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SYNTHESIS AND BLEND OF BIO-BASED BENZOXAZINES FROM CARDANOL AND DIPHENOLIC ACID

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Abstract. In this study, two benzoxazine monomers, m-alkylphenyl-3,4-dihydro-2H-benzoxazine (CA-Bz) and 4,4′ -Bis-[6-(3-phenyl-3,4-dihydro-2H-1, 3-benzoxazine)] pentanoic acid (DPA-Bz) were successfully synthesized from fully bio-based phenols (cardanol and diphenolic acid). Their structures were confirmed by FTIR and NMR spectroscopy. CA-Bz/DPA-Bz blend was prepared at weight ratio of 3:1. Polymerization behavior of the blend was investigated by DSC. The ring-opening polymerization temperature of CA-Bz was found to decrease significantly by incorporation of carboxyl groups in DPA-Bz showing thereby the catalytic effect of acid functionality. The modified polybenzoxazine also showed an enhancement of the thermal properties.

Keywords: diphenolic acid, cardanol, ring-opening polymerization, benzoxazine blend.

Classification numbers: 2.9.3, 2.10.2, 2.10.3.

1. INTRODUCTION

Polybenzoxazines (PBzs) are relatively a new class of high performance polymers which display good mechanical strength, low moisture absorption, high service temperature, high char yield and structure design flexibility, in addition to their zero shrinkage or a slight expansion upon curing. These fascinating characteristics have made polybenzoxazine more attractive from both industry and academic parties in recent years, leading to a wide range of applications such as electronics, composites, blends, and alloys and so on [1-3].

Most of the chemicals used for the synthesis of benzoxazine (Bz) are based on petroleum resources, which is not easily renewable. Currently, with the rapid development of bio-based materials, using renewable phenolic derivatives to replace the petroleum-based raw materials for the synthesis of benzoxazine monomers has gained considerable interest. Cardanol is an industrial pale-yellow oil extracted from cashew nut shell liquid which is also a promising renewable phenol resource. Cardanol is the main component of the technical CNS which is sustainable, inexpensive and largely available as agricultural waste in major parts of the world, particularly in Viet Nam. Cardanol have been used with other neat resins for properties improvement in various applications such as structural composites, adhesives, and paints [4-7].

Cardanol-based benzoxazines demonstrated high flexibility due to the presence of the long soft aliphatic chain, which provides a better processability. However, this benzoxazine has relatively low mechanical properties due to the low crosslink density of cured products and still requires a high polymerization temperature [8-9].

It is widely reported that bisphenol A (BPA)-based benzoxazine stands out from many types of benzoxazines due to its high structural integrity and superior properties [1, 9]. Diphenolic acid (DPA), which has a structure similar to BPA (Figure 1), can be prepared from low-grade lignin and cellulose biomass resources. DPA is commercially available and much cheaper than BPA and has the ability to introduce functional carboxyl group into the polymer structure. Therefore, DPA is believed to be a cheap bio-based compound in large scale and it can be a good candidate to replace BPA for the synthesis of benzoxazine resin with low curing temperature [10].

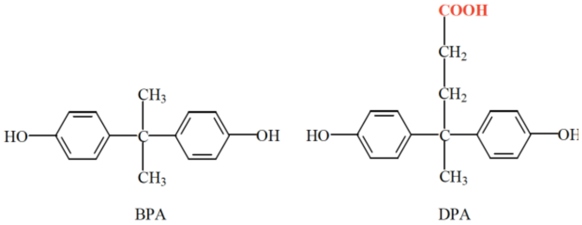

Figure 1. The structure difference between BPA and DPA.

It is well known that one main drawback in benzoxazine chemistry is the high curing temperature. Two methods have been used to solve this problem: application of highly active initiators and blending with different benzoxazine monomers. Benzoxazine monomers have been modified to lower ring-opening polymerization (ROP) by using catalysts such as lithium iodide (LiI), phosphorus pentachloride (PCl_5), p-toluene sulfonate. However, the excess of catalyst used remain trapped in the polymer network might cause problems such as low thermal stability and brittleness of obtained materials. The latter approach can overcome such disadvantages since the added monomer become a part of PBz network and accelerate the ROP [11-12].

In this work, we have synthesized and used a DPA-Bz monomer containing acid functionality based on diphenolic acid (DPA) to blend with CA-Bz monomer. It is expected that such a monomer will catalyze the ROP and reduce the curing temperature of cardanol-based benzoxazine.

2. MATERIALS AND METHODS

2.1. Materials

Cardanol was obtained from Son Chau Co., Ltd (Viet Nam) (Table 1). Prior to synthesis of CA-Bz, cardanol ($C_{21}H_{36-n}O$, n = 0, 2, 4, 6) was distilled at 230–240 ^{o}C under 2–4 mm Hg. Diphenolic acid (4,4ʾ-bis(4-hydroxyphenyl) pentanoic acid) (95 %), sodium sulfate (99 %) and sodium hydroxide (97 %) were purchased from Sigma-Aldrich. Paraformaldehyde (95 %), aniline (99.5 %) and chloroform (99 %) were purchased from Merck. Toluene (99 %) was provided by Prolabo. The 1,3,5-triphenylhexahydro-1,3,5 triazine was synthesized following a procedure described by Brunovska, Z. [13]. All chemicals (except cardanol) were used without further purification. Synthesis reactions were carried out in oven-dried flask.

Table 1. Main characteristics of cardanol.

Characteristic	Test Method	Values
Water Content (by vol/mass) (%)	ASTM D 95-13e1	0.1
Relative Density at 25 °C (g/cm^3)	ASTM D 4052-11	0.94
Kinematic Viscosity at 25 °C (mm^2/s)	ASTM D 445-12	51.47
Acid Number (mgKOH/g)	ASTM D 664-11a	0.8
Hydroxyl Value (mgKOH/g)	ASTM D 1957-86	184.8
Non-volatile Content (by mass) (%)	ASTM D 1353-13	99.5

2.2. Synthesis of 4,4′-Bis-[6-(3-phenyl-3,4-dihydro-2H-1, 3-benzoxazine)] pentanoic acid (DPA-Bz)

DPA-Bz were synthesized according to the reported procedure as illustrated in Figure 2 [14]. Into a 250 ml round-bottomed flask equipped with a condenser, 1,3,5-Triphenylhexahydro-1,3,5-triazine (0.02 mol), paraformaldehyde (0.06 mol), 4,4′-bis(4-hydroxyphenyl) pentanoic acid (0.03 mol) and 100 ml of toluene were added. The mixture was heated with stirring at 110 °C for 6 h. The mixture was cooled to room temperature, filtered and concentrated under reduced pressure to obtain a light orange syrup. Subsequently, the syrup was dried under high vacuum to form DPA-Bz as a yellowish powder with a yield of 89 %.

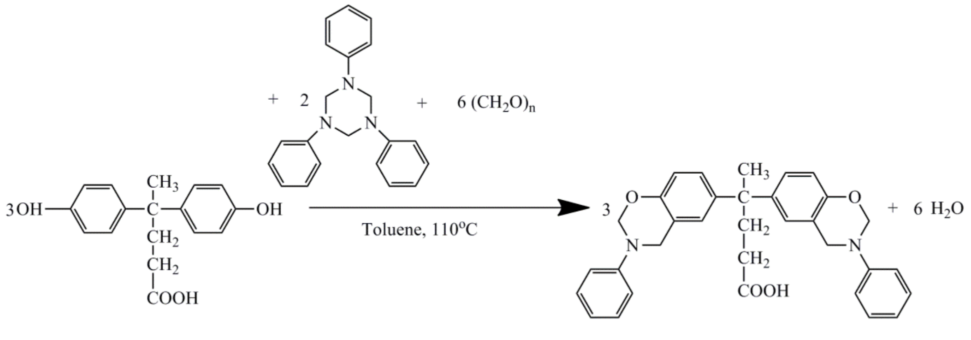

Figure 2. Schematic pathway of synthesis of DPA-Bz monomer.

2.3. Synthesis of m-alkylphenyl-3,4-dihydro-2H-benzoxazine (CA-Bz)

CA-Bz was prepared by our earlier reported solventless method [15]. A mixture of cardanol (10 g, 0.033 mol), paraformaldehyde (1.98 g, 0.066 mol) and aniline (3 ml, 0.033 mol) was added into a 100 ml three-necked round-bottomed flask and stirred at 80 °C under nitrogen atmosphere for 5 h. The mixture was cooled to room temperature and dissolved in chloroform. The mixture was washed with NaOH 2M and thoroughly washed by distilled water using a separating funnel. Then, the organic phase was collected, dried with anhydrous sodium sulfate and filtered to give a red oil. The solvent was evaporated under reduced pressure and then dried at 60 °C for 12 h under vacuum to obtain CA-Bz monomer with a yield of 73 %.

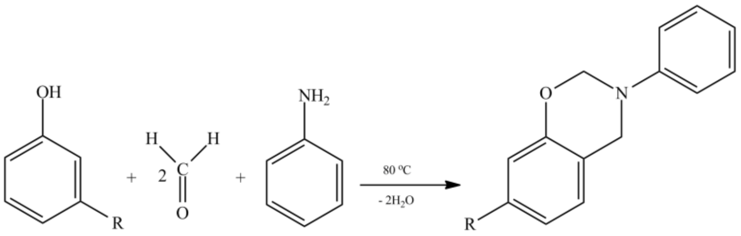

Figure 3. Schematic pathway of synthesis of CA-Bz monomer [15].

2.4. Blend of CA-Bz and DPA-Bz

CA-Bz and DPA-Bz monomers with blend ratio (w/w) of 3:1 were dissolved in chloroform (10 %, w/w) and stirred at room temperature for at least 1 h to obtain a homogenous solution form. Subsequently, the solution was dropped and casted on a glass plates. The sample was dried under vacuum for 2 h at 100 °C. Thermal curing of blend was carried out in a heating oven at 220 °C/2h and further characterized by DSC and FTIR. Similar process was used to prepare CA-Bz and DPA-Bz resin.

2.5. Measurements

Fourier transform infrared (FTIR) spectra were obtained on a Bruker Tensor37 spectrophotometer with a resolution from 4000 – 400 cm^{-1}. The measurement was performed at Institute of Chemistry Technology, Vietnam Academy of Science and Technology (VAST), Ho Chi Minh City.

^{1}H (500 MHz) and ^{13}C (125.8 MHz) nuclear magnetic resonance (NMR) spectra were taken on a Bruker Avance AM500 FT-NMR spectrometer with $CDCl_3$ as solvent. The NMR measurements and analysis were done at Center for Apply Spectroscopy, Institute of Chemistry Technology, Vietnam Academy of Science and Technology (VAST), Ha Noi.

Differential scanning calorimetry (DSC) measurement was done using a Mettler Toledo thermal analyzer to monitor the polymerization of benzoxazines. Each dynamic scan was performed by heating a sample at 10 °C/min under nitrogen purge from room temperature to 300 °C. The thermal stability of polymer was studied by thermogravimetric analysis (TGA) using a TGA Q500 instrument. The thermograms were obtained at a temperature rate of 10 °C/min from 25 °C to 800 °C under nitrogen environment. DSC and TGA characterization were performed at Central Laboratory for Analysis, University of Science–VNUHCM.

3. RESULTS AND DISCUSSION

3.1. Determination of the structure of DPA-Bz and CA-Bz monomers

The structures of DPA-Bz and CA-Bz monomers were supported by the FTIR spectra shown in Figure 4. The presence of cyclic ether of DPA-Bz structure was confirmed by the absorbance peaks at 1232 and 1028 cm^{-1} due to the C-O-C symmetric stretching and asymmetric stretching modes, respectively. For CA-Bz, these peaks displayed at 1241 and 1031 cm^{-1}, respectively. There was an obvious characteristic peak of out-of-plane C-H of oxazine ring at 947 cm^{-1} (959 cm^{-1} for CA-Bz). The absorbance peak at 1119 cm^{-1} (1113 cm^{-1} for CA-Bz) was attributed to the C-N-C symmetric stretching mode [16].

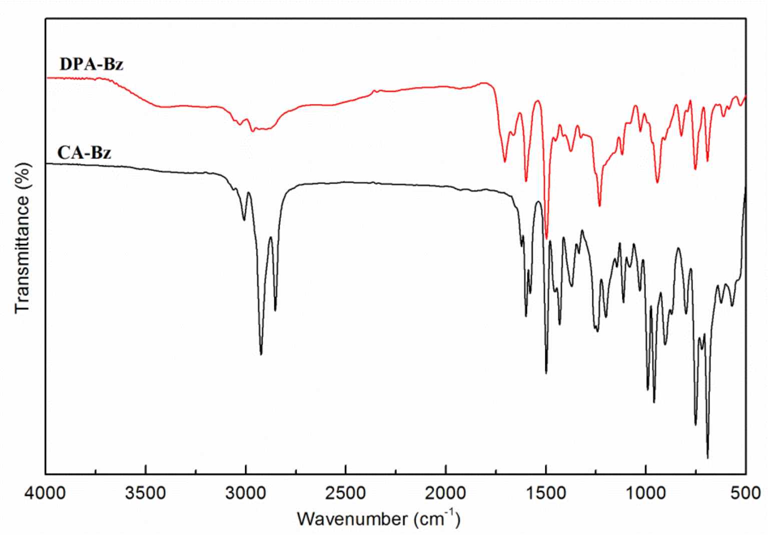

Figure 4. FTIR spectra of DPA-Bz and CA-Bz monomers.

The expected structure of DPA-Bz was further examined by the NMR results (Figure 5). In ^{1}H NMR spectrum, the oxazine protons (O-CH$_2$-N and Ar-CH$_2$-N) gave two signals at 5.32 ppm (singlet, 4H) and 4.56 ppm (singlet, 4H), respectively. Methyl protons of the DPA appeared at 1.51 ppm (singlet, 3H) while methylene protons of the DPA observed at 2.35 ppm (triplet, 2H) and 2.13 ppm (triplet, 2H) respectively. The COOH proton was not found in ^{1}H NMR when CDCl$_3$ is used as solvent. The corresponding ^{13}C NMR spectrum also supported the structure of DPA-Bz. The oxazine ring carbons (O-CH$_2$-N and Ar-CH$_2$-N) appeared as two singlets at 79.23 ppm and 50.6 ppm, respectively. Most importantly, the signal appeared at 179.1 ppm confirmed the presence of COOH group in the monomer structure [16].

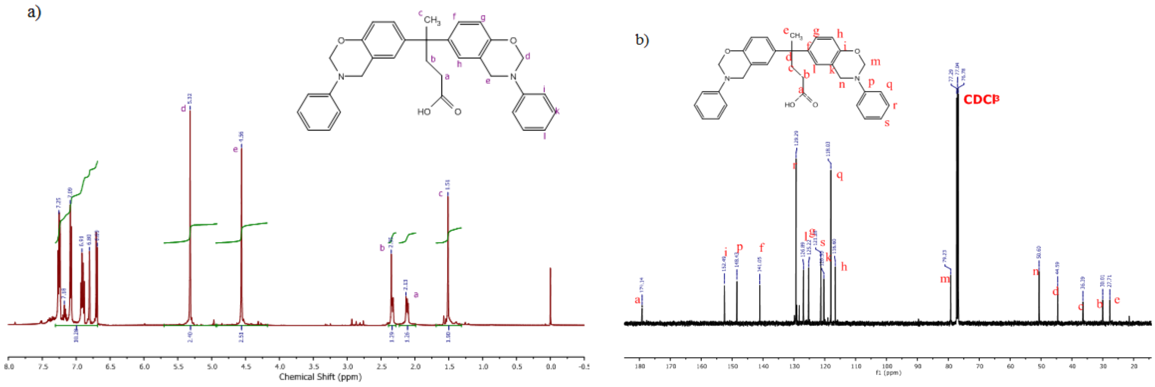

Figure 5. ^{1}H NMR (a), ^{13}C NMR (b) spectra of DPA-Bz monomer.

Similarly, the CA-Bz monomer structure was further confirmed by ^{1}H NMR spectrum in Figure 6. The resonances peaks at 4.58 and 5.3 ppm were assigned to (Ar-CH$_2$-N) and (O-CH$_2$-

N) of the oxazine ring, respectively. The aromatic protons were observed as multiplet in position at 6.63–7.26 ppm. The peaks observed at 0.90, 1.29, 1.55, 2.05 and 2.80 ppm appeared due to the long alkyl chain of cardanol [15].

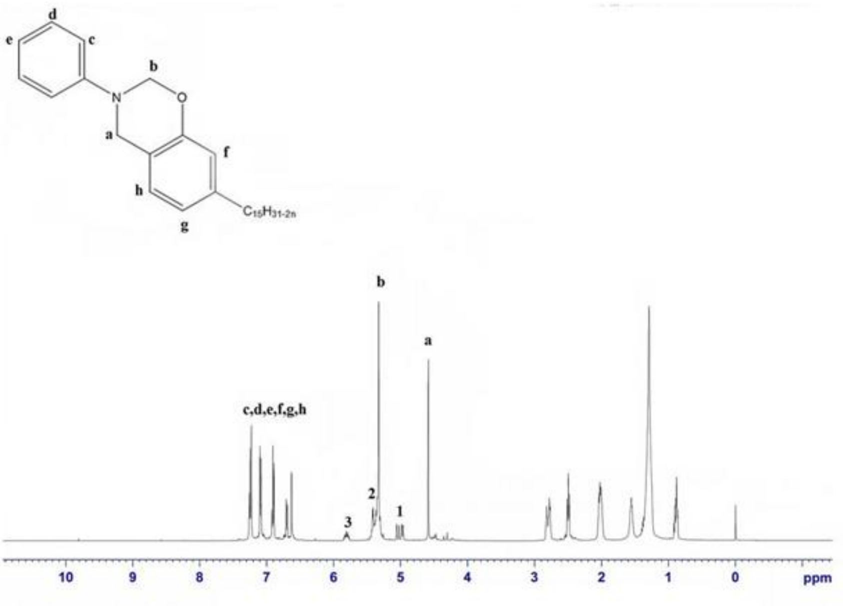

Figure 6. ^{1}H NMR spectrum of CA-Bz monomer.

3.2. Thermal polymerization of CA-Bz/DPA-Bz blend

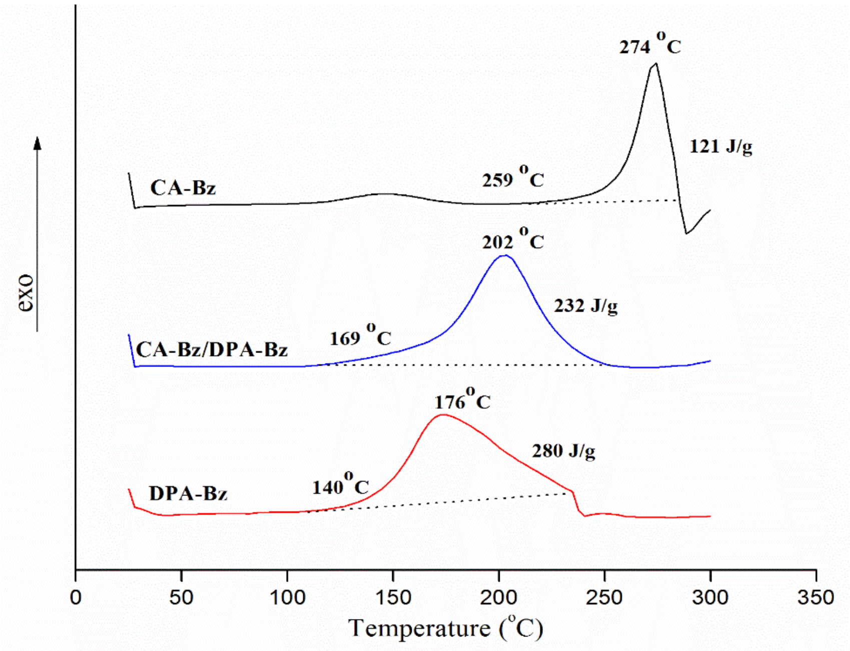

Figure 7. DSC thermograms of CA-Bz, DPA-Bz and their blend.

Table 2. Data collected from DSC curves of CA-Bz, DPA-Bz and their blend.

Sample	T $_{onset}$ (^oC)	T $_{peak}$(^oC)	ΔH(J/g)
CA-Bz	259	274	121
CA-Bz/DPA-Bz	169	202	232
DPA-Bz	140	176	280

Thermal polymerization of individual monomers and CA-Bz/DPA-Bz mixtures was studied using DSC at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere from 30 °C to 300 °C. Figure 7 showed the DSC thermograms with the data summarized in Table 2 including onset curing temperature (T_{onset}), temperature of exothermic peak (T_{peak}), and heat of curing reaction (ΔH). The exothermic transitions observed at high temperature region associated to the ring opening polymerization (ROP of oxazine rings. Heating of benzoxazine produced the ROP by cleavage of C-O bond, resulted in structure transformation from oxazine ring to a linear open chain structure. The exothermic peak observed at 274 °C was corresponded to the polymerization temperature of CA-Bz which was relatively high compared to other benzoxazines (around 200-250 °C). The onset temperature and peak temperature of DPA-Bz were 140 and 176 °C respectively, which were much lower than those of CA-Bz. This result could directly be related to the presence of carboxylic group (COOH) in the structure of DPA-Bz [14, 17].

Interestingly, the presence of carboxylic group in DPA-Bz showed a profound lowering in the polymerization temperature of benzoxazine blend with T_{onset} at 169 and T_{peak} at 202 °C. An increase in the acidity of phenolic groups generated during ROP might be responsible for the reduction in curing temperature of blend. Despite the difference in the exothermic peak temperatures of CA-Bz and DPA-Bz, the DSC curve of blend featured only one main peak. This might indicate the formation of a co-crosslinked polymer network by the copolymerization of benzoxazines. Therefore, the presence of DPA-Bz was believed to promote the curing reaction of CA-Bz and improve the crosslinking density of cured resin [11, 18]. Thermal-induced ring opening polymerization of benzoxazine monomers resulted in formation of polybenzoxazine. Possible crosslinked network of benzoxazine resin formed by ring opening of two monomers was depicted in Figure 8.

Thermal stability of cured benzoxazines was further investigated by TGA under nitrogen atmosphere. The TGA thermograms of polymers from CA-Bz and DPA-Bz and blend were shown in Figure 9 and TGA data collected from these curves presented in Table 3. Thermal stability was characterized by determining temperatures for 5 % and 10 % mass loss ($T_{5\%}$, and $T_{10\%}$ respectively), and char yield at 800 ^oC. The TGA curve of poly (DPA-Bz) showed that more than one degradation step occurs. The first step (160 to 250 ^oC) corresponding to a very small mass loss which could be related to the decomposition of COOH groups and alkyl chain in pentanoic acid moiety. The major weight loss at temperatures between 260 and 500 ^oC was due to the evaporation of amines and degradation of the phenolic moieties, respectively. The final step was the degradation of the aromatic ring occurred at the temperature above 500 ^oC.

It can be seen that the main degradation of poly (DPA-Bz) occurred at lower temperature than poly (CA-Bz), thus the T5%, and T10% of blend was found to be higher in the blend compared to those of poly (DPA-Bz). A higher char yield of Poly (DPA-Bz) was due to higher aromatic content in its monomer structure. Moreover, slight increase in char yield of the blend was observed, suggesting that higher crosslink density might be obtained [10, 18].

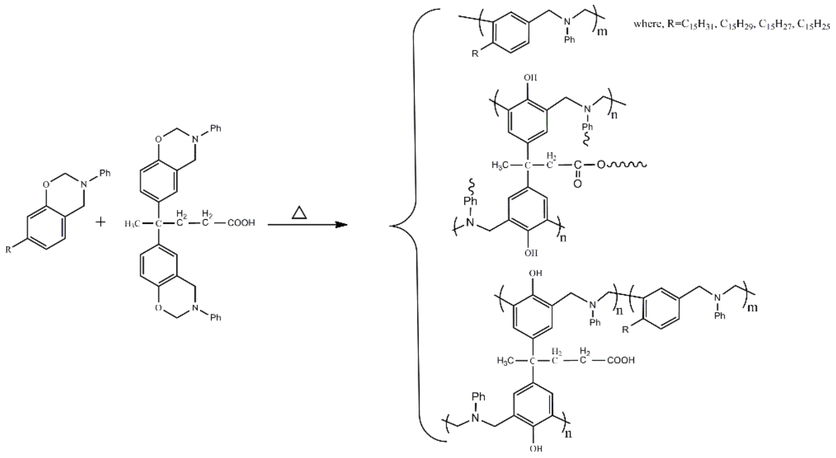

Figure 8. Possible crosslinked network formed upon ROP of CA-Bz/DPA-Bz blend.

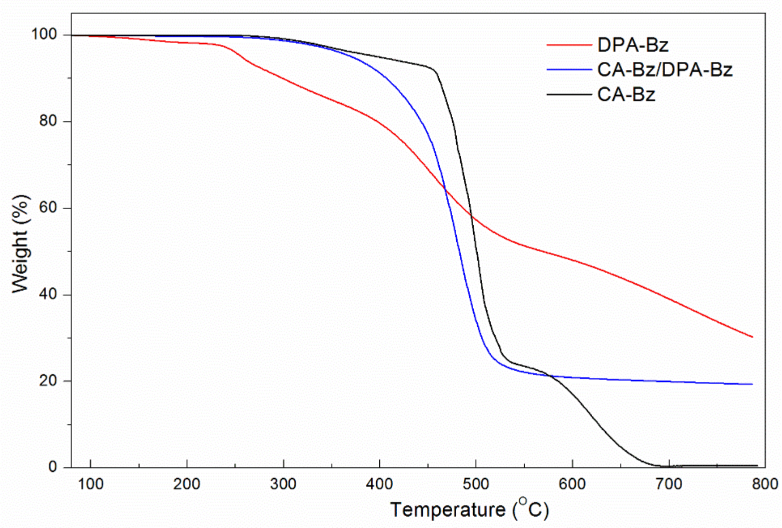

Figure 9. TGA thermograms of CA-Bz, DPA-Bz and their blend.

Table 3. Data collected from TGA curves of cured resin from CA-Bz, DPA-Bz and their blend.

Sample	**$T_{5\%}$ (°C)**	**$T_{10\%}$ (°C)**	**Char yield at 800 °C (%)**
Poly (CA-Bz)	397	461	0.6
Cured CA-Bz/DPA-Bz	371	407	19
Poly (DPA-Bz)	257	299	30

4. CONCLUSIONS

In this work, we have reported the synthesis and structural characterization of two benzoxazine monomers, CA-Bz and DPA-Bz from fully bio-based phenols. Benzoxazine with much lower curing temperature was achieved with CA-Bz/DPA-Bz blend as indicated by DSC analysis. The addition of DPA-Bz containing acid functonality was found to have beneficial effect on the polymerization of CA-Bz monomer such as accelerating effect on the curing process and enhancement in crosslink density. Therefore, DPA-Bz has a great potential for blending with other benzoxazines to overcome the high thermal curing temperature of the conventional benzoxazine system.

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