Supporting information

Nature's Empowerment: Unraveling Superior Performance and Green Degradation Closure in Self-Curing Fully Bio-based Benzoxazine

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Total number of pages: 10 (S1-S10)

Total number of figures: 11 (Figure S1-S9, Scheme S1-S2)

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Measurement

The FTIR spectra were acquired using a Nicolet Nexus 670 spectrometer operating in absorbance mode over a range from 4000 to 400 cm^{-1}. Three benzoxazine monomers were meticulously ground with potassium bromide powder, subsequently compressed into a disk, and their respective spectra were recorded. To confirm the structures of the fully biobased benzoxazine resin VE-BZ, as well as the control groups BPA-BZ and VA-BZ, ^{1}H NMR spectroscopy was employed. For this purpose, ^{13}C and ^{1}H NMR spectra were obtained utilizing a Bruker Advance 400 spectrometer operating at a frequency of 400 MHz, with DMSO-d6 serving as the solvent. The ^{1}H measurements involved an averaging of 16 transients, with integrated intensity determination facilitated using a relaxation time of 10 s.

DSC measurements were conducted using a TA Q2000 DSC instrument equipped with an RCS 90 cooling system, employing varying heating rates of 2, 5, 10, 15, and 20 °C per minute. The glass transition temperature was determined utilizing a TA TMA Q400, employing a heating rate of 10 °C/min within a temperature range spanning from 30 ℃ to 350 ℃. Throughout the text, technical term abbreviations were defined upon their initial usage. The language utilized was objective, devoid of bias or ornamentation, adopting a passive tone and impersonal structure. Thermomechanical properties were evaluated using Dynamic Mechanical Analysis (DMA, TA Instruments Q800) at a heating rate of 5 ℃/min in the temperature range of 40 to 350 ℃.

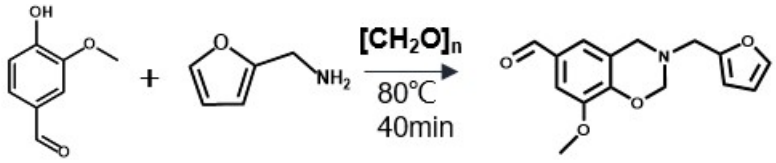
Thermal stability analysis was performed using a Thermogravimetric analyzer (TGA, TA Instruments Q600) employing diverse heating rates ranging from 5 to 25 °C/min, spanning from room temperature to 800 ℃ under N_2 flow conditions (50 mL/min). The text adhered strictly to American English spelling, grammar, and style conventions, ensuring it was devoid of grammatical errors, spelling mistakes, and punctuation errors.

Flammability properties were meticulously evaluated utilizing a microscale combustion calorimeter (MCC) developed and manufactured by Fire Testing Technology of East Grinstead, UK, under the supervision of the Federal Aviation Administration. Shear strength was precisely quantified employing a Universal Materials Testing Machine (MTS CMT4204, GB/T 1040.2–2006) at a stretching rate of 50 mm/min.

1. Synthesis of control benzoxazine resins

1.1 Synthesis of 3-(furan-2-ylmethyl)-8-methoxy-3,4-dihydro-2H-benzo[e]-[1,3]oxazine-6-carbaldehyde.(VA-BZ)

In a 250 mL volumetric flask, furfurylamine (7.09 g, 0.0723 mol) and paraformaldehyde (4.47 g, 0.144 mol) were added. The reaction was carried out at room temperature for 20 minutes. Vanillin (10.10 g, 0.0657 mol) was added, and the system was heated to 80 ℃, causing the vanillin crystals to melt. After stirring for 40 minutes, the reaction was cooled and left to stand. After decompression filtration, the unreacted furfurylamine was removed using ethanol. Then, the unreacted paraformaldehyde and vanillin were washed with a strong alkali solution and deionized water. The crude product was then baked in an oven at 80 °C for 3 hours to obtain the final white solid product (VA-BZ). The yield was 69.6% (12.48 g). ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) = 9.79 (s, 1H), 7.63-7.62 (dd, J = 1.9, 0.9 Hz, 1H), 7.30-7.28 (m, 2H), 6.43-6.42 (dd, J = 3.2, 1.9 Hz, 1H), 6.35-6.33 (dd, J = 3.2, 0.8 Hz, 1H), 4.99 (s, 2H), 4.05 (s, 2H), 3.85 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ (ppm) = 191.81, 151.91, 149.43, 148.45, 143.27, 129.03, 124.62, 120.62, 110.92, 109.36, 108.92, 82.95, 56.00, 48.59, 47.91.



Scheme. S1 Synthesis of the benzoxazine monomer VA-BZ

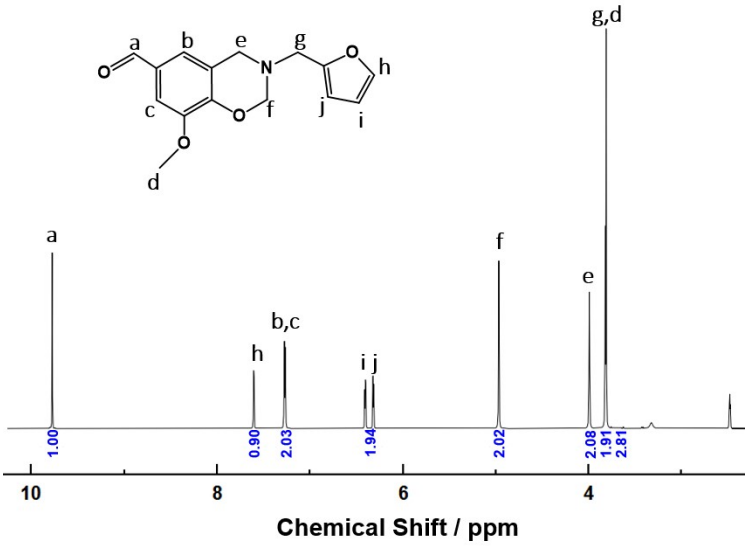


Fig. S1 ^{1}H NMR Spectrum of VA-BZ

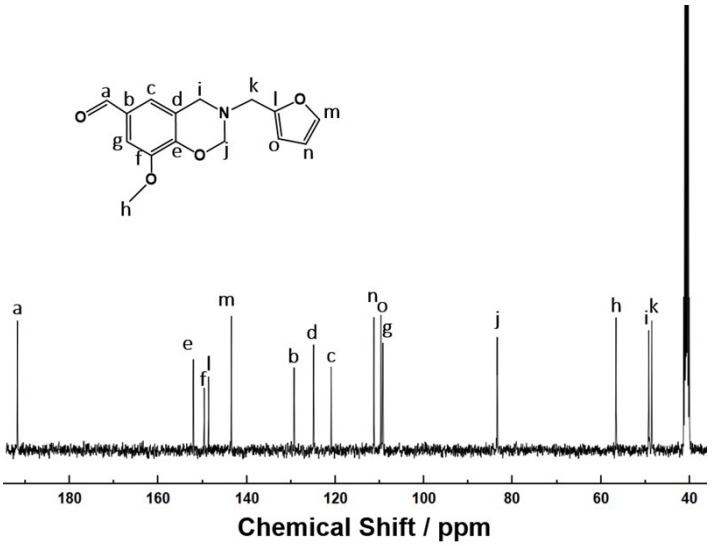
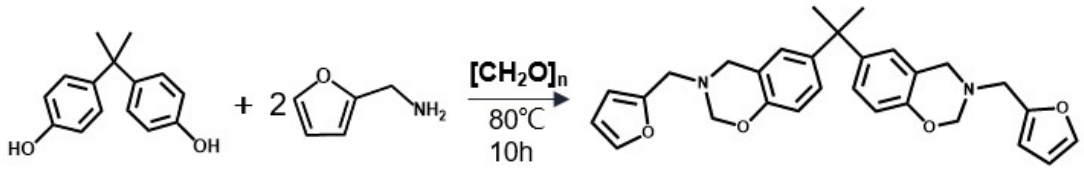


Fig. S2 ^{13}C NMR Spectrum of VA-BZ

1.2 **Synthesis of 6,6'-(propane-2,2-diyl)bis(3-(furan-2-ylmethyl)-3,4-dihydro-2H-benzo[e][1,3]oxazine) (BPA-BZ)**

Due to the fact that the melting point of bisphenol A is above 155 °C, which is located in the curing window of bisphenol A-type benzoxazines.The solvent method was used to synthesize benzoxazine resins. The reaction of furfurylamine (9.45 g, 0.0963 mol) with paraformaldehyde (5.96 g, 0.193 mol) was carried out in an ice bath for 30 min, and BPA (10.10 g, 0.0438 mol) was added after the formation of a white turbid liquid with sufficient stirring, and then the temperature was raised to 80 ℃ and refluxed for 10 h. The solvent was removed by spin evaporation, and the crude products were solubilized by adding CH_2Cl_2, and washed 4-5 times each with a strong base and deionized water. The final product (BPA-BZ) was obtained by evaporating CH_2Cl_2 and recrystallizing in ethanol. Yield (74.7%, 15.39 g). ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) = 7.61-7.56 (d, J = 4.8 Hz, 2H), 6.91-6.89 (d, J = 5.9 Hz, 4H), 6.70-6.59 (d, J = 4.2 Hz, 2H), 6.42-6.36 (m, 2H), 6.30-6.17 (m, 2H), 4.77 (s, 4H), 3.83 (s, 4H), 3.57 (s, 4H), 1.58 (s, 6H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ (ppm) = 152.28, 151.87, 143.08, 142.76, 126.37, 125.63, 119.53, 115.91, 110.88, 109.05, 81.73, 49.63, 49.01, 48.03, 31.18.



Scheme. S2 Synthesis of the benzoxazine monomer BPA-BZ

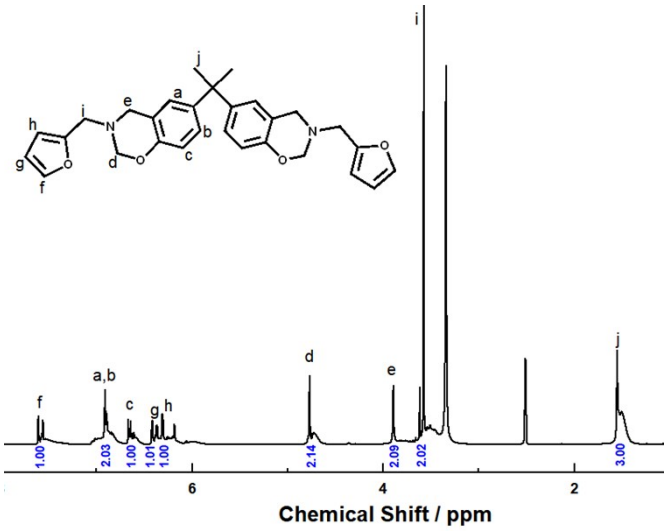


Fig. S3 ^{1}H NMR Spectrum of BPA-BZ

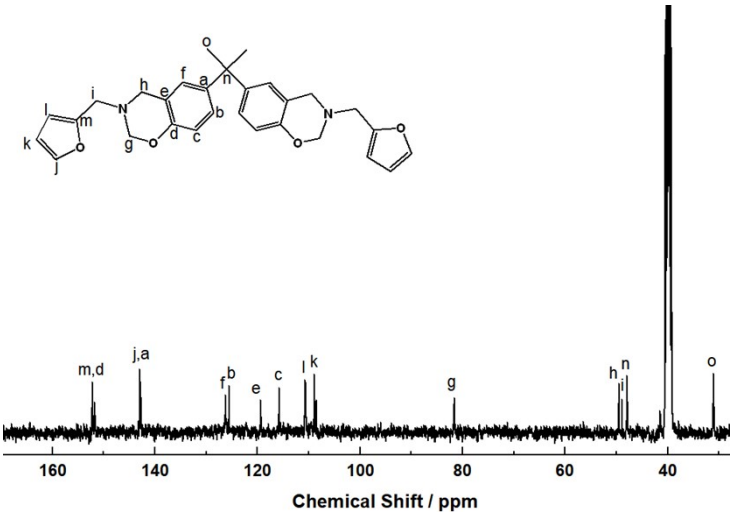


Fig. S4 ^{13}C NMR Spectrum of BPA-BZ

1.3 Synthesis of 2,6-bis(3-(furan-2-ylmethyl)-8-methoxy-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)tetrahydro-[1,3]dioxino[5,4-d][1,3]dioxine. (VE^{P}-BZ)

The synthesis of VE^{P}-type benzoxazine (VE^{P}-BZ) followed the same procedure as VE-BZ, with the only modification being the substitution of benzylaldehyde with paraformaldehyde. The resulting product was a light yellow solid. Yield (59.57%, 5.8 g). ^{1}H NMR (D_2O, 400 MHz):δ(ppm)=

6.90 (s, 2H), 6.83-6.82 (d, J = 10.4 Hz, 2H), 6.81-6.80 (d, J = 11.2 Hz, 2H), 6.53-6.51 (d, J = 8.1 Hz, 2H), 5.66 (s, 2H), 4.70 (s, 4H), 4.21-4.19 (d, J = 13.9 Hz, 2H), 3.99-3.96 (d, J = 9.3 Hz, 4H), 3.89-3.86 (d, J = 20.2 Hz, 4H), 3.69 (s, 6H), 3.25 (s, 4H). ^{13}C NMR (D_2O, 101 MHz):δ(ppm) = 158.22, 158.09, 150.95, 149.61, 129.10, 121.20, 120.57, 110.02, 108.75, 103.27, 100.62, 84.99, 73.24, 68.01, 55.79, 48.67, 47.93.

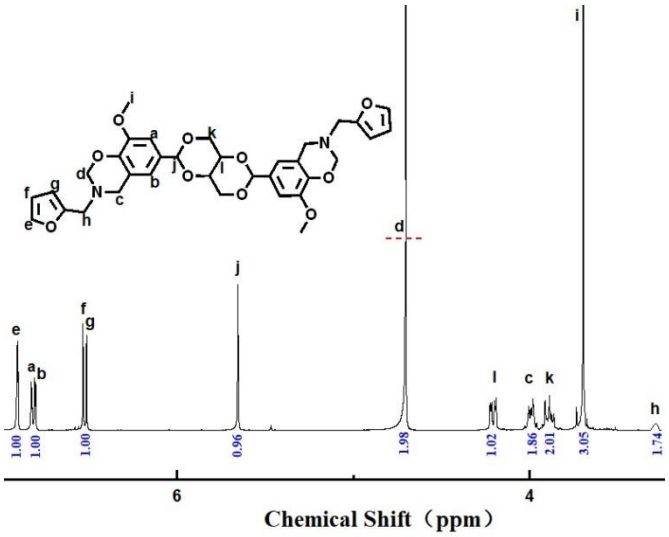


Fig. S5 ^{1}H NMR Spectrum of VE^{P}-BZ

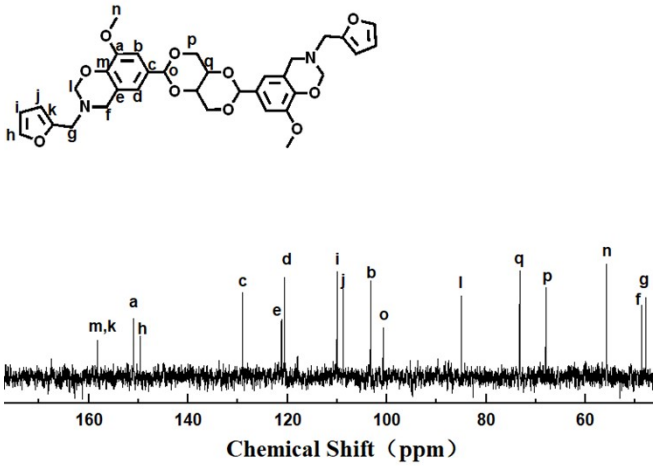


Fig. S6 ^{13}C NMR Spectrum of VE^{P}-BZ

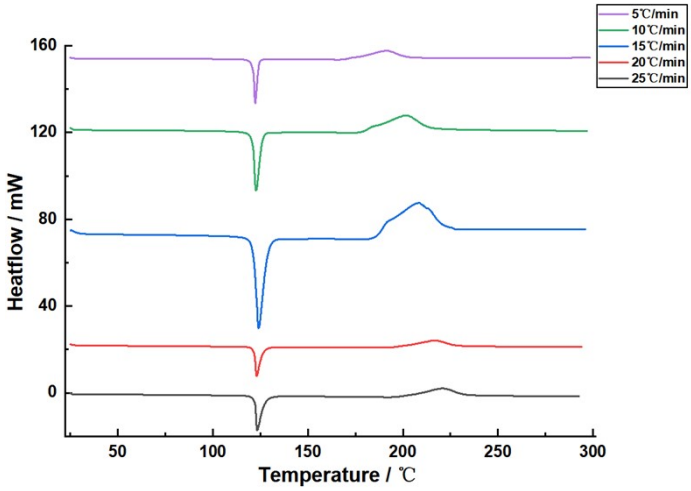


Fig.S7 DSC curves of VA-BZ system

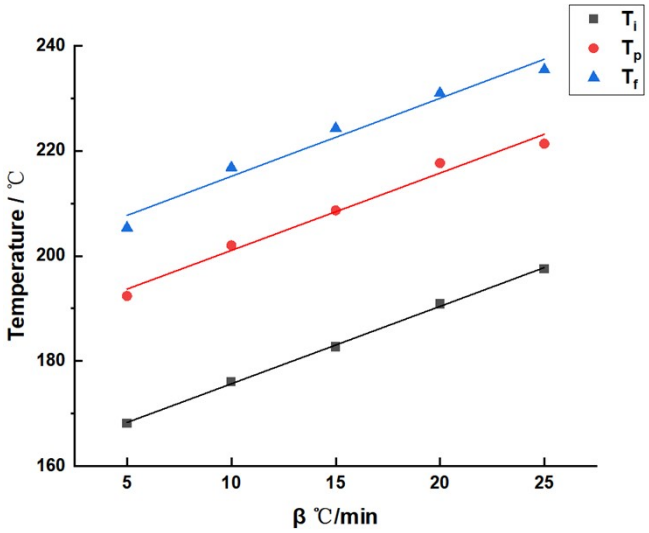


Fig.S8 Plots of linear fit relationship for T-β in VA-BZ

2. Preparation of acid solutions

To prepare a 1 M citric acid (CA) solution, dissolved 1.9212 g of CA solid particles in 10 mL of deionized water. Since CA was a weak acid, it did not completely ionize 1 M of c(H^+). After being stabilized for 10 minutes, the results of precision pH paper showed that the pH of the 1 M CA solution was only about 2.5. According to the relationship between c(H^+) and pH:

$$pH = -\log_{10} c(H^+)$$

At this time, the concentration of H^+ in CA solution can be calculated as 3.162×10^{-3} mol/L, which represents only 1/31.65 of the concentration in the hydrochloric acid (HCl) solution. The concentration gradient of the solution was 2 mol/L, and it was observed that the pH value was nearly identical to that of the HCl solution with a gradient of 1, 2, and 4 mol/L, as determined by a precision pH test paper when the CA concentration was 4 mol/L. At this time, under the condition of maintaining the fixed amount of solvent, the CA solute was increased and recorded accordingly. A high-precision pH tester was utilized to detect the change in pH value. Once the display stabilized at around 0.01, the addition of solute was recorded, and the molar concentration of the solution was calculated to be approximately 5 mol/L. The accuracy of the results was confirmed through colorimetric comparison using precision pH test paper. Since the study aimed to investigate the laws of the degradation process of weak and strong acids, no additional acid-base titration was conducted to enhance the accuracy of acid concentration determination.

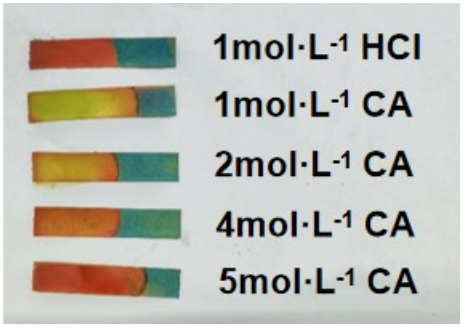


Fig.S9 Color changes of CA solution under precision pH paper at different concentrations