of benzoxazines with appropriate functional substituent in the precursor materials (preferably using substituted phenols and amines with varying nature of molecular structure) used for the preparation of benzoxazines. In the case of amines substituted with electron withdrawing groups are expected to reduce the curing temperature of benzoxazines [21]. 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 3). Consequently, the formation of Zwitterion intermediate during polymerization reduces the curing temperature of substituted benzoxazines, when compared to that of non-substituted amine (aniline) based benzoxazines [22].



Scheme 3. Plausible curing mechanism of aminophenol based benzoxazine

FTIR spectral analyses of polybenzoxazines

After the thermal treatment, the chemical structure of cardanol based polybenzoxazines namely, poly(C-a), poly (C-pt), poly(C-ap), poly (C-fa), poly(C-aap) and poly (C-na) was confirmed by FTIR spectroscopy. The absorption band at 961 cm⁻¹ of oxazine ring

disappeared after thermal curing at 260 °C for 3 h, which confirms the occurrence of complete ring opening and in turn leads to form cross-linked network structure of benzoxazines.

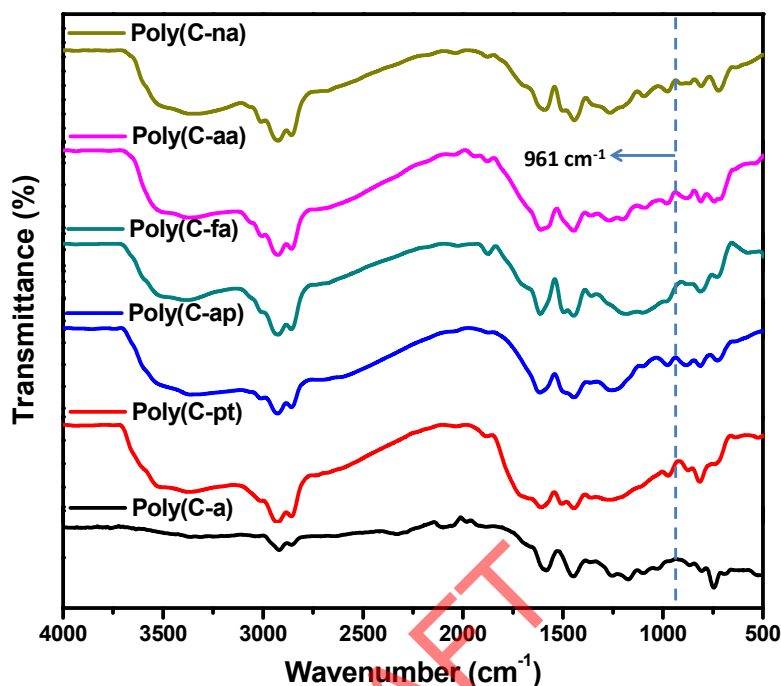


Figure 5. FTIR spectra of polybenzoxazines

Thermal stability of polybenzoxazines

The thermal stability of cardanol based polybenzoxazines was studied by thermogravimetric analysis (Figure 6) and the results obtained are presented in Table 2. Thermal stability of polybenzoxazine matrix is one of the most important factors to be considered in device fabrication with varied nature of substrates. TGA provides a valuable data with regard to the thermal stability of polymeric materials, the trace of impurities or solvents present in the samples and the nature of degradation by measuring the weight loss at each instant. The cardanol based benzoxazines obtained using different amines namely poly(C-a), poly(C-pt), poly(C-ap), poly(C-fa), poly(C-aap) and poly(C-na), the 5% weight loss was noticed at 361, 331, 360, 370, 358 and 369 °C, respectively. The maximum degradation takes place at 461, 466, 468, 470, 465 and 467 °C, respectively. The char yield of respective samples was obtained from TGA carried out at 850°C from Figure 6. The residual char yield obtained for poly(C-a), poly(C-pt), poly(C-ap), poly(C-fa), poly(C-aap) and poly(C-na) based polybenzoxazines are 6, 13, 27, 34, 18 and 14% respectively. Among the polybenzoxazines studied in the present work, poly(C-fa) possesses the higher char yield than that of poly(C-a),

poly(C-pt), poly(C-ap), poly(C-aap) and poly (C-na), due to the presence of fluoro substitution.

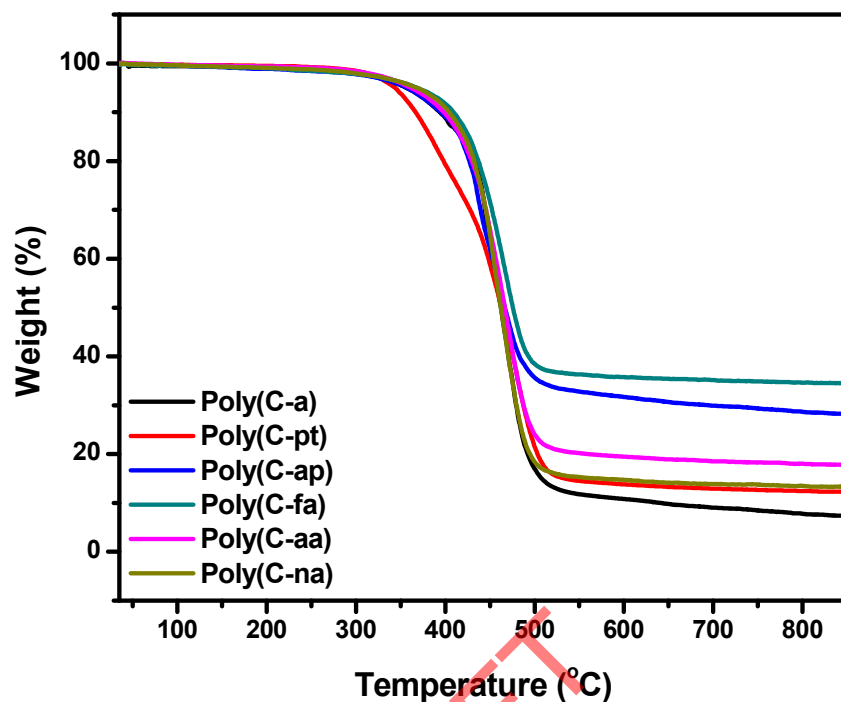


Figure 6. TGA traces of polybenzoxazines

Table 2. Thermal behavior of cardanol based benzoxazines

Cardanol based benzoxazines	Curing temperature (°C)	5% weight loss (°C)	10% weight loss (°C)	T _{max} (°C)	Char yield % at 850°C	LOI
Poly(C-a)	282	361	392	461	6	20.7
Poly(C-pt)	262	331	358	466	13	22.7
Poly(C-ap)	191	360	396	468	27	28.3
Poly(C-fa)	258	370	411	470	34	31.1
Poly(C-aa)	251	358	399	465	18	24.7
Poly(C-na)	227	369	405	467	14	23.1

Flame retardant behaviour

The flame retardant behaviour of the cured polybenzoxazines is also ascertained from the values of limiting oxygen index (LOI) calculated using the residual char yield values obtained from thermogravimetric analysis at 850°C. The value of limiting oxygen index (LOI) calculated from van Krevelen and Hoftzyer equation [eq. 1] [5,23] are presented in Table 2.

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

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

The char yield of the polybenzoxazines poly(C-a), poly(C-pt), poly(C-ap), poly(C-fa), poly(C-aap) and poly(C-na) was found to be 6, 13, 27, 34, 18 and 14%, respectively. It is generally accepted that the value of LOI of the polymers having above the threshold value of 26 is considered to be self-extinguishing and suitable for flame resistance applications. Among the polybenzoxazines synthesized in the present work, the poly(C-fa) possesses the highest LOI value of 31.1 and it possess better flame retardant property than other polybenzoxazine samples studied due to the presence of fluorine atoms in its moiety. The LOI values calculated for other samples of poly(C-a), poly (C-pt), poly(C-ap), poly(C-aa) and poly (C-na) are 20.7, 22.7, 28.3, 24.7 and 23.1, respectively (Table 1).

Water contact angle

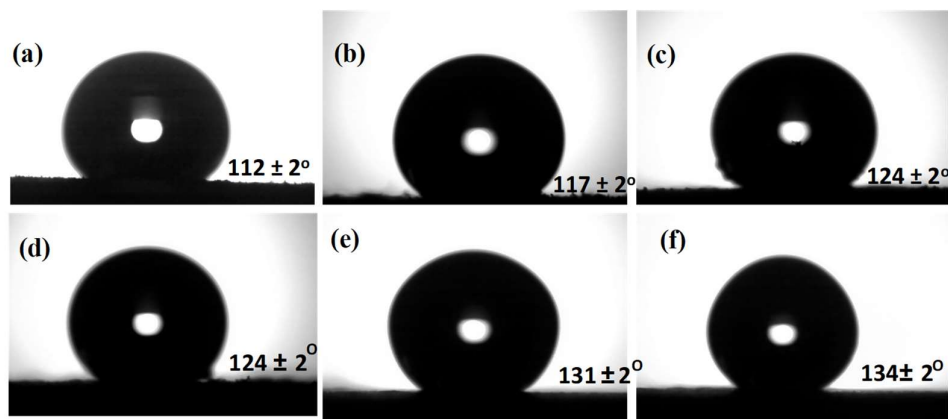


Figure 7. The water contact angle of (a) poly(C-a), (b) poly(C-pt), (c) poly(C-na), (d) poly(C-aa), (e) poly(C-ap) and (f) poly(C-fa) polybenzoxazines

The value of water contact angle and images of poly(C-a), poly (C-pt), poly(C-ap), poly(C-fa), poly(C-aa) and poly(C-na) obtained from goniometer are presented in Figure 7.

The value of water contact angle was obtained in the following order, poly(C-a) $112^\circ >$ poly(C-pt) $117^\circ >$ poly(C-na) $124^\circ >$ poly(C-aa) $124^\circ >$ poly(C-ap) $131^\circ >$ poly(C-fa) 134° . It can be observed again that among the polybenzoxazines prepared the poly(C-fa) possesses the highest value of contact angle when compared to other samples due to the influencing effect of the presence of fluorine atom in the benzoxazine moiety. However, it is interesting to note that all the cardanol based polybenzoxazine samples synthesized in the present work exhibited hydrophobic behaviour due to the presence of inherent long chain alkyl moiety, which in turn contributes to good water repellent character. Further, the presence of an intra-molecular hydrogen bonding in the polybenzoxazine molecular systems also contributes to an enhanced value of water contact angle and in turn influences the behaviour of resistance to moisture. Data obtained from the water contact angle studies suggest that these materials can be used as an effective insulation materials for different industrial applications under humid environments.

Conclusion

In the present work, an attempt has been made to develop a series of cardanol based benzoxazines by reacting different aryl amines with varied functional substituents (aniline (a), p-toluidine (pt), p-fluoroaniline (fa), p-aminophenol (ap), p-acetylaniline (aa), p-nitroaniline (na)) with cardanol (C) in presence of formaldehyde at appropriate experimental conditions with a view to assess their cure behavior, thermal stability and hydrophobic property in order to utilize them for high performance applications. The curing behavior of different benzoxazines obtained follows in the order i.e., C-a- $282^\circ\text{C} >$ C-pt- $262^\circ\text{C} >$ C-fa- $258^\circ\text{C} >$ C-aa- $251^\circ\text{C} >$ C-na- $227^\circ\text{C} >$ C-ap- 191°C . Among the different polybenzoxazine systems studied, the poly(C-fa) possesses the highest thermal stability and higher char yield than those of other polybenzoxazines. Similarly, the values of water contact angle obtained are follows in the order *viz.*, poly(C-a) $112^\circ >$ poly(C-pt) $117^\circ >$ poly(C-na) $124^\circ >$ poly(C-aa) $124^\circ >$ poly(C-ap) $131^\circ >$ poly(C-fa) 134° . Data obtained from different studies, it is concluded that the cardanol based polybenzoxazine developed in the present work can be conveniently used in the form insulators, coatings, sealants, adhesives, encapsulants, matrices and composites where demands at high performance industrial and engineering applications.

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Conflict of interest

The authors declare no conflict of interest.

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