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Thermal behaviour of cardanol-based benzoxazines

Monomers and polymers

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Abstract A novel benzoxazine monomer (Bz-C) based on agrochemical renewable resource—cardanol (by-product of cashew nut tree, *Anacardium occidentale*) was synthesized. Bz-C, a liquid monomer, was used as reactive diluent for the solventless synthesis of bisphenol-A benzoxazine monomer (Bz-A). Benzoxazine monomer based on cardanol and bisphenol-A in 3:1, 1:1 and 1:3 blend ratio were prepared by this method. The resins had Brookfield viscosity at 316 K in the range of 145–81,533 mPa s. The resins were characterized by ^{1}H-NMR, FTIR and elemental analysis. Curing characteristics were studied by DSC analysis. Thermal stability of cured resins was found to improve with increase in Bz-C content in the blends.

Keywords Benzoxazine · Cardanol · Brookfield viscosity · Renewable · Curing · Thermal stability

Introduction

Polybenzoxazines (PBzs) are a relatively new class of thermosetting phenolic resins developed in the past few years [1–4]. These resins have the capability to overcome the shortcomings of conventional phenolic resins as they exhibit (a) nearly zero shrinkage upon curing, (b) low water absorption, (c) usually T_g much higher than the cure temperature, (d) high char yield, (e) no strong acid catalysts required for curing, (f) ideally very long shelf life (g) and no release of by-products thereby leading to crack-free mouldings. Besides these properties they have good thermal stability and chemical resistance.

The monomers of PBz have been prepared using phenols, primary amines and formaldehyde. Therefore, the chemistry of benzoxazine synthesis offers a wide range of molecular design flexibility by using appropriate starting materials and thus molecular structure can be tailored for specific applications. Benzoxazines (Bzs) monomers are bicyclic heterocycles generated by the Mannich-like condensation of a phenol, formaldehyde and an amine [5] either by employing solution or solventless methods.

A typical reaction scheme for the synthesis of bisphenol-A based benzoxazine monomer is depicted in Scheme 1. This monomer has been designated as Bz-A in subsequent text. A variety of benzoxazine monomers have been synthesized by using different substituted phenols and amines [6–8].

Benzoxazine monomers have been prepared either by mixing formaldehyde and amine in dioxane or methanolic KOH and then adding the phenol. The mixture is heated at reflux for few hours and cooled when a crystalline product is obtained. It is then recrystallised from 95% ethanol. The major disadvantage of this process is that a large amount of solvent is needed and the rate of reaction is slow. A solventless process [9], where an aldehyde, amine and phenol are physically mixed together and heated to above melting point, is a better approach.

Melt polymerization has been extensively used for the synthesis of benzoxazines [10–14]. Several aromatic amines such as aniline, *o*-toluidine, *p*-toluidine, *m*-toluidine, etc. have been used for the synthesis of benzoxazine monomers. However, the major problem encountered

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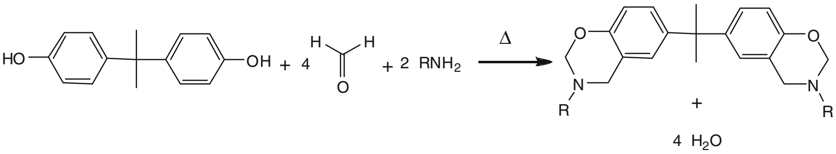
Scheme 1 Synthesis of bisphenol-A based benzoxazine-A (Bz-A) monomer



during solventless synthesis of these monomers is a significant increase in viscosity of the reaction mixture which creates problem during stirring at a later stage of the reaction (high conversion). It would be better if a low viscosity benzoxazine monomer is used as a solvent for the preparation of the desired monomer.

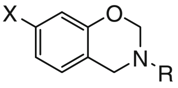
PBzs may be low or high viscosity liquids or solids. In the low viscosity resin, it is possible to achieve good wettability, processability and ease in applicability without the use of high temperature and pressure. In high viscosity resin, generally a reactive diluent is blended with neat base resins to reduce viscosity, extend pot life and improve cure. Reactive diluents are mono-functional low-viscosity liquids and used in forming structural composites, marine and protective coatings, adhesives, flooring and paints. Several varieties of reactive diluents have been reported for epoxy resins [15].

In the present studies, we have synthesized a new low viscosity cardanol-based benzoxazine monomer [designated as Bz-C (Fig. 1) in subsequent discussion]. Calo et al. [16] have reported the synthesis of cardanol-based benzoxazine using ammonia (30% w/w) and aqueous formaldehyde (37% w/w in aqueous solution).

However, no reports are available on Bz-C. It was used as reactive diluent for the preparation Bz-A. The other advantages of Bz-C monomer over the state-of-the-art benzoxazine monomers are:

(a) Phenolic raw material (cardanol) used for the synthesis of Bz-C is based on agricultural renewable resources of cashew industry (cashew nut tree, *Anacardium occidentale*),
(b) Monofunctional benzoxazine is of low viscosity due to the presence of long alkyl side-chain in the phenolic ring, and
(c) PBz based on cardanol may be more flexible due to internal plasticization of the alkyl substituent.

A series of resins were prepared by using Bz-C:Bz-A as 1:0, 3:1, 1:1, 1:3 and 0:1 by changing the feed ratio of phenolic compound, aniline and paraformaldehyde. Structural characterization was done using ^{1}H-NMR, FTIR, elemental analysis and Brookfield viscosity measurements. Curing behaviour of the various resin samples was studied using differential scanning calorimetry (DSC). Thermal stability of the cured resins was evaluated using thermogravimetry analysis (TG) in nitrogen atmosphere.



where, $X = C_{15}H_{31}, C_{15}H_{29}, C_{15}H_{27}, C_{15}H_{25}$

$R = C_6H_5$

Fig. 1 Structure of Bz-C monomer

Experimental

Materials

Cardanol was procured from Satya Cashew Chemicals Pvt. Ltd. (India), paraformaldehyde and chloroform from Rankem, aniline from Merck, bisphenol-A from SRL Pvt. Ltd. and sodium sulphate from CDH. All the reagents were used as received.

Characterization techniques

Structural characterization

FTIR spectrometer (Nicolet 200) was used for recording the IR spectra of starting material and monomer as thin film on KBr disc. Bruker AC 300 MHz FT-NMR spectrometer was used to record the ^{1}H-NMR of the samples. ^{1}H-NMR was recorded in $CDCl_3$ using tetramethyl silane as an internal standard. Brookfield viscosity was determined using Brookfield digital viscometer at 316 K with a spindle BS29.

Thermal characterization

The curing behaviour of monomer blends was evaluated by using TA 2100 thermal analyzer having 910 DSC module. A heating rate of 10 K min^{-1} in static air atmosphere and a sample mass of 2–3 mg in aluminium pans was used. The benzoxazine monomers were dried under vacuum at 323 K for 1 h before DSC analysis. Isothermal curing of resins was done by heating at 323 K for 1 h, 423 K for 1 h and 473 K for 1 h in an air oven. However, for 1:0 and 3:1 Bz-C:Bz-A required further additional curing at 523 K for an hour in an air oven. A Perkin Elmer Diamond SDTA thermal analyzer was used for thermal characterization of isothermally cured PBz resins in nitrogen atmosphere (flow rate 60 mL min^{-1}). A sample mass of 5–6 mg was used and the rate of heating was 10 K min^{-1}.

Synthesis

Benzoxazine-cardanol monomer (Bz-C)

A mixture of cardanol (100 g, 0.33 mol), paraformaldehyde (19.8 g, 0.66 mol), aniline (30.1 mL, 0.33 mol) was gradually heated from 323 to 343 K over a period of an hour, then at 353 K for 1 h followed by heating at 363 K for 2 h. The reaction starts at 343 K as indicated by evolution of water and reaction colour changed at 353 K from yellow to red brown. On cooling, water (500 mL) was added and organic layer was extracted with chloroform (2 × 100 mL). The organic layers were combined and washed with water (3 × 100 mL), dried over sodium sulphate and filtered to give red oil. The solvent was removed under reduced pressure and the residue was dried at 343 K under vacuum to give cardanol benzoxazine (Bz-C) in quantitative yield as red brown oil. $\nu_{\max}$ (film, KBr disc)/cm^{-1} 3008, 2926, 2853, 1623, 1601, 1579, 1257, 1241, 1031; ^{1}H-NMR (300 MHz, $CDCl_3$, δ ppm): 0.86–0.93 (*m*, CH_3), 1.2–1.7 (*m*, aliphatic CH_2 protons), 1.92–2.20 (*m*, $CH_2CH=$), 2.50 (*t*, CH_2Ar), 2.80–2.90 (*m*, $CH_2(CH=)_2$), 4.58 (s, $ArCH_2N–$), 4.92–5.12, 5.20–5.50, 5.80–5.89 (*m*, CH=, $CH_2=CH–$, $–OCH_2N–$, $HC=CH_2$), 6.63–6.74 (ArH, *m*, 2H), 7.05–7.30 (ArH, *m*, 4H). The calculated values of elemental composition of Bz-C ($C_{29}H_{41}NO$) are C%: 83.0, H%: 9.6 and N%: 3.84. The observed percentages of C, H, and N for Bz-C were 83.54, 9.85 and 3.34, respectively.

Bz-C:Bz-A, 1:1

The Bz-C monomer was prepared as described above. To this bisphenol-A (37.64 g, 165 mmol), paraformaldehyde (19.8 g, 0.66 mol) and aniline (30.1 mL, 0.33 mol) was added. The mixture was allowed to homogenize at 363 K for 1/2 h, then temperature was raised slowly to 403 K at a heating rate of 20 K h^{-1} with a temperature interval of 10 K. The contents were heated at 403 K for 1 h. On cooling, water (500 mL) was added and organic layer was extracted with chloroform (2 × 150 mL). The organic layer was combined and washed with water (3 × 100 mL), dried over sodium sulphate and filtered to give red solution. The solvent was removed under vacuum and the residue was dried at 343 K under vacuum to give the blend of benzoxazine-cardanol and benzoxazine-bisphenol-A monomers in quantitative yield as yellowish red oil. Thus, in situ reaction for the preparation of Bz-A in the presence of Bz-C as reactive diluent was successful and no problems were encountered during mechanical stirring of the reaction mixture. The other resins were prepared following the same synthetic procedure. The low viscosity of Bz-C modifies the viscosity of the medium thereby facilitating the formation of Bz-A. A neat Bz-A monomer was also synthesized under similar reaction conditions for comparison studies and stirring at later stages was observed to be problematic.

Results and discussion

The condensation reaction of cardanol hydroxyl groups with aniline and paraformaldehyde resulted in the formation of Bz-C in quantitative yield. The characteristic absorption bands [17, 18] of cardanol due to phenolic O–H (3344 cm^{-1}) was absent in Bz-C suggesting a complete conversion of hydroxyl groups of cardanol to oxazine ring (Fig. 2). The formation of oxazine ring in Bz-C was further supported by the appearance of new absorption bands due to Ar–C–O oxazine asymmetric and symmetric stretch [19] at 1241 and 1031 cm^{-1}, respectively. The absence of N–H and C–N stretch (3360–3442 cm^{-1}, 1281 cm^{-1}), and N–H bending (1619 cm^{-1}) vibrations of aniline of Bz-C further suggests the absence of unreacted aniline in the Bz-C monomer and a complete condensation reaction. In addition, the other absorption bands observed are aromatic, vinylic, aliphatic C–H (3008, 2926 and 2854 cm^{-1}) and aromatic, aliphatic C=C (1580–1623 cm^{-1}) supporting the structure of Bz-C.

The ^{1}H-NMR spectrum of Bz-C (Fig. 3) showed characteristic signals at 5.3 ppm (olefin, $ArOCH_2N$), 4.8 ppm (s, $ArCH_2N$) suggesting thereby the formation of oxazine structure and hence successful formation of cardanol-based benzoxazine monomer. The ^{1}H-NMR spectra of Bz-C: Bz-A blends also showed the formation of the two monomers.

Bz-A is solid while Bz-C is liquid at ambient temperature. Brookfield viscosity of Bz-C and other resin mixtures with varying amounts of Bz-A was recorded at 316 K. Bisphenoxazine-A is a structural rigid monomer and Bz-C is flexible due to longer alkyl/alkylene chain at *m*-position.

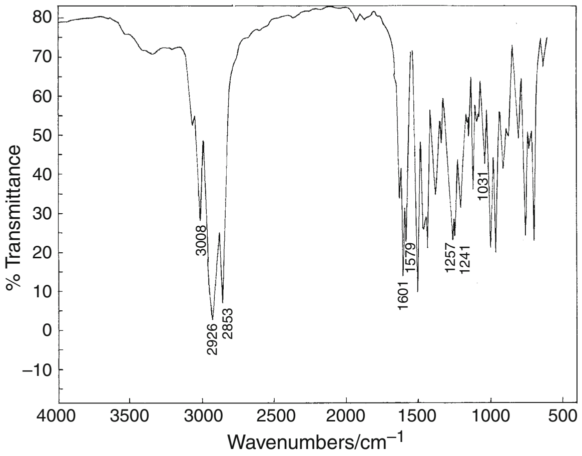


Fig. 2 FTIR spectrum of Bz-C

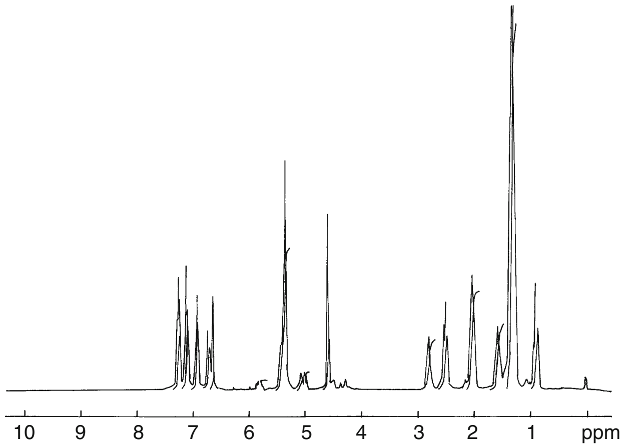


Fig. 3 ^{1}H-NMR spectrum of Bz-C in $CDCl_3$

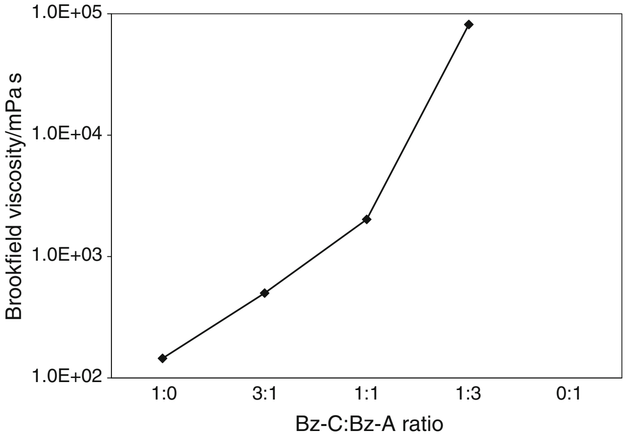


Fig. 4 Brookfield viscosity of Bz-C:Bz-A monomers at 316 K

Addition of Bz-C to Bz-A resulted in a significant reduction of viscosity Bz-A. The variation in Brookfield viscosity with the change in blend ratio of the monomers is shown in Fig. 4.

Thermal curing of the benzoxazine monomers forms the corresponding polymer PBzs. The architecture of backbone of PBz is formed by thermally activated ring-opening of the oxazines of the two monomers (Fig. 5). The conformation of the repeat unit in the polymer backbone may be head-to-head or head-to-tail or a mixture of the two.

A good agreement was observed in the experimental elemental analysis results of the Bz-C with the calculated data supporting the chemical structure of monomer. Bz-C monomer was isothermally cured to form polymer (PBz-C). The observed C%, H% and N% for PBz-C were 82.52, 9.04 and 2.65, respectively. A slight decrease in C, H and N content is observed in the cured resin. This may be due to partial oxidation of the monomer during thermal curing in air atmosphere.

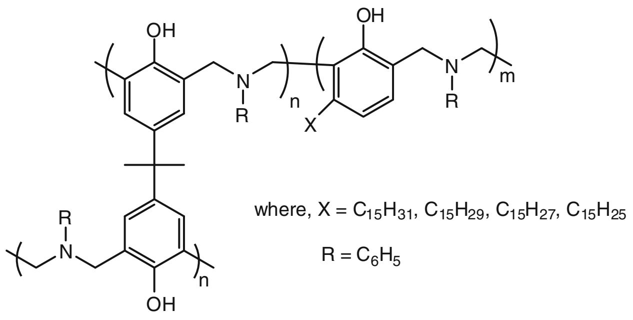


Fig. 5 Repeat unit structure of polybenzoxazines. The ratio of *m*:*n* will depend on the monomer feed composition

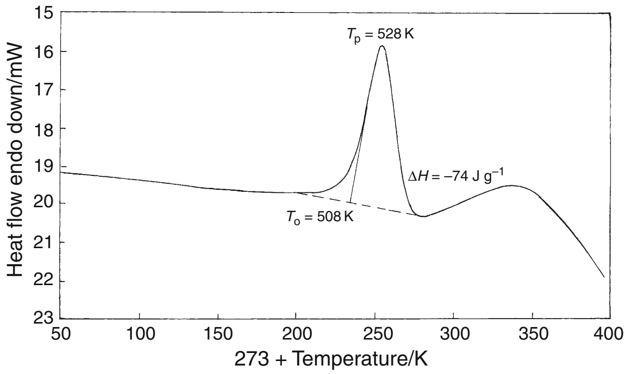


Fig. 6 DSC trace of Bz-C:Bz-A (3:1) resin

The curing characteristics of various resins were studied by DSC. A typical DSC scan is shown in Fig. 6. The exothermic transition observed was characterized by determining onset curing temperature (T_o), temperature of exothermic peak (T_p) and heat of curing reaction (ΔH) from the area under the curve. The curing characteristics (T_o, T_p and ΔH) of neat and Bz-C:Bz-A resins are summarized in Table 1.

The Bz-C monomer showed a higher T_o and T_p and a lower ΔH as compared to the Bz-A. The polymerization enthalpy of Bz-C is fourfold lower than Bz-A. This could be attributed to the monofunctional nature of Bz-C monomer while Bz-A is difunctional. Moreover, presence of longer

Table 1 Results of DSC analysis of benzoxazine resins (Bz-C and Bz-A, static air, heating rate 10 K min^{-1})

S. no.	Resin sample Bz-C: Bz-A	T_o/K	T_p/K	ΔH/J g^{-1}
1	1:0	515	536	71.1
2	3:1	508	528	74.1
3	1:1	506	523	114.2
4	1:3	484	504	223.4
5	0:1	460	492	271.1

alkylene chain substituent at the meta position in Bz-C causes dilution effect of oxazine functionality as compared to Bz-A. The blends of Bz-C with Bz-A showed a progressive decrease in T_o and T_p values with increase in Bz-C content in the blend ratio. A single exothermic transition was observed in the DSC curves of the blends suggesting co-curing of the monomers. As expected, an increase in ΔH values was found by an increase in Bz-A content in the resins.

Thermal stability of isothermally cured benzoxazines was studied by TG. A typical TG and DTG trace is shown in Fig. 7. The relative thermal stability of these samples was estimated by comparing initial decomposition temperature (IDT), temperature of maximum rate of mass loss (T_{max}, from DTG trace) and char yield at 1,073 K. The TG results are summarized in Table 2. PBz-C cured sample was flexible while PBz-A was brittle. Cardanol-based polymer (PBz-C) is thermally more stable than the bisphenol-A (PBz-A). The thermal stability of the blends improved by 100 K with increase in cardanol-based moieties in the polymer network. With the increase in Bz-A content in the blend ratio the char yields of copolymers were found to increase. This is because of increase in aromatic content of the polymeric structure. The bifunctionality of bisphenol-A benzoxazine structure yield higher crosslink density accounting for higher char yields with more bisphenol-A content in the blends.

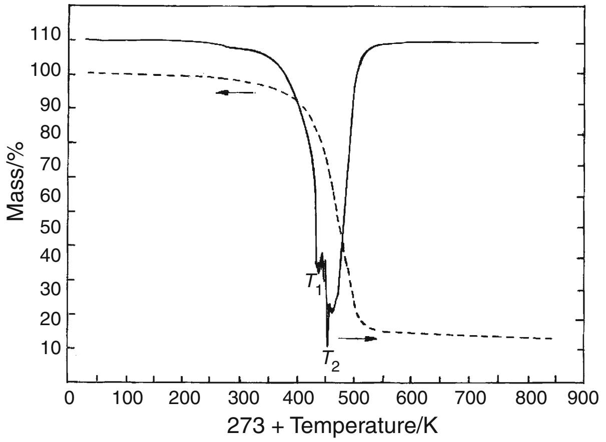


Fig. 7 TG/DTG curve of isothermally cured Bz-C:Bz-A (3:1) resin

Table 2 Decomposition temperatures of isothermally cured polybenzoxazine blends (nitrogen atmosphere, heating rate 10 K min^{-1})

S. no.	Resin sample PBz-C:PBz-A	IDT/K	T_{max}/K		Char yield/% at 1,073 K
			T_1	T_2	
1	1:0	671	703	740	12
2	3:1	667	703	738	14
3	1:1	652	703	729	17
4	1:3	650	–	720	20
5	0:1	547	583	723	39

The DTG traces showed a bimodal weight loss distribution with maximum weight loss at centred at 703 K (T_1) and 733 K (T_2) (Fig. 7) in Bz-C and Bz-C:Bz-A 3:1 and 1:1 resins. However, further increase in Bz-A content in Bz:C (3:1), a single step degradation was observed.

Summary and conclusions

A solventless synthesis of cardanol-based benzoxazine monomer, which was liquid in nature, was carried out successfully. The use of renewable source cardanol could effectively replace part of the petroleum-based bisphenol-A in benzoxazine polymers by this synthetic procedure. Bz-C monomer was used as a viscosity modifier and co-reactant for the synthesis of Bz-A monomer. The thermoset polymer formed was obtained by co-curing of Bz-C and Bz-A as demonstrated by DSC analysis. Benzoxazine moieties were shown to readily undergo thermally activated ring-opening reaction to form cross-linked polymer networks. The crosslink density of the polymer formed reflected in the cured polymers, which increased with increase in bisphenol content. Harder cured resins were obtained with higher content of bisphenol-A in the reaction mixture blend ratio. The co-cured resins exhibited higher thermal stability than PBz-A polymer. The enhanced thermal stability was attributed to the presence of cardanol units in the polymer network.

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