Syntheses and characterization of skeletally modified cardanol based asymmetric benzoxazines with enhanced thermal and hydrophobic properties

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Abstract:

Two different skeletally modified cardanol based asymmetric benzoxazines monomers [(cardanol-aminophenol/p-toludine (C-ap-pt) and cardanol-aminophenol/4-fluoroaniline(C-ap-fa)] were synthesized using cardanol, 4-aminophenol, p-toludine/4-fluoroanilineand paraformaldehyde through Mannich condensation reaction. The molecular structure of the benzoxazine monomers was confirmed by FTIR and ^{1}H-NMR spectral analyses. Cure behaviour and thermal stability were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) respectively. The results from DSC analysis indicated that these benzoxazines exhibit marginally lower polymerization temperature than that of conventional benzoxazines. The formation of polybenzoxazine was confirmed by FTIR analysis after the thermal curing through the cleavage of benzoxazine ring and subsequently led to the formation of three dimensional cross-linked network structure. Results from TGA infer that among the polybenzoxazines studied, poly(C-ap-fa) possess better thermal stability than that of poly(C-ap-pt) due to fluoro substitution in the molecular structure of benzoxazine. Further, the values of LOI calculated using char yield obtained at $850°C$ from TGA for poly(C-ap-pt) and poly(C-ap-fa) are 26 and 29 respectively. The values of water contact angle obtained for poly(C-ap-pt) and poly(C-ap-fa) are $115°$ and $117°$ respectively. It is inferred that both benzoxazine samples exhibit an excellent thermal behavior and hydrophobic behaviour.

Keywords: Benzoxazines, curing temperature, thermal stability, char yield, limiting oxygen index, water contact angle, hydrophobic behaviour.

Introduction

Polybenzoxazines, a new class of modified phenolic resins [1,2], recently received attention over traditional phenol-formaldehyde resins due to their advantages in terms of performance and design flexibility towards synthesis [3,4]. These resins offer suitability for a wide area of applications ranging from composite materials for aerospace, construction, microelectronics industry, etc.[5,6], Since, these polymers offer a wide range of molecular design flexibility in order to produce a large array of molecular structures to tailor to the desired set of properties [7]. The flexibility is due to their versatile preparation from an extensive variety of phenolic precursors including bio-phenols and primary amines viz., aliphatic, aromatic, cycloaliphatic, heterocyclic, polymerized and substituted amines as raw materials [8].

Currently, there is a huge dependence on these non-renewable starting materials, which has led to an increase in an environmental concern and rapid depletion of petrochemical resources [9]. Among various possible alternatives, cardanol has been considered as an attractive resources due to its abundant availability from agro-source, simplest extraction methodology, non-toxicity and bio-degradability [10].Cardanol is a naturally occurring phenolic compound extracted from cashew nutshell liquid [11]. Its chemical structure is interesting because cardanol is bearing a phenolic hydroxyl function and an unsaturated alkyl chain in meta position [12]. Numerous chemical reactions can thus be considered for its chemical and skeletal modifications.

With this in view, the present work is proposed to synthesize a new class of cardanol based structurally modified skeletal extended benzoxazine monomers using4-aminophenol, p-toludine/4-fluoro aniline and paraformaldehyde through Mannich condensation reaction. The structure of synthesized benzoxazines was ascertained from FTIR and ^{1}H-NMR spectral analyses. The curing behavior of C-ap-pt and C-ap-fa benzoxazine monomers was studied using DSC technique and followed by the ring opening polymerization of benzoxazines confirmed by FTIR spectroscopy. Thermal stability of polybenzoxazines was analyzed using TGA technique. Moisture resistant behavior of benzoxazine samples was ascertained from water contact angle measurements using goniometer. Data obtained from different studies are correlated, discussed and reported.

Experimental

Materials

In this work, the materials that required for the synthesis of benzoxazines are cardanol, paraformaldehyde, 4-aminophenol, p-toludine,4-fluroaniline. Cardanol was purchased from Sathya cashew products, Chennai. Analytical grade of chemicals, 4-aminophenolwas

obtained from Alfa Asser (Britain), paraformaldehyde and4-fluroaniline were purchased from Sigma-Aldrich (India), p-toludine from TCI (Japan).

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 ˚C min^{-1}. Thermogravimetric analysis (TGA) was obtained using NETZSCH STA 449F3 taking 5 mg of sample under N_2 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 5μl of water as probe liquid.

Synthesis of Cardanol–aminophenol-para-toludine based benzoxazine(C-ap-pt)

10g(0.034mol) of cardanol was mixed with 3.6g (0.034mol) of 4-aminophenol and 2.0g (0.067mol) 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 110ºC and maintained for more than 3h. Afterwards 3.589g(0.033mol) of para-toludine and 2.0g(0.067mol) of paraformaldehyde were added 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 50ml of ethyl acetate and washed twice with 2N NaOH for the removal of unreacted phenolic compounds.

Further organic layer was washed twice with 100ml of distilled water. Then, the organic phase was dried over anhydrous Na_2SO_4 and ethyl acetate was removed using the rotary evaporator, and the purified product was recovered and preserved. The synthesized cardanol- aminophenol/para-toludine based asymmetric benzoxazine was labelled as C-ap-pt.(Scheme 1)
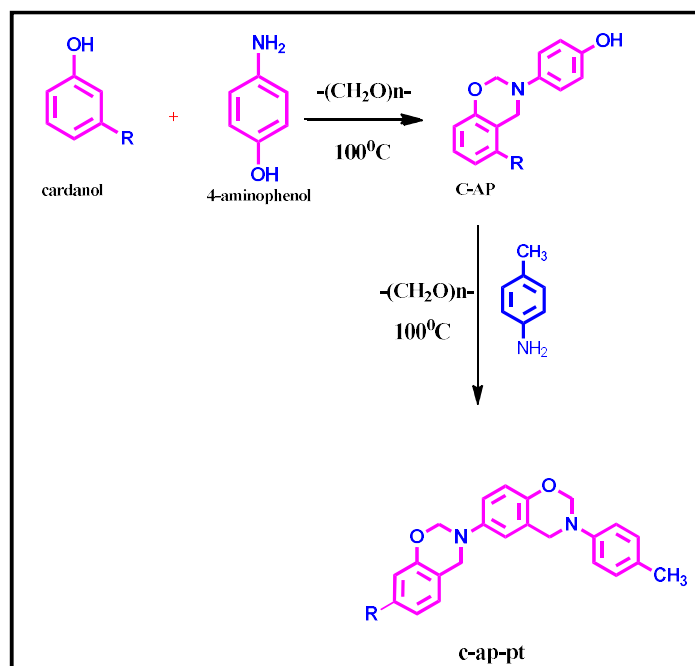
Scheme 1.   Synthesis of C-ap-pt

Synthesis of cardanol–aminophenol-fluroaniline based benzoxazine(C-ap-fa)

10g (0.033mol) of cardanol was mixed with 3.65g (0.0335mol) of 4-aminophenol and 2.0g (0.067mol)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 followed by the addition of3.75g(0.0167mol) of fluroaniline, 2.0g (0.067 mol) of paraformaldehyde and continued the reaction for another 2 h until the completion of benzoxazine formation. Rest of the steps had been followed according to the synthesis procedure adopted for (C-ap-pt). The synthesized cardanol-4-aminophenol/4-fluoroanilinebased asymmetric benzoxazine was labelled as C-ap-fa (Scheme 2).
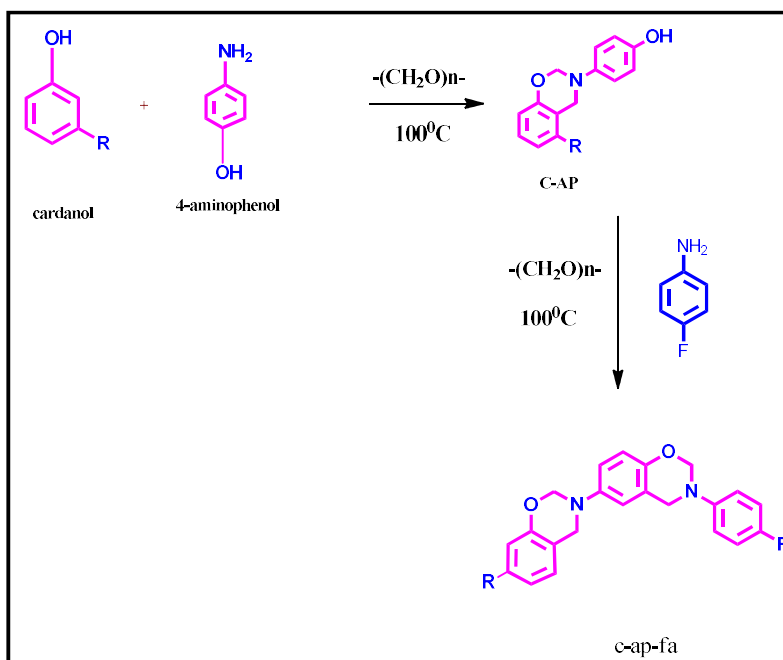
Scheme 2. Synthesis of C-ap-fa

Preparation of polybenzoxazines

The thermal ring opening polymerization of cardanol based benzoxazine was carried out according to the reported procedure [13,2,14]. 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, if any present viz., moisture and trace of solvent. After stabilization, the temperature was raised to 220°C at a heating rate of 20°C/h. The heating was continued for another 3 h at 220°C for the completion of the curing process. At this temperature, the monomer undergoes ring opening polymerization to form polybenzoxazine with cross-linked network structure (Schemes S1 and S2). The process of polymerization was confirmed by FTIR spectrum.

RESULTS AND DISCUSSION

The cardanol-based benzoxazines (C-ap-pt) and (C-ap -fa) were prepared by the condensation reaction of cardanol with different amino compounds and paraformaldehyde at an appropriate stoichiometric as shown in Schemes 1 and 2. Due to the presence of meta-substituted long alkenes/alkyl (15carbons) chain groups, the cardanol derived benzoxazines are liquid [15,16]. Consequently, resulted benzoxazines possess an improved flexibility, good water repellence. The molecular structure of prepared cardanol based benzoxazine monomers was confirmed by FTIR and ^{1}H-NMR spectral analyses. Curing behaviour and thermal stability of benzoxazines were studied by DSC and TGA techniques respectively.

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FTIR spectral analyses of benzoxazines

The FTIR spectra of cardanol based benzoxazines are presented in Figure 1. The bands at around 1229 cm^{-1} and 1592 cm^{-1} were attributed to the asymmetric and symmetric stretching vibrations of C-O-C bond in the benzoxazine respectively. The peak at 1105 cm^{-1} obtained due to the asymmetric stretching of C-N-C. Similarly, the appearance of bands at around 941cm^{-1} and 1496cm^{-1} are correspond to a tri-substituted benzene ring which confirms the formation of benzoxazine ring [2, 17]. Further, the band at around 3009 cm^{-1}corresponds to C-H stretching vibrations of the benzene ring. The characteristic absorption peaks at around 2920 cm^{-1} and 2853 cm^{-1} represent the asymmetric and symmetric stretching vibrations of CH$_2$ of oxazine ring[18], as well as alkyl side chain of cardanol moiety.
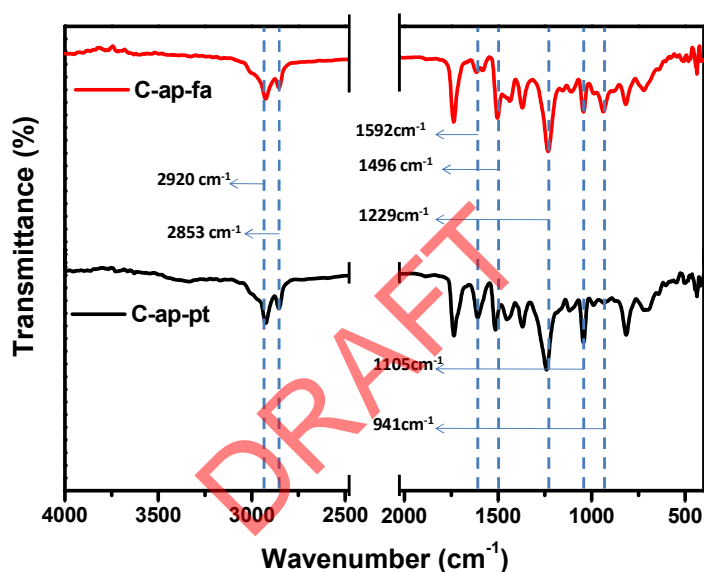

Figure 1. FTIR spectra of benzoxazine monomers C-ap-pt and C-ap-fa

^{1}H-NMR analysis of benzoxazines

Additionally, the structure of benzoxazines viz., C-ap-pt and C-ap-fa has been confirmed by ^{1}H-NMR analysis. The formation of benzoxazine ring in C-ap-pt and C-ap-fa was confirmed with the appearance of different environment resonance peaks. For the para-toludine attached with benzoxazine ring peaks at around 4.5 ppm (singlet, 2H, a type signal in Figures 2 and 3) for methylene group of Ar-CH$_2$–N and around 5.5 ppm (singlet, 2H, b type signal in Figures 2 and 3) for (O-CH$_2$ -N) from ^{1}H-NMR spectroscopy.
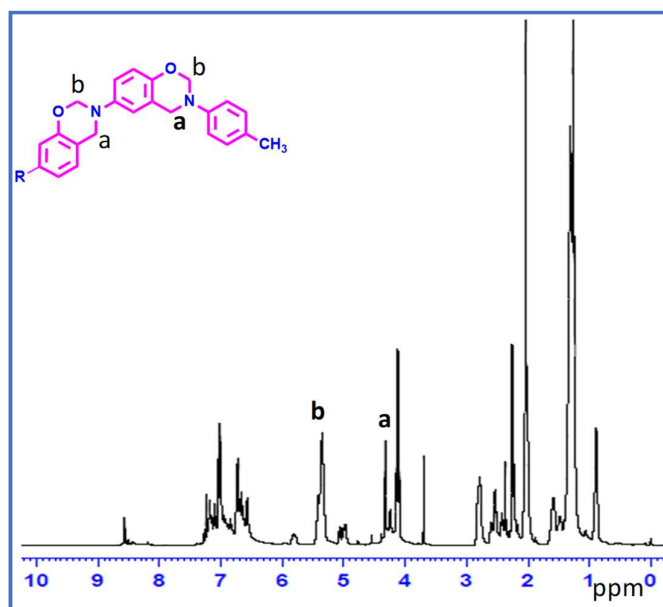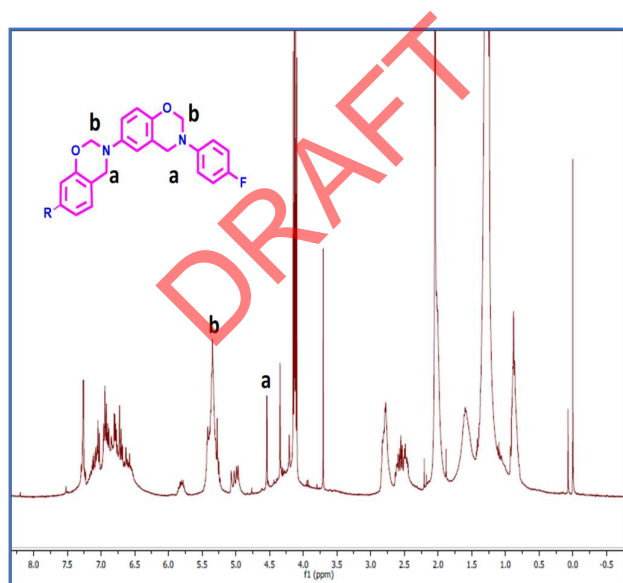
Figure 2. ¹H-NMR spectrum of C-ap-pt benzoxazine

Figure 3.¹H-NMR spectrum of C-ap-fa benzoxazine

Curing behavior of benzoxazine

The curing behavior of all the synthesized benzoxazine monomers was examined by DSC analysis at the heating rate of 10°C/min. Figure 4, shows the DSC thermograms of cardanol based benzoxazines with two different amines, p-toludine and 4-fluroaniline. The appearance of exothermic peaks with regard to the benzoxazines, C-ap-pt and C-ap-fa confirm the polymerization reaction proceeds through thermal ring-opening mechanism [19,20](S2). The

curing temperature (exothermal maxima – T_p) of C-ap-pt and C-ap-fa benzoxazines were observed at 207°Cand 219 °C (Table 1) respectively.
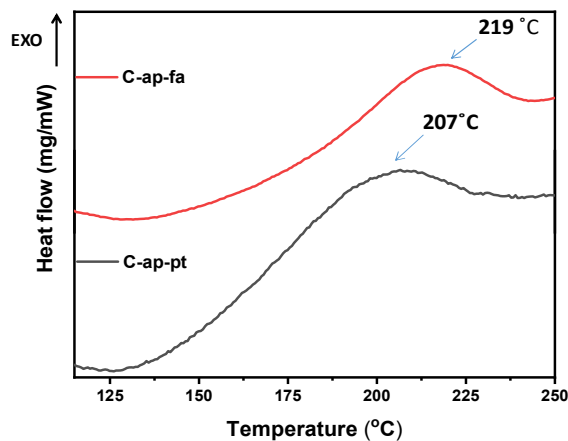

Figure 4. DSC traces of benzoxazine monomers C-ap-pt and C-ap-fa

Table 1.The curing behaviour of cardanol based benzoxazines (C-ap-pt andC-ap-fa)

Cardanol basedbenzoxazines	Curing behaviour at the rateof 10°C per min		
	T_i(°C)	T_p(°C)	T_f(°C)
C-ap-pt	187	207	226
C-ap-fa	190	219	238

T_i initial peak temperature
T_p exothermic peak maximum temperature
T_f final peak temperature

The curing temperature of di-functional benzoxazine C-ap-pt is lower than that of C-ap-fa based benzoxazines. The lowering of cure temperature may be explained due to the formation of Zwitterions intermediate (S3) followed by the proton exchange in the case of benzoxazines moiety [18,19,21], Consequently, the formation of Zwitterions intermediate reduces the polymerization temperature when compared to that of aniline based benzoxazines.

FTIR spectral analysis of polybenzoxazines

After the thermal treatment, the chemical structure of cardanol based polybenzoxazines namely poly(C-ap-pt) and poly(C-ap-fa) was confirmed by FTIR spectral analyses (Figure 5). The absorption band at941cm^{-1}ofoxazine ring disappeared after thermal curing at 220°C for 3 h which confirms the occurrence of complete ring opening and subsequent occurrence of cross-linking due to polymerization.
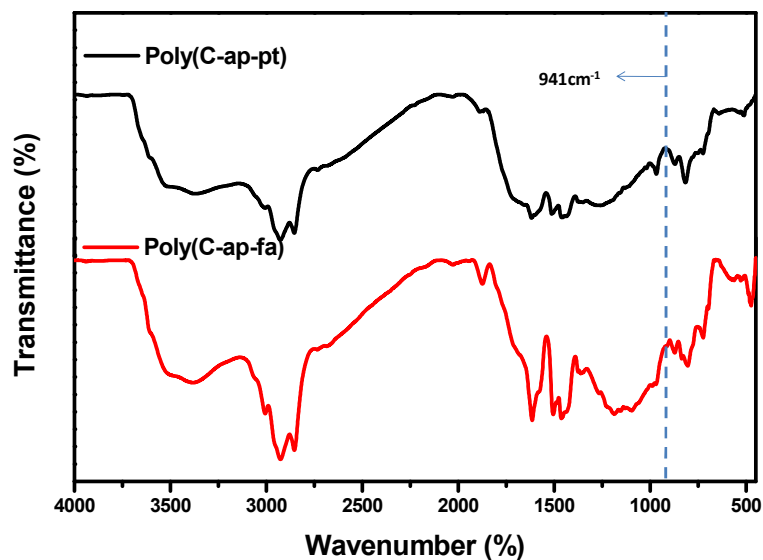
Figure 5. FTIR spectra of poly(C-ap-pt) and poly(C-ap-fa)

Thermal stability of polybenzoxazines

The thermal stability of cardanol based polybenzoxazines was studied using thermogravimetric analysis (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.TGA provides a valuable data with regard to the thermal stability of materials, the impurities or solvents present and the nature of degradation by measuring the weight loss. For the cardanol based polybenzoxazines viz., poly(C-ap-pt) and poly(C-ap-fa), 5% weight loss was noticed at 338, 344°Crespectively. The maximum degradation takes place at 446°C and 454°C, respectively. The chair yield of poly(C-ap-pt) and poly(C-ap-fa) observed at 850 °Care 21% and 29%respectively. Among the benzoxazines viz., poly(C-ap-fa) possesses higher char yield than that of poly(C-ap-pt), due to the presence of highly cross-linked network structure obtained from di-functional benzoxazine moiety [2,22].
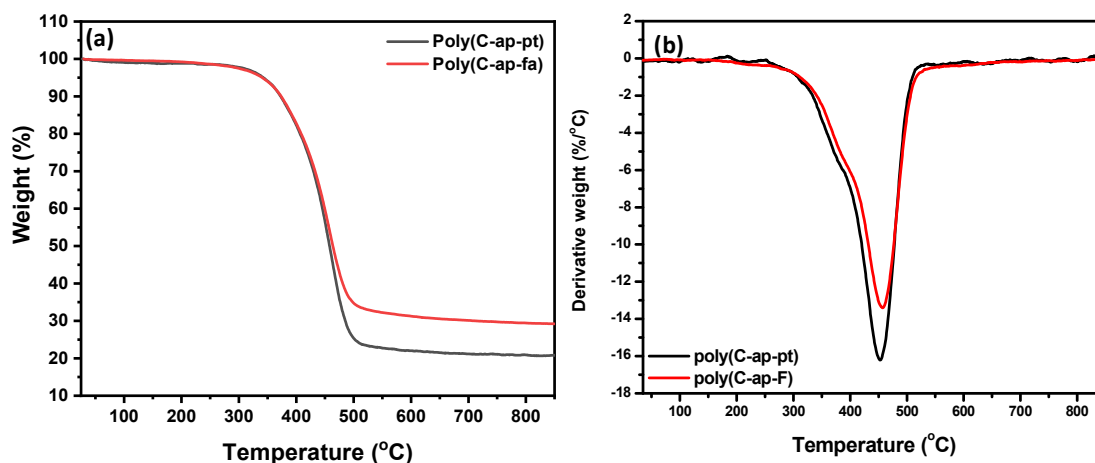
Figure 6. Thermal stability of polybenzoxazines (a) TGA thermogram and (b) DTG thermogram of polybenzoxazines.

Table 2. Thermal behavior of cardanol based benzoxazines.

Cardanol basedbenzoxa zines	5% weight loss (^{o}C)	10% weight loss(^{o}C)	T_{max} (^{o}C)	Char yield % at 850°C	LOI
Poly(C-ap-pt)	338	371	454	21	26
Poly(C-ap-fa)	344	375	458	29	29

Flame retardant behavior

The flame retardant behavior of the cured polybenzoxazines was also ascertained by calculating limiting oxygen index (LOI) value based on the obtained residual char yield at 850ºCfrom TGA analysis. The value of limiting oxygen index (LOI) is calculated from van Krevelen's and Hoftyzer equation [23,24], [eq. 1] and the results obtained are presented in Table 2.

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

Whereθ is the percentage char yield of materials remains at850°C.

The char yield of the polybenzoxazines viz., poly(C-ap-pt) and poly(C-ap-fa) was found to be 26% and 29% respectively. The LOI values of the polymers should be above the threshold value of 26 to render them self-extinguishing and for their utility for many applications requiring good flame resistance [25]. The synthesized polybenzoxazines show the value of LOI greater than 26 confirming their good flame retardant behaviour. The higher the LOI value of poly(C-ap-fa) is may be due to the presence of three dimensional cross-linked network structure.
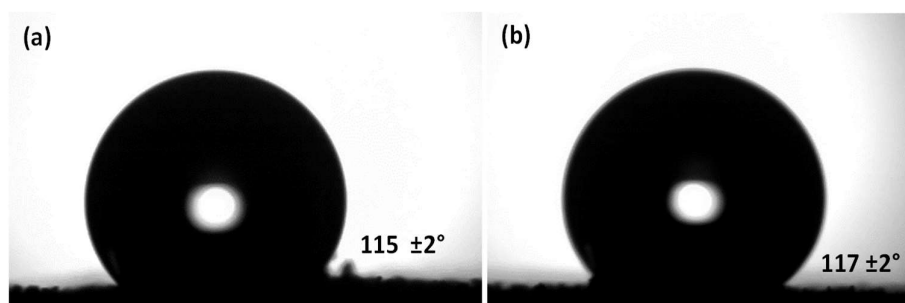
Water contact angle studies

Figure 7. The water contact angle of (a) poly(C-ap-pt) and (b) poly(C-ap-fa)

The value of water contact angle and images of poly(C-ap-pt) and poly(C-ap-fa) are given in Figure 7. The values of water contact angle obtained for poly(C-ap-pt) and poly(C-ap-fa) are 115° and 117° respectively. The lower affinity of the developed polybenzoxazine matrices towards water indicates their hydrophobic behavior [17, 26], this may be due to the presence of long aliphatic chain of cardanol moiety. In addition, the intra-molecular hydrogen bonding results in enhanced value of water contact angle. Consequently, the developed benzoxazine matrices possess lower surface free energy and enhanced hydrophobic behavior suggest that these materials can be used as an effective insulation material under humid environmental conditions.

CONCLUSION

Bio-based asymmetric benzoxazines (C-ap-pt and C-ap-fa) were synthesisedthrough Mannich condensation reaction. The benzoxazines were prepared using cardanol,4-aminophenol, paraformaldehyde and p-toludine / 4-fluroanilineunder an appropriate experimental condition. The molecular structure of synthesized monomers was confirmed by FTIR and ^{1}H-NMR spectral analyses. The curing behaviour of C-ap-pt and C-ap-fa benzoxazines was studied and confirmed the exothermic ring-opening polymerisation reaction of oxazine moieties. The polymerization temperature (T_P) obtained for C-ap-pt and C-ap-faare207°C and 218°C respectively. The formation of polybenzoxazine structure was confirmed by FTIR analysis after the thermal curing which ascertains the cleavage of benzoxazine ring through ring-opening and results three dimensional cross-linked network structure. The thermal stability of cured poly(C-ap-pt) and poly(C-ap-fa) was studied by TGA analysis. The maximum degradation in TGA thermograms indicated that the bond cleavage of aromatic group. The char yield of poly(C-ap-pt) and poly(C-ap-fa) at 850°C was noticed at 21% and

29%, respectively. The value of LOI of poly(C-ap-pt) and poly(C-ap-fa) was found to be 26 and 29 respectively and this indicates that poly(C-ap-fa) possesses a higher value of LOI than that of poly(C-ap-pt).Data obtained indicate that the synthesized polybenzoxazines may be exploited for flame retardant application. The value of water contact angle of poly(C-ap-pt) and poly(C-ap-fa) are observed at $115°$ and $117°$ respectively. These values infer an excellent hydrophobicity. Among the synthesized benzoxazines viz., poly(C-ap-pt) possesses better hydrophobic character than that of poly(C-ap-fa). Data obtained from different studies, it is concluded that the polybenzoxazines developed in the present work can be used in the form of sealants, adhesives, coatings and matrices where applications demand thermally stable and resistance to moisture.

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