Supporting Information

Chemically Recyclable and Reprogrammable Epoxy Thermosets Derived from Renewable Resources

Tankut Türel,[a†] Özgün Dağlar,[a†] Christos Pantazidis,[a] and Željko Tomović[a*]

a) Polymer Performance Materials Group, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands.

Contents

1) Synthesis and Characterization of 2-((2-(Vinyloxy)ethoxy)methyl)oxirane (VE2), C2 and the model compound
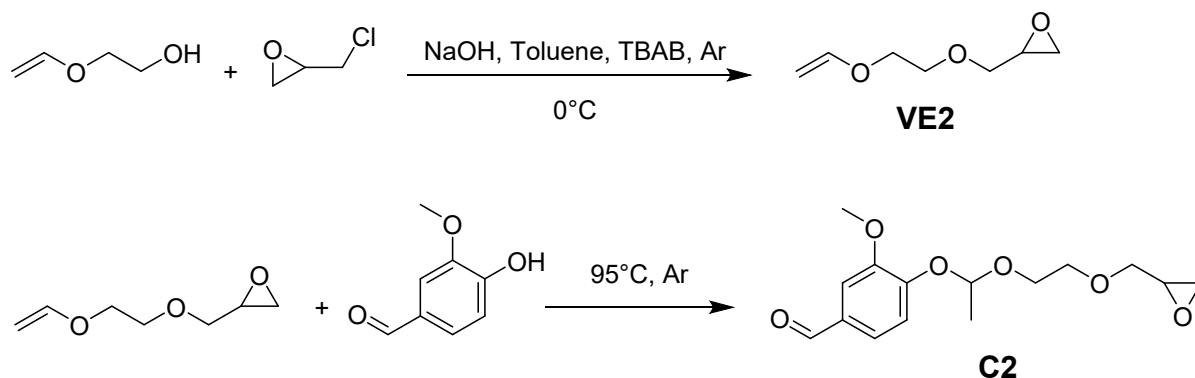
Synthesis of VE2

Ethylene glycol vinyl ether (39.0 g, 0.44 mol) and tetrabutyl ammonium bromide (TBAB, 4.7 g, 15 mmol) were dissolved in 260 mL of the toluene/NaOH (50wt %) mixture (1:1 by volume) in a 1 L three-necked round-bottom flask equipped with a reflux condenser, an Ar inlet, and a dropping funnel, and the mixture was cooled to 0 °C. Epichlorohydrin (65.81 g, 0.71 mol) was added dropwise over 1 h. After completion ofthe addition, the reaction temperature was raised to room temperature and the mixture was allowed to stir for 24 h at this temperature under Ar flow. The reaction mixture was extracted with distilled water and dried over magnesium sulfate. Upon removal of the solvent, the crude product was purified upon distillation under reduced pressure to give a colorless liquid with a yield of 57.2 g, 90.1%.^{1}H NMR (399 MHz, Chloroform-d) δ 6.50 (dd, J = 14.3, 6.8 Hz, 1H), 4.19 (dd, J = 14.3, 2.2 Hz, 1H), 4.02 (dd, J = 6.8, 2.2 Hz, 1H), 3.90 – 3.77 (m, 4H), 3.44 (dd, J = 11.7, 5.9 Hz, 1H), 3.17 (ddt, J = 5.8, 4.2, 2.8 Hz, 1H), 2.80 (dd, J = 5.0, 4.1 Hz, 1H), 2.62 (dd, J = 5.0, 2.7 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 151.84, 86.89, 72.17, 69.86, 67.35, 50.94, 44.33.

Synthesis of C2

Vanillin (4.93 g, 32.4 mmol) and **VE2** (7.01 g, 48.6 mmol) were mixed in a 100 mL three-necked round-bottom flask equipped with a reflux condenser and an Ar inlet. The mixture was heated to 95 °C for 24 hours under Ar flow. After cooling to room temperature, the crude product was purified using column chromatography with ethyl acetate and cyclohexane as eluents. The **C2** monomer was obtained as a yellow liquid with a yield of 5.05 g, 52.6%.

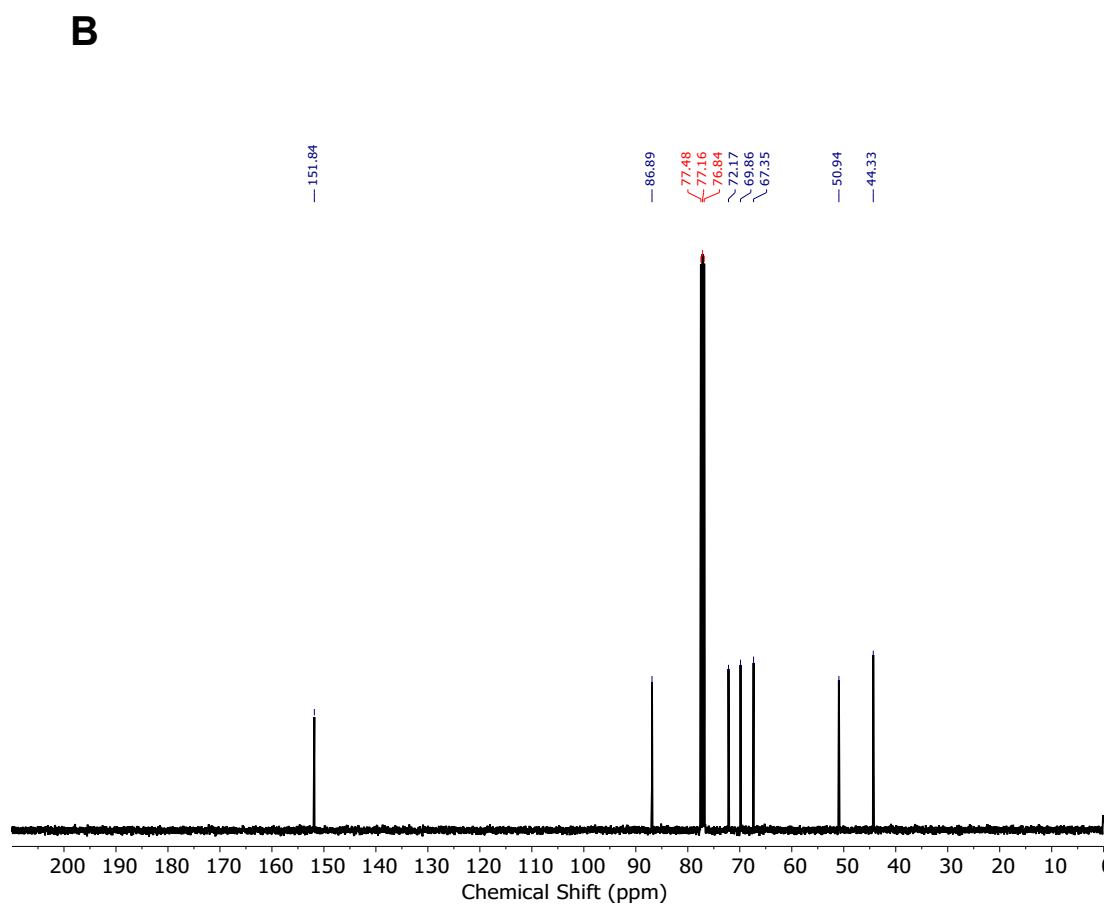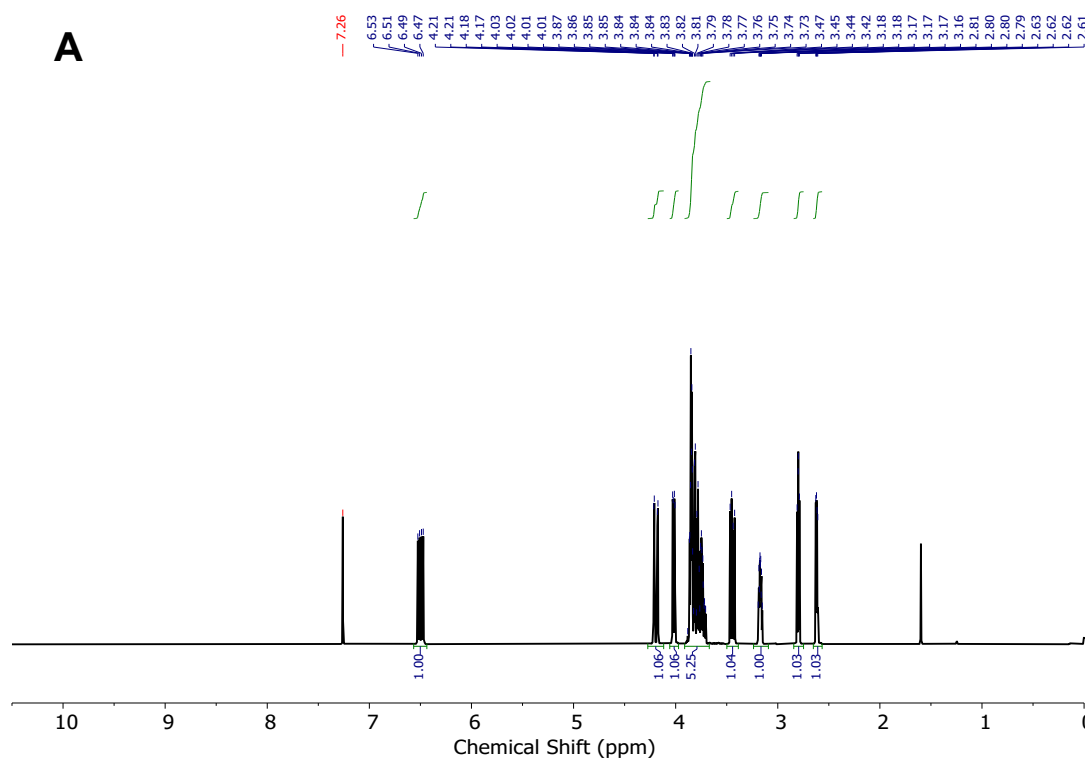Scheme S1. Synthetic pathway towards **VE2** and **C2**.

A

B

Figure S1. ^{1}H NMR (A) and ^{13}C NMR (B) spectra of 2-((2-(Vinyloxy)ethoxy)methyl)oxirane (**VE2**) recorded in CDCl$_3$.
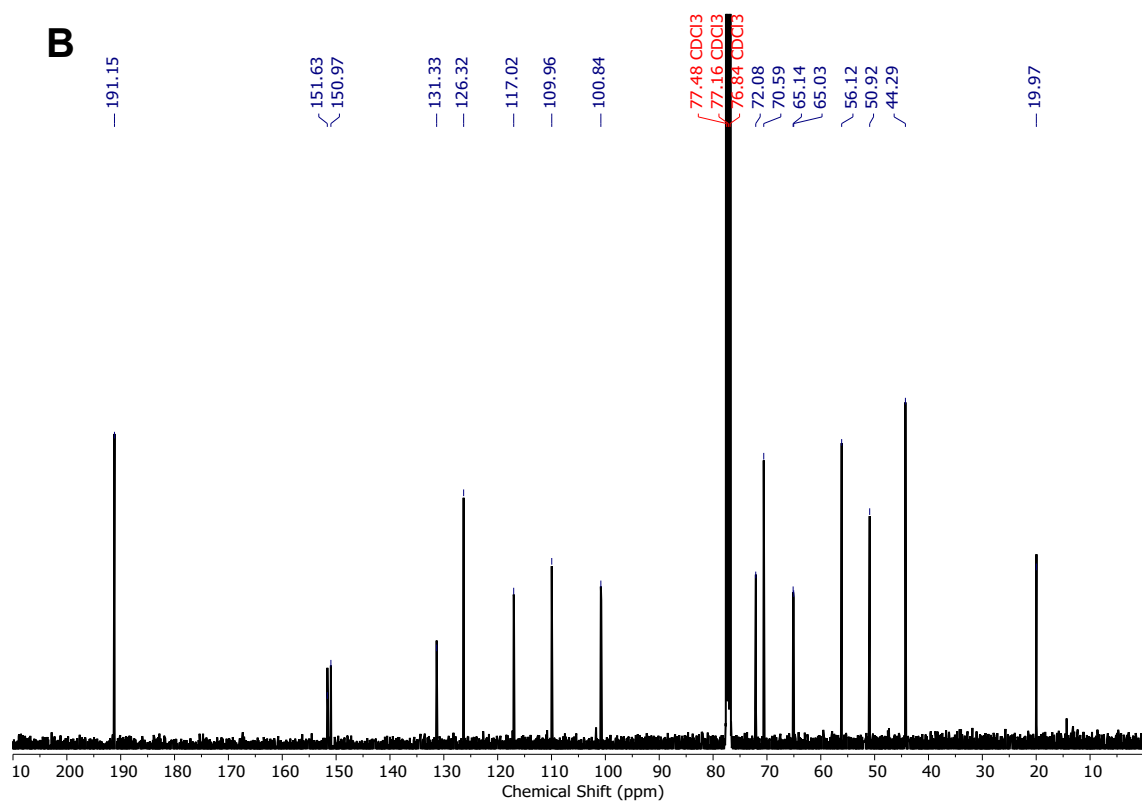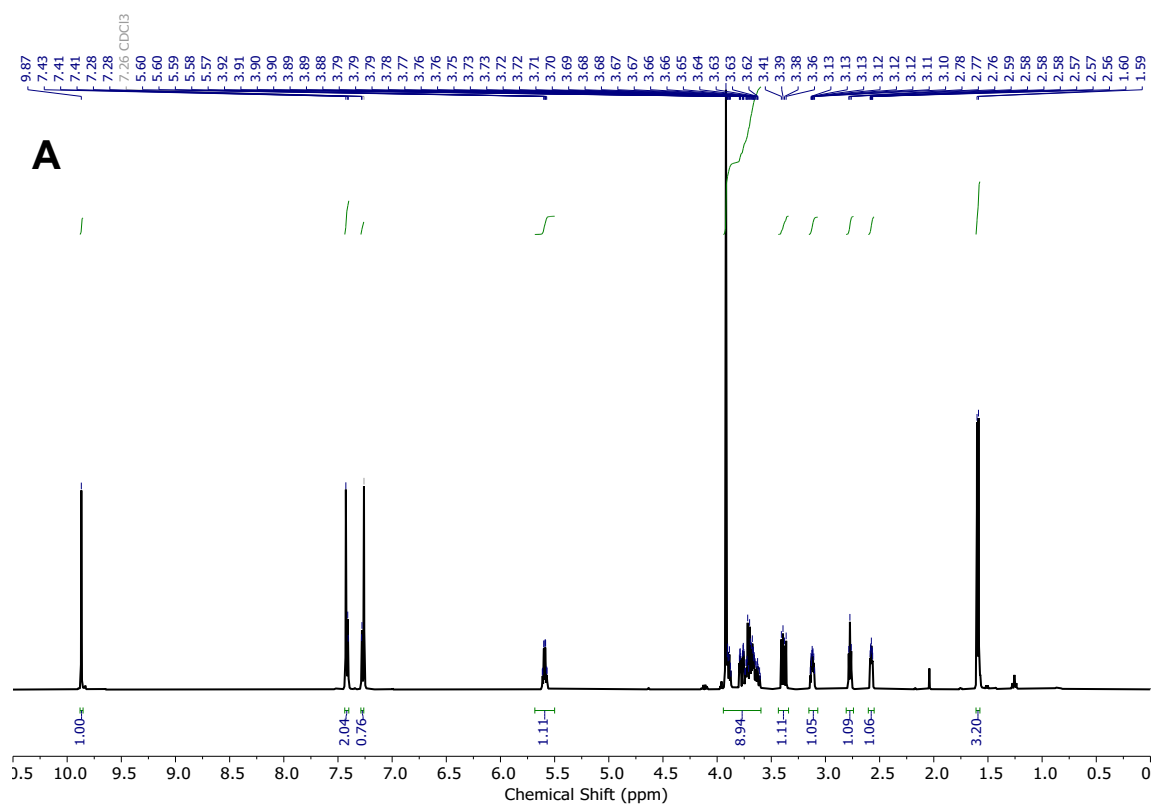
Figure S2. ^{1}H NMR (A) and ^{13}C NMR (B) spectra of **C2** recorded in CDCl$_3$.

Synthesis of model compound

805 mg of **C2** was mixed with 400 mg of furfuryl amine at room temperature. The mixture was then heated to 100°C. For a duration of 2 hours, ^{1}H NMR measurements were taken at 30-minute intervals.
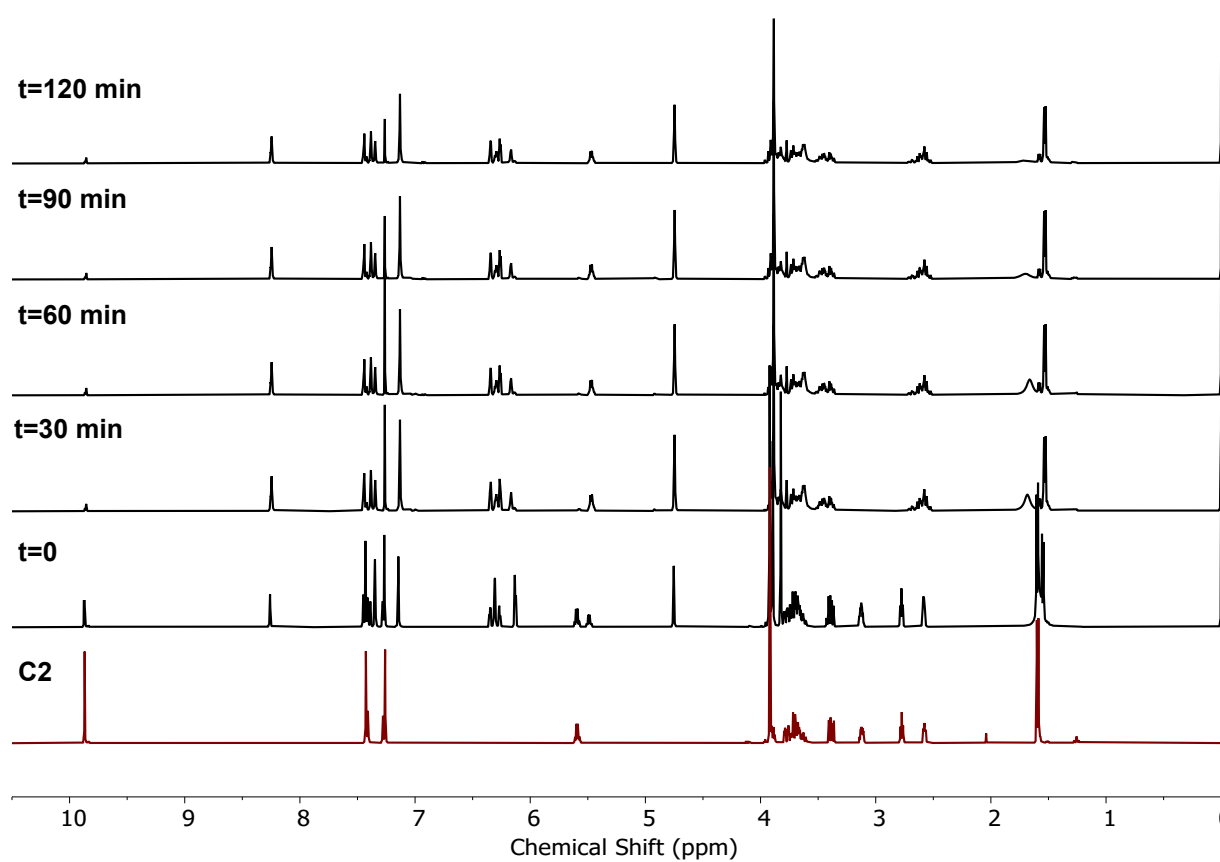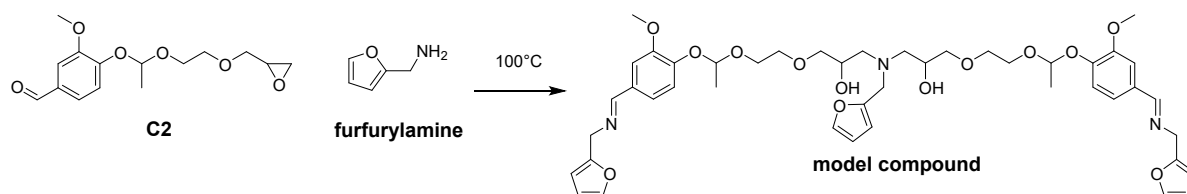
Scheme S2. Model reaction.

Figure S3. Time-dependent ^{1}H NMR spectra of the reaction between **C2** monomer and furfuryl amine recorded in CDCl$_3$.

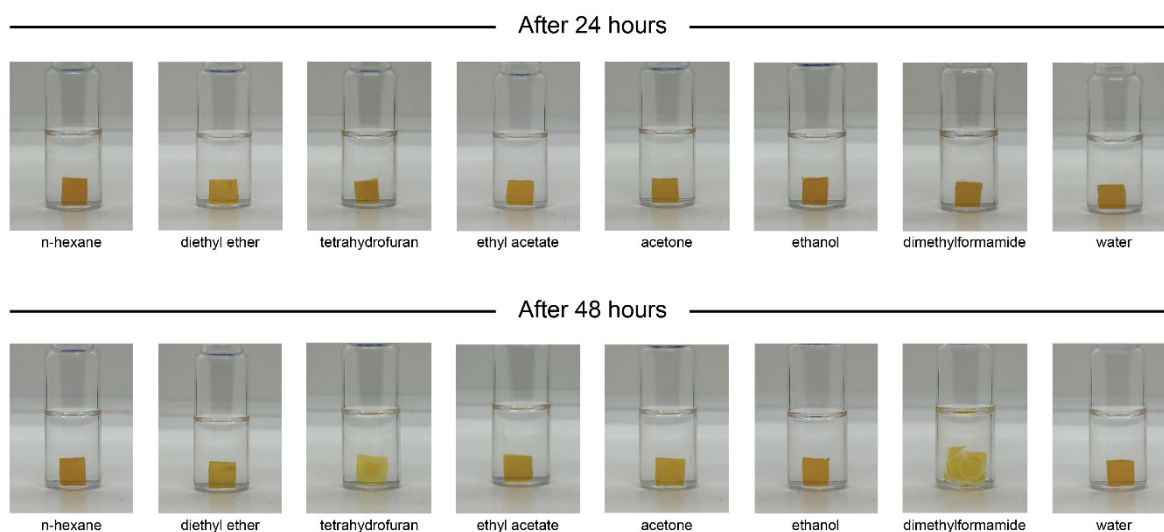## 2) Solvent and Water Resistivity of C2PDA and C2FDA Networks

After 24 hours

n-hexane	diethyl ether	tetrahydrofuran	ethyl acetate	acetone	ethanol	dimethylformamide	water

After 48 hours

|							
n-hexane	diethyl ether	tetrahydrofuran	ethyl acetate	acetone	ethanol	dimethylformamide	water

Figure S4. Solvent-immersion tests of **C2PDA**.

Table S1. Swelling ratio and gel fractions of the **C2PDA** network, upon immersion into various organic solvents and water for 2 days at room temperature.

C2PDA	Swelling Ratio (%)	Gel Content (%)
n-hexane	0	100
Diethyl ether	4.7	100
Tetrahydrofuran	159.8	85.8
Ethyl acetate	40.1	97.9
Acetone	51.6	100
Ethanol	44.3	99.7
Dimethylformamide	254.2	84.1
Water	15.5	100
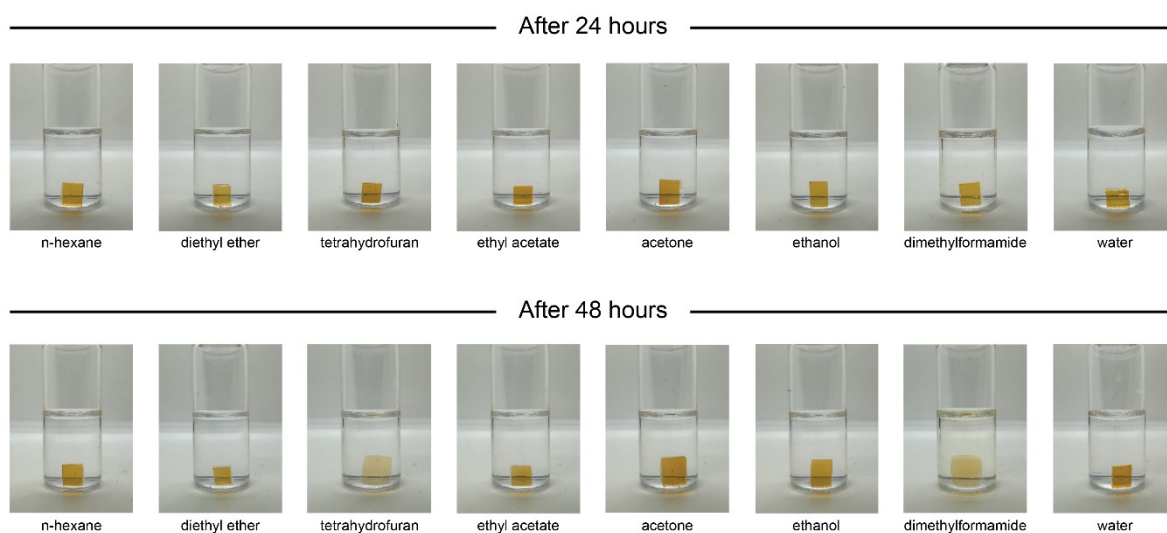
Figure S5. Solvent-immersion tests of **C2FDA**.

Table S2. Swelling ratio and gel fractions of the **C2FDA** network, upon immersion into various organic solvents and water for 2 days at room temperature.

C2FDA	Swelling Ratio (%)	Gel Content (%)
n-hexane	0	99.3
Diethyl ether	0	99.3
Tetrahydrofuran	85.3	100
Ethyl acetate	11.8	100
Acetone	23.1	100
Ethanol	5.6	100
Dimethylformamide	151.1	97.2
Water	3.1	98.9
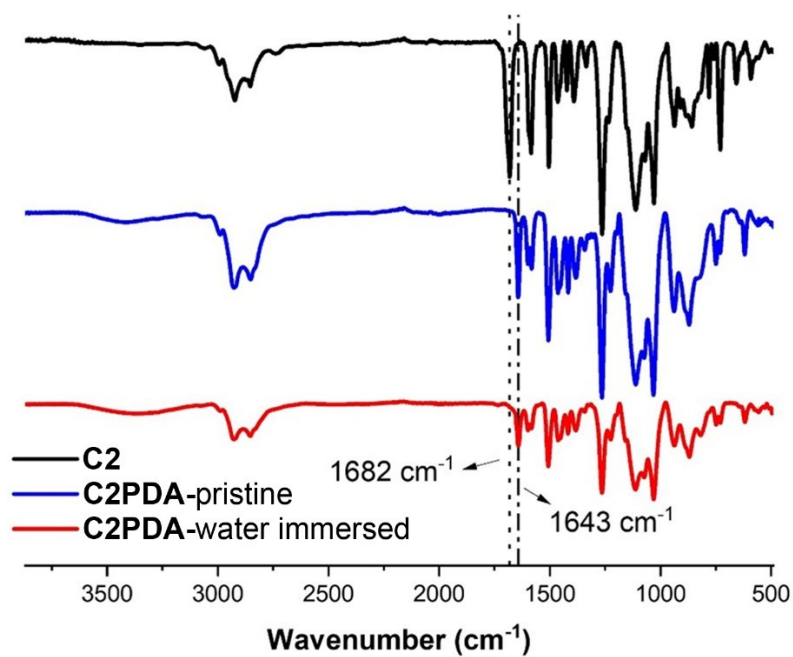
Figure S6. FTIR comparison of **C2** monomer, pristine **C2PDA** network and water immersed **C2PDA** network.
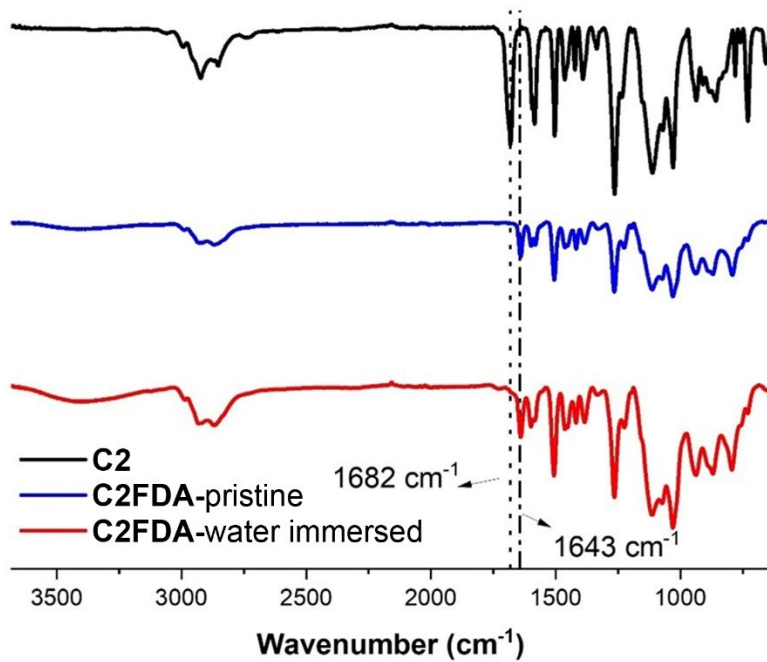
Figure S7. FTIR comparison of **C2** monomer, pristine **C2FDA** network and water immersed **C2FDA** network.

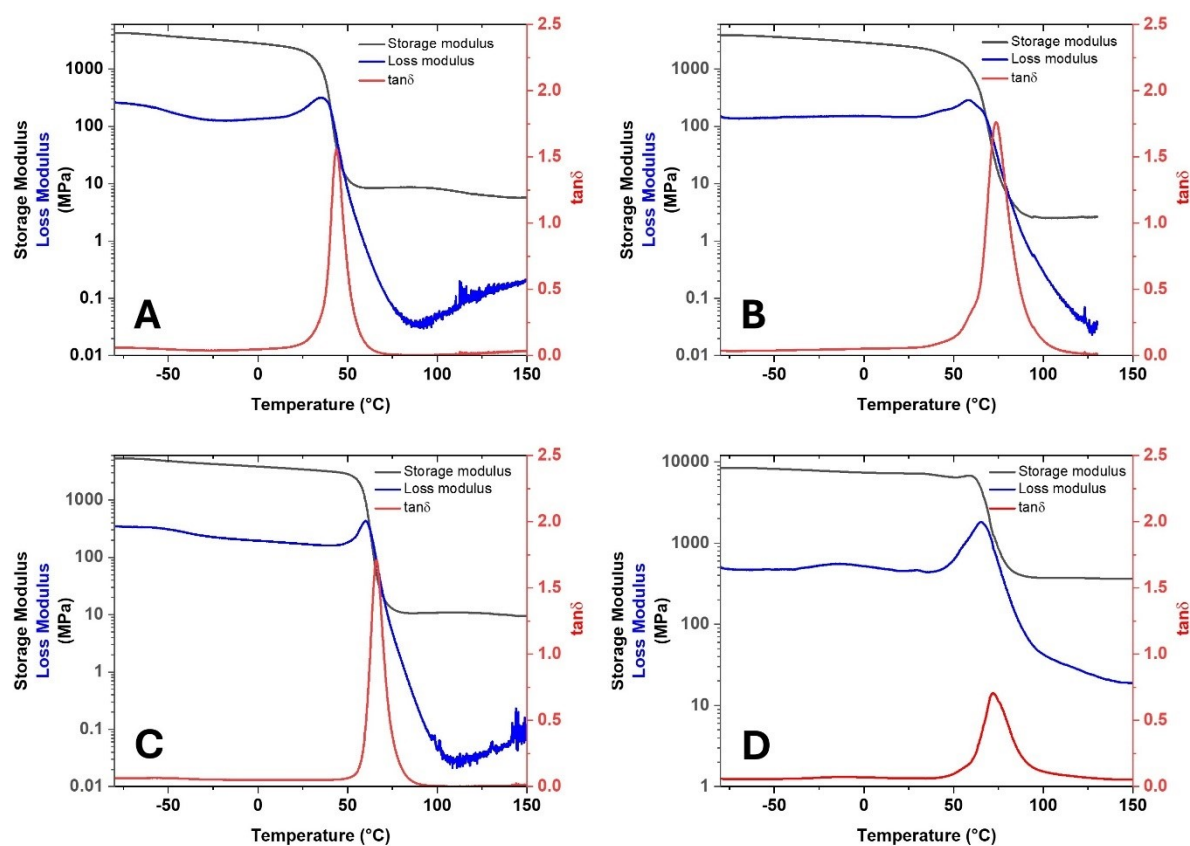## 3) Dynamic Mechanical Analysis of the Original Networks

Figure S8. Dynamic mechanical analysis of **C2PDA** (A), **C2MDA** (B), **C2FDA** (C) and **C2FDA-CFC** (D).

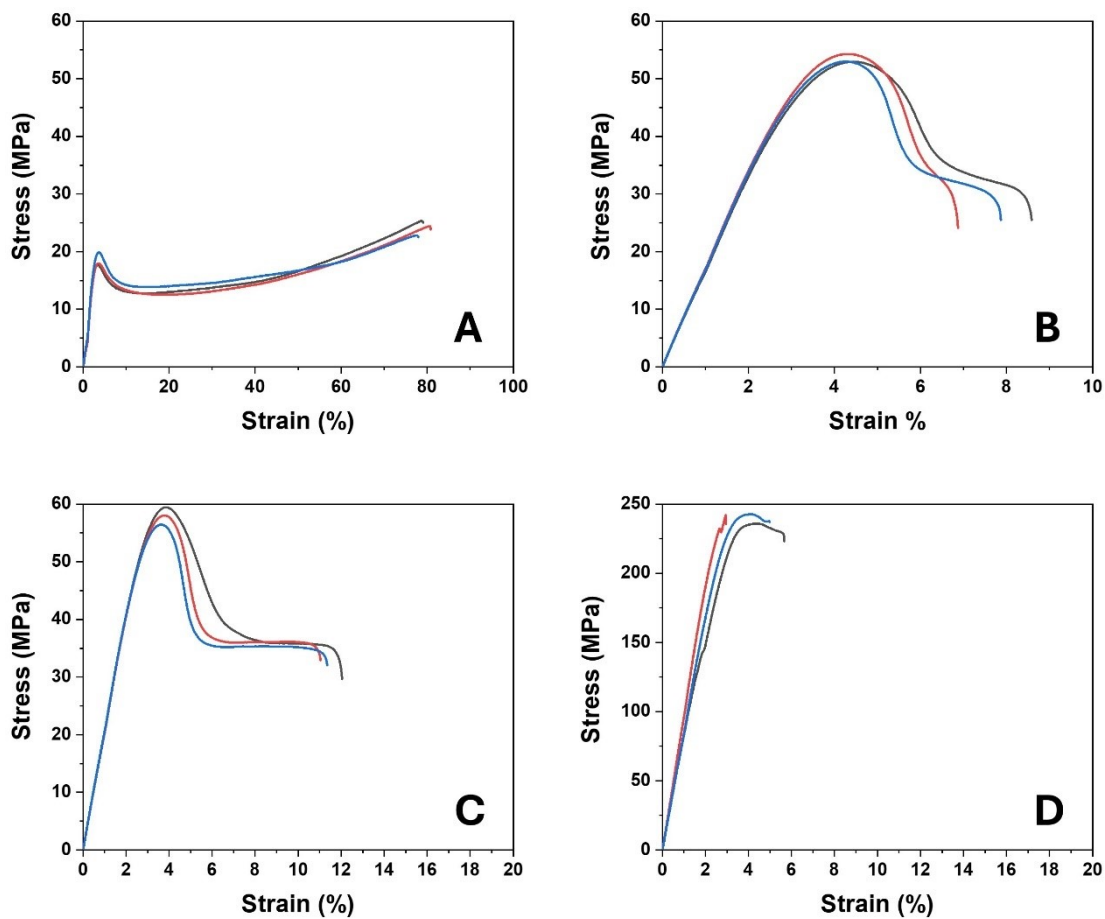## 4) Mechanical Characterization of the Original Networks and Composite

Figure S9. Mechanical characterization of **C2PDA** (A), **C2MDA** (B), **C2FDA** (C), and **C2FDA-CFC** (D).

5) Interface Characterization of the Composite through Scanning Electron Microscopy
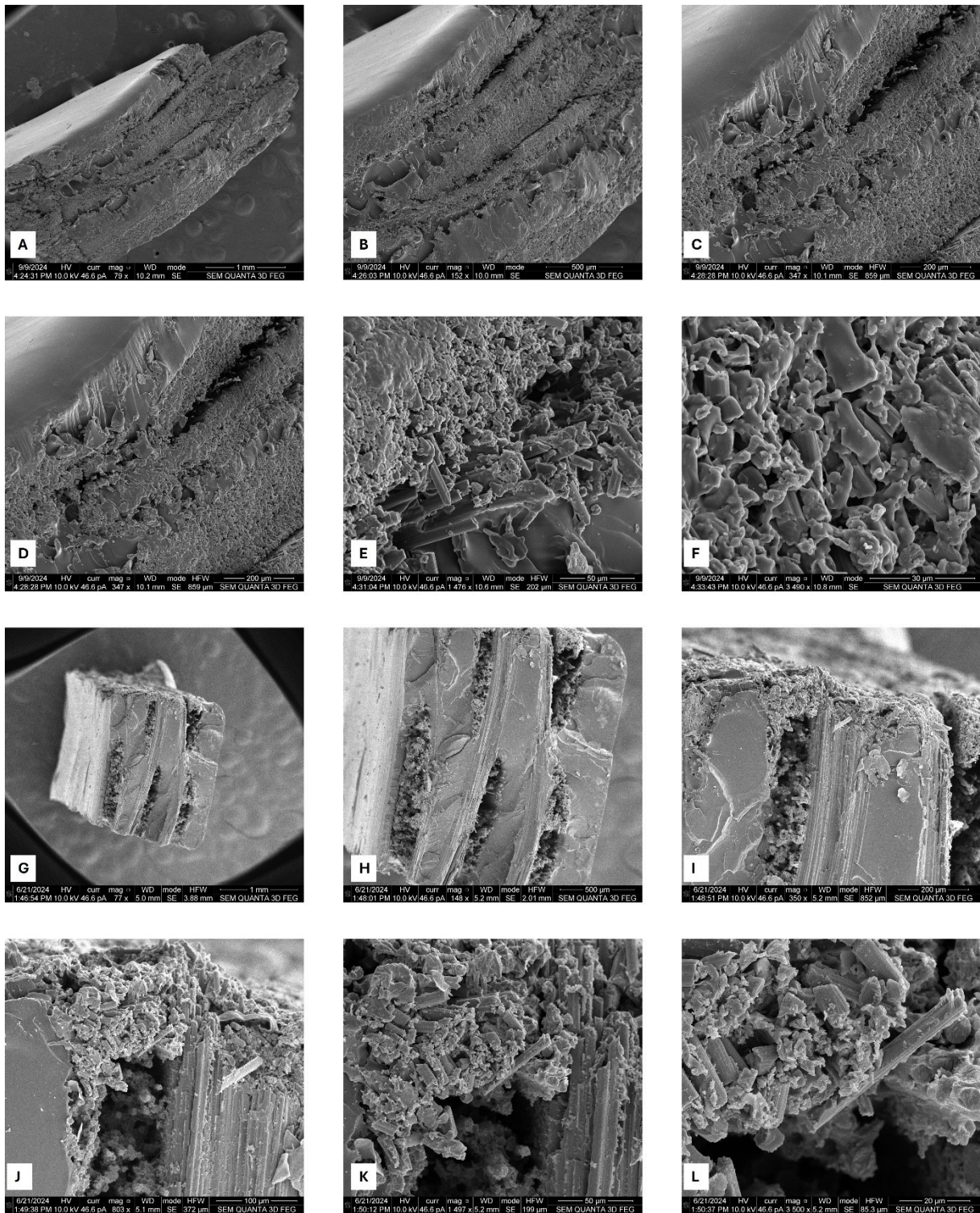
Figure S10. Scanning electron micrographs of the original (A-F) and fractured (G-L) **C2FDA-CFC** at 80X (A, G), 150X (B, H), 350X (C, I), 800X (D, J), 1500X (E, K) and 3500X (F, L) magnifications.

6) Structural Characterization of the Acid Depolymerization Products
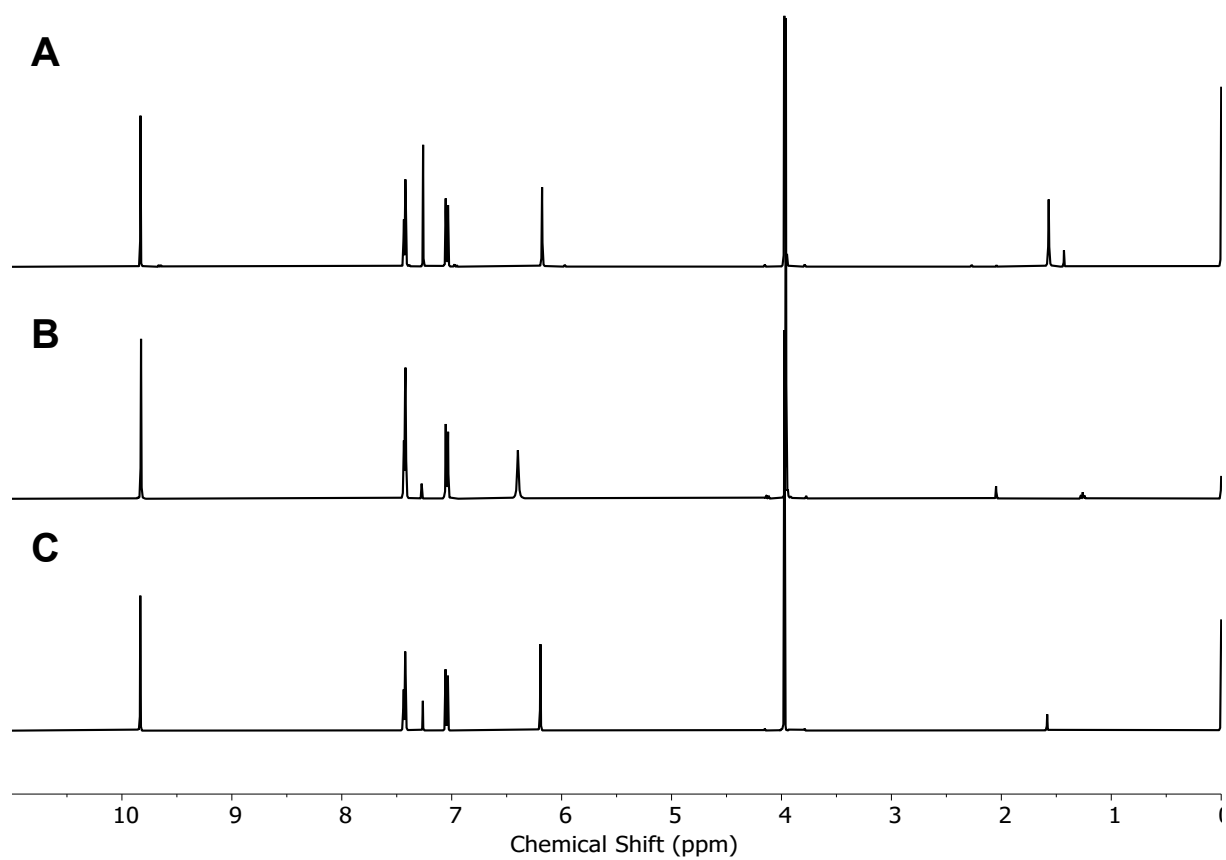
Figure S11. ^{1}H NMR spectra of recovered vanillin as depolymerization product: from **C2FDA** (A) and **C2PDA** (B), as compared with original vanillin (C), recorded in CDCl$_3$.
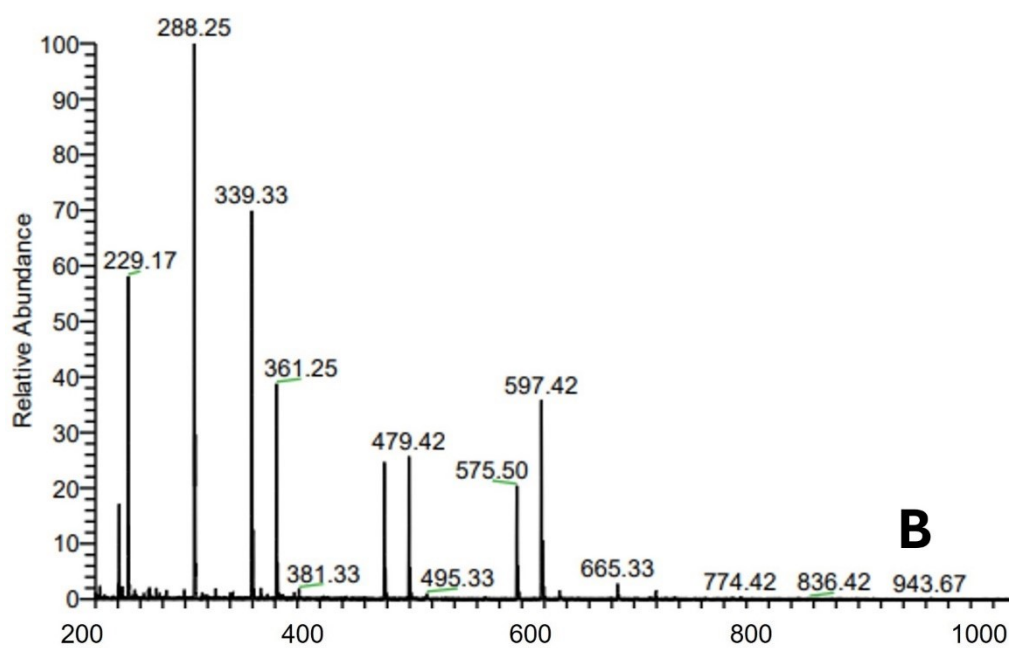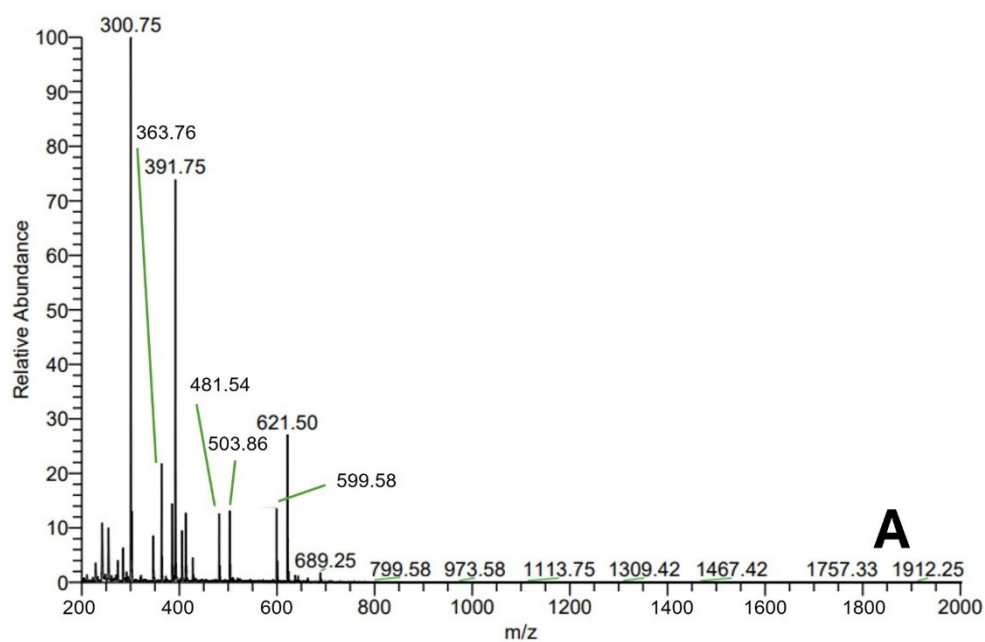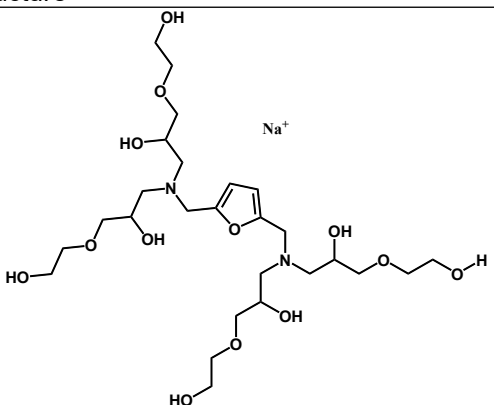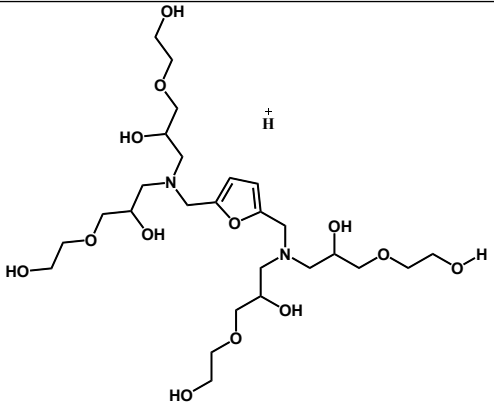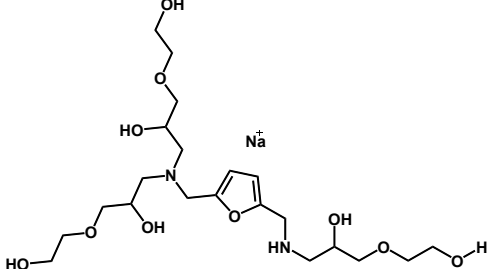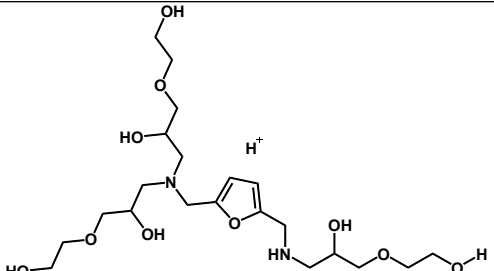
Figure S12. ESI-MS spectra of the polyol mixtures obtained from the acidic depolymerization of **C2FDA** (A) and **C2PDA** (B).

Table S3. Structure elucidation of the corresponding m/z values for the polyol mixtures of **C2FDA** obtained from the acidic depolymerization.

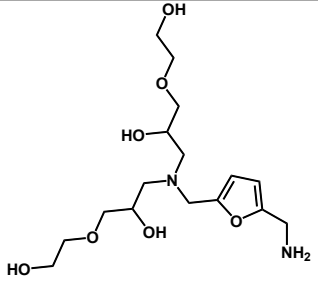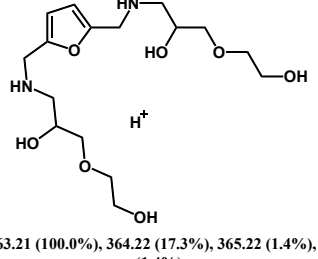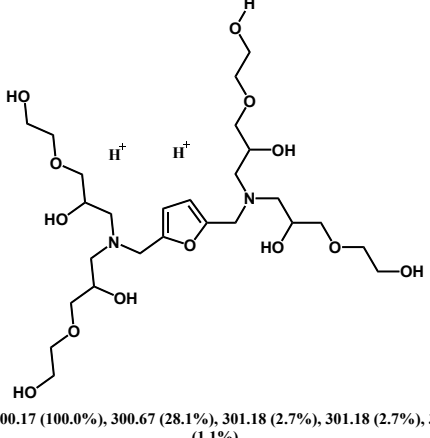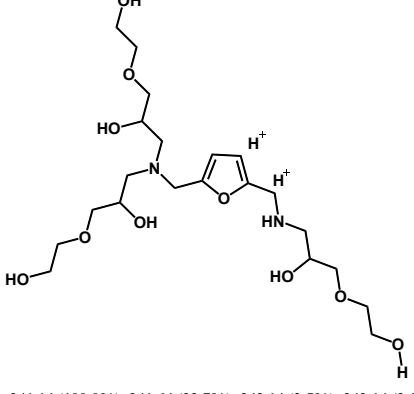| Structure	m/z
 m/z: 621.32 (100.0%), 622.32 (28.1%), 623.33 (3.8%), 623.32 (2.7%)	621.50
 m/z: 599.34 (100.0%), 600.34 (28.1%), 601.35 (3.8%), 601.34 (2.7%)	599.58
 m/z: 503.26 (100.0%), 504.26 (22.7%), 505.26 (2.5%), 505.26 (2.1%)	503.86
 m/z: 481.28 (100.0%), 482.28 (22.7%), 483.28 (2.5%), 483.28 (2.1%)	481.54
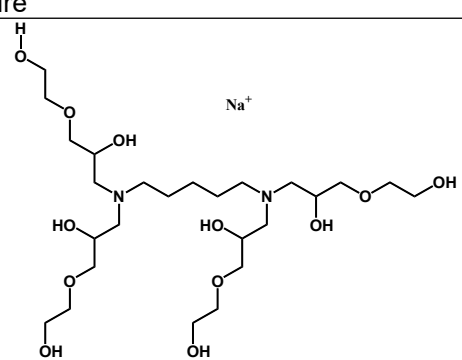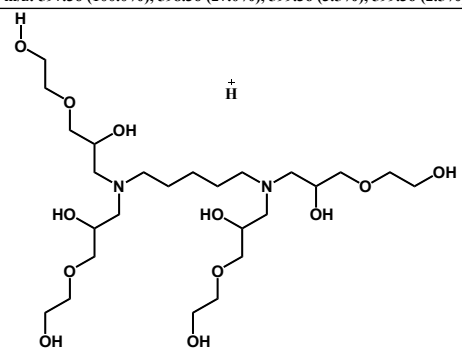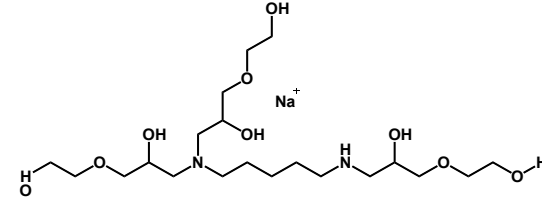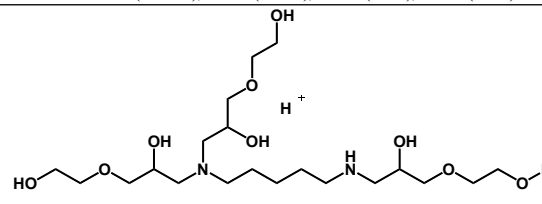
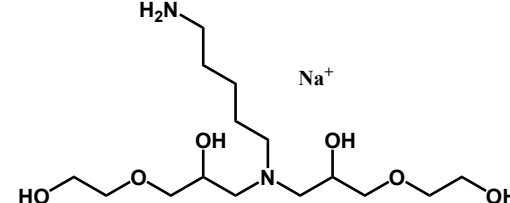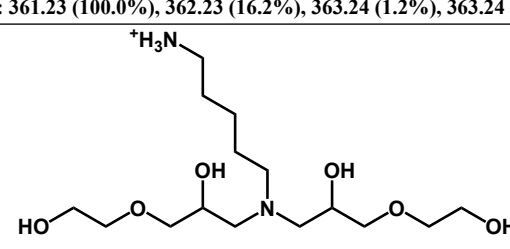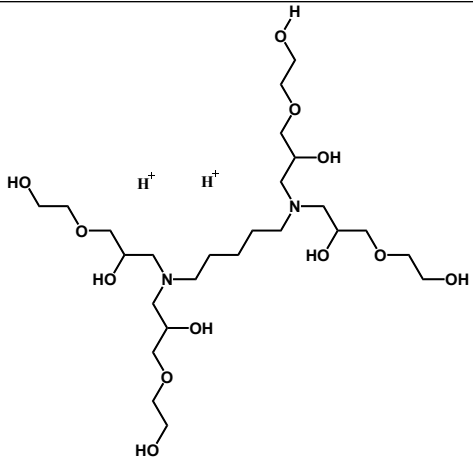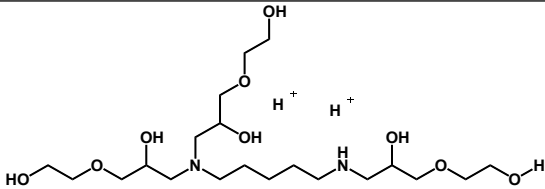|	385.41
m/z: 402.24 (100.0%), 403.24 (20.5%), 404.24 (2.0%), 404.24 (1.4%)	
m/z: 363.21 (100.0%), 364.22 (17.3%), 365.22 (1.4%), 365.22 (1.4%)	363.76
m/z: 300.17 (100.0%), 300.67 (28.1%), 301.18 (2.7%), 301.18 (2.7%), 301.18 (1.1%)	300.75
m/z: 241.14 (100.0%), 241.64 (22.7%), 242.14 (2.5%), 242.14 (2.1%)	240.94

Table S4. Structure elucidation of the corresponding m/z values for the polyol mixtures of **C2PDA** obtained from the acidic depolymerization.

Structure	m/z
m/z: 597.36 (100.0%), 598.36 (27.0%), 599.36 (3.5%), 599.36 (2.5%)	597.42
m/z: 575.37 (100.0%), 576.38 (27.0%), 577.38 (3.5%), 577.38 (1.6%)	575.50
m/z: 479.29 (100.0%), 480.30 (21.6%), 481.30 (2.2%), 481.30 (1.8%)	479.42
m/z: 457.31 (100.0%), 458.32 (21.6%), 459.32 (2.2%), 459.32 (1.8%)	457.31
m/z: 361.23 (100.0%), 362.23 (16.2%), 363.24 (1.2%), 363.24 (1.2%)	361.25
m/z: 339.25 (100.0%), 340.25 (16.2%), 341.25 (1.2%), 341.26 (1.2%)	339.33

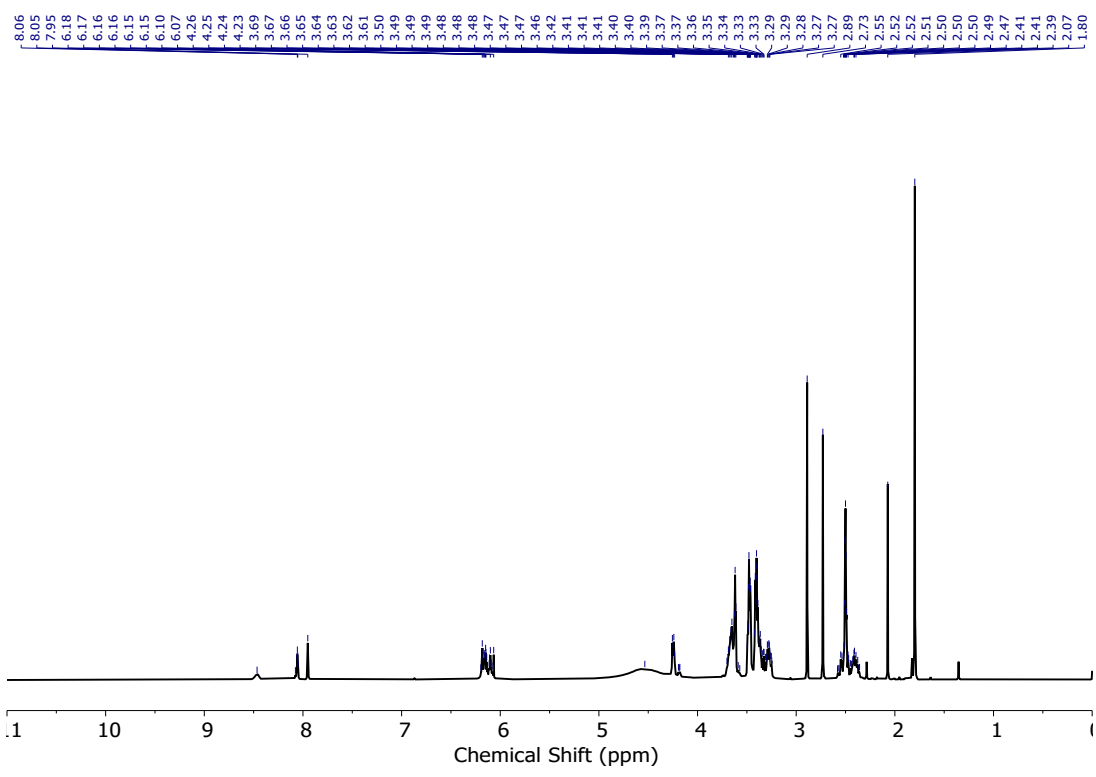|	
m/z: 288.19 (100.0%), 288.69 (27.0%), 289.19 (2.7%), 289.19 (2.5%)	288.25
m/z: 229.16 (100.0%), 229.66 (21.6%), 230.16 (2.2%), 230.16 (1.8%)	229.17

Figure S13. ^{1}H NMR spectra of recovered polyol mixture of **C2FDA** as depolymerization product, recorded in DMSO-d$_6$.
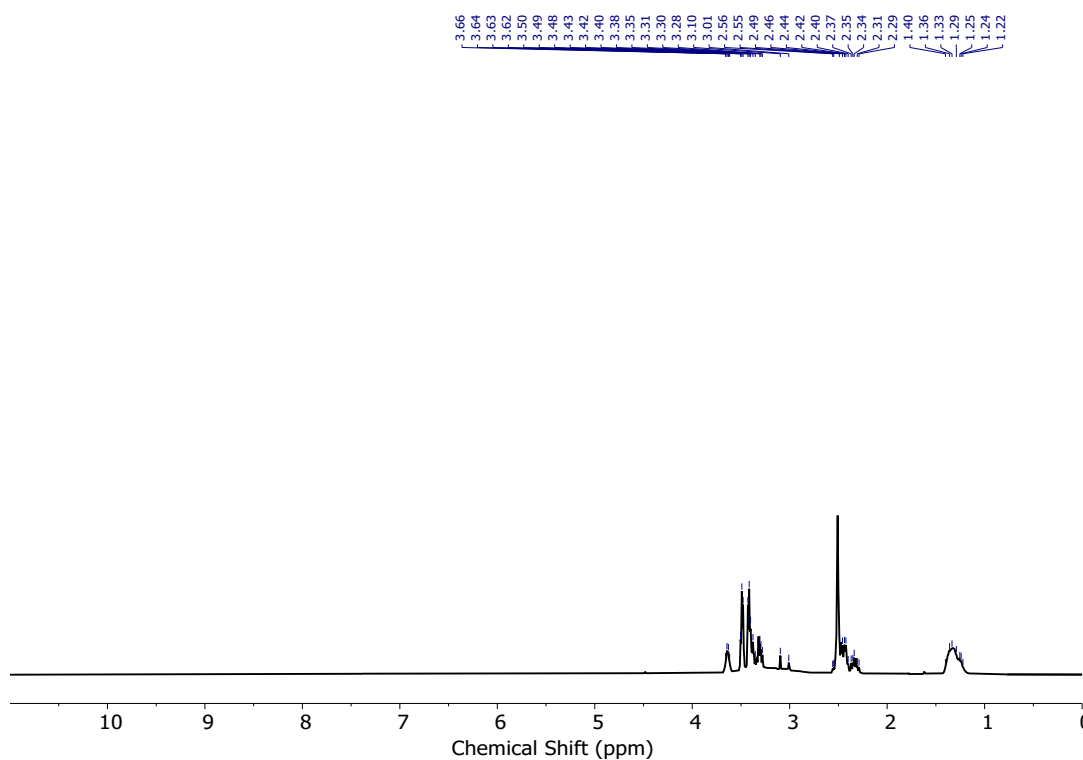
Figure S14. ^{1}H NMR spectra of recovered polyol mixture of **C2PDA** as depolymerization product, recorded in DMSO-d$_6$.

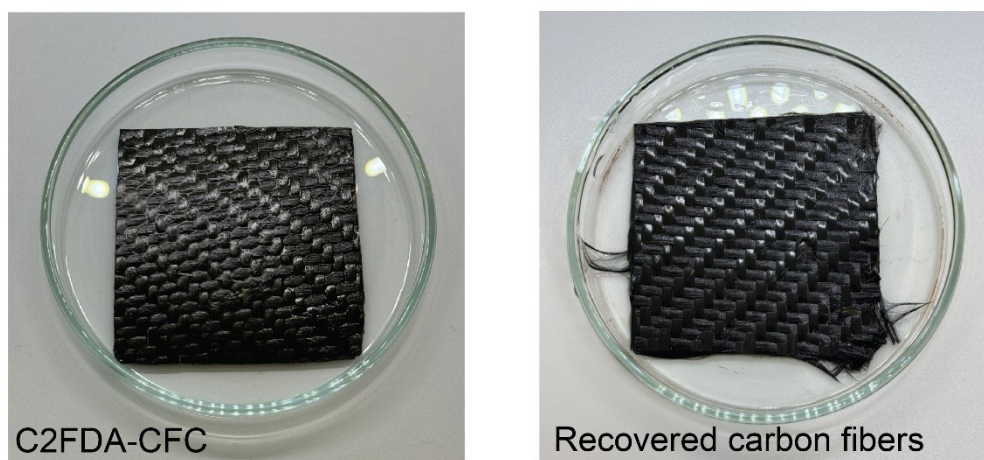## 7) Recycling of Carbon Fibers from the C2FDA-CFC

Figure S15. Images of **C2FDA-CFC** and recovered carbon fiber cloth from the acidic depolymerization pathway.
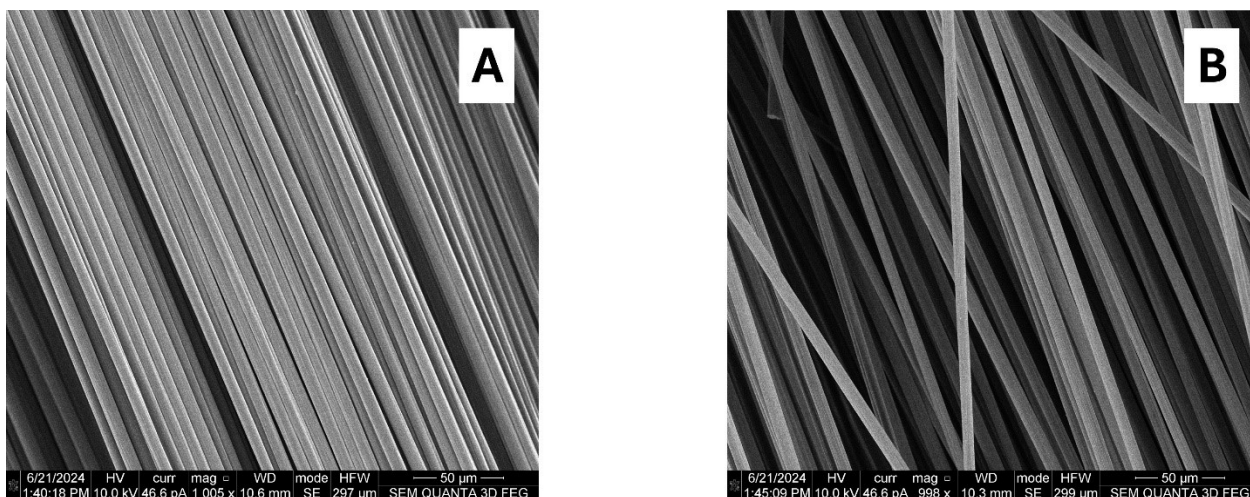
Figure S16. Scanning electron micrographs of virgin (A) and recovered carbon fibers (B) from the acidic depolymerization of **C2FDA-CFC** (scale bar is 50 μm).

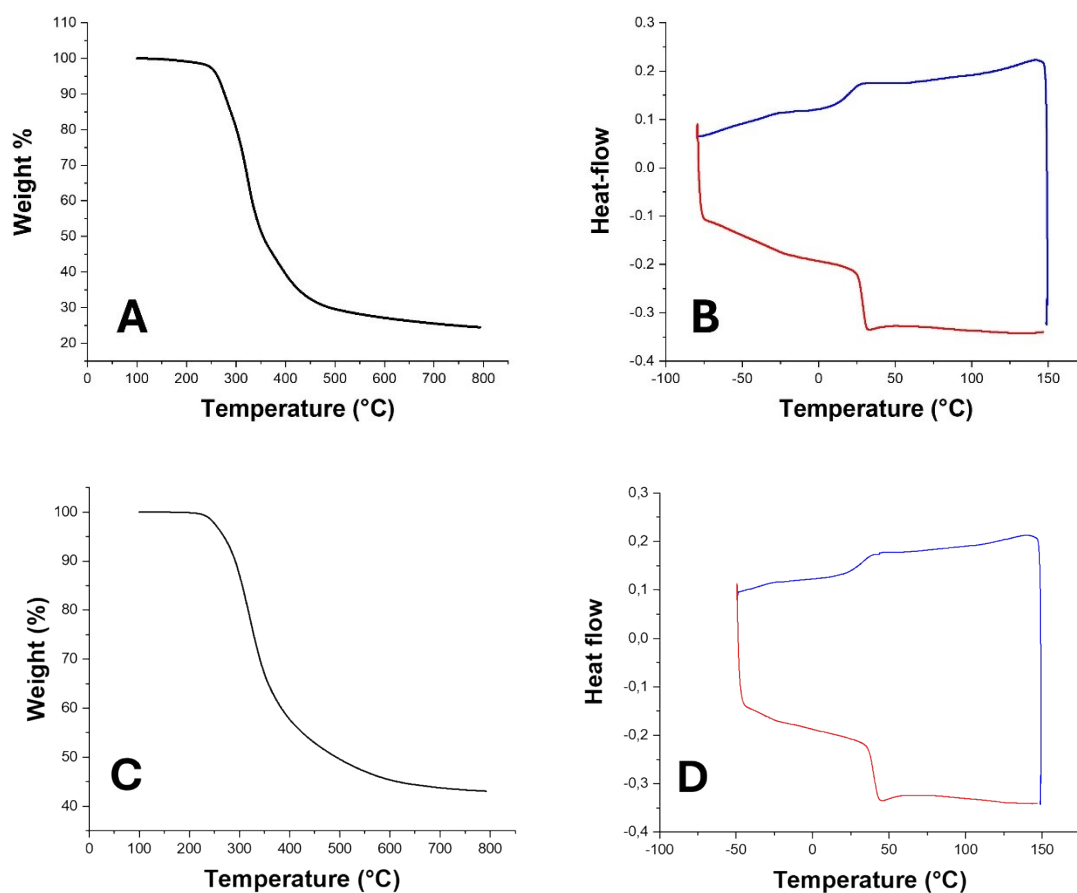## 8) Thermal Characterization of Recycled Networks

Figure S17. TGA (A, C) and DSC (B, D) thermographs of recycled networks: **rC2PDA** (A, B) and **rC2FDA** (C, D).

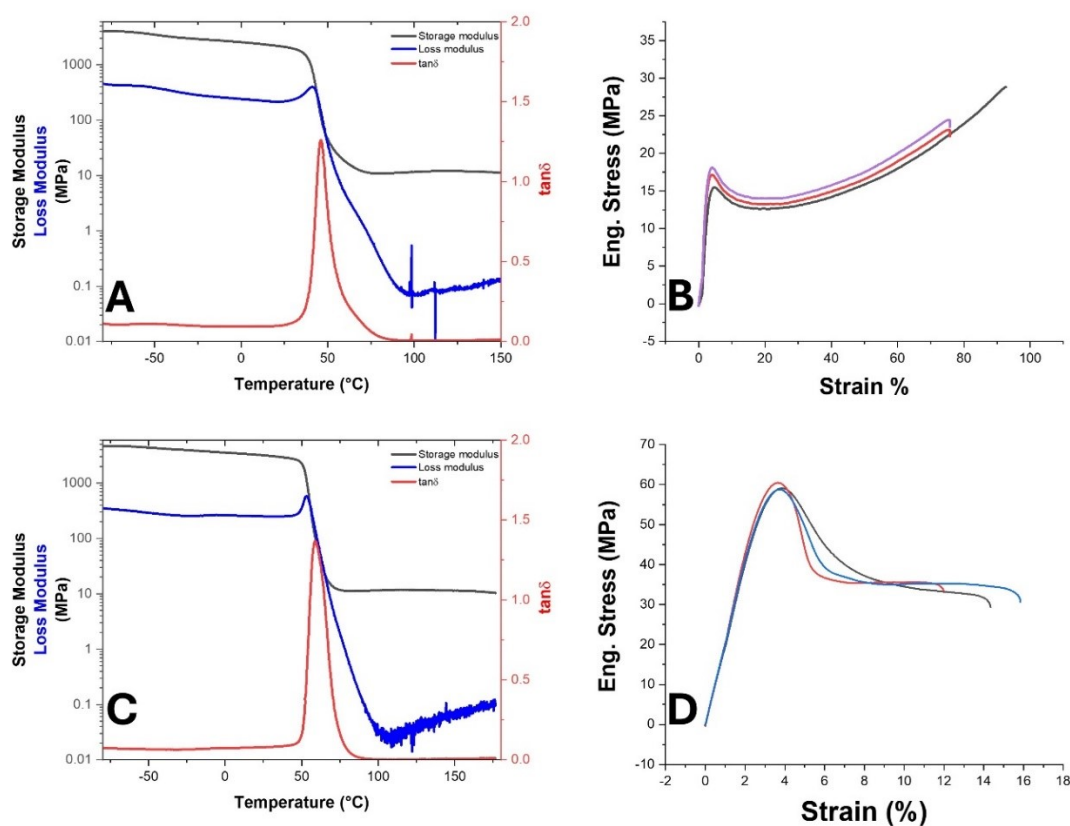# 9) Thermomechanical and Mechanical Characterization of Recycled Networks

Figure S18. DMA (A, C) and stress-strain (B, D) plots of recycled networks: **rC2PDA** (A, B) and **rC2FDA** (C, D).

10) Thermomechanical and Mechanical Characterization of Reprogrammed C2PDAFDA Network
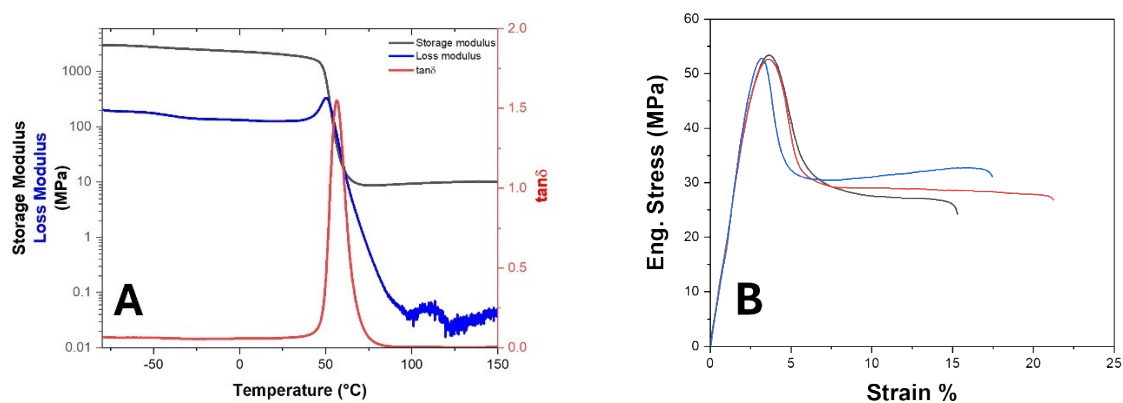

Figure S19. DMA (A) and stress-strain (B) plots of reprogrammed **C2PDAFDA** networks.

11) Extended Data

Table S5. Extended data for thermomechanical characteristics of original, recycled and reprogrammed networks.

Networks	T_g^a (°C)	T_g^b (°C)	T_g^c (°C)	E_{30}' (MPa)	E_{100}' (MPa)
C2PDA	34.7	35.0	43.9	1684.3	8.2
C2MDA	62.6	58.2	73.6	2369.5	2.5
C2FDA	57.8	60.0	66.2	3355.1	10.8
C2FDA-CFC	63.2	65.2	71.9	7206.0	373.3
rC2PDA	38.9	41.3	46.1	1958.0	11.6
rC2FDA	50.3	53.2	59.0	3087.3	11.6
C2PDAFDA	47.8	50.0	56.6	1970.3	9.4

*T_g^a: glass-transition temperature identified by the intercept between two tangential lines—one from the glassy plateau of the storage modulus and the other from the sharp decline in the transition region. T_g^b: glass-transition temperature identified by the maxima of the loss modulus curves, T_g^c: glass-transition temperature identified by the maxima of the tanδ curves.