

Supplementary Information

A thermally remendable epoxy resin

Qiao Tian^a, Yan Chao Yuan^a, Min Zhi Rong^{*b}, Ming Qiu Zhang^b

^aKey Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, OFCM Institute, School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510275, P. R. China

^bMaterials Science Institute, Zhongshan University, Guangzhou 510275, P. R. China

Synthesis of DGFA

Epichlorohydrine 92.8 g (1 mol) was charged into a 250 mL four-necked round-bottom flask equipped with a stirrer, a thermometer, and an inlet of dry nitrogen. When the solution was heated to 40 °C, furfural amine 48.5 g (0.5 mol) was added dropwise while keeping the solution temperature below 60 °C. The reaction mixture was stirred for 5 h at 60 °C under N₂ atmosphere and then cooled down to room temperature. After that, 160 mL sodium hydroxide aqueous solution (50 % (w/v)) was added dropwise within 1 h. The reaction proceeded for additional 5 h at 30 °C. Afterwards, 200 ml ethyl acetate was added, and the organic layer was collected, washed with water for several times before it was dried with anhydrous sodium sulfate, filtrated, and evaporated to give a 80 % liquid. The liquid was further purified by chromatography on a silica gel column using mixed solvent of ethyl acetate/hexane (1/3). The solvent was removed on a rotary evaporator, and lastly, a light yellow liquid was obtained with a yield of 50%.

Characterization of DGFA

Oxirane ring of DGFA is present as reflected by the FTIR absorption peaks (Fig. S1) at 3051 cm⁻¹ (C-H in oxirane ring), 1250 and 851 cm⁻¹ (C-O-C), and 918 cm⁻¹ (oxirane ring breathing). Furan ring of DGFA is proved by the peaks at 3144 and 3117 cm⁻¹ (C-H in furan ring), 1503 cm⁻¹ (C=C in furan ring), 1148 cm⁻¹ (C-O in furan ring), 1013 cm⁻¹ (furan ring breathing), and 752 cm⁻¹ (representing mono-substituted furan ring).¹⁵ Besides, the characteristic peak at 1346 cm⁻¹ is attributed to stretching vibration of C-N.

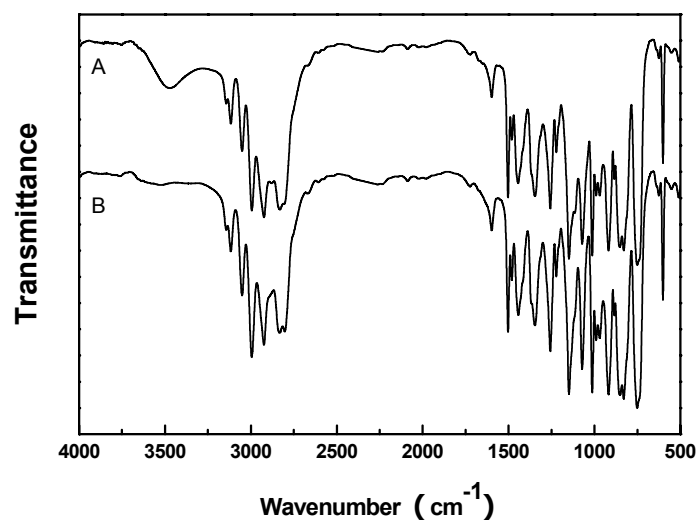


Fig. S1 FTIR spectra of (A) raw DGFA and (B) its purified version.

In ¹H-NMR spectrum of the reaction product (Fig. S2), the peaks at $\delta_{\text{H}} = 3.1\text{--}2.4$ ppm are due to the protons designated as “5” in the oxirane rings. Furan ring is identified with the peaks at $\delta_{\text{H}} = 6.2\text{--}6.3$ ppm (=CH-CH=, 2H) and $\delta_{\text{H}} = 7.3$ ppm (-O-CH=C-, 1H) corresponding to the protons “2”, “3” and “1”, respectively. The characteristic peak at $\delta_{\text{H}} = 3.8$ ppm (-NCH₂-furan ring, 2H) indicates existence of group “4” that links glycidyl amine to furan ring. Fig. S3 shows ¹³C-NMR spectrum of DGFA with the assignments: 151, 141, 110, 109 (C₁₋₄ for furan ring), 66.6, 66.1 (C₅, -N-CH₂-oxirane ring), 61.1, 60.9 (C₆, oxirane ring), 60.6 (C₇, -N-CH₂-furan), and 44.8, 44.5 (C₈, oxirane ring), respectively. Moreover, result of element analysis also coincides with the chemical structure of DGFA.

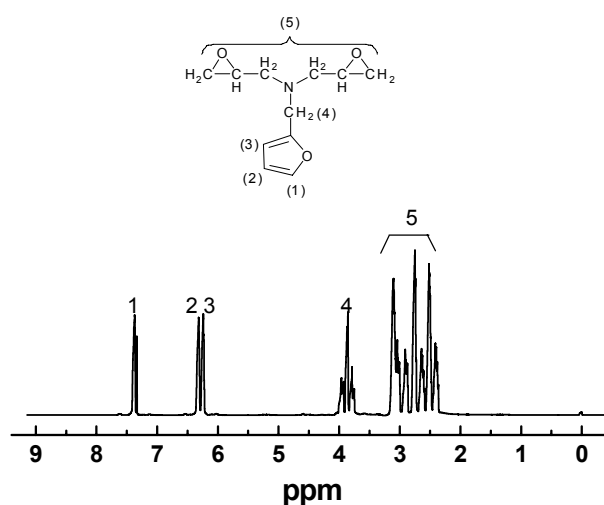


Fig. S2 ¹H-NMR spectrum of DGFA.

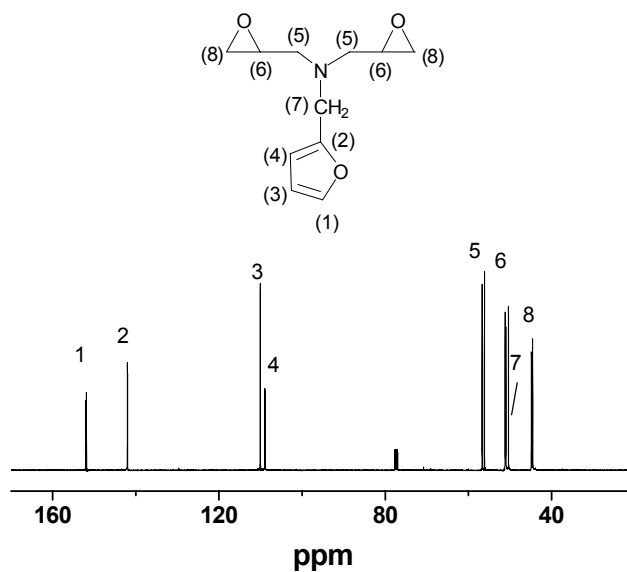


Fig. S3 ¹³C-NMR spectrum of DGFA.

Table S1 Curing kinetic parameters of stoichiometric DGFA/MHHPA mixture obtained from isothermal DSC tests at different temperatures and calculated according to the modified Avrami equation¹⁷

Temperature (°C)	<i>n</i>	<i>k</i> × 10 ⁻² (s ⁻¹)	<i>E_a</i> (kJ/mol)	ln <i>A</i>
100	1.13	1.03		
110	1.04	3.13		
120	1.05	4.82	61.5	16
130	1.06	6.62		

A: pre-exponential factor.

E_a: activation energy.

n: reaction order.

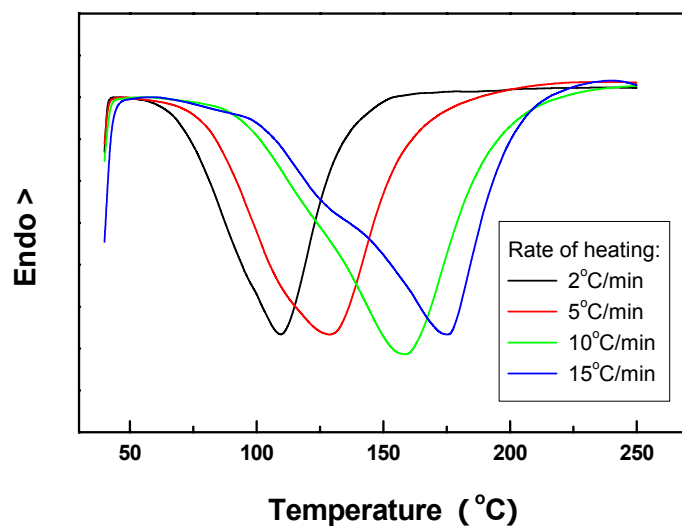


Fig. S4 DSC heating traces of the mixture of DGFA and MHPA at stoichiometric ratio.

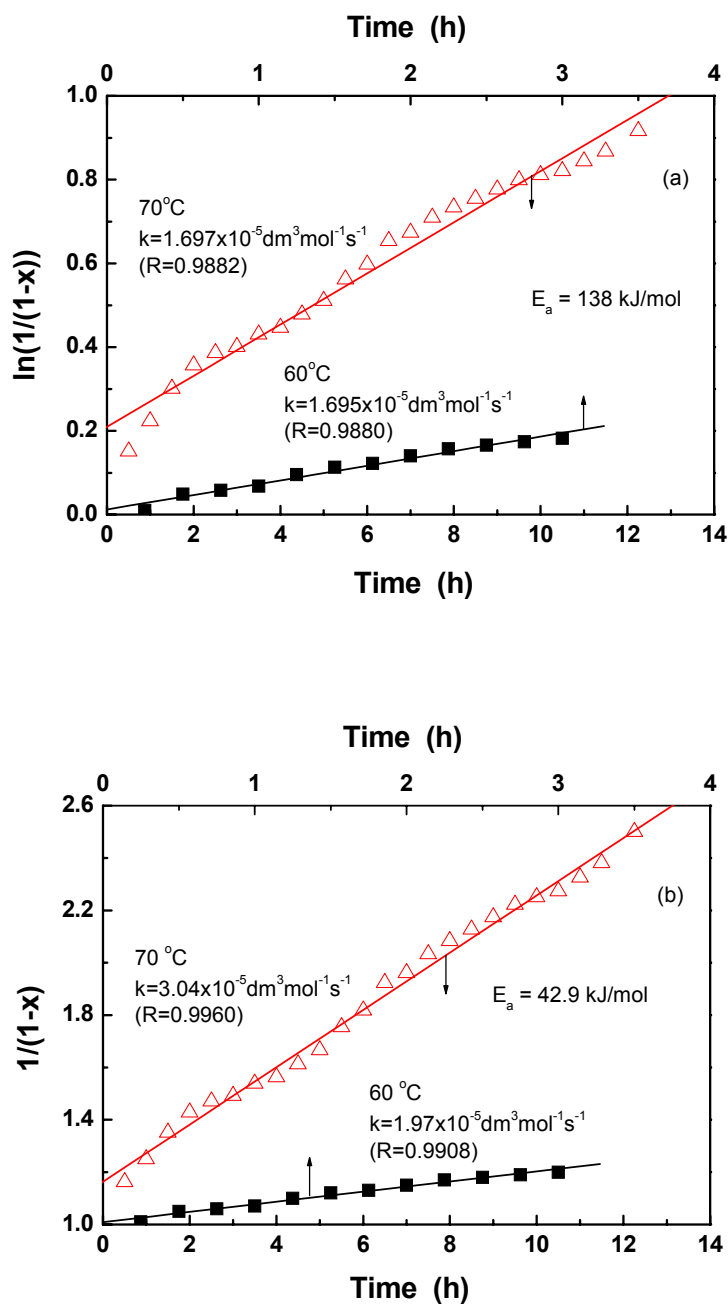


Fig. S5 Time dependences of DA conversion, x , of the reaction between DGFA and DPMBMI. Linear fit of the data is conducted according to (a) first-order and (b) second-order kinetics. The values of x are obtained from $^1\text{H-NMR}$ measurements at 60 and 70 °C, respectively.