Supplementary information

Poly(carbonate acetal) Vitrimers with Enhanced Thermal Properties and Closed-Loop Thermal Recyclability Derived from Waste Polycarbonate-Derived Polyaldehyde and Pentaerythritol/Erythritol/$_D$-Sorbitol

Yi-Chun Chen[†‡], Kamani Sudhir K. Reddy[†], and Ru-Jong Jeng [‡*], Ching-Hsuan Lin[†*]

[†]Department of Chemical Engineering, National Chung Hsing University, Taichung 40227, Taiwan.

[‡] Institute of Polymer Science and Engineering, National Taiwan University, Taipei 106319, Taiwan.

Corresponding Email: rujong@ntu.edu.tw; linch@nchu.edu.tw

Synthesis of WPC-CHO

Dry WPC 10 g (39.32 mmol of repeating unit) and VNEP 16.35 g (78.65 mmol) were taken into mortar and ground vigorously to get a homogeneous mixing. The fine powder of reactants were then carefully poured into a schlenk flask, then a catalytic amount of DMAP or TBAB (1 wt% to VNEP) was then added into the reactor, degassed the vessel using a vacuum for 10 min, purged with N_2 gas, and heated to 150 ^oC for 3 h. Upon cooling to room temperature, the rock-solid substance was scratched out (otherwise dissolved into a minimum amount of DMAc) and washed with 1000 mL MeOH/H_2O (1/1, v/v) twice. The precipitate was then washed with 200 mL of hot ethanol (70 ^oC) twice and then dried under reduced pressure at 80 ^oC. WPC-CHO (brown color, yield 97% for DMAP-catalyzed; light brown color, yield 95% for TBAB-catalyzed) was obtained. 1H-NMR (DMSO-d6, δ ppm, 400 MHz): 9.83 (H1, 2H), 9.18 (-OH, 2H), 7.51 (H3, 2H), 7.39 (H7, 2H), 7.20 (H4, 2H), 7.03 (H14, 4H), 6.83 (H15, 4H), 5.35 (H10, 2H), 4.4 – 4.02 (H9, and H11, 8H), 3.88 – 3.72 (H8, 6H), and 1.54 (H18, 6H). 13C NMR (DMSO-d6, δ ppm, 150 MHz): 191.3, 156.2, 155.7, 153.6, 152.7, 149.3, 143.1. 142.6, 130.21, 129.7, 127.7, 126.0, 125.7, 114.6, 113.9, 112.7, 112.3, 110.2, 109.7, 74.4, 70.1, 69.1, 67.3, 66.9, 65.8, 39.9, 39.1, and 30.7. FTIR (KBr-pellet, cm-1): 3570 (phenolic –OH), 3060 - 2763 (aromatic CH), 1753 (aliphatic carbonate), 1681 (aldehyde carbonyl), 1256 (C-O, of carbonate), and 1129, 1025 (aromatic-aliphatic C-O). Number-average molecular weight 7251 g/mol, weigh-average molecular weight 13842 g/mol.

Note: VNEP is prepared as per the literaute.[1]

Table S1. The thermal and mechanical properties of original PCAs with x=1-4.

Sample code.	$T_{d5\%}$ (°C)[a]	CY (%)[b]	T_g(°C) DMA	E' at T_g +40 °C (MPa)	Crosslinking density (mmol* cm^{-3})	σ (MPa)[f]	ε (%)[g]
PCA-P1	358	24.8	176	23.94	1.96	36.2	2.5
PCA-P2	354	25.4	178	29.52	2.41	34.9	2.7
PCA-P3	351	24.5	178	29.53	2.41	37.8	2.7
PCA-P4	347	26.1	178	29.64	2.42	31.3	2.7
PCA-E1	337	20.1	142	10.32	0.91	33.8	2.3
PCA-E2	342	18.8	142	10.0	0.88	33.5	2.6
PCA-E3	338	19.7	142	8.86	0.78	37.7	2.3
PCA-E4	337	19.7	142	9.18	0.81	32.8	2.8
PCA-S1	369	24.6	178	39.21	3.20	46.8	4.1
PCA-S2	373	23.4	178	45.92	3.75	46.4	4.3
PCA-S3	352	23.9	178	49.26	4.02	45.8	4.2
PCA-S4	350	25.0	178	44.23	3.61	45.4	4.5

[a] TGA was measured at a heating rate of 20 °C/min. [b] Residual weight % at 800 °C. [c] TMA was measured at a heating rate of 5 °C/min.[d] DMA was measured at a heating rate of 5 °C/min. [f] Tensile strength. [g] Elongation at the break.

Table S2. The thermal and mechanical properties of the first reprocessed PCAs with x=1-4.

Sample code	$T_{d5\%}$ (°C)[a]	CY (%)[b]	T_g(°C) DMA[d]	E' at T_g +40 °C (MPa)	Crosslinking density (mmol* cm^{-3})	σ (MPa) [f]	ε (%)[g]
PCA-P1-R1	347	23.9	174	23.9	1.97	33.7	3.2
PCA-P2-R1	354	25.9	175	21.3	1.75	35.8	3.1
PCA-P3-R1	358	26.0	176	20.9	1.71	35.4	3.5
PCA-P4-R1	356	26.7	176	30.9	2.53	34.0	3.6
PCA-E1-R1	339	20.7	135	5.6	0.50	24.2	2.2
PCA-E2-R1	345	22.5	141	6.6	0.58	23.6	2.1
PCA-E3-R1	355	20.3	142	5.2	0.46	23.6	2.3
PCA-E4-R1	350	20.8	142	4.2	0.37	27.0	2.4
PCA-S1-R1	371	23.9	168	30.12	2.51	44.8	3.7
PCA-S2-R1	363	24.5	169	33.01	2.75	46.1	3.6
PCA-S3-R1	362	25.8	168	30.62	2.55	40.4	3.9
PCA-S4-R1	357	26.1	170	35.17	2.92	39.8	3.9

a TGA was measured at a heating rate of 20 °C/min. *b* Residual weight % at 800 °C. *d* DMA was measured at a heating rate of 5 °C/min. *f* Tensile strength. *g* Elongation at the break.

Table S3. The thermal and mechanical properties for the orignal , the first reprocessed , and the second reprocessed PCAs with x=2.

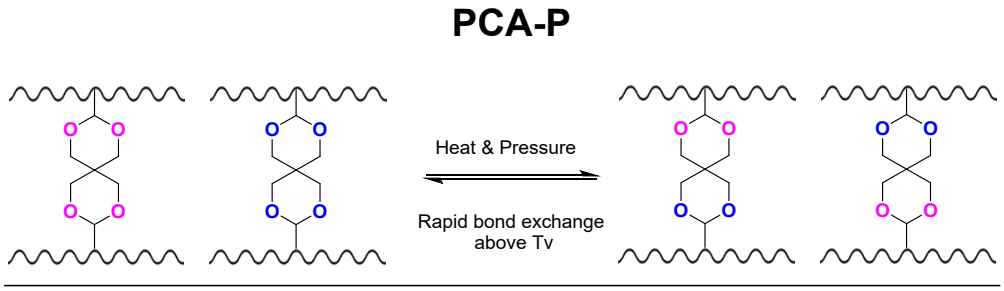
Sample code.	$T_{d5\%}$ (°C)[a]	CY (%)[b]	T_g (°C) DMA	E' at T_g + 40 °C (MPa)	Crosslinking density (mmol* cm^{-3})	σ (MPa)[f]	ε (%)[g]
PCA-P2	354	25.4	178	29.52	2.41	34.9	2.7
PCA-P2-R1	354	25.9	175	21.3	1.75	35.8	3.1
PCA-P2-R2	348	25.5	173	19.7	1.63	32.6	2.9
PCA-E2	342	18.8	142	10.0	0.88	33.5	2.6
PCA-E2-R1	345	22.5	141	6.6	0.58	23.6	2.1
PCA-E2-R2	333	19.9	142	9.8	0.86	22.1	2.1
PCA-S2	373	23.4	178	45.92	3.75	46.4	4.3
PCA-S2-R1	363	24.5	169	33.01	2.75	46.1	3.6
PCA-S2-R2	370	25.6	172	35.82	2.96	46.0	3.3

a TGA was measured at a heating rate of 20 °C/min. *b* Residual weight % at 800 °C. *d* DMA was measured at a heating rate of 5 °C/min. *f* Tensile strength. *g* Elongation at the break.

Table S4. Recovery yields of R-WPC-CHO-1 to 4, and R-PT-1 to 4 after acid hydrolysis of PCA-P1 to 4.

PCA used	Recovered product	Yield (%)
PCA-P1	R-WPC-CHO-1	91
	R-PT-1	62
PCA-P2	R-WPC-CHO-2	93
	R-PT-2	60
PCA-P3	R-WPC-CHO-3	94
	R-PT-3	63
PCA-P4	R-WPC-CHO-4	92
	R-PT-4	62

Scheme S1. Acetal metathesis of PCA-Px.



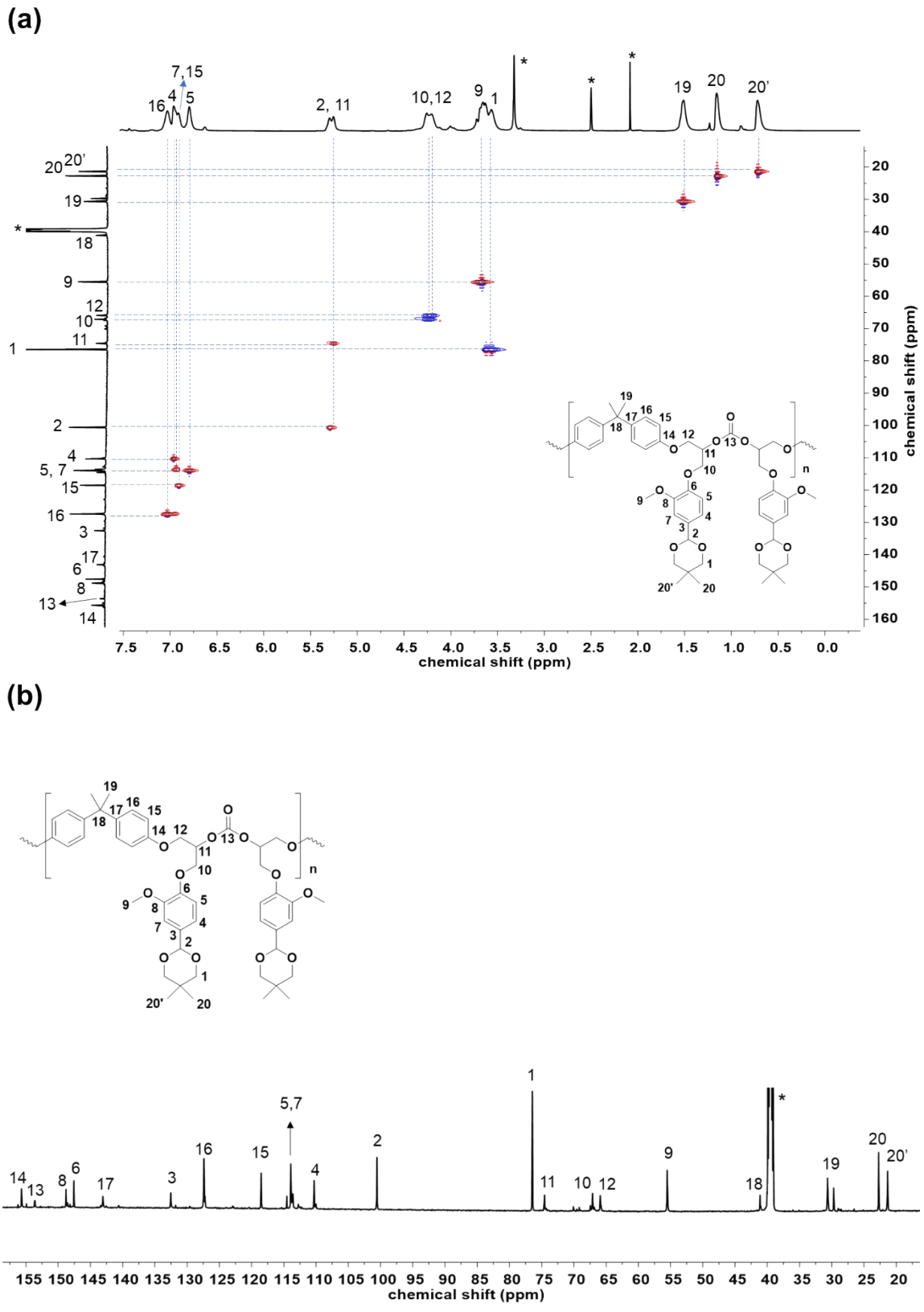


Figure S1. (a) HSQC, (b) ^{13}C NMR spectrum of WPC-CHO/NG.

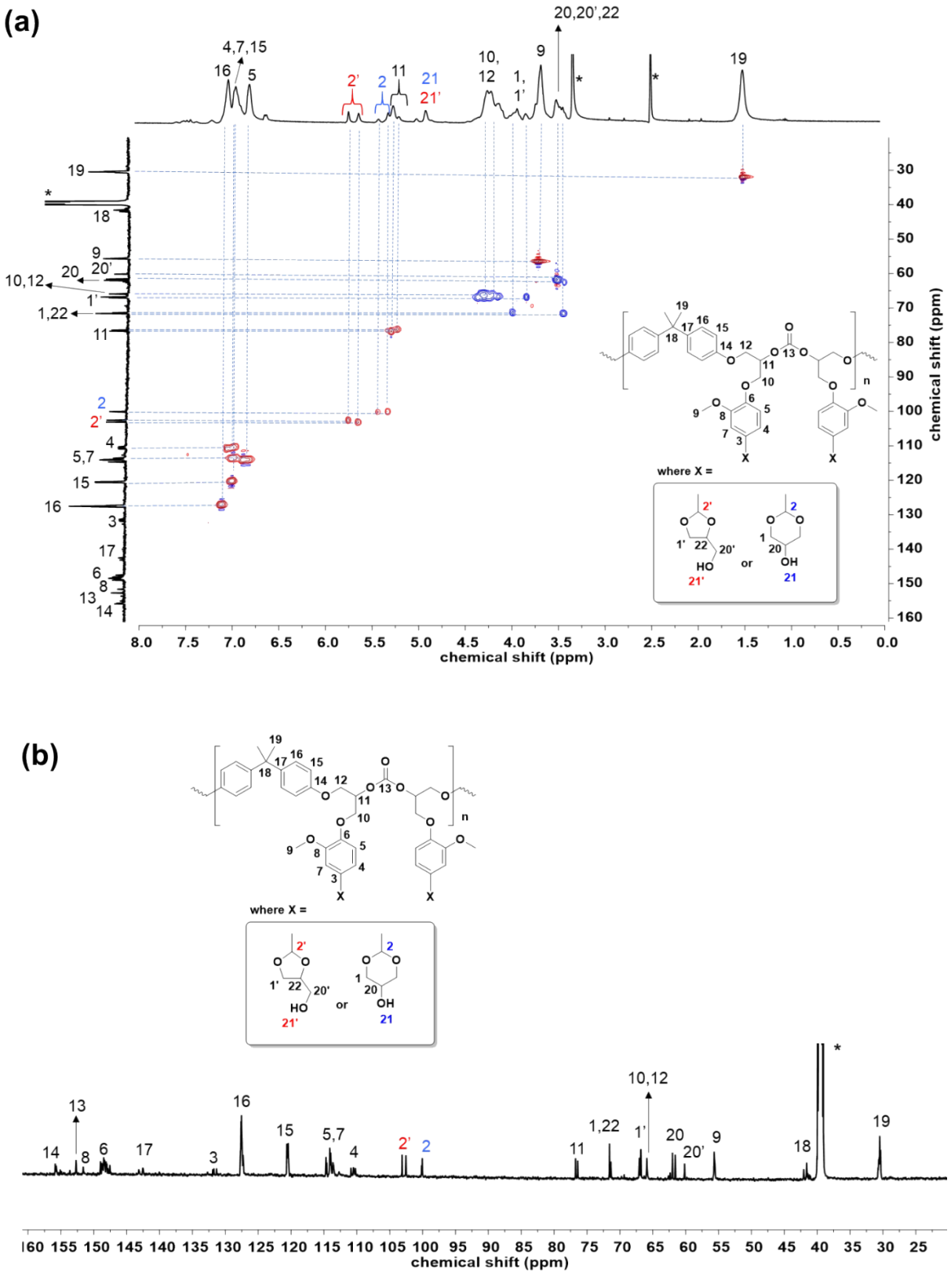


Figure S2. (a) HSQC, (b) ^{13}C NMR spectrum of WPC-CHO/GC.

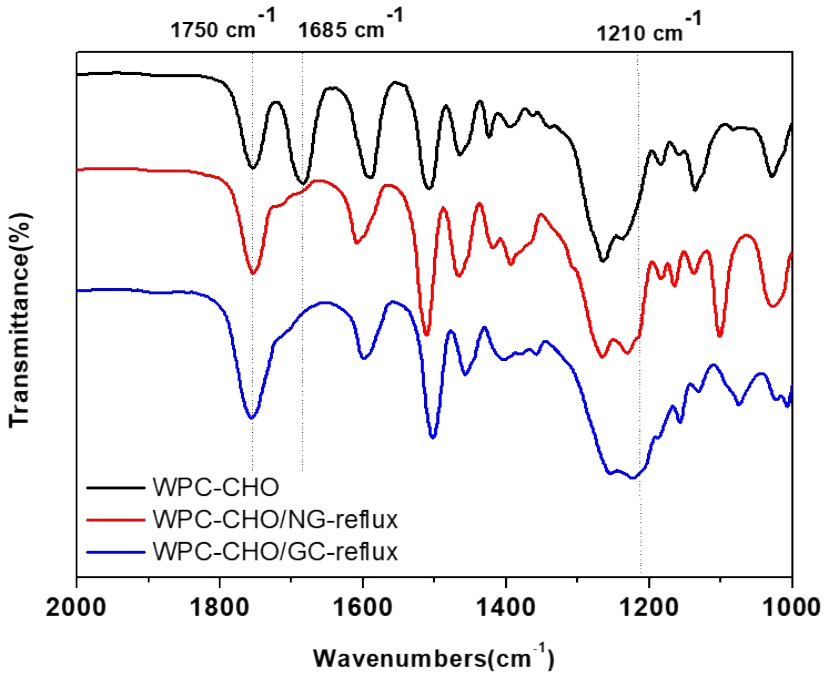


Figure S3. Enlarged FTIR spectra of WPC-CHO, WPC-CHO/NG and WPC-CHO/GC.

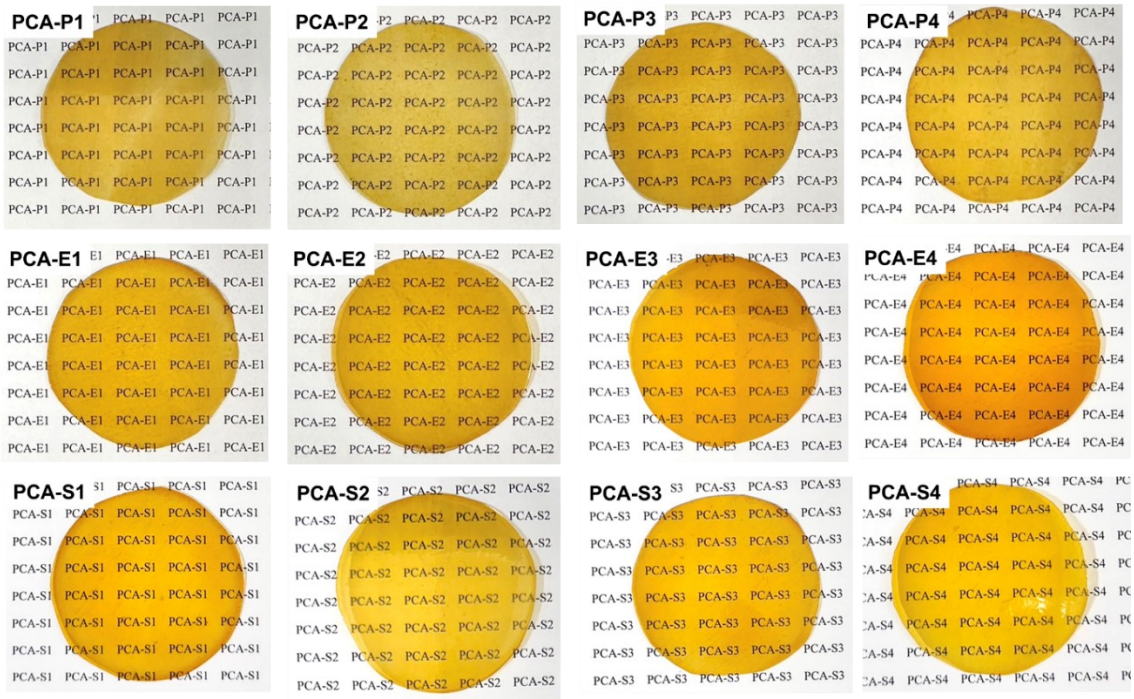


Figure S4. Photos of PCA-Px, PCA-Ex and PCA-Sx films where 'x' denotes the mole percentage of pTSA used. Brittle films were obtained if x=0.5, while flexible PCA films can be obtained if x = 1-4.

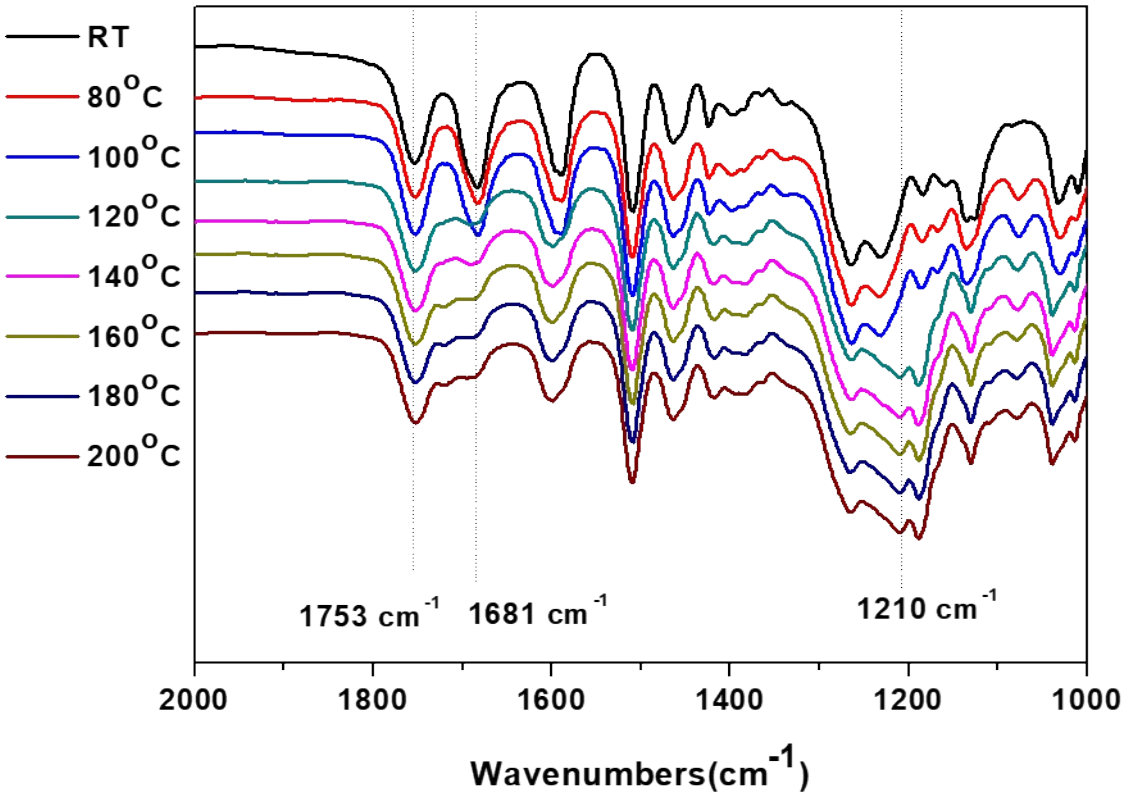


Figure S5. The overlapping presentation of FTIR spectra of the acetal formation of PCA-P2 at accumulative curing at each temperature for 20 min.

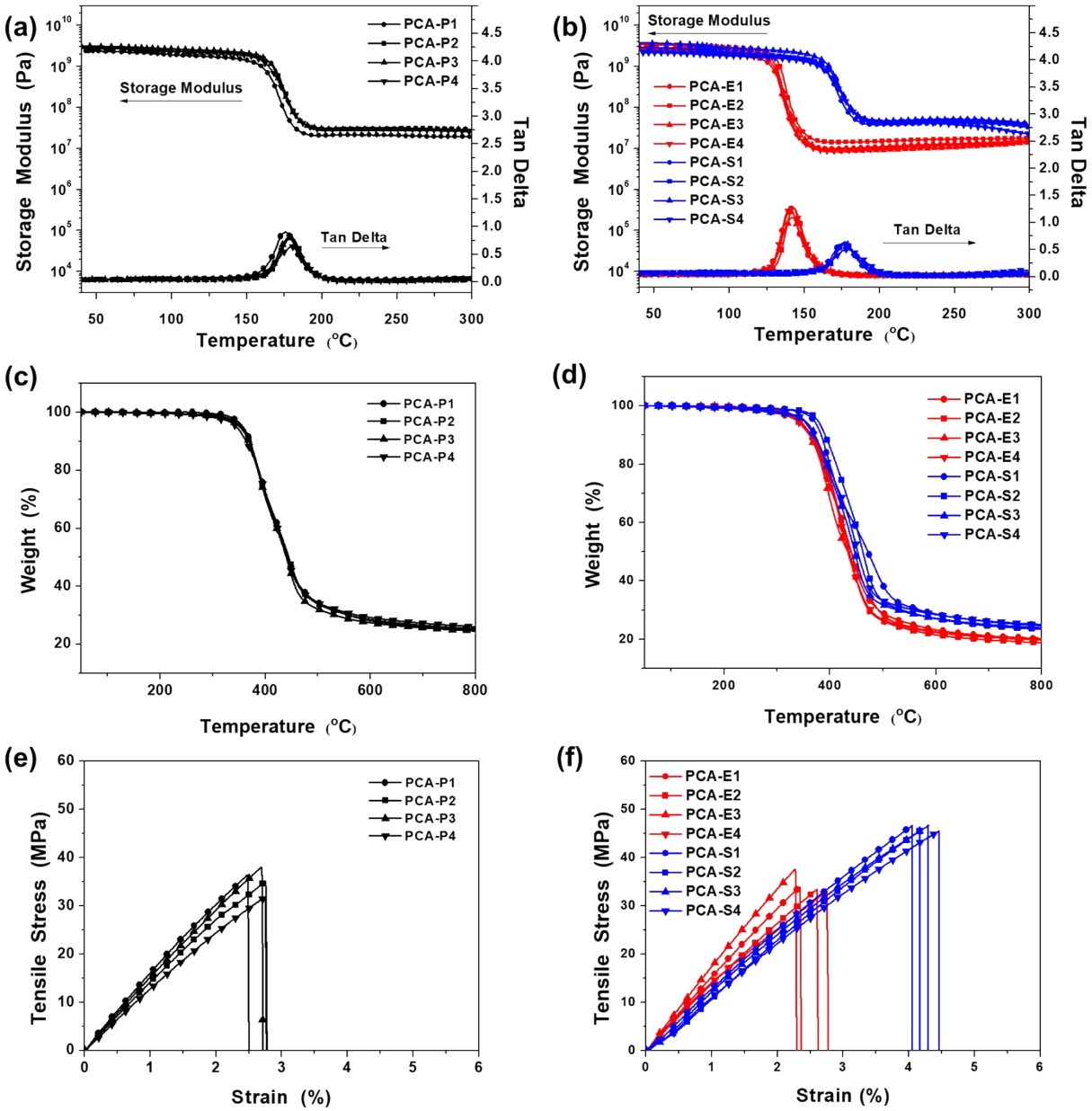


Figure S6. (a) DMA thermogram, (b) TGA thermogram, and (c) stress-strain curves of original PCAs with x = 1-4.

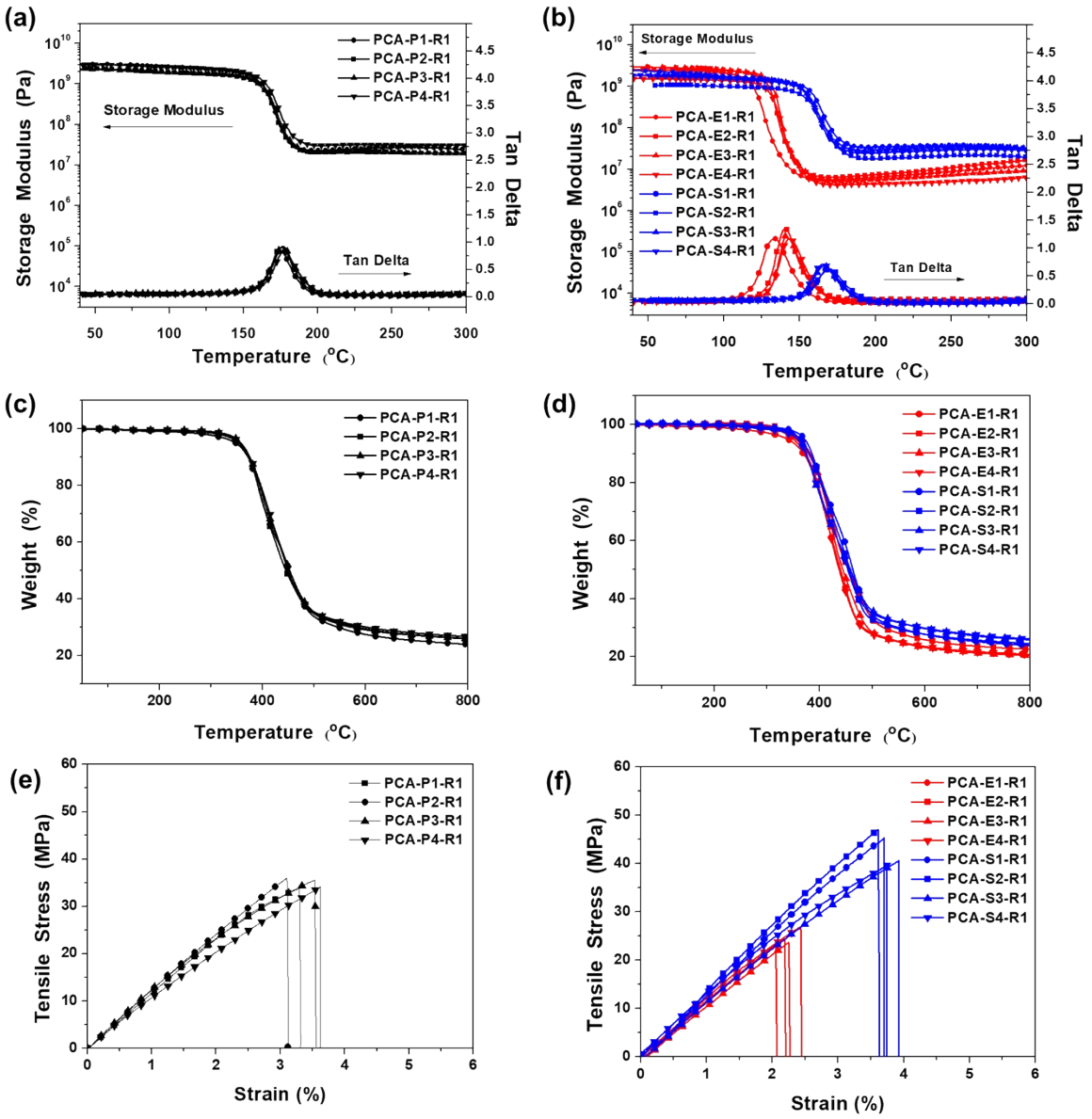


Figure S7. (a-b) DMA thermograms, (c-b) TGA thermograms, and (e-f) stress-strain curves of the first reprocessed PCAs with x = 1-4.

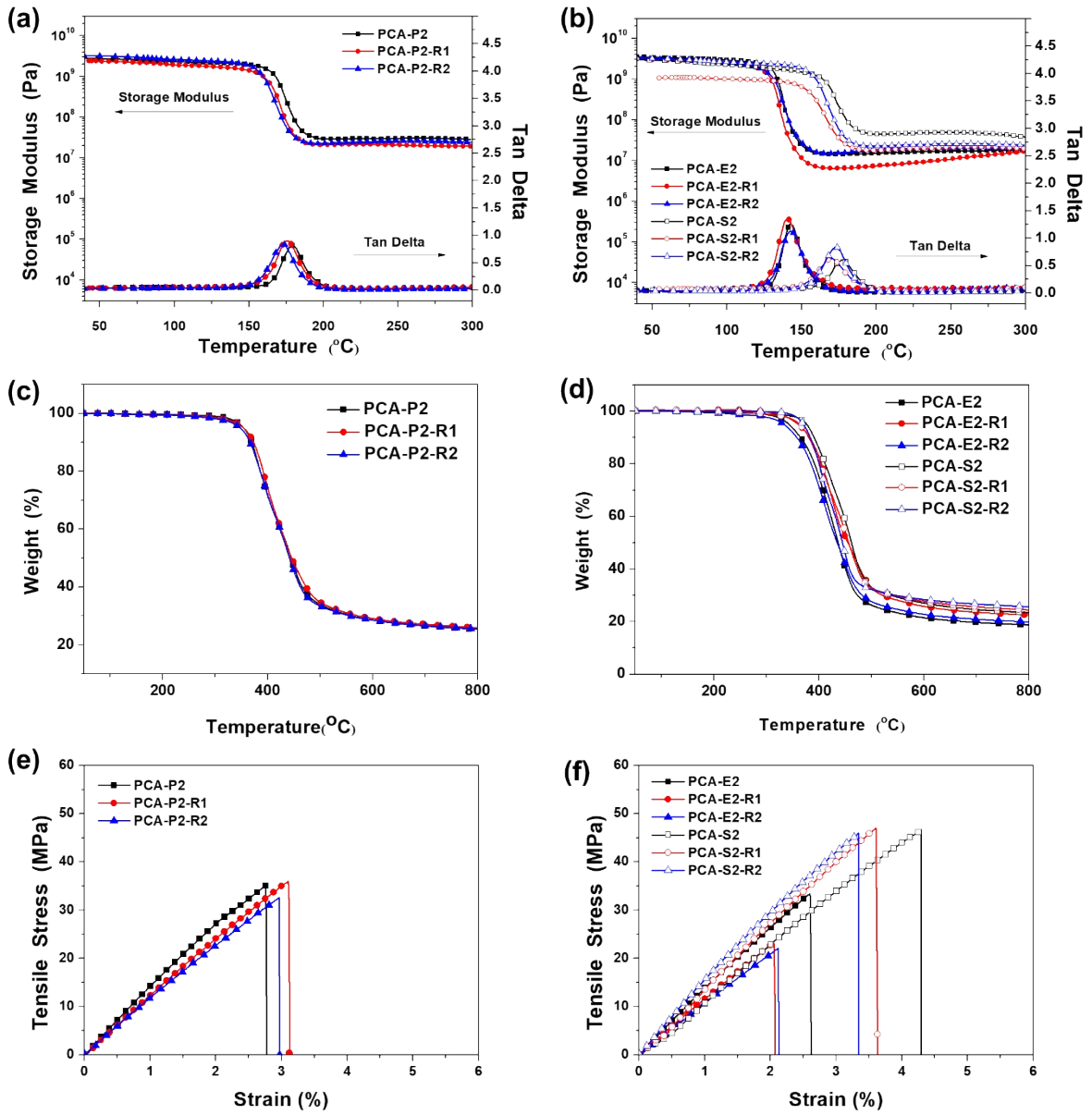


Figure S8. (a-b) DMA thermograms, (c-b)TGA thermograms, and (e-f) stress-strain curve for the orignal , the first reprocessed , and the second reprocessed PCAs with x=2.

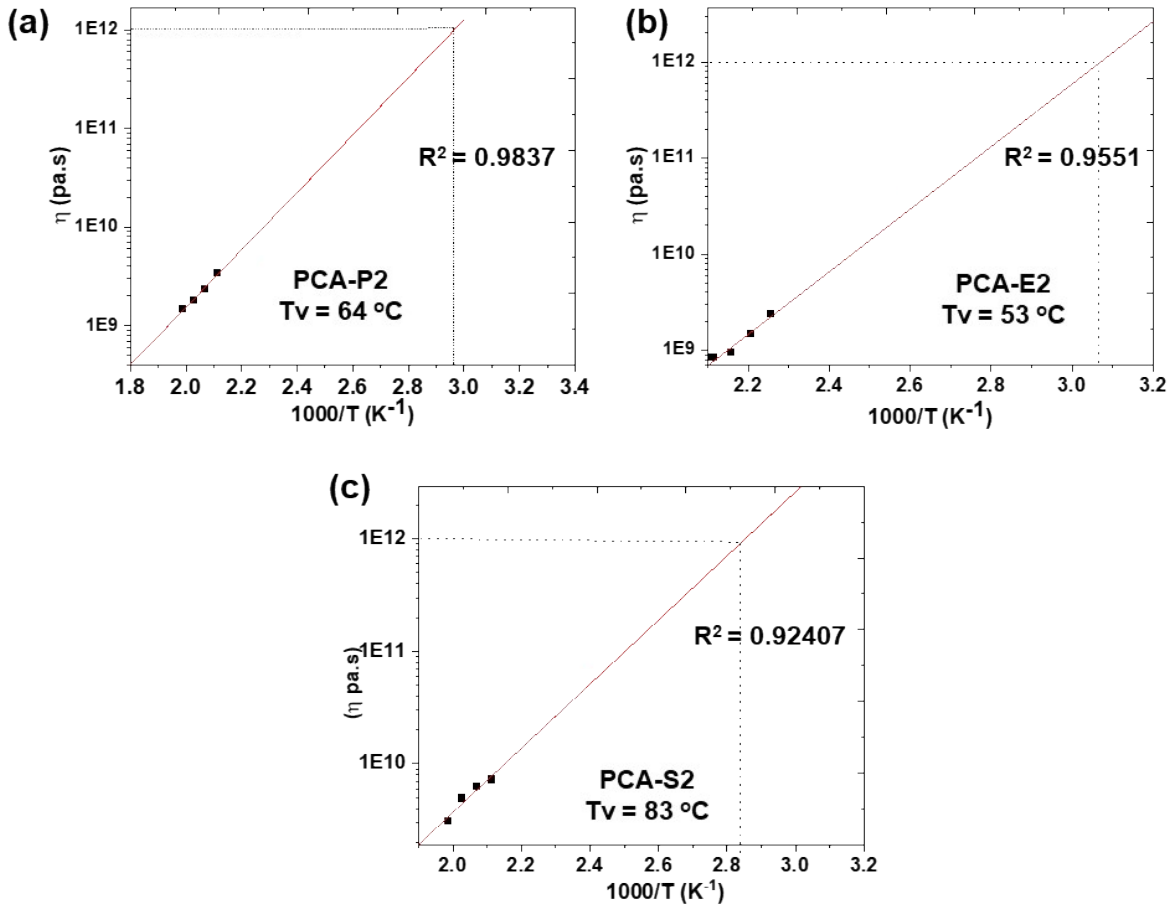


Figure S9. The graph of log η vs 1000/T for T_v determination.

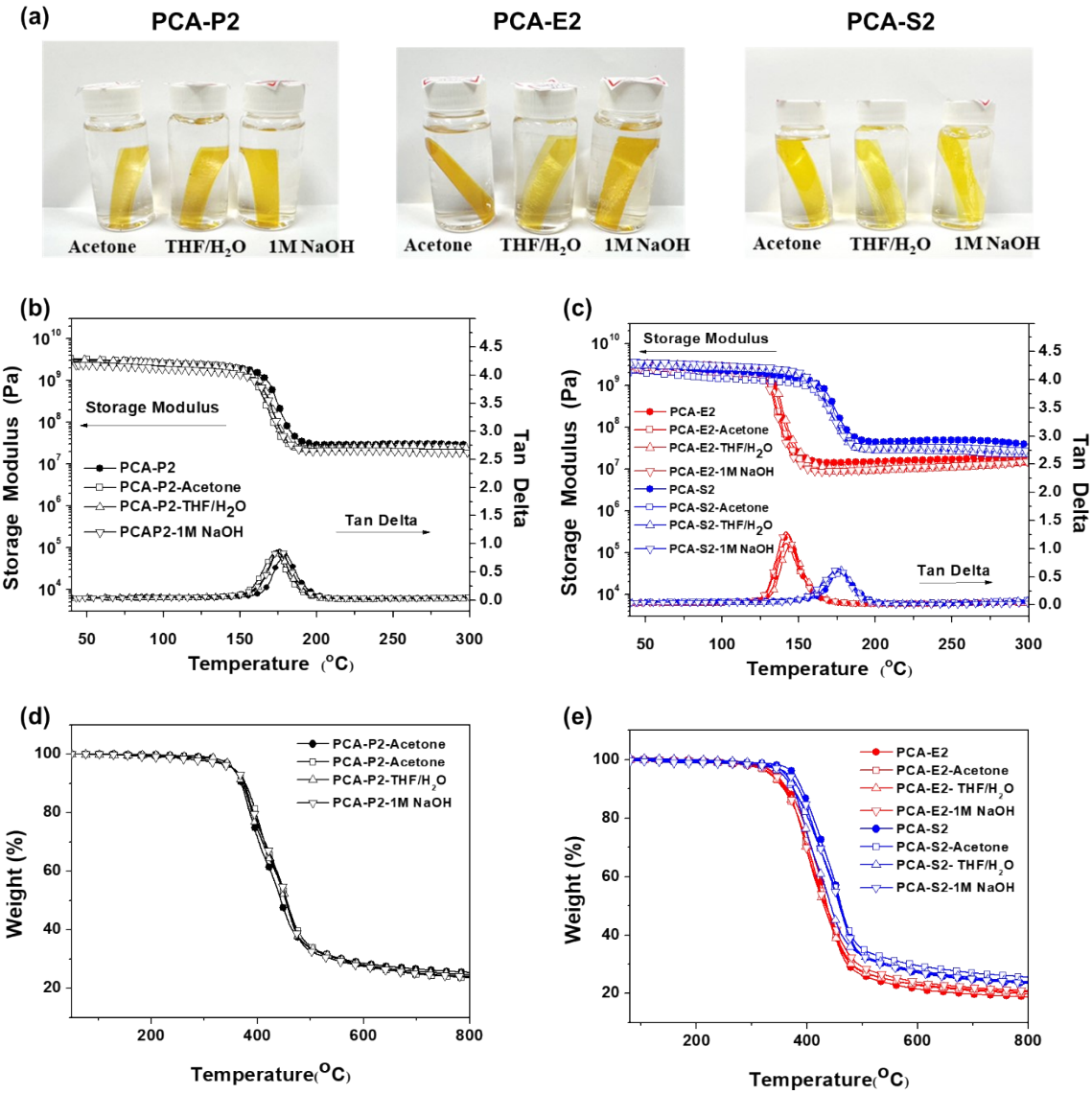


Figure S10. (a) Solvent resistance test of PCA-P2, PCA-E2, and PCA-S2. (b-c) DMA thermograms and (d-e) TGA thermograms of original PCA and solvent-immersed PCA films.

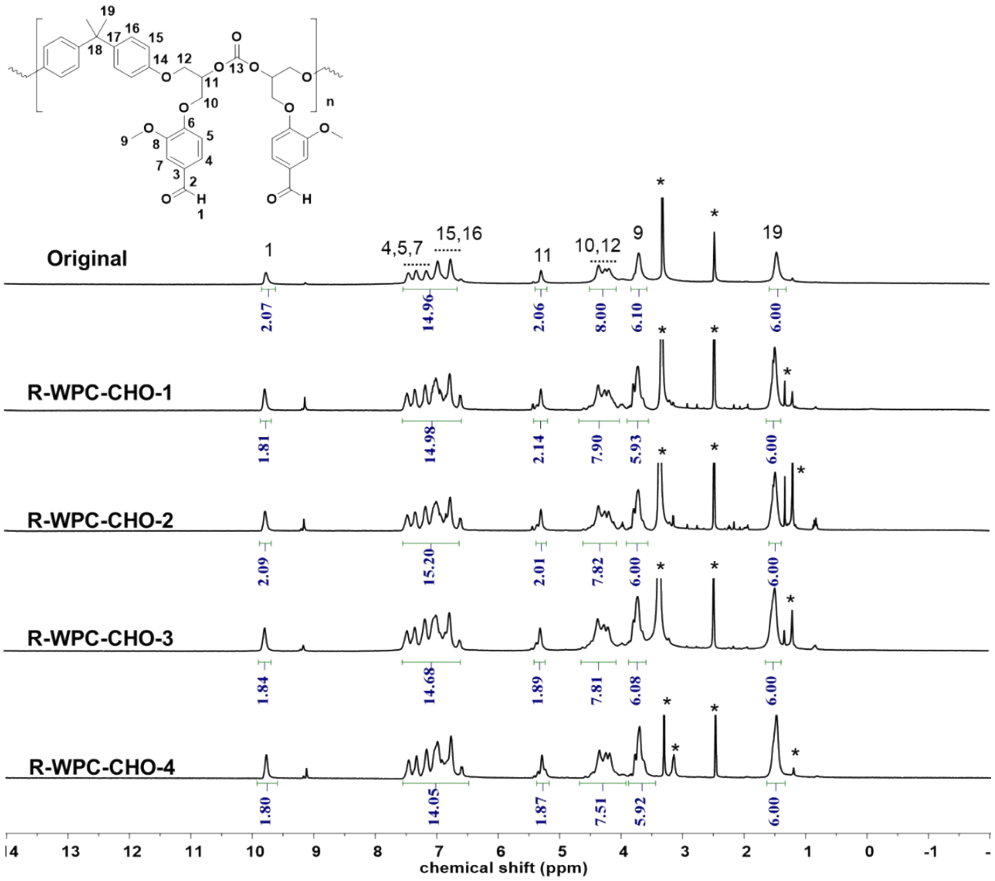


Figure S11. [1]H-NMR spectra of the precipitate in the acid degradation of PCA-Px.

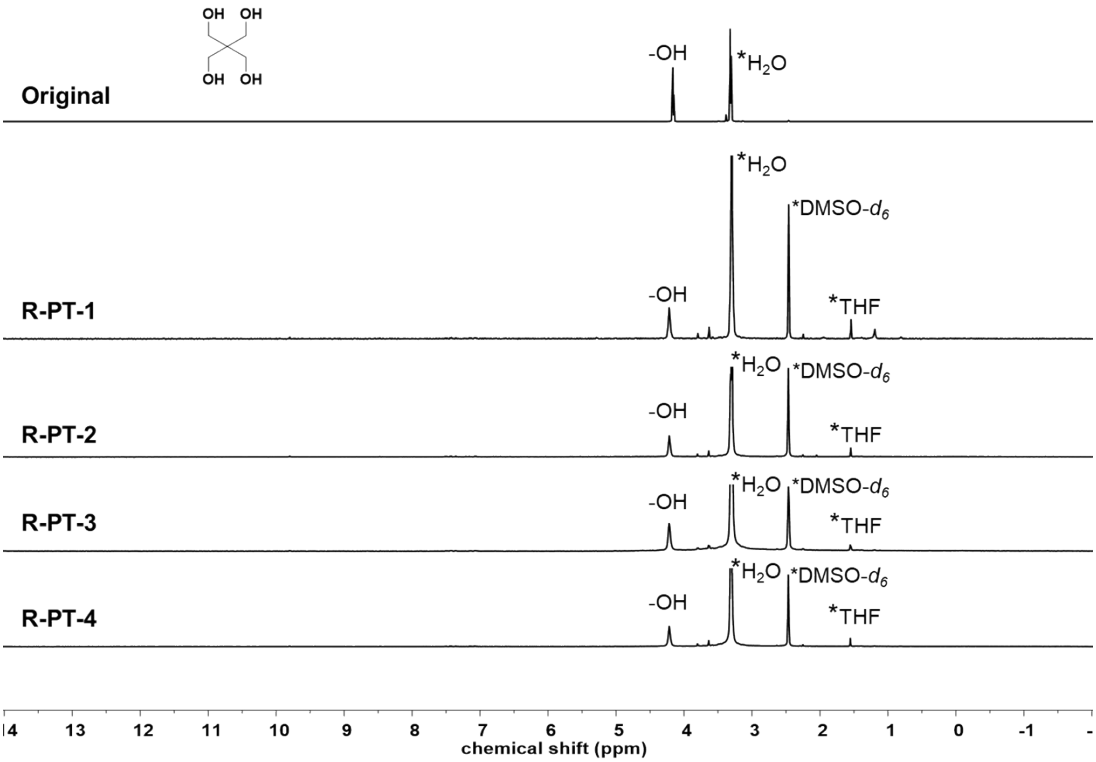


Figure S12. [1]H-NMR spectra of the fresh and recycled pentaerythritol.

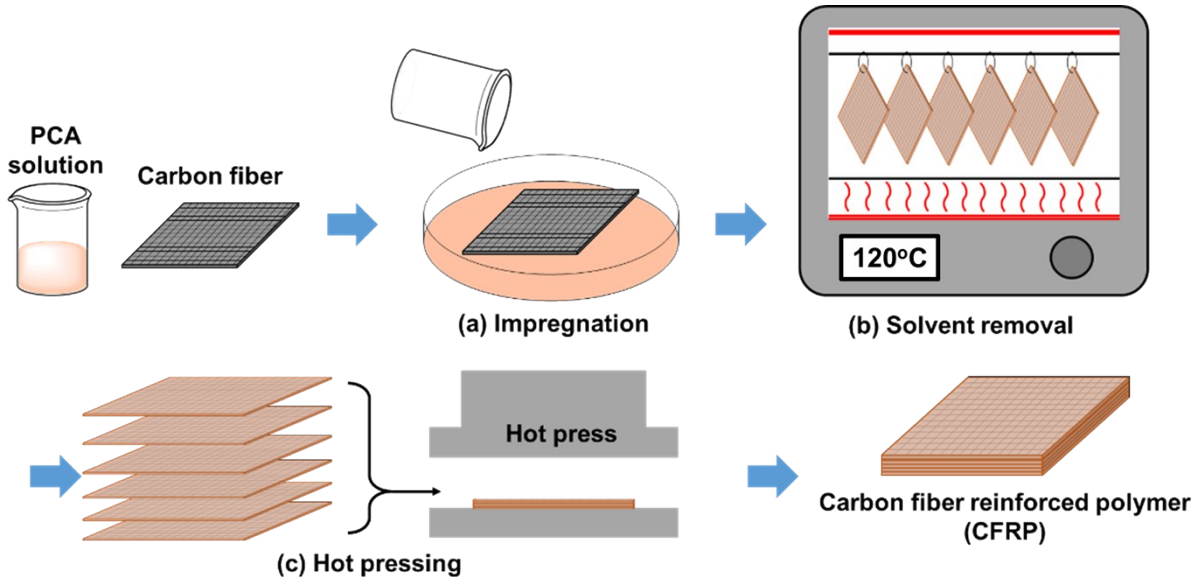


Figure S13. Schematic procedure used for preparing the CFRPs.

References

1. S. Wang, S. Ma, Q. Li, X. Xu, B. Wang, W. Yuan, S. Zhou, S. You and J. Zhu, *Green chemistry*, 2019, **21**, 1484-1497.