

BIO-BASED BENZOXAZINE MONOMER AND POLYMER BASED ON VANILLIN AND DIFURFURYL DIAMINE

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ABSTRACT

A type of bio-based benzoxazine monomer based on difurfuryl diamine (DFDA) obtained by the coupling of furfuryl amine using formaldehyde will be discussed. The benzoxazine monomer was synthesized by reacting DFDA with renewable phenolic vanillin and formaldehyde. This benzoxazine system was purified by precipitation to obtain solid powders that melt at 55 °C to form low viscosity liquids that can be readily used to impregnate fiber reinforcements. Onset cure temperature is 163 °C and the autocatalytic reaction behavior was observed. The resulting polybenzoxazine has about 244 °C after post curing. It was found that the polybenzoxazine network containing high content of furan rings in the backbone provides the improvement of 800 °C char yield compared with Bisphenol A (BPA) based polybenzoxazines greater than 50% measured by TGA temperature ramps in an inert environment. This paper will discuss processing and thermal characteristics of this highly renewable material, which are useful for high temperature applications.

Keywords: Bio-based, Polybenzoxazine, vanillin, furfurylamine
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1. INTRODUCTION

Benzoxazines belong to heterocyclic compounds based on an aromatic ring connected with a six-membered heterocycle containing one oxygen and one nitrogen atom. These monomers are usually synthesized by the Mannich reaction of phenols, formaldehyde, and amines.^{1,2} Polybenzoxazines possess good performance characteristics, especially thermal performance, such as high char yield, high glass transition temperature, and fire resistance performance. They also possess advantages including good electric properties, low melt viscosity of the precursors, curing without a strong catalyst, and near-zero volume change upon cure.^{3,4} Therefore, they can be used for electronics applications and as matrix materials for fiber-reinforced composite materials that require high temperature capabilities.

An increasing number of researchers have focused on bio-based materials as replacements for petroleum-based materials to mitigate environmental concerns and limited resources. For polybenzoxazines, a number of bio-based building blocks have been used to synthesize benzoxazine monomers. Lochab and Varma synthesized difunctional benzoxazines derived from bisphenol-A and cardanol.⁵ Sini and coworkers synthesized furfurylamine- and vanillin-based

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benzoxazines and their curing behavior.⁶ Shen and his group synthesized DFDA- and phenol-based polybenzoxazines with good thermal stability and adhesion properties.⁷ To our knowledge there is no work available combining bio-based phenols and DFDA to synthesize benzoxazine monomers with higher bio-based content. In this investigation, DFDA- and vanillin-based benzoxazine was synthesized and characterized. Cure kinetics were evaluated using FTIR spectroscopy. Additionally, thermomechanical behavior of the system was assessed by dynamic mechanical analysis (DMA) using carbon fiber fabric composites impregnated with the benzoxazine monomer powder.

2. EXPERIMENTATION

2.1 Materials

Vanillin, furfurylamine, paraformaldehyde, chloroform, sodium hydroxide, diethyl ether, magnesium sulfate anhydrous, formaldehyde solution (37 %), and hydrochloric acid solution (37 %) were purchased from Sigma Aldrich and used as received.

2.2 Synthesis of (5,5'-methylenebis(furan-5,2-diyl))dimethanamine (DFDA) and benzoxazine monomer

DFDA was synthesized by following the method provided by Holfinger et al. and resulted in a brown viscous liquid.⁸ DFDA- and Vanillin-based benzoxazine (BZ-DFDA-Vanillin) was synthesized by Mannich reaction in the presence of solvent. Chloroform, paraformaldehyde and DFDA were introduced into the round bottomed flask and mixed at room temperature for 30 min. After adding vanillin, the mixture was stirred at 70 °C and refluxed for 20 h. The liquid of mixture was washed with sodium hydroxide solution and distilled water, and last, a crystalized yellow powder was obtained by crystallization (Yield: 65 %, Purity: 95 %). ¹H-NMR of BZ-DFDA-Vanillin (500 MHz, CDCl₃, ppm): δ 9.82 (s, 2H); 7.45 (s, 2H); 7.15 (s, 2H); 6.19 (d, 2H); 6.03 (d, 2H); 5.03 (s, 4H); 4.10 (s, 6H); 3.98 (s, 4H); 3.94 (s, 4H); 3.89 (s, 2H).

2.3 Preparation of polybenzoxazine-carbon fiber fabric composites

PolyBZ-DFDA-Vanillin/CF composites were prepared by powder impregnation and compression molding. Carbon fiber (AS4 G', 5HS 12K) was cut to 110 mm × 110 mm and placed in a steel mold with the cavity size 110 mm × 110 mm × 1.5 mm. Six alternating layers of carbon fiber and benzoxazine powder were pressed into the cavity, and the mold was preheated first to 100 °C for 1h and then 130 °C 1h to melt powder in the press at 3 MPa pressure. Then the composite was cured under 150 °C 1 h, 180 °C 2 h, 200 °C 1 h. The fiber volume fraction of the resulting composite was about 45%.

3. RESULTS

3.1 Structure characterization of BZ-DFDA-Vanillin

The structure of the new benzoxazine monomer was confirmed by ¹H NMR spectra, shown in Fig. 1A). The protons of oxazine rings -Ar-CH₂-N- and -OCH₂-N- give rise to characteristics peaks at 4.10 and 5.03 ppm, respectively. The resonances at 6.03 and 6.09 ppm are assigned to furan ring protons. The spectrum also displays two resonances centered at 4.10 and 9.82 ppm that correspond to the formyl and methyl groups consistent with the structure of vanillin. In addition, the theoretical

values calculated for the molecular structure of this novel benzoxazine correlates well with the ^1H NMR elemental analysis of BZ-DFDA-Vanillin shown in the experiment section. The Mid-FTIR spectra shown in Fig. 1B) is also consistent with the structure of BZ-DFDA-Vanillin. Characteristic absorption peaks for the furan rings are observed at 1584 and 785 cm^{-1} . The presence of the formyl group of vanillin is confirmed by the peak absorption at 1686 cm^{-1} . Moreover, the absorption peaks at 1020 cm^{-1} (asymmetric stretching of C-N-C) and 1220 cm^{-1} (Ar-C-O stretch), indicate that an oxazine ring fuses to the benzene ring of vanillin.⁹

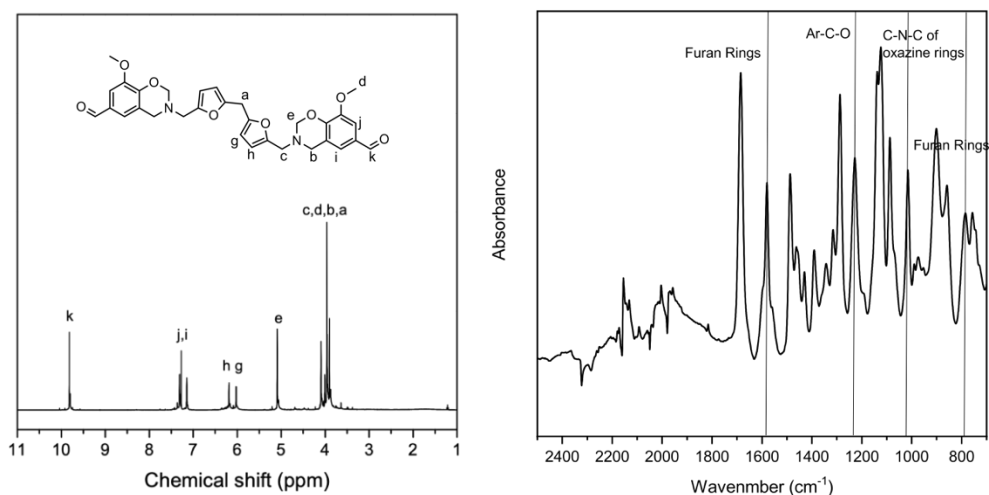


Fig. 1 A) ^1H -NMR spectra of BZ-DFDA-Vanillin; B) FTIR spectra of BZ-DFDA-Vanillin.

3.2 Curing behavior of BZ-DFDA-Vanillin

The thermal behavior of BZ-DFDA-Vanillin was monitored using Differential Scanning Calorimetry (DSC) as shown in Fig. 2A). The BZ-DFDA-Vanillin benzoxazine monomer exhibited a melting transition at $55\text{ }^\circ\text{C}$ that is $45\text{ }^\circ\text{C}$ lower than the $100\text{ }^\circ\text{C}$ melting point of di-benzene-based benzoxazines, indicating the furan rings have an impact on reducing melting temperature. In addition to the melting endotherm, BZ-DFDA-Vanillin exhibits an exothermic peak that starts around $160\text{ }^\circ\text{C}$ and ends around $200\text{ }^\circ\text{C}$. From the previous work of other groups, it is known that the ring-opening curing process of benzoxazines typically show exothermic peaks between $200\text{--}280\text{ }^\circ\text{C}$.¹⁰ This novel difuran based benzoxazine exhibited exothermic behavior in a range $50\text{ }^\circ\text{C}$ lower than incumbent systems. Additionally, the processing window of BZ-DFDA-Vanillin, as defined by the temperature difference between the onset curing temperature and the melting point, is wider than that of benzene containing systems. It was found that the BZ-DFDA-Vanillin followed a ring-opening polymerization mechanism with the elimination of carboxylic groups of vanillin, which was observed by Sini's group who studied furfurylamine- and vanillin-based benzoxazine.^{6,11} More details regarding the curing mechanisms of BZ-DFDA-Vanillin will be discussed in a future paper from our group.

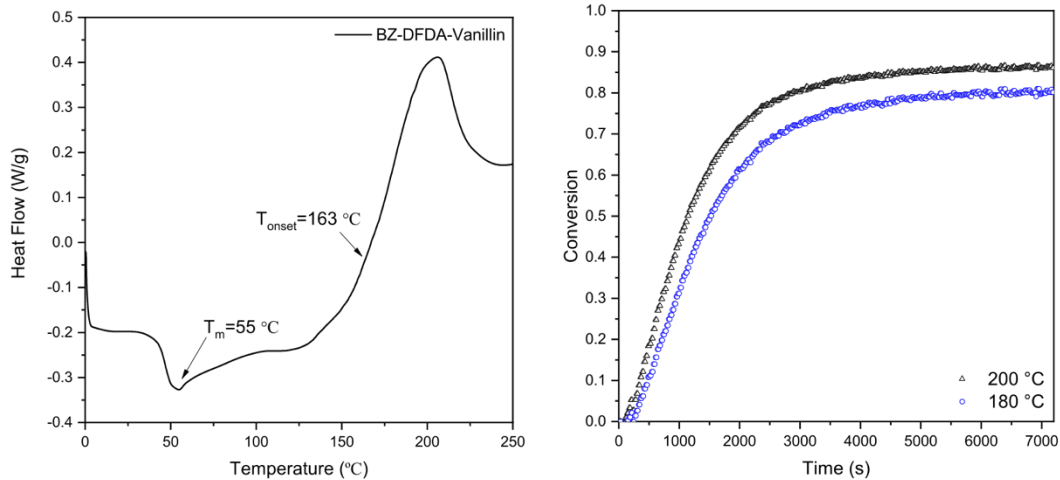


Fig. 2 A) DSC thermogram of BZ-DFDA-Vanillin showing melt transition and peak exotherm; B) conversion as a function of time of BZ-DFDA-Vanillin at 180° and 200 °C isothermal cure conditions.

The curing kinetics of benzoxazine monomers were characterized by FTIR isothermal experiments. The conversion of benzoxazines was calculated by quantifying the height change of absorption bands of oxazine rings (1220 cm^{-1}). Fig. 2B) shows cure profiles at 180° and 200 °C. The shape of these curves is consistent with autocatalytic reaction behavior. The polymerization of BZ-DFDA-Vanillin reached a steady state of conversion within about 1 hour without the use of a catalyst. At 200 °C, the material achieved about 90 % final conversion, which is consistent with the exothermic behavior from the DSC thermogram.

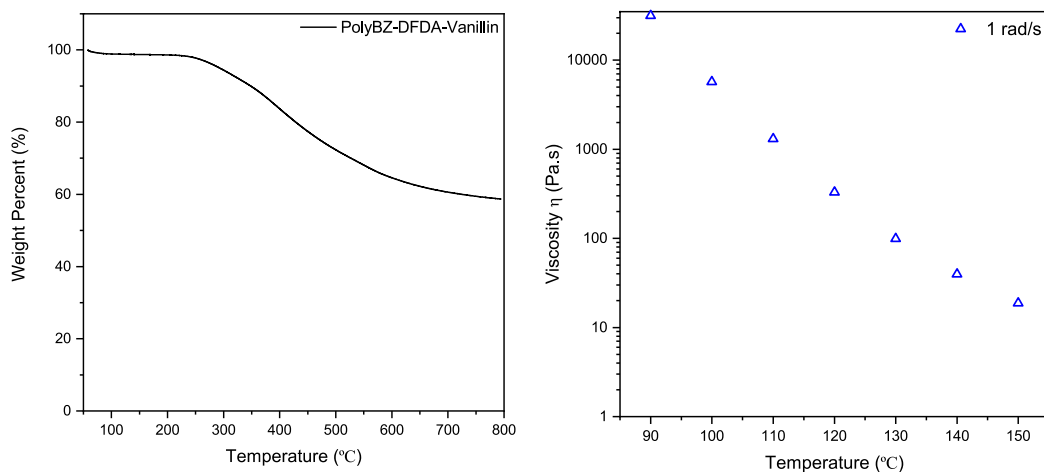


Fig. 3 A) TGA thermogram of PolyBZ-DFDA-Vanillin; B) viscosity of melted BZ-DFDA-Vanillin versus temperature.

3.3 Thermal stability of the bio-based polybenzoxazine

The thermal stability of PolyBZ-DFDA-Vanillin was observed by Thermogravimetric Analysis (TGA) in argon atmosphere. Fig. 3A) shows the thermogram obtained at 10 °C/minute and Table

1 includes the char yield at 800°C from the thermogram (Row 7). Also included for comparison in Table 1 are char yield literature values for other systems. The TGA curve in Fig. 3A) indicates that difuran-containing polybenzoxazine has 61% char yield at 800 °C. It should be noted that BZ-DFDA-Vanillin lost about 10% weight due to the elimination of carboxylic groups during curing process, so PolyBZ-DFDA-Vanillin possesses around 50 % char yield based on initial weight of precursors. Compared with 62% char yield of DFDA- and phenol-based polybenzoxazine PolyBZ-F that was studied by Shen’s group (Row 6), the DFDA-vanillin based polybenzoxazine is similar but contains significantly higher renewable content. Furthermore, comparison with typical dibenzene-based polybenzoxazine, such as Bisphenol A-based polybenzoxazine (Rows 1–5 in Table 1), show that the furan-containing network has a positive impact on enriching the char formation of polybenzoxazines.¹⁰

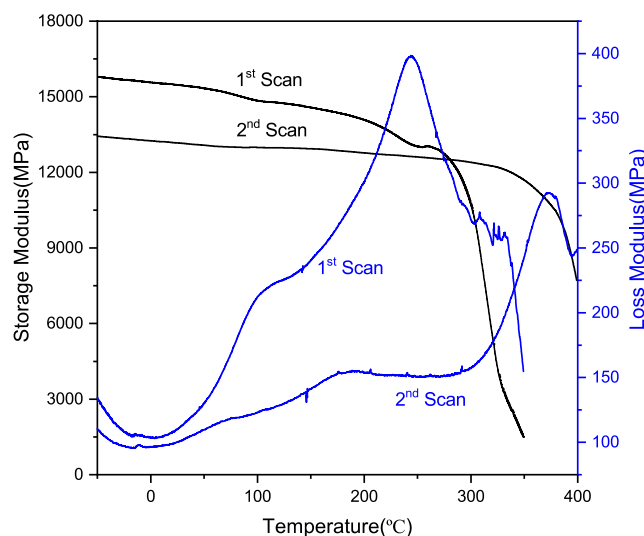


Fig. 4 DMA curves of PolyBZ-DFDA-Vanillin/ CF composites.

3.4 Dynamic mechanical properties of PolyBZ-DFDA-Vanillin/Carbon Fiber composites

Prior to the preparation of polybenzoxazine carbon fiber composites, the viscosity of the monomer was measured using TA Instruments DHR-3 determine if the melted precursor is able to infiltrate into the carbon fiber fabric. The viscosity as a function of temperature of BZ-DFDA-Vanillin is shown in Fig. 3B). The viscosity decreases steadily after the melt transition and is 1000 Pa·s at 100 °C, which is low enough to infiltrate the fabric. This value was selected as the starting temperature for compression processing of the composite bar for DMA testing. DMA was used to investigate the dynamic mechanical properties of bio-based polybenzoxazine carbon fiber composites. Fig. 4 presents the storage modulus and loss modulus curves of this cured material and were obtained using a ramp rate of 2 °C/min from -50 °C to 350 °C followed by a second scan. The storage modulus of the composite is well above 10 GPa at room temperature as is expected because of the 3 layers carbon fiber reinforcement. The glass transition temperature (T_g) of the material shows significant difference between the two scans. The first run following a 200 °C post curing temperature resulted in T_g of 244 °C, however, the T_g increased to 372 °C on the second scan because the material was heated to 350 °C during the first run. The curing kinetics study of the BZ-DFDA-Vanillin showed 90% benzoxazine conversion at a 200 °C isothermal cure

temperature. The 244°C T_g could be a result of the first run temperature ramp causing continued benzoxazine conversion. This would not explain the much higher T_g (372 °C) obtained on the second run. It was found that PolyBZ-DFDA-Vanillin starts to decompose and form char beginning at 280 °C from TGA curves, so the heating to 350°C would certainly affect the network structure via reactions other than benzoxazine ring opening polymerization.

Table 1 Thermal and mechanical properties of polybenzoxazines derived therefrom.

Abbr.	Phenol	Amine	Char Yield at 800°C (%)	T_g (°C)
BA-a	BPA	Aniline	30 ⁴	170 ⁴
BA-ot	BPA	o-Toluidine	32 ⁴	114 ⁴
BA-mt	BPA	m-Toluidine	31 ⁴	210 ⁴
BA-pt	BPA	p-Toluidine	32 ⁴	158 ⁴
BA-35x	BPA	3,5-Xylidine	28 ⁴	245 ⁴
BZ-F	Phenol	DFDA	62 ⁷	270 ⁷
BZ-DFDA-Vanillin	Vanillin	DFDA	61	244

Table 1 also contains T_g data for a number of BZ resins. Of the BPA-based polybenzoxazines, only BZ-35x has a T_g close to that of the BZ-DFDA-Vanillin system. But this system has only 28% char yield, The T_g 's of the rest of the BPA-based polybenzoxazines are significantly lower. It is clear that the DFDA- and vanillin-based polybenzoxazines performed better both in terms of T_g and char yield.¹² PolyBZ-F has a 270 °C T_g but these systems were post cured at 220 °C. Thus, the performance of the fully bio-based polybenzoxazine has similar performance characteristics to those of the Phenol-DFDA system, suggesting that the furan building block is responsible for the improved performance characteristics.

4. CONCLUSIONS

A novel bio-based benzoxazine monomer derived from furfurylamine and vanillin was synthesized with high purity. ¹H NMR and FTIR characterization of this material was used to confirm the structure of BZ-DFDA-Vanillin. BZ-DFDA-Vanillin exhibited autocatalytic ring-opening curing kinetics as observed by Mid-IR spectroscopy. The PolyBZ-DFDA-Vanillin system showed better thermal stability and higher T_g than BPA-based polybenzoxazines. PolyBZ-DFDA-Vanillin has higher renewable content and similar performance characteristics when compared to DFDA-phenol-based polybenzoxazine reported in the literature.

5. ACKNOWLEDGMENTS

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6. REFERENCES

1. Lligadas G, Tüzün A, Ronda JC, Galià M, Cádiz V. Polybenzoxazines: New players in the bio-based polymer arena. *Polym Chem.* 2014;5(23):6636-6644. doi:10.1039/c4py00914b
2. Ghosh NN, Kiskan B, Yagci Y. Polybenzoxazines-New high performance thermosetting resins: Synthesis and properties. *Prog Polym Sci.* 2007;32(11):1344-1391. doi:10.1016/j.progpolymsci.2007.07.002
3. Takeichi T, Kawauchi T, Agag T. High Performance Polybenzoxazines as a Novel Type of Phenolic Resin. *Polym J.* 2008;40(12):1121-1131. doi:10.1295/polymj.pj2008072
4. Ishida H, Agag T. Handbook of Benzoxazine Resins. *Handb Benzoxazine Resins.* 2011:740480. doi:10.1016/C2010-0-66598-9
5. Lochab B, Varma IK, Bijwe J. Thermal behaviour of cardanol-based benzoxazines: Monomers and polymers. *J Therm Anal Calorim.* 2010;102(2):769-774. doi:10.1007/s10973-010-0736-6
6. Sini NK, Bijwe J, Varma IK. Renewable benzoxazine monomer from Vanillin: Synthesis, characterization, and studies on curing behavior. *J Polym Sci Part A Polym Chem.* 2014;52(1):7-11. doi:10.1002/pola.26981
7. Shen X, Dai J, Liu Y, Liu X, Zhu J. Synthesis of high performance polybenzoxazine networks from bio-based furfurylamine: Furan vs benzene ring. *Polymer (Guildf).* 2017;122(March 2018):258-269. doi:10.1016/j.polymer.2017.06.075
8. Holfinger MS, Conner AH, Holm DR, Hill CG. Synthesis of Difurfuryl Diamines by the Acidic Condensation of Furfurylamine with Aldehydes and Their Mechanism of Formation. *J Org Chem.* 1995;60(6):1595-1598. doi:10.1021/jo00111a017
9. Wang C, Sun J, Liu X, Sudo A, Endo T. Synthesis and copolymerization of fully bio-based benzoxazines from guaiacol, furfurylamine and stearylamine. *Green Chem.* 2012;14(10):2799-2806. doi:10.1039/c2gc35796h
10. Ishida H, Sanders DP. Regioselectivity and network structure of difunctional alkyl-substituted aromatic amine-based polybenzoxazines. *Macromolecules.* 2000;33(22):8149-8157. doi:10.1021/ma991836t
11. Sini NK, Bijwe J, Varma IK. Thermal behaviour of bis-benzoxazines derived from renewable feed stock “vanillin.” *Polym Degrad Stab.* 2014;109:270-277. doi:10.1016/j.polymdegradstab.2014.07.015
12. Ishida H, Allen DJ. Physical and mechanical characterization of near-zero shrinkage polybenzoxazines. *J Polym Sci Part B Polym Phys.* 1996;34(6):1019-1030. doi:10.1002/(SICI)1099-0488(19960430)34:6<1019::AID-POLB1>3.0.CO;2-T