Supporting Information
Sustainable Bio-based Furan Epoxy Resin with Flame Retardancy
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Supporting Experimental Section

Experimental

Unless otherwise noted, all reactions were carried out in an oven-dried flask under a nitrogen or argon atmosphere. Column chromatography was performed with silica gel Merck 60 (300-400 mesh). Analytical thin layer chromatography (TLC) was performed on TLC silica gel plates (0.9 mm) precoated with a fluorescent indicator. Visualization was effected with ultraviolet light, KMnO$_4$, or ethanol sulfuric acid. A positive ion mass spectrum of sample was acquired on a Thermo LTQ-FT mass spectrometer with an electrospray ionization source. All synthetic furan-derivatives were stored at 0 °C and kept dry.

Materials

All reagents and solvents were used without further purification. 5-(hydroxymethyl)-furfural (5-HMF, >98% purity) was purchased from Macklin Reagent Company, China. Epichlorohydrin (ECH), p-Toluenesulfonic acid (PTSA), 2,2'-oxybis(ethan-1-amine) (DEGA), 2,2'-ethane-1,2-diylbis(oxy)bis(ethan-1-amine) (TEGA) and 2,2'-((oxybis(ethane-2,1-diyl))bis(oxy))bis(ethan-1-amine) (TGDE) were obtained from J&K Scientific LTD.

Characterization

**Nuclear Magnetic Resonance (NMR) test**: NMR spectra were recorded on Bruker ADVANCED III (400 MHz) spectrometers for $^1$H and $^{13}$C NMR. DMSO-$d_6$ and CDCl$_3$ were the solvents used for the NMR analysis, with tetramethylsilane as the internal standard. Chemical shifts were reported upfield to TMS (0.00 ppm) for $^1$H NMR and relative to CDCl$_3$ (77.0 ppm) for $^{13}$C NMR.

**Fourier transform infrared (FT-IR) determination**: FT-IR spectra were obtained using a Bruker a Vertex 70 spectrometer (USA) over the wavenumber ranging from 400 to 4000 cm$^{-1}$. All samples are scanned for 16 times.

**Differential scanning calorimetry (DSC) analysis**: The thermal behaviors of monomers and polymers were examined by DSC, using a Discovery DSC (TA250) apparatus. The thermograms were obtained from 4 to 6 mg samples at heating and cooling rates of 10 °C·min$^{-1}$ from -70 °C to 200 °C under a nitrogen flow of 20 mL·min$^{-1}$.

**Thermogravimetric analysis (TGA) analysis**: TGA analysis was performed on a Discovery TGA-550 System under a nitrogen flow of 20 mL·min$^{-1}$ at a heating rate of 20 °C·min$^{-1}$ within a temperature range from 40 to 900 °C.

**Burning determination**: The horizontal burning tests were conducted using the cured epoxy resins. The specimens with thickness of 3 mm and width of 20 mm was horizontally located, and the front of the samples were ignited (10 s). The entire burning processes were recorded using a digital camera.

**Micro calorimeter flammability test**: Microscale combustion calorimetry (MCC-2, GOVMARK) was employed to reveal the flammability of epoxy polymer according to ASTM D7309. About 5 mg sample was heated to 900 °C with a heating rate of 1 °C/s at a stream of nitrogen flowing of 80 cm$^3$/ min. The volatile and anaerobic thermal degradation molecules in the nitrogen stream were mixed with a 20 cm$^3$/min stream comprised of 20% oxygen and 80% nitrogen before approaching a combustion furnace at 900 °C.

**Scanning electron microscope (SEM)**: Microscopy analysis was performed on each burned sample with scanning electron microscope (SEM TM3000, Hitachi) with the largest magnification up to 10000.

General procedures for furan diepoxide synthesis

Two types of furan-containing monomers are obtained, and detailed procedures are listed in Fig. 1 and Fig. 2.

i) **Synthesis of 2,5-bis((oxiran-2-ylmethoxy)methyl)furan (BOF)**

![Fig. 1 Route for BOF synthesis](#)
Furan-2, 5-diylmethanol (2, FDM) synthesis

To a 250 mL Erlenmeyer flask, 5-hydroxymethylfurfural (50.4 g, 400 mmol) was added in portions to deionized water (100 mL), and then the mixture was chilled on an ice bath. Sodium borohydride (16 g, 423 mmol) was carefully added to the open flask in a well-ventilated fume hood as it was stirred magnetically. The reaction mixture was stirred on ice for 1 h then allowed to react at room temperature overnight. The reaction was added sodium chloride and extracted with ethyl acetate at 0°C several times until no product in the aqueous phase are available. The organic mixture are then dried (Na₂SO₄). The white crystalline solid (49.6g, 97% yield) was directly used in next step without further purification.

2, 5-Bis((oxiran-2-ylmethoxy)methyl)furan synthesis (3, BOF)

Epichlorohydrin (EPC) (25.9 g, 280 mmol), 50% w/w aqueous NaOH (9.6 g, 240 mmol), and tetrabutylammonium bromide (0.644 g, 2 mmol) were added to a three-necked round-bottomed flask (250 mL), mixed at 25°C and stirred vigorously for 30 min. Furan-2,5-diylmethanol (2.56 g, 20 mmol) in THF (20 mL) was added dropwise into the flask, the system was subsequently stirred at 50°C. When the FDM was complete (for 6 h), the mixture was concentrated to remove THF and recovered the remained EPC. The reaction was extracted with ethyl acetate (40 mL) three times and dried with MgSO₄. The slightly yellow liquid was purified by silica gel column chromatography (PE/EA= 4/1 ~ 1/1) to yield the colorless liquid 3.61 g in 75% yield.

ii) Synthesis of 5, 5’-(oxybis(methylene))bis(2-((oxiran-2-ylmethoxy)methyl)furan) (OmbFdE)

Commercial 5-hydroxymethylfurfural (50 g, 395 mmol) dissolved in 200 mL toluene was charged into a three-necked round-bottomed flask equipped with a water Dean-Stark trap. p-Toluenesulfonic acid monohydrate (4.5 g, 25 mmol) was also added. The mixture was then refluxed at 110°C for 5 h. Thin layer chromatography (TLC) was employed to indicate the reaction process. The reaction was extracted with DCM three times after washing with saturated bicarbonate solution. The solvent-free mixture was then isolated by column chromatography using a gradient (PE/EA=100/1 ~ 2/1). The combined, concentrated by rotary evaporation under reduced pressure, and recrystallized from 2-propanol to furnish crystalline solid 28.1 g, in 60%.

((Oxybis(methylene))bis(furan-5,2-diyl))dimethanol (5) synthesis

To a 250 mL Erlenmeyer flask, 4 (14 g, 60 mmol) was added in portions to deionized water (40 mL), and then the mixture was chilled on an ice bath. Sodium borohydride (2.28 g, 60 mmol) was carefully added to the open flask in a well-ventilated fume hood as it was stirred magnetically. The reaction mixture was stirred on ice for 1 h, then it was allowed to react at room temperature overnight. The reaction was added sodium chloride and extracted with ethyl acetate at 0°C several times until no product in the aqueous phase are available. The organic mixture are then dried (Na₂SO₄). The white crystalline solid (13.7 g) in 98% yield was directly used in following step without further purification.

5, 5’-(Oxybis(methylene))bis(furan-2-carbaldehyde) synthesis (4)

((Oxybis(methylene))bis(furan-5,2-diyl))dimethanol (5) synthesis

To a 250 mL Erlenmeyer flask, 4 (14 g, 60 mmol) was added in portions to deionized water (40 mL), and then the mixture was chilled on an ice bath. Sodium borohydride (2.28 g, 60 mmol) was carefully added to the open flask in a well-ventilated fume hood as it was stirred magnetically. The reaction mixture was stirred on ice for 1 h, then it was allowed to react at room temperature overnight. The reaction was added sodium chloride and extracted with ethyl acetate at 0°C several times until no product in the aqueous phase are available. The organic mixture are then dried (Na₂SO₄). The white crystalline solid (13.7 g) in 98% yield was directly used in following step without further purification.

5, 5’-(Oxybis(methylene))bis(2-((oxiran-2-ylmethoxy)methyl)furan) (6, OmbFdE) synthesis

Epichlorohydrin (EPC) (26 g, 280 mmol), 50% w/w aqueous NaOH (9.6 g, 240 mmol), and tetrabutylammonium bromide (0.64 g, 2 mmol) were mixed vigorously for 30 min in a three-necked round-bottomed flask (250 mL) at 25°C. ((Oxybis(methylene))bis(furan-5,2-diyl)) dimethanol (4.76 g, 20 mmol) in THF (20 mL) was added dropwise into the flask, and the system was subsequently stirred at 50°C for 7 h. When the
furan stock was complete, the mixture was concentrated to remove THF and remained EPC. The reaction was extracted with EA (30 mL) three times and dried with MgSO\(_4\). The slightly yellow liquid was purified by silica gel column chromatography (PE/EA= 4/1 ~ 1/1) to yield the yellowish liquid (5.11 g) in 73% yield.

**General procedure for the synthesis of cured epoxy resins**

To obtain cured resin samples with optimal structure and performance, the molar ratio of epoxy group to NH was kept at the ratio of 1:1. The following processes were carried out in nitrogen atmosphere.

The epoxy-amine resins were blended with an equivalent molar ratio of functional groups at room temperature, wherein the light viscosity property allowed a mixing processes and degasification. After 30 min, the homogeneous clear liquid was then carefully poured into a polytetrafluoroethylene (PTFE) mold, and put it into vacuum oven. In order to remove any trapped air, the mixture was degassed at room temperature approximately 3~5 min. Remarkably, the epoxy-amine mixtures appear clear and homogeneous. Then the fully miscible mixture was cured at 50\(\degree\)C for 2 h, and post-cured at 70 \(\degree\)C for an additional 2 h (curing time and temperature optimization, seeing Table 1). Subsequently, the ejection of the casting from the mold after the mold was naturally cooled to room temperature to obtain cured epoxy resin. All samples were cured at the same conditions to achieve fully cured epoxy resins.

### Table 1. curing time and temperature optimization\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>diamine</th>
<th>epoxy</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
<th>Average value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DEGA</td>
<td>OmbFdE</td>
<td>0.118</td>
<td>0.099</td>
<td>0.083</td>
<td>0.082</td>
<td>0.073</td>
<td>0.091</td>
</tr>
<tr>
<td>2</td>
<td>BOF</td>
<td></td>
<td>0.244</td>
<td>0.225</td>
<td>0.217</td>
<td>0.194</td>
<td>0.168</td>
<td>0.209</td>
</tr>
<tr>
<td>3</td>
<td>TEGA</td>
<td>OmbFdE</td>
<td>0.083</td>
<td>0.082</td>
<td>0.0828</td>
<td>0.079</td>
<td>0.058</td>
<td>0.077</td>
</tr>
<tr>
<td>4</td>
<td>BOF</td>
<td></td>
<td>0.36</td>
<td>0.293</td>
<td>0.264</td>
<td>0.254</td>
<td>0.191</td>
<td>0.272</td>
</tr>
<tr>
<td>5</td>
<td>TGDE</td>
<td>OmbFdE</td>
<td>0.106</td>
<td>0.086</td>
<td>0.085</td>
<td>0.068</td>
<td>0.056</td>
<td>0.08</td>
</tr>
<tr>
<td>6</td>
<td>BOF</td>
<td></td>
<td>0.255</td>
<td>0.233</td>
<td>0.213</td>
<td>0.2</td>
<td>0.143</td>
<td>0.209</td>
</tr>
</tbody>
</table>

\(^a\) Curing condition: for sample 1: 50 \(\degree\)C, 1 h; sample 2: 50 \(\degree\)C, 2 h; sample 3: 50 \(\degree\)C, 2 h; then 70 \(\degree\)C, 1 h; sample 4: 50 \(\degree\)C, 2 h; then 70 \(\degree\)C, 2 h; sample 5: 50 \(\degree\)C, 2 h; then 70 \(\degree\)C, 3 h.

**Differentiation analysis of TGA curves of monomers**

In order to investigate the stability of different monomers used in these new epoxy resin polymers, TGA were employed in the temperature ranging from 25\(\degree\)C to 900\(\degree\)C under N\(_2\). Three aliphatic curing reagents, i.e. DEGA TEGA TGDE were evaluated herein. Besides, the epoxy monomer, such as BOF, OmbFdE were determined under the same conditions. The DTG curves are shown in Fig. 3.
Characterization data of products

furan-2, 5-diyldimethanol (2, FDM) ¹

¹H NMR (400 MHz, DMSO-d⁶)  δ 6.19 (s, 2H), 4.35 (s, 4H), 3.50 (br, 2H).

2, 5-bis((oxiran-2-ylmethoxy)methyl)furan (3, BOF) ¹

¹H NMR (400 MHz, CDCl₃)  δ 6.30 (s, 2H), 4.51 (q, J = 12.8 Hz, 4H), 3.77 (dd, J = 11.5, 3.0 Hz, 2H), 3.43 (dd, J = 11.5, 5.9 Hz, 2H), 3.16 (ddt, J = 5.9, 4.1, 2.9 Hz, 2H), 2.85-2.76 (m, 2H), 2.61 (dd, J = 5.0, 2.7 Hz, 2H).

¹C NMR (100 MHz, DMSO-d⁶)  δ 178.88, 157.72, 152.79, 124.28, 112.80, 64.15.

((oxybis(methylene))bis(furan-5,2-diyl))dimethanol (5)²

¹H NMR (500 MHz, CDCl₃)  δ 6.27 (d, J = 3.0 Hz, 1H), 6.23 (d, J = 3.0 Hz, 1H), 4.56 (s, 2H), 4.47 (s, 2H).

¹C NMR (125 MHz, CDCl₃)  δ 153.56, 150.32, 109.45, 107.37, 62.83, 56.45.

5, 5'-(oxybis(methylene))bis(2-((oxiran-2-ylmethoxy)methyl)furan) (6, OmbFdE)

¹H NMR (400 MHz, CDCl₃)  δ 6.29 (s, 4H), 4.52 (t, J = 11.2 Hz, 4H), 4.46 (s, 4H), 3.77 (dd, J = 11.5, 3.0 Hz, 2H), 3.43 (dd, J = 11.5, 5.9 Hz, 2H), 3.16 (ddt, J = 5.9, 4.1, 2.9 Hz, 2H), 2.79 (t, J = 4.6 Hz, 2H), 2.61 (dd, J = 5.0, 2.7 Hz, 2H).

¹C NMR (100 MHz, CDCl₃)  δ 151.77, 151.75, 110.46, 110.35, 70.70, 65.16, 63.74, 50.72, 44.30.

HRMS-ESI⁺ (m/z): C₉₂H₂₂O₇Na [M+Na]⁺ calcd for 373.1258, found 373.1254.

Copy of NMR spectra

furan-2, 5-diyldimethanol (2, FDM)

2, 5-bis((oxiran-2-ylmethoxy)methyl)furan (3, BOF)
5, 5'-oxybis(methylene)bis(furan-2-carbaldehyde) (4)
((-oxybis(methylene))bis(furan-5,2-diyl))dimethanol (5)
5, 5'-oxybis(methylene)bis(2-((oxiran-2-ylmethoxy)methyl)furan) (6, OmbFdE)
References:
