Supporting Information

Tandem CO_2 Valorisation to Polycarbonate Vitrimer and Ethylene Carbonate

Seiyoung Yoon,[a] Ling-Jo Wu,[a] Sophia Aracri,[a] Satej S. Joshi,[a] Vishal Kumar,[b] Wenbin Kuang,[b] Mark D. Foster,[a] James M. Eagan,*[a] and Junpeng Wang*[a]

[a] School of Polymer Science and Polymer Engineering, University of Akron, Akron, Ohio 44325, United States.

[b] Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, Washington, United States.

Contents

Materials

Tri-PCHC-COOH was synthesized according to literature.[1] EPON 828 (bisphenol A diglycidyl ether, DGEBA) was obtained from Hexion and used as received. Malic acid was purchased from Thermo Scientific. Zinc acetate dihydrate was purchased from Acros Organics, and zinc stearate dihydrate from Sigma-Aldrich.

Tri-PCHC-COOH, malic acid, zinc acetate and zinc stearate were ground into a fine powder and stored in anhydrous condition until curing.

Instruments

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR NMR spectra were obtained using a Varian 500 MHz spectrometer at the University of Akron Magnetic Resonance Center with chloroform-d as the solvent. Chemical shifts were referenced to residual chloroform signal (δ = 7.26 [^{1}H]). T1 measurements were performed to obtain the longest ^{1}H relaxation delay needed for quantitative analysis.

Cryogenic Ball-Milling

A CryoMill from Retsch was used to perform cryogenic ball-milling of materials. A 50 mL stainless steel jar and six stainless steel balls with 7 mm diameter were used. 5 g of vitrimer material were subjected to ball-milling each time. Cryogenic ball-milling was conducted by pre-cooling the jar at 5 Hz while circulating liquid nitrogen for 30 minutes followed by 5 minutes of shaking at 30 Hz under liquid nitrogen circulation.

Scanning Electron Microscopy

SEM images were obtained using a JEOL JEOL-7401 FE-SEM operated in secondary electron (SE) mode at an accelerating voltage of 1.0 kV and a working distance of 12.7 mm. Samples were mounted on aluminum stubs using carbon conductive tape prior to imaging.

Synthesis and Characterization of Vitrimers

Synthesis of PCHC Vitrimer

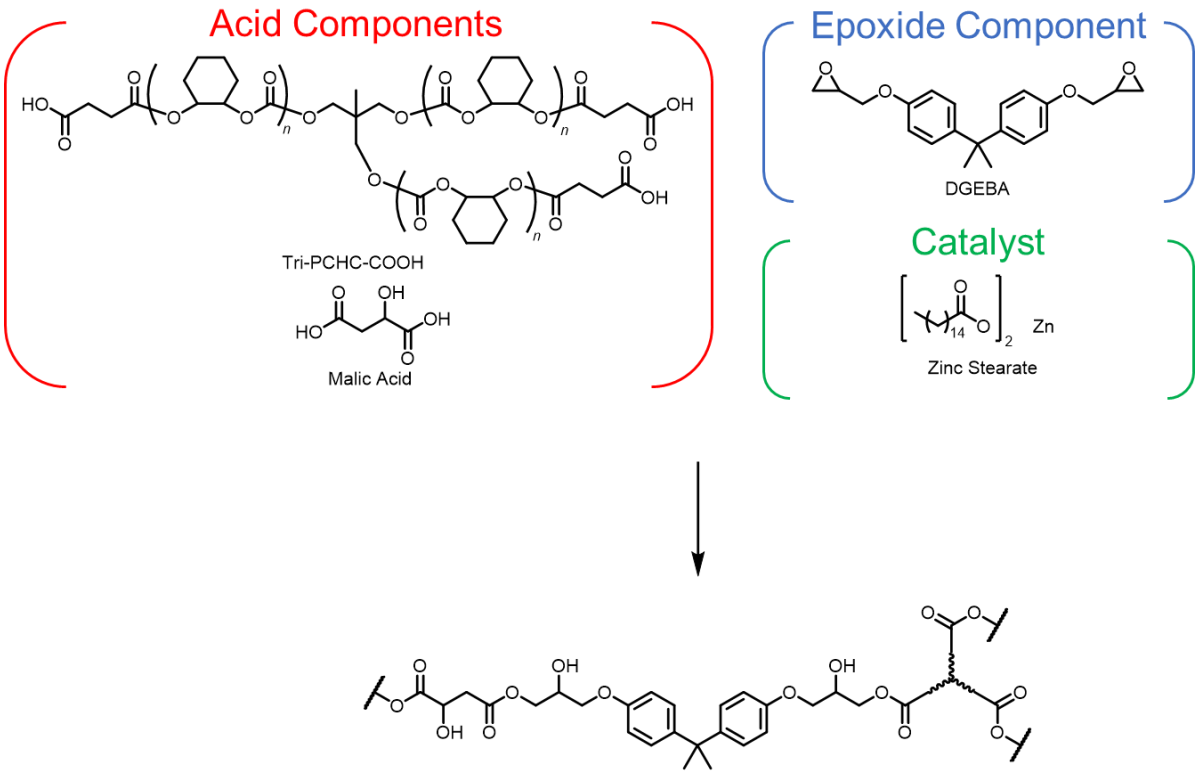

Figure S1. Synthesis of PCHC vitrimer with zinc stearate.

The representative curing conditions are as follows:
Tri-PCHC-COOH (4.99 g, 2.35 mmol, 1.0 eq.), malic acid (0.473 g, 3.53 mmol, 1.5 eq.) and DGEBA (2.73 g, 7.06 mmol, 3.0 eq.) were mixed at 130 °C until homogenization. Zinc stearate (0.268 g, 0.424 mmol, 0.18 eq.) was added to the mixture while stirring at 130 °C. The mixture was degassed at 130 °C for 1 h and heated to 150 °C for 8 h in a Carver Press at 2000 psi.

Gel-Fraction Analysis

Gel-fraction was characterized by swelling 50 mg of vitrimer resin in 50 mL acetone for 16 hours followed by swelling in 50 mL THF for another 16 hours. The retrieved swollen resin was dried under vacuum before weighing. The mass of the dried gel was compared to original mass (50 mg) to calculate the gel-fraction.

Curing Kinetics Analysis (Temperature Effect)

A mixture of tri-PCHC-COOH, malic acid, DGEBA and zinc stearate was separated into 100 mg batches. The samples were subjected to heating at either 130 °C or 150 °C. Samples were taken out at different times for gel-fraction analyses. The results suggest that the mixture can be heated for 1 h at 130 °C for degassing without reaching a gel-point.

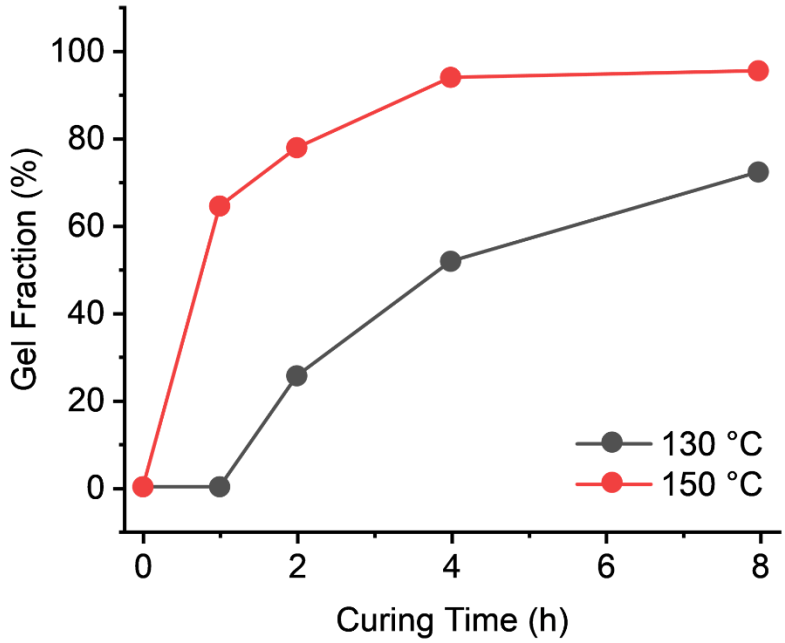

Figure S2. Curing kinetics of PCHC vitrimer with 3 mol% zinc stearate at two temperatures.

Zinc Catalyst Comparison

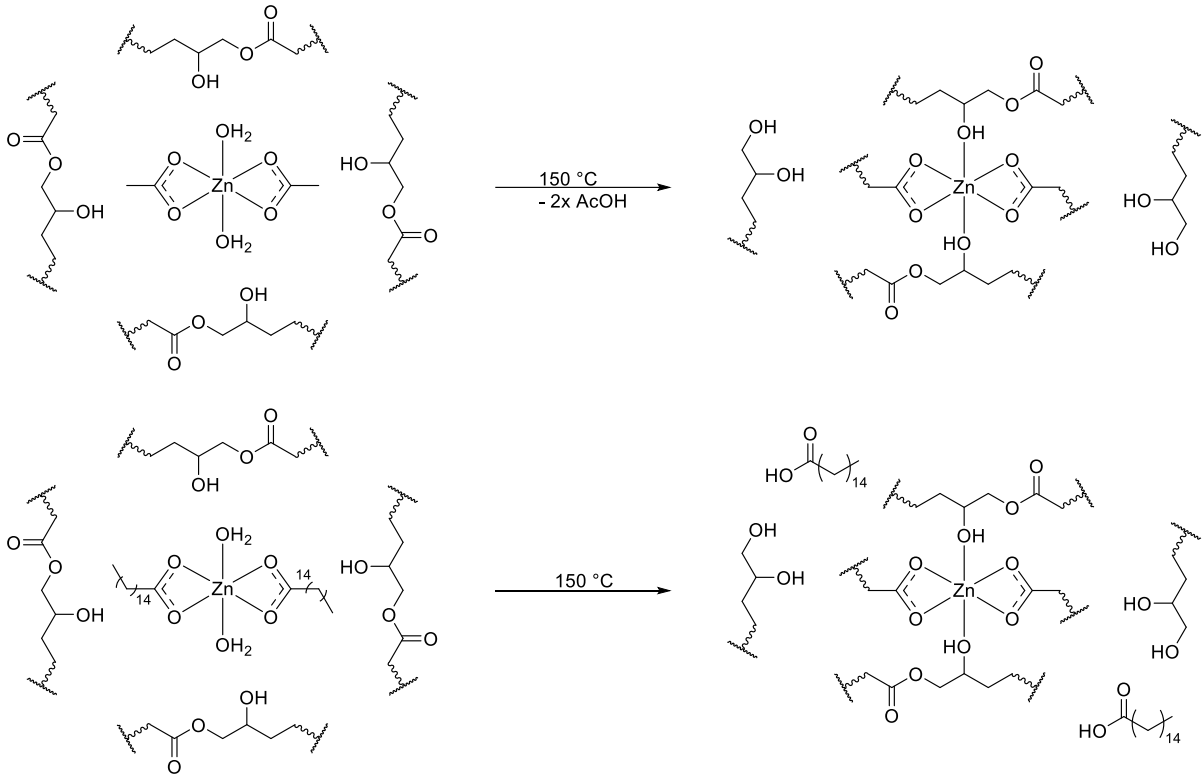

Figure S3. Mechanism of zinc incorporation into transesterification vitrimer for zinc acetate (top) and zinc stearate (bottom).

Creep of PCHC Vitrimers

Non-isothermal creep experiments were conducted on a TA-RSA G2 DMTA instrument in tension geometry. Rectangular samples with dimensions of 60 mm (L) × 6 mm (W) × 1.5 mm (T) were prepared. The temperature was set to 80 °C, and the sample was given 15 min to thermally equilibrate. The experiment was conducted using a constant axial force of 0.2 ± 0.1 N and heating the sample from 80 to 250 °C at a rate of 2 °C/min.

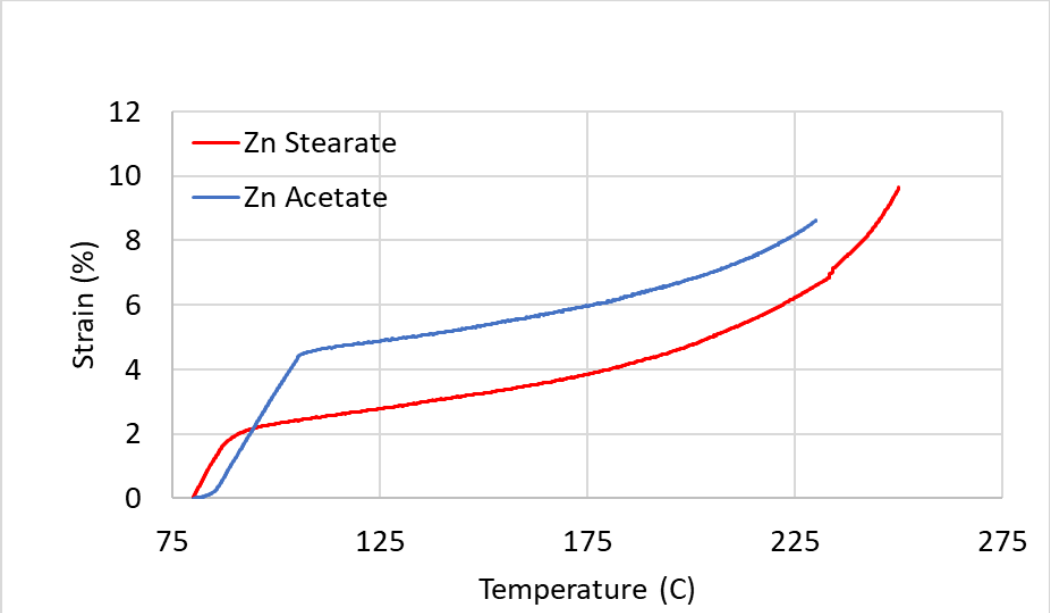

Figure S4. Non-isothermal creep for the samples with 5 mol% zinc acetate and samples with 3 mol% zinc stearate.

Temperature Sweep Experiments

Temperature sweep experiments were conducted in a TA-RSA G2 Dynamic mechanical thermal analysis (DMTA) instrument in tension geometry. Samples were shaped as rectangles of dimension 10 mm (L) × 3 mm (W) × 2 mm (T) and tested at a frequency of 1 Hz and 0.1% strain. Samples were heated from 50 to 200 °C at a ramp rate of 2 °C/min. All measurements were made in the linear viscoelastic region.

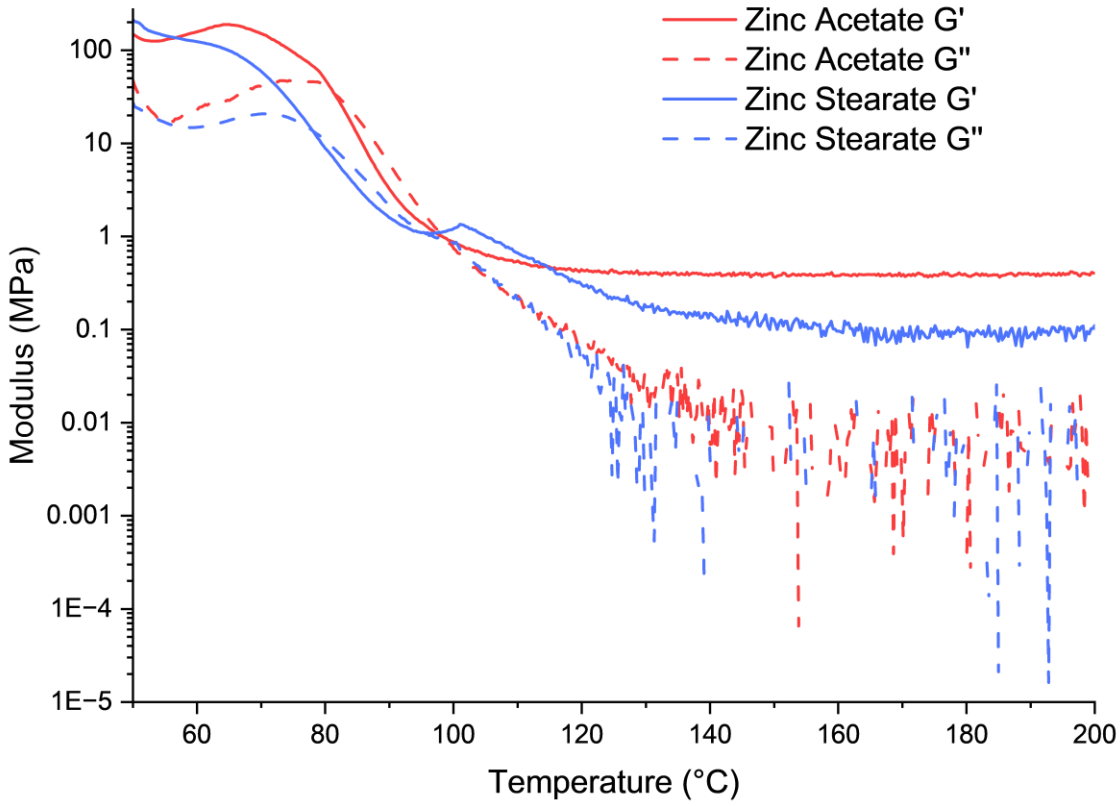

Figure S5. Temperature sweep for the samples with 5 mol% zinc acetate and samples with 3 mol% zinc stearate.

[1]H NMR Analyses

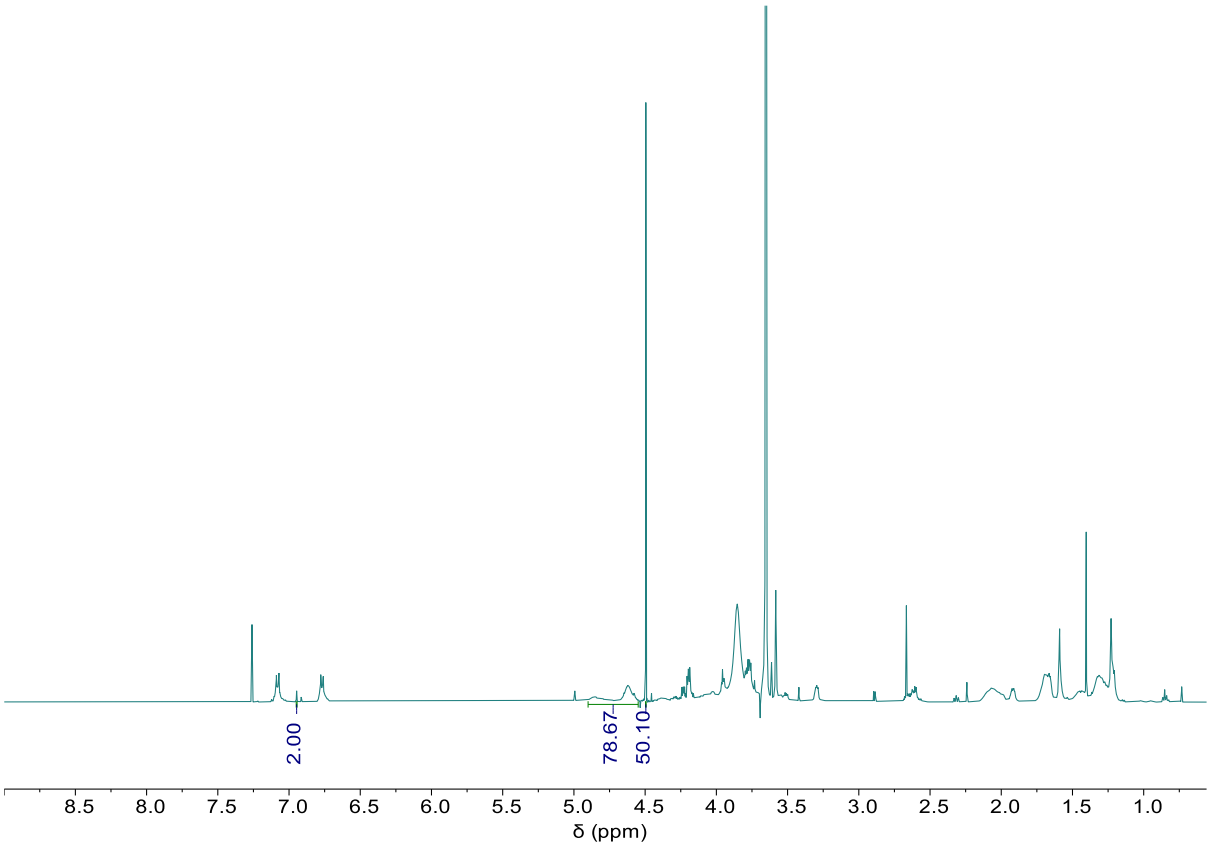

Figure S6. [1]H NMR (500 MHz, $CDCl_3$) spectrum of PCHC vitrimer after 4 h of glycolysis.

PCHC vitrimer resin: 907 mg

BHT: 16.1 mg

$$Conversion\ of\ PCHC = 1 - \frac{PCHC}{EC + PCHC} = 1 - \frac{78.67}{50.1 + 78.67} = 39\%$$

$$Yield\ of\ EC$$

$$= \frac{\frac{Mass\ of\ BHT}{MW\ of\ BHT} \times \frac{12.5\ mol\ EC}{1\ mol\ BHT}}{Mass\ of\ vitrimer \times \frac{0.59\ g\ PCHC - COOH}{1\ g\ vitrimer} \times \frac{1700\frac{g}{mol}CHC}{2120\frac{g}{mol}PCHC - COOH} \times \frac{1}{MW\ of\ CHC}}$$

$$= \frac{\frac{16.1\ mg}{220.35\ g/mol} \times \frac{12.5\ mol\ EC}{1\ mol\ BHT}}{907\ mg \times \frac{0.59\ g\ PCHC - COOH}{1\ g\ vitrimer} \times \frac{1700\frac{g}{mol}CHC}{2120\frac{g}{mol}PCHC - COOH} \times \frac{1}{142.15\ g/mol}}$$

$$= 30\%$$

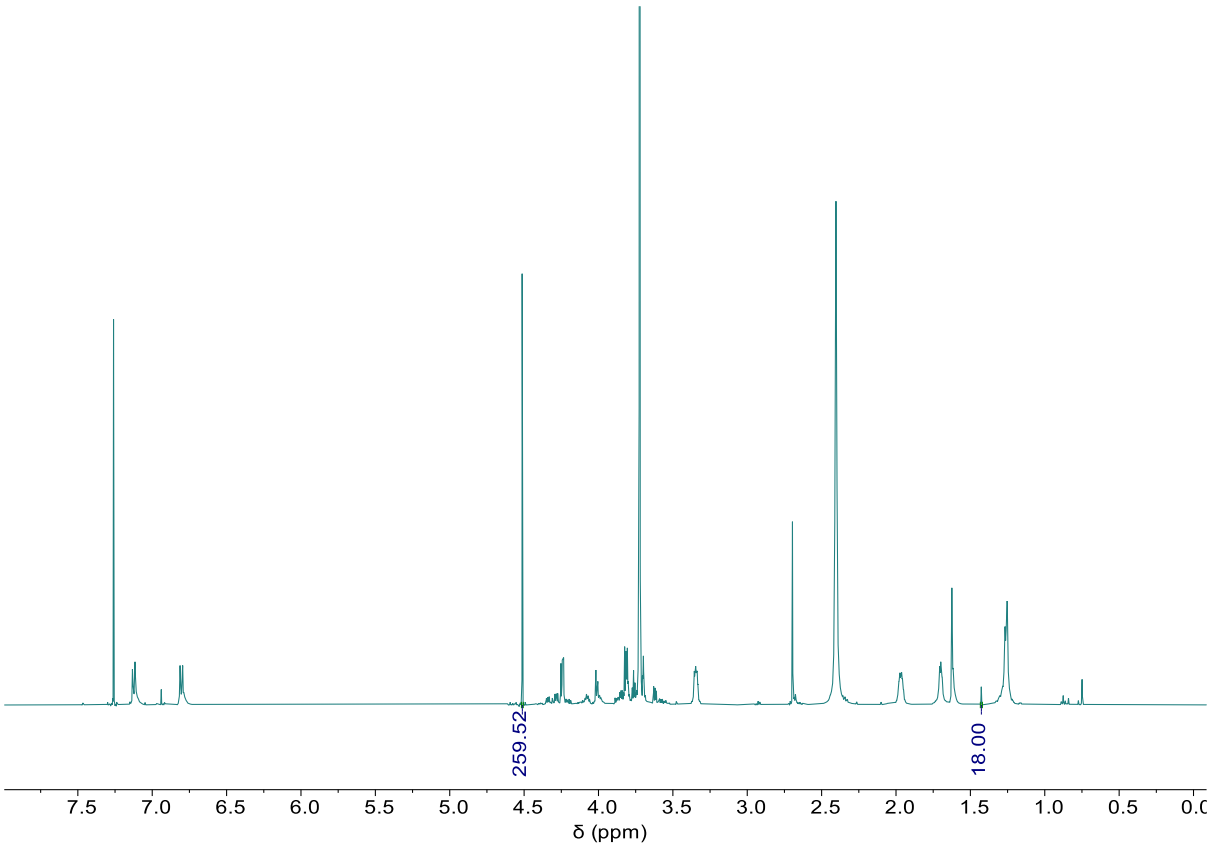

Figure S7. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of PCHC vitrimer after 8 h of glycolysis.

PCHC vitrimer resin: 905 mg

BHT: 9.8 mg

$$Conversion\ of\ PCHC = 1 - \frac{PCHC}{EC + PCHC} = 1 - \frac{0}{259.52 + 0} = 100\%$$

$$Yield\ of\ EC$$

$$= \frac{\frac{Mass\ of\ BHT}{MW\ of\ BHT} \times \frac{64.88\ mol\ EC}{1\ mol\ BHT}}{Mass\ of\ vitrimer \times \frac{0.59\ g\ PCHC - COOH}{1\ g\ vitrimer} \times \frac{1700\frac{g}{mol}CHC}{2120\frac{g}{mol}PCHC - COOH} \times \frac{1}{MW\ of\ CHC}}$$

$$= \frac{\frac{9.8\ mg}{220.35\ g/mol} \times \frac{64.88\ mol\ EC}{1\ mol\ BHT}}{905\ mg \times \frac{0.59\ g\ PCHC - COOH}{1\ g\ vitrimer} \times \frac{1700\frac{g}{mol}CHC}{2120\frac{g}{mol}PCHC - COOH} \times \frac{1}{142.15\ g/mol}}$$

$$= 96\%$$

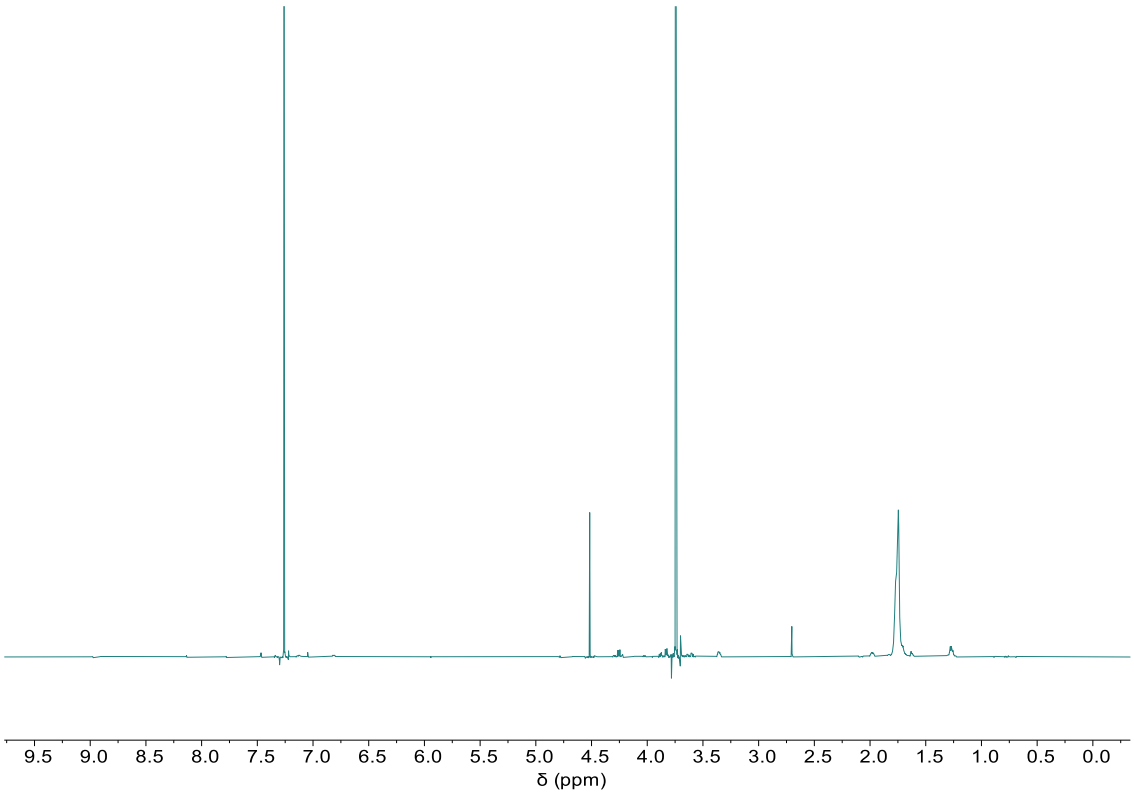

Figure S8. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of PCHC CFRP after 16 h of glycolysis.

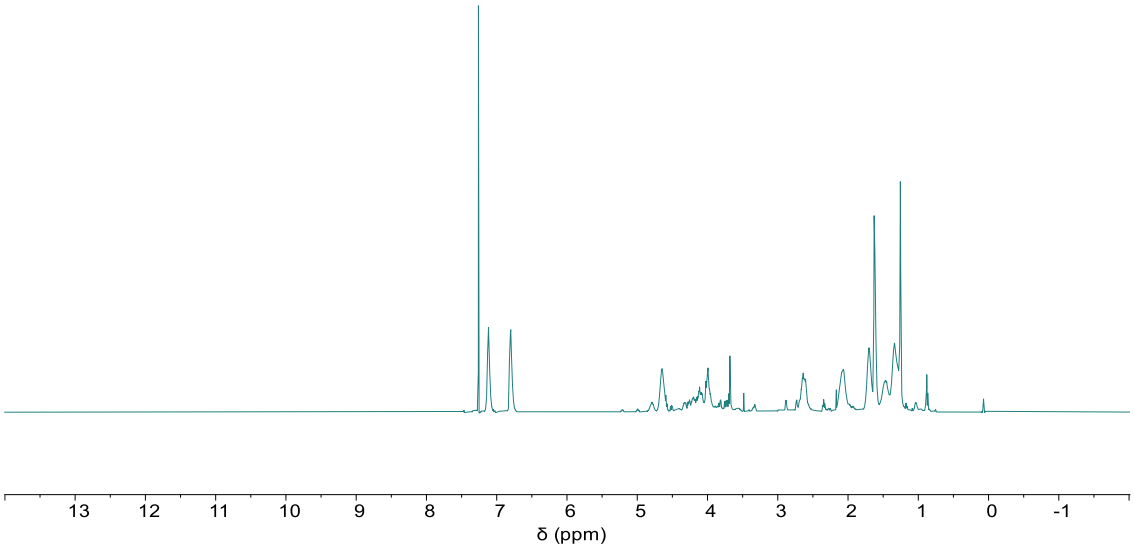

Figure S9. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of PCHC vitrimer sol fraction after 16 h of heating at 180 °C

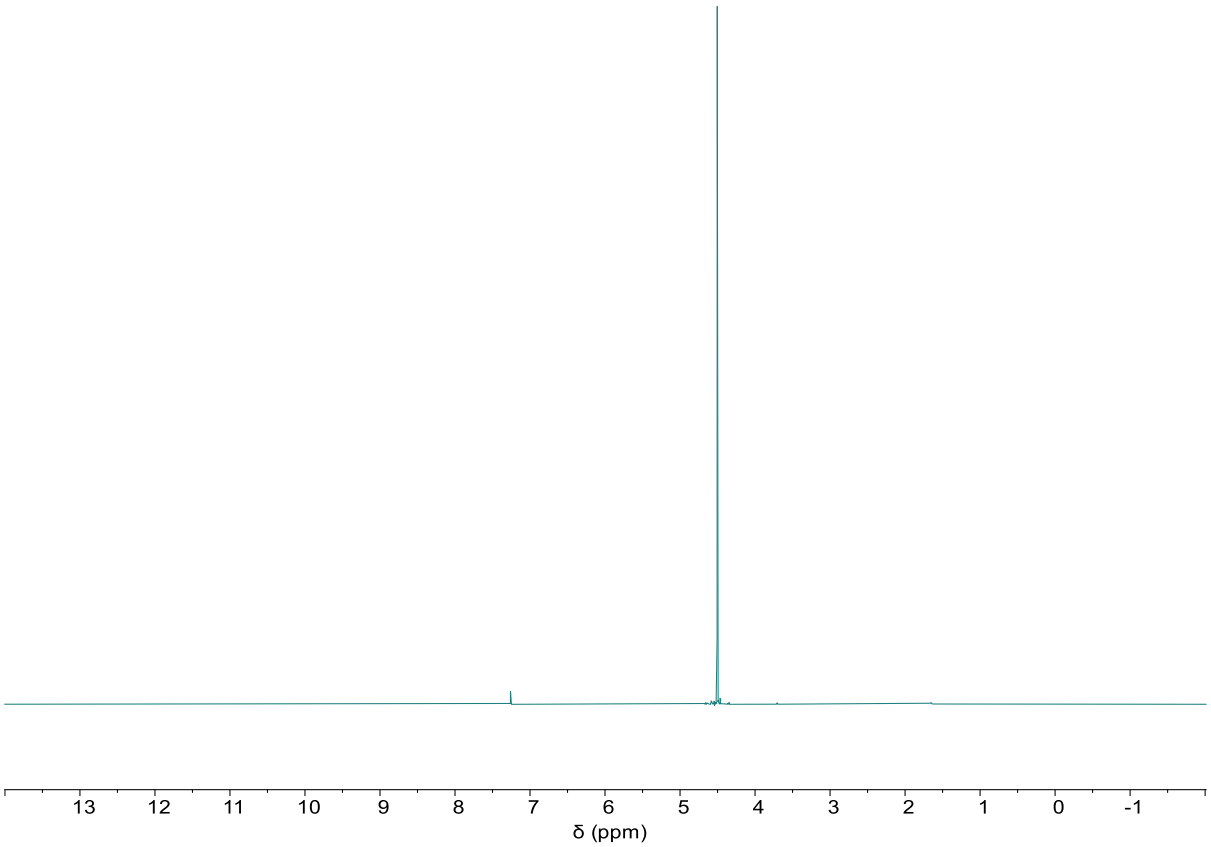

Figure S10. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ethylene carbonate distilled from decomposed PCHC.

Carbon Fibre Recovery

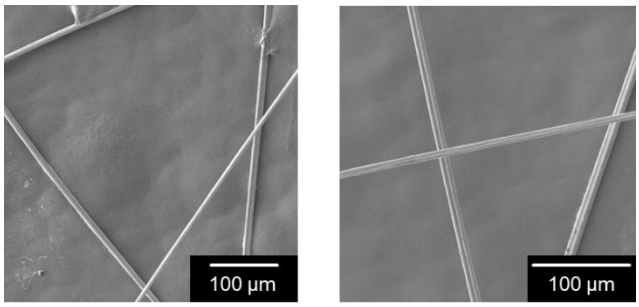

Figure S11. Additional SEM images of recovered carbon fibres.

References

1. S. Yoon, S. S. Joshi, S. Aracri, Y. Ospina-Yepes, D. Sathe, M. D. Foster, J. Wang and J. M. Eagan, *ACS Appl. Polym. Mater.*, 2025, **7**, 4561-4571.