

Thermal Curing of Benzoxazine Blends from Cardanol-Furfurylamine and Diphenolic Acid-Aniline

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Abstract. Cardanol-furfurylamine benzoxazine (CFB) is a bio-based resin thanks to cardanol as a by-product of cashew nut shell liquid. Polybenzoxazine obtained from CFB exhibited high thermal stability, however, it requires a high thermal curing temperature. This research was aimed to reduce the curing temperature of CFB by blending it and diphenolic acid-aniline benzoxazine (DAB). The blend molar ratio of CFB:DAB was 4:1. Under thermal curing, carboxyl group in DAB was degraded and accelerated ring-opening polymerization of CFB/DAB blend so that no catalyst was used. Different curing temperatures of CFB/DAB blend was investigated. Results from fourier transform infrared (FTIR) and differential scanning calorimetry (DSC) proved that the ring-opening initiated at 115.2 °C for DAB, 141.6 °C for blend and 206.2 °C for CFB. It proved that CFB/DAB blend could start thermal curing at an obvious lower temperature. Moreover, polybenzoxazine synthesized from CFB/DAB blend exhibited good thermal stability compared to DAB-polybenzoxazine and obtained higher char yields compared to CFB-polybenzoxazine.

1. Introduction

Polybenzoxazines (PBzs) appeared as attractive candidates over traditional phenolic polymers due to their superior properties including high thermal stability, superior modulus properties, low water absorption, near zero shrinkage, and no release of by-products [1]. Recently, polybenzoxazine technology is now finding a breakthrough through the preparation of their monomers from renewable resources in the same way as other petroleum-based polymers. Among these renewable resource materials, cardanol is considered as an important starting material bio-based benzoxazine synthesis purposes due to its unique structural features, abundant availability and low cost. Cardanol is a major constituent of the cashew nut shell liquid (CNSL) which is an agricultural by-product abundantly available in many parts of the world, particularly in ASEAN countries. In other hand, the bio-based polybenzoxazines containing furan units has demonstrated excellent properties due to the aromatic characters of furan ring, like the high performance furan-based epoxy systems [2]. The furanic ring of furfurylamine is highly reactive and promotes an increase of the crosslinking density. When comparing cardanol-based monofunctional benzoxazines to other amine derivatives, such as aniline or benzylamine (T_g around 55 °C), was observed for the furfurylamine-based PBz material. Moreover, furfurylamine is synthesized from furfural which is a green platform product derived from a variety of agricultural by-products such as corncobs and wheat bran like other fatty amines containing a long hydrocarbon chain [3].



However, cardanol-furfurylamine benzoxazines (CFB) still requires a relatively high polymerization temperature. In the present research, an attempt was done to lower curing temperature of CFB by blending with benzoxazine derived from diphenolic acid (DPA) which is also commercially produced from cellulose-rich biomass. The presence of a carboxylic acid in DPA monomer should lower the high temperature needed to complete curing of these benzoxazines [4].

2. Experimental

2.1. Materials

All reagents and solvents were used as received from commercial suppliers. Cardanol was procured from Son Chau Co., Ltd (Viet Nam). Cardanol ($C_{21}H_{36-n}O$, $n = 0, 2, 4, 6$) was distilled at 230–240 °C under 2–4 mm Hg. Diphenolic acid (95%), furfuryl amine (99%), sodium sulfate (99%) and sodium hydroxide (97%) were purchased from Sigma-Aldrich. Paraformaldehyde (95%), aniline (99.5%) and chloroform (99%) were obtained from Merck. Toluene (99%) was provided by Prolabo. All reactions were carried out in oven-dried flask.

2.2. Synthesis of Cardanol – Furfurylamine Benzoxazine (CFB)

Cardanol-furfurylamine benzoxazine was synthesized by a method adopted from earlier report [4]. Cardanol (0.033 mol) was heated to 50 °C in a 100 ml three-necked round flask equipped with magnetic stirrer and thermometer. Then paraformaldehyde (0.066 mol) and aniline (0.033 mol) were added drop wise under vacuum environment. The temperature was gradually raised to 80–90 °C and kept at this temperature for half an hour until the mixture becomes homogenous and turns dark brownish red color.

Then, the temperature was further raised to 120–130 °C and refluxed for another 2h. The reaction mixture was then cooled to room temperature. The product was washed with 2N NaOH followed by washing with distilled water in a separating funnel. The organic phase was dried over sodium sulphate (Na_2SO_4) and filtered to give a red brown oil. The solvent was removed under reduced pressure and then dried at 60 °C for 12h under vacuum to obtain the final product which is CFB with a yield of 88%.

2.3. Synthesis of Diphenolic Acid-Aniline Benzoxazine (DAB)

Diphenolic acid-aniline (DAB) were synthesized according to the reported procedure [5]. 1,3,5-Triphenylhexahydro-1,3,5-triazine and (0.02 mol), paraformaldehyde (0.06 mol), 4,4-bis(4-hydroxyphenyl) pentanoic acid (0.03 mol) and 100 ml of toluene were placed into 250 ml two-necked round-bottom flask. The reaction mixture was heated at 110 °C for 6 h. The resulting light orange solution was filtered and concentrated under vacuum to obtain a syrup that was subsequently dried under high vacuum giving a yellowish solid with a yield of 89% of DAB.

2.4. Preparation of CFB/DAB Blend – Thermal Curing

CFB/DAB blend was prepared in a 4:1 molar ratio. CFB and DAB were taken and dissolved in 10 ml of chloroform and stirred at room temperature for 1 h to obtain a homogenous solution form. Afterwards, the mixture was dropped and casted on a glass plates. The solution was dried under vacuum for 2h at 80 °C. Thermal curing of blends was carried out in an oven at 150 °C, 180 °C and 220 °C for 1 hour and further characterized by DSC and FTIR. Similar process was used to prepare CFB and DAB polybenzoxazine.

2.5. Measurements

2.5.1. Structural Characterization

^1H (500 MHz) and ^{13}C (125.8 MHz) nuclear magnetic resonance (NMR) spectra were obtained using a Bruker Avance AM500 FT-NMR spectrometer with Fourier transform and CDCl_3 as solvent. The chemical shift are given relative to tetra methyl silane (TMS). The NMR measurements and analysis were performed at Center for Apply Spectroscopy, Institute of Chemistry, Vietnam Academy of Science and Technology (VAST), Hanoi, Vietnam. Fourier transform infrared (FTIR) spectra of the samples were recorded on a Bruker Tensor 37 spectrophotometer with a resolution from 4000 – 400 cm^{-1} in the absorbance and transmittance modes.

2.5.2. Thermal Characterization

Differential scanning calorimetric (DSC) studies were carried out on a NETZSCH DSC 204F1 Phoenix thermal analyzer using N_2 as a purge gas, heated from room temperature to 300 °C at scanning rate of 10 °C/min. The thermal stability of polymer was studied by thermogravimetric analysis (TGA) using a TGA Q500 instrument. Cured samples at 230 °C were analyzed at a temperature rate of 10 °C /min from 25 °C to 800 °C under nitrogen environment.

3. Results and Discussion

3.1. NMR Spectroscopy of the Synthesized Benzoxazines

The ^1H NMR spectra shown in Figure 1 confirm the structure of CFB benzoxazine. The oxazine ring protons (Ar-CH₂-N and O-CH₂-N) give resonance peaks at 3.9 and 4.8 ppm. The furan ring was characterized with the peaks at 6.3 to 7.3 ppm. The peaks from 0.8 to 2.7 ppm, at 5.0 ppm, and 5.4 ppm, were attributed to the unsaturated alkyl side chain of the cardanol [4].

Figure 2 shows ^1H NMR and ^{13}C NMR spectra of DAB. It can be seen that the nuclear magnetic resonance spectroscopy (^1H NMR) spectrum of the DPA-b exhibits not only the specific signals of the benzoxazine ring, but also chemical shifts that belong to the alkyl chain and the aromatic signals. Notably, while the two signals at 4.56 and 5.32 ppm correspond to -CH₂ protons of benzoxazine ring, methyl protons of the pentanoic acid appears at 1.51 ppm (singlet, 3H). Alkyl protons of the propionic acid moiety resonate at 2.13 ppm (triplet, C-CH₂, 2H) and 2.35 ppm (triplet, -CH₂-COOH, 2H). The COOH proton is not observed in ^1H NMR when CDCl_3 is used as solvent [6].

The corresponding ^{13}C NMR spectrum also supports the structure of the monomer. The two singlets at 79.23 ppm and 50.6 ppm are typical of the carbon resonances of -N-CH₂-O- and -N-CH₂-Ph of the oxazine ring, respectively. Most importantly, the signal appears at 179.1 ppm confirmed the presence of COOH group in the monomer structure [5].

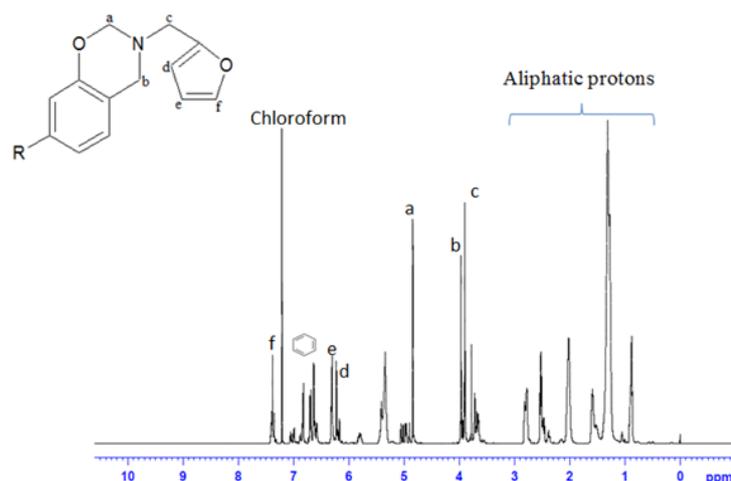


Figure 1. ^1H NMR spectrum of synthesized CFB

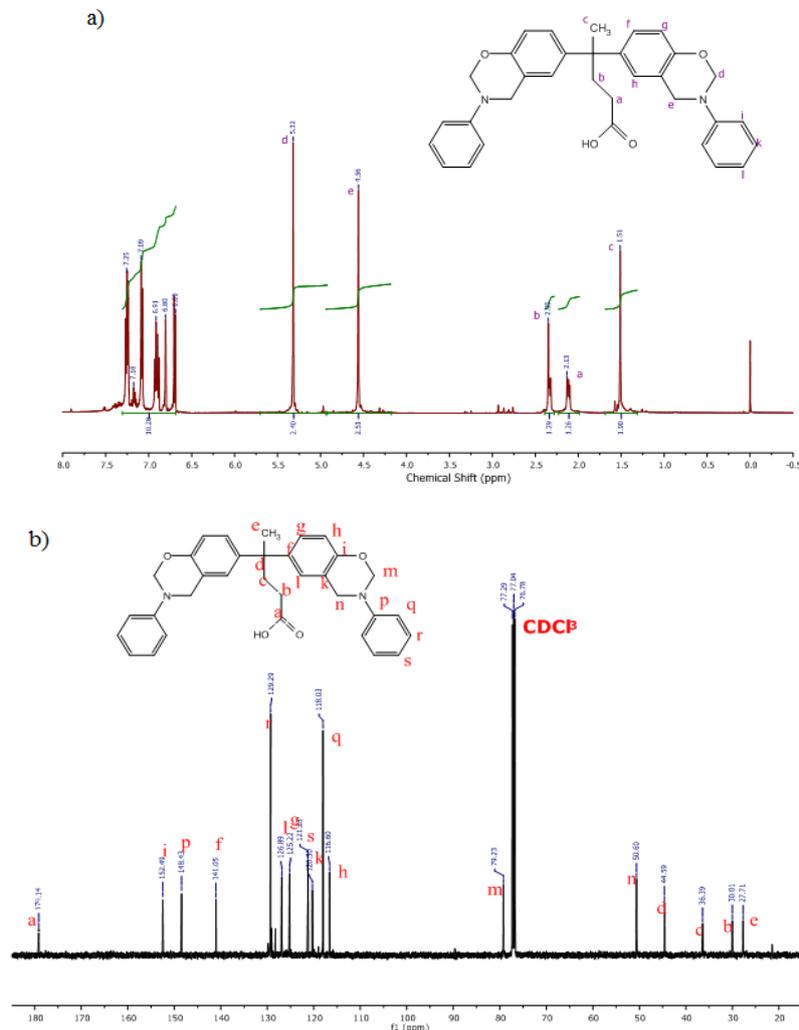


Figure 2 (a): ^1H NMR, (b) ^{13}C NMR spectra of synthesized DAB.

Figure 3 shows the distinguished curing behaviour of CFB, DAB and their blend. DAB could have the earliest curing temperature due to its carbonyl group, while CFB has the highest one. However, the curing energy of DAB was more than 10 times higher than that of CFB. As expected, the blend could have lower ROP initiation and endset temperature. It means carbonyl group of DAB could also accelerate the ROP reaction of CFB, even the high molar ratio of 4 CFB: 1 DAB.

CFB/DAB blend was cured at 150 °C, 180 °C, and 220 °C; and its curing energy and residue cure of were recorded seen in Figure 4. The curing energy of CFB/DAB blend was 93.8 J/g (Table 1), so its residue cure was calculated as 52.24% at 150°C and 3.2% at 180°C. In the other words, CFB/DAB blend was cured 47.76% at 150 °C, 96.8% at 180 °C and fully cured at 220 °C. Glass transition was detected from the DSC curve of CFB/DAB blend cured at 220°C. CFB/DAB blend was able fully cured at 220°C which is significantly lower than the curing temperature of CFB. Suggestion of polymerization of CFB and DFB are shown in Figure 5(a) and (b). It is noted that not all the COOH group will be esterification.

Table 1: Thermal curing behaviour of CFB, DAB and their blend using DSC

Monomer	T _{initiation} (°C)	T _{peak} (°C)	T _{endset} (°C)	ΔH(J/g)
CFB	206.2	251.6	281.2	25.49
CFB/DAB blend	141.6	210.0	243.0	93.88
DAB	115.2	177.2	242.7	272.6

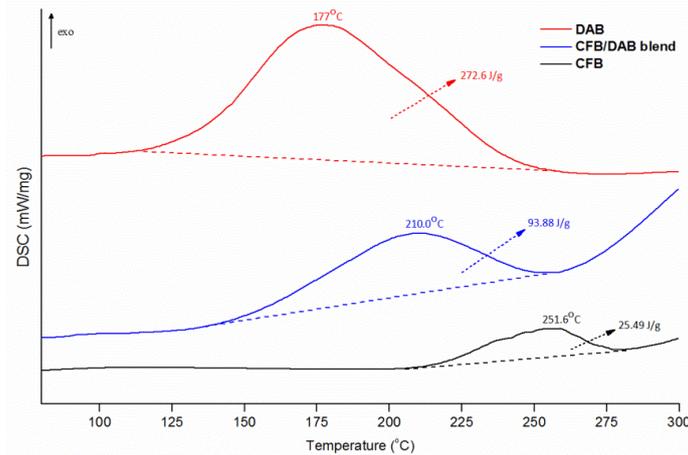


Figure 3. Thermal curing of DAB, CFB and their blend by using DSC

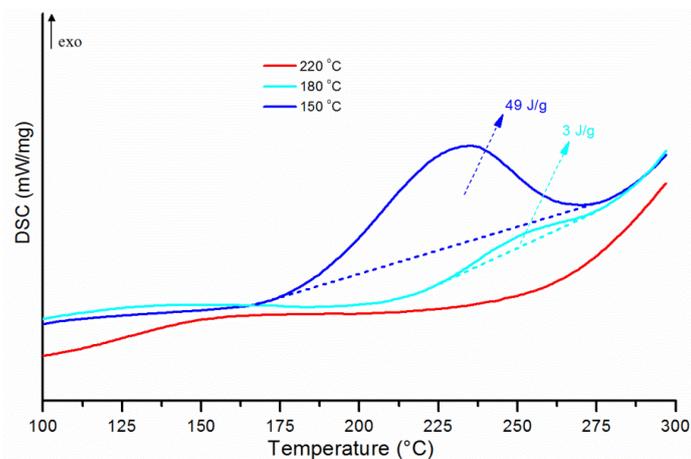


Figure 4. DSC of CFB/DAB blend after cured at 150 °C, 180 °C, and 220 °C

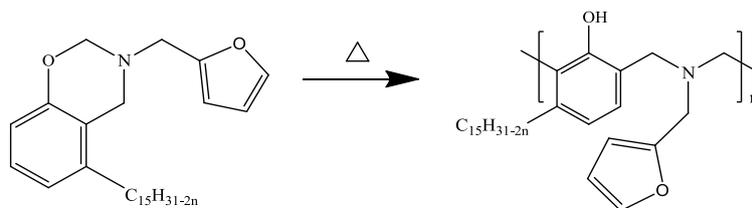


Figure 5(a). Thermal curing reaction of CFB

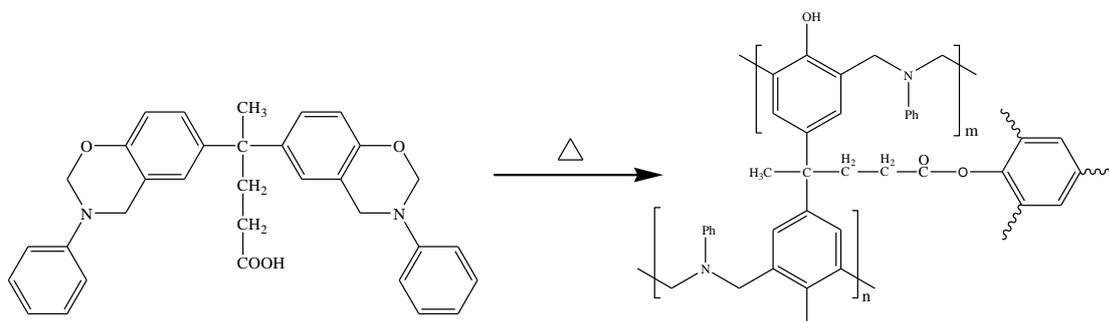


Figure 5(b). Thermal curing reaction of DAB

FTIR spectra of monomers blend and poly-benzoxazine after cured at 150 °C, 180 °C and 220 °C. The peaks at 1721cm^{-1} and 1410cm^{-1} of COOH group in DAB disappeared in all poly-benzoxazines. The carboxyl group could react with hydroxyl group to form ester (Figure 5(b)). Therefore the peak 1410cm^{-1} of OH belonged to COOH group reduced. Similar finding was also reported by Zuniga et. al [4]. In the other side, three main groups of benzoxazine are 1360cm^{-1} (CH_2 wagging), $\sim 1248\text{cm}^{-1}$ (Ar-CO-asymmetric stretching) and 960cm^{-1} (benzene attached to oxazine ring), which also decreased in all poly-benzoxazines proving the occurrence of ROP reaction. The peak 690cm^{-1} of tri-substituted aromatic ring of benzoxazine also reduces.

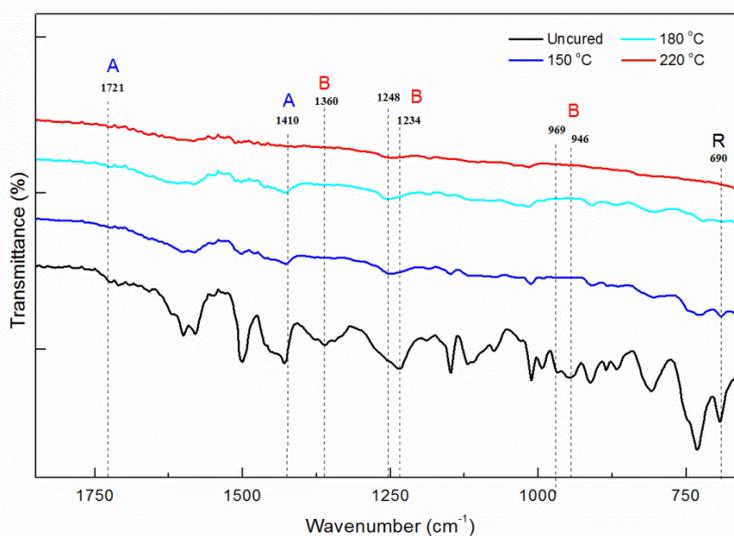


Figure 6. FTIR of CFB/DAB blend before and after cured, A: COOH, B: peaks of benzoxazine, R: tri-substituted.

Thermal stability of poly-benzoxazines synthesized from CFB, DAB and their blend is reported in Table 2 and Figure 7. DAB -benzoxazine exhibited the early degradation at $221.1\text{ }^\circ\text{C}$ because of the degradation of remained carboxyl group or new ester groups. CFB poly-benzoxazine had a significantly high thermal stability compared to DAB. Therefore, the poly-benzoxazine of CFB/DAB blend also performed well thermal stability.

Table 2: Thermal properties of Poly-benzoxazine from CFB, DAB and their blend

	T_{onset} ($^{\circ}\text{C}$)	$T_{5\%}$ ($^{\circ}\text{C}$)	$T_{10\%}$ ($^{\circ}\text{C}$)	Char yield (%)
CFB	436.9	402.5	428.5	14.7
Blend	427.8	360.5	399.5	18.3
DAB	221.1	255.5	297.5	30.3

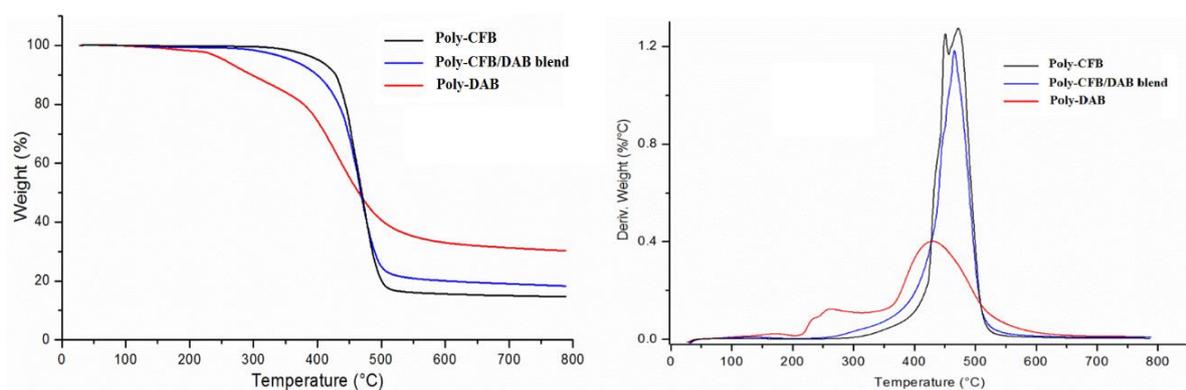


Figure 7. TGA and DTG curves of polybenzoxazine from CFB, DAB and their blend

4. Conclusion

Cardanol-furfurylamine benzoxazine as a bio-benzoxazine was synthesized. Its poly-benzoxazine exhibited a distinguished high thermal stability. However, cardanol-furfurylamine benzoxazine needed a high temperature for thermal curing. Addition of dibisphenol acid – aniline benzoxazine with the blend ratio of 4 CFB/1 DAB was successfully reduced the peak temperature of thermal curing from 251.6 $^{\circ}\text{C}$ of CFB to 210.0 $^{\circ}\text{C}$ of CFB/DAB blend. Further investigation on the ability to form interpenetrating polymer network of CFB and DFB could be carried out, as well as the reaction of CFB and DFB during thermal curing can be examined.

References

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