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Supporting Information for

Glycidyl Azide Polymer-Based Polyurethane Vitrimers with Disulfide Chain Extenders

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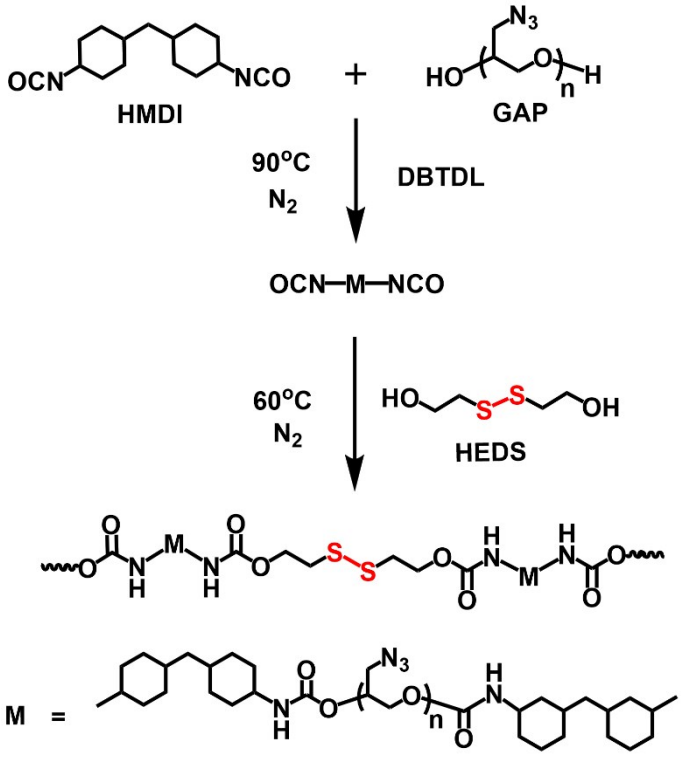
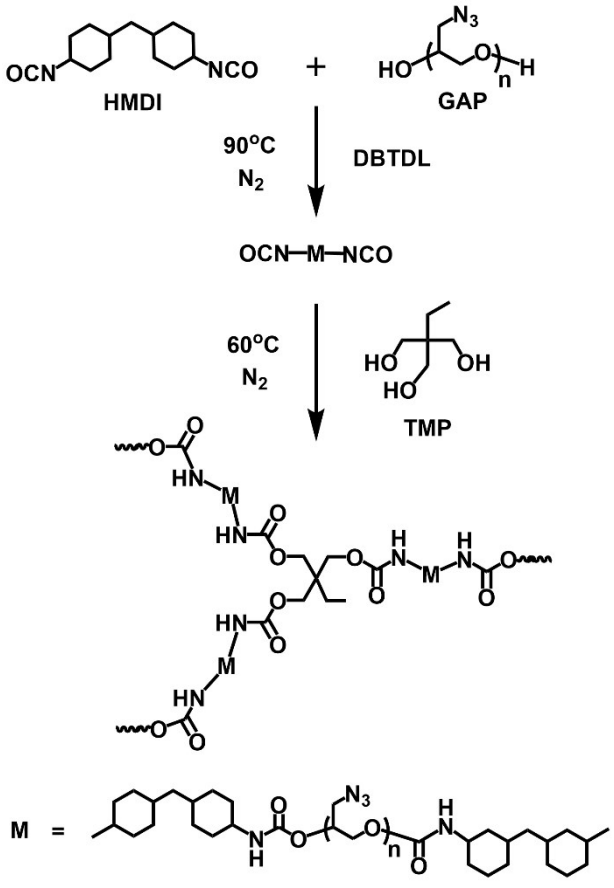


Scheme S1. Synthesis route of the GAPUs with pure HEDS.



Scheme S2. Synthesis route of the GAPUs with pure TMP.

The components of the GAPUVs are calculated according to the following equations,

$$\begin{cases} x = \dfrac{m(\mathrm{HMDI}) + m(\mathrm{HEDS}) + m(\mathrm{TMP})}{m(\mathrm{GAP}) + m(\mathrm{HMDI}) + m(\mathrm{HEDS}) + m(\mathrm{TMP})} * 100\% & (eq.S1) \\ y = \dfrac{n(\mathrm{HEDS}) * 2}{n(\mathrm{HEDS}) * 2 + n(\mathrm{TMP}) * 3} * 100\% & (eq.S2) \end{cases}$$

where x stands for the weight percentage of hard segment, y for the molar percentage of the HEDS hydroxyl groups within the total amount of hydroxyl groups from the chain extenders and crosslinkers, and r for the ratio between isocyanate and hydroxyl groups.

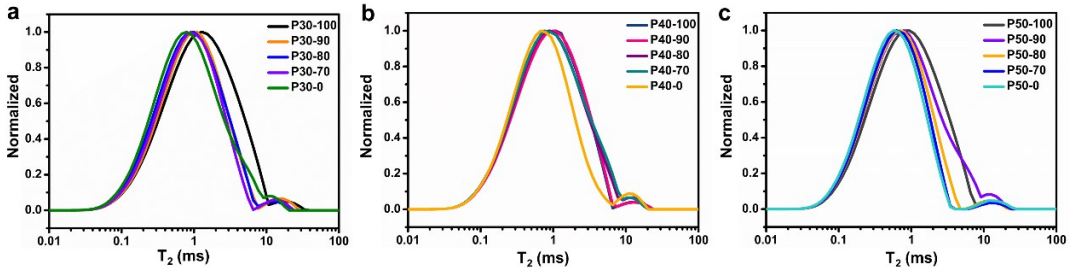


Figure S1. Inversion curves of GAPUVs by low-field nuclear magnetic resonance.

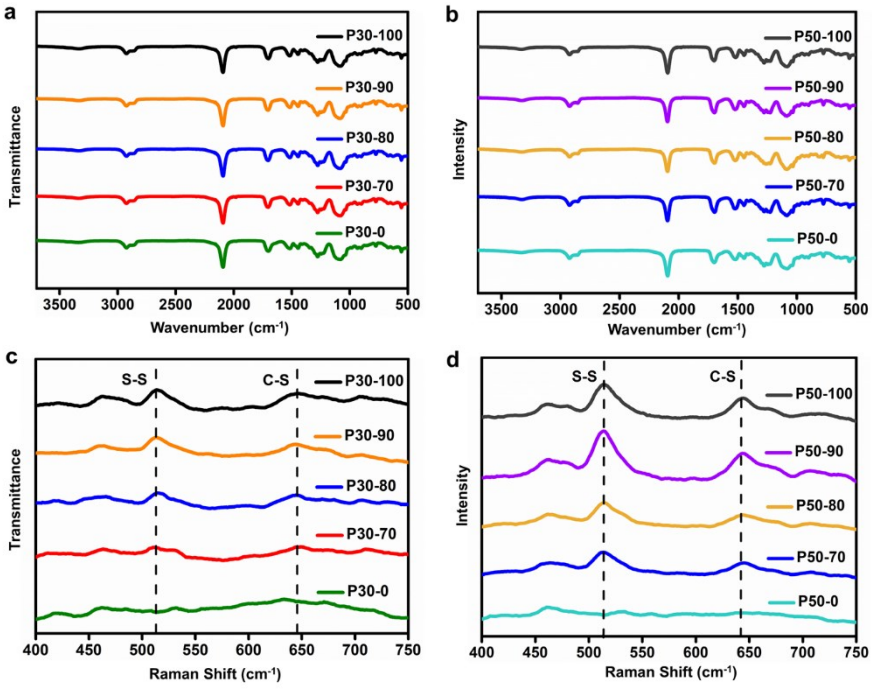


Figure S2. (a) FT-IR spectra of all P30 samples. (b) FT-IR spectra of all P50 samples. (c) Raman spectra of all P30 samples. (d) Raman spectra of all P50 samples.

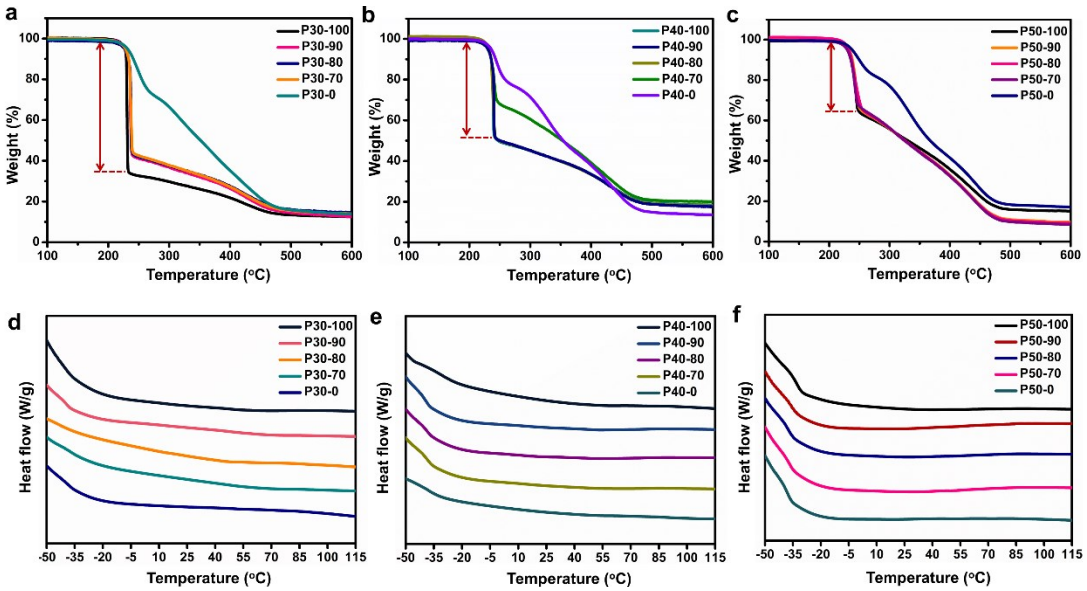


Figure S3 traces of (a) P30 samples, (b) P40 samples, (c) P50 samples; and DSC traces (obtained from the second heating scan) of (d) P30 samples, (e) P40 samples, (f) P50 samples.

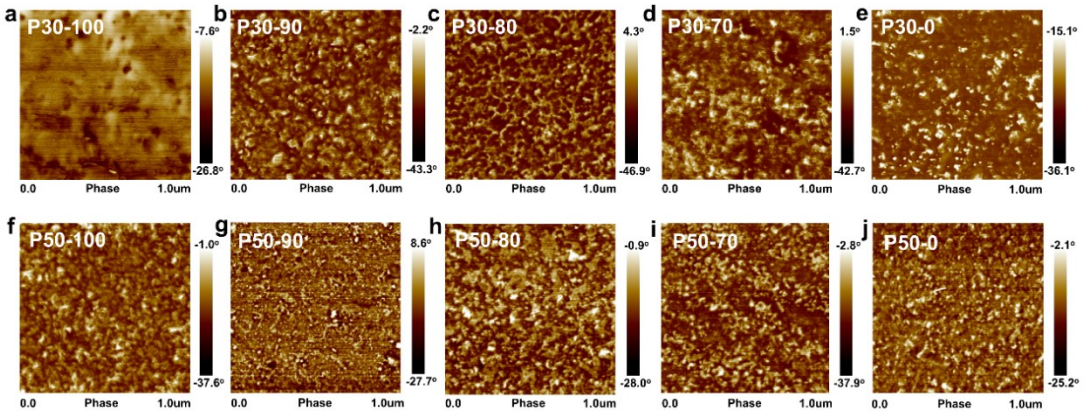


Figure S4. AFM phase images of P30 and P50 sample films.

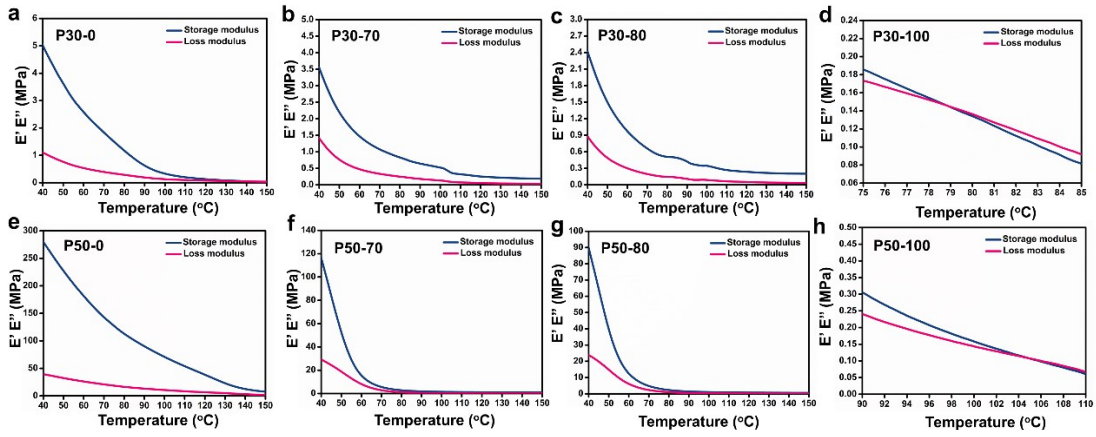


Figure S5. DMA results of (a) P30-0, (b) P30-70, (c) P30-80, (d) P30-100, (e) P50-0, (f) P50-70, (g) P50-80, (h) P50-100 samples obtained at different temperatures at 1 Hz.

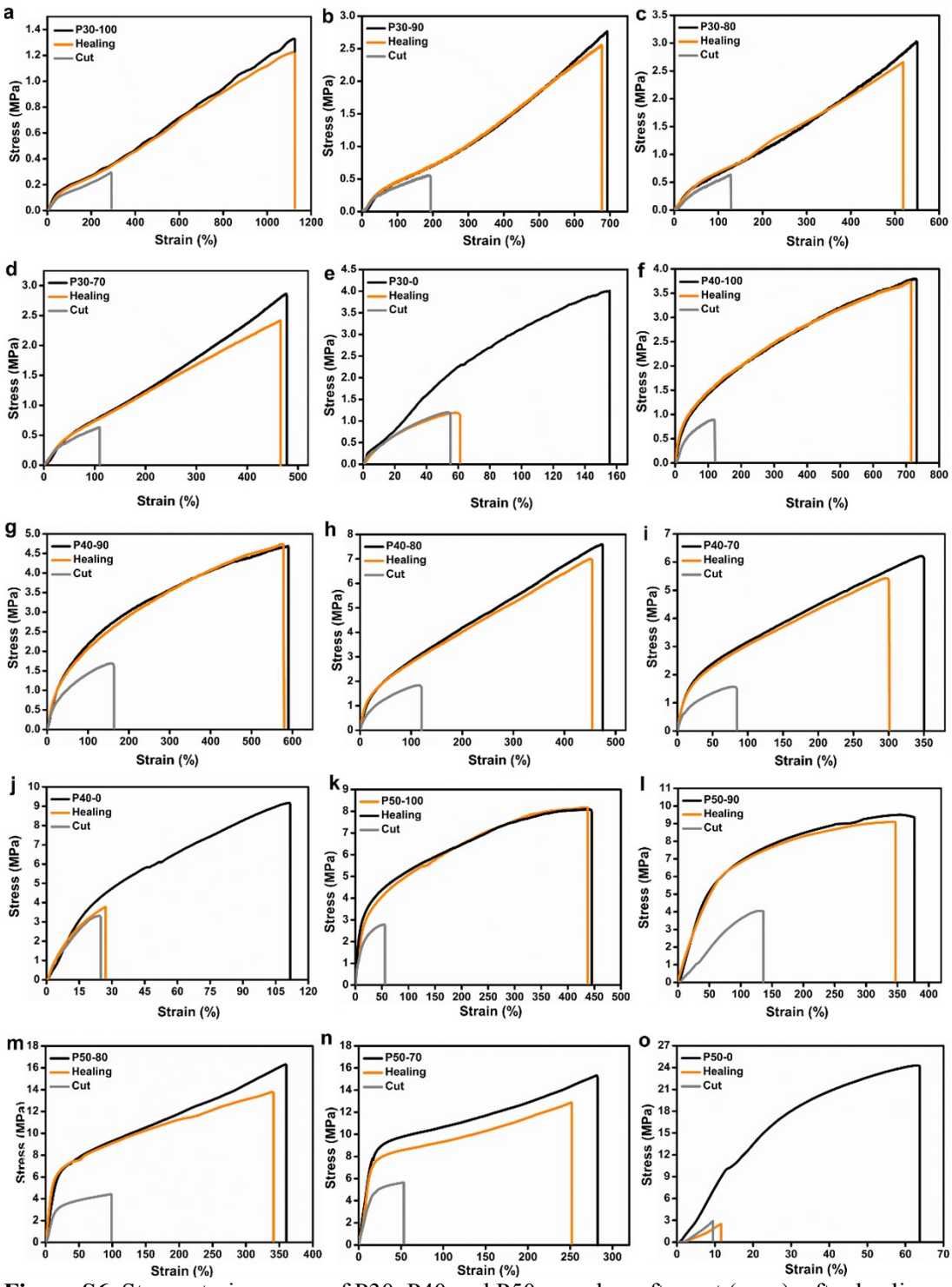


Figure S6. Stress-strain curves of P30, P40 and P50 samples: after cut (gray), after healing (orange) and pristine sample (black).

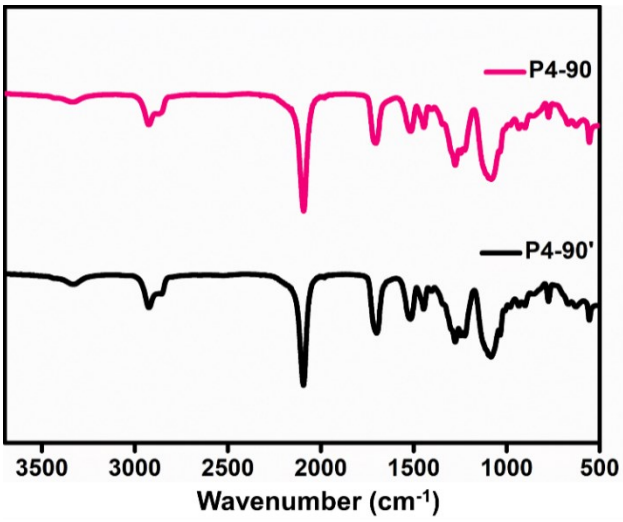


Figure S7. FT-IR spectra of P40-90 sample before (red) and after (black) heating at 85 °C for 24 h.

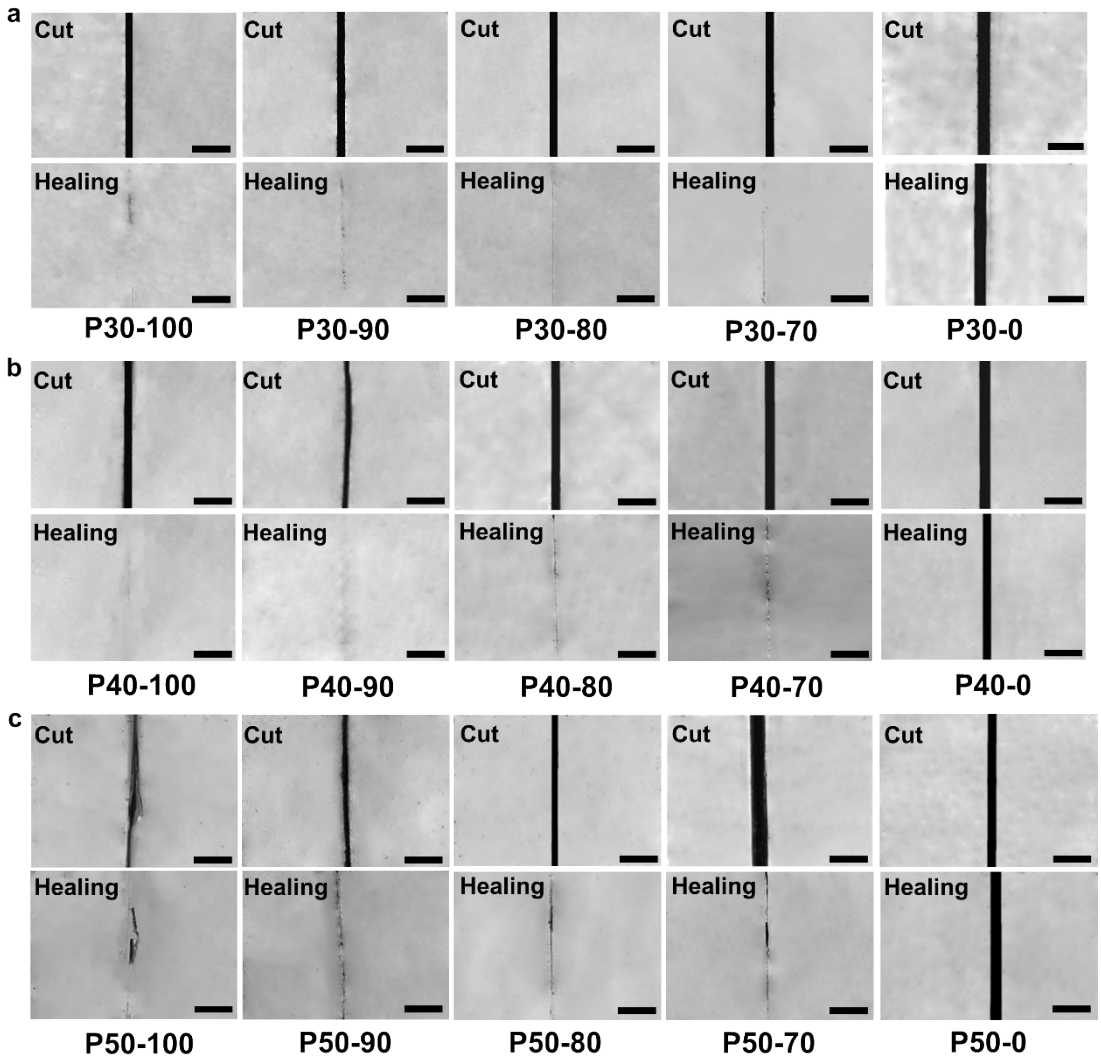


Figure S8. Optical pictures of P30, P40 and P50 samples with cut and after healing. Scale bars is 100 μm.

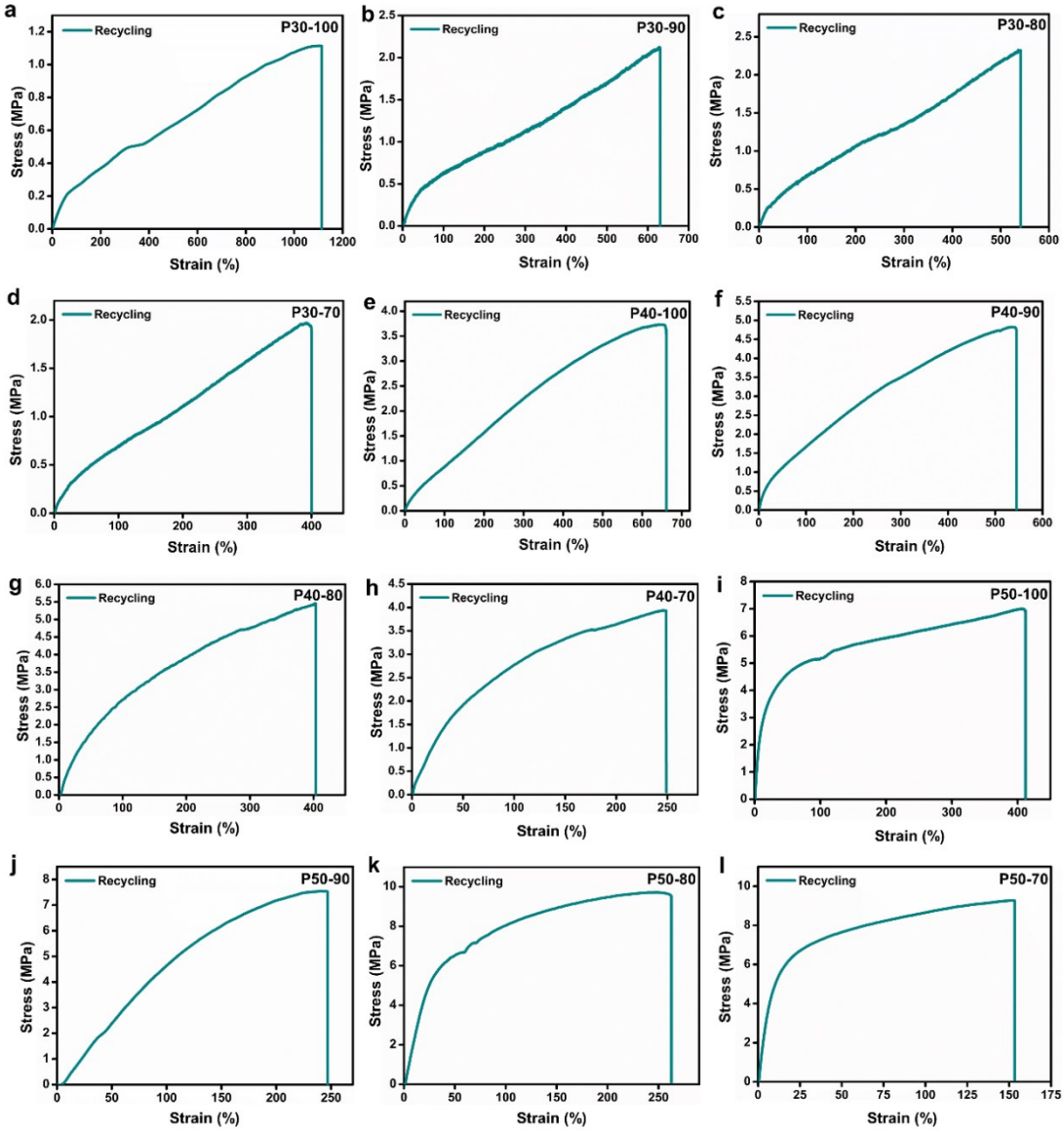


Figure S9. Stress-strain curves of P30, P40 and P50 samples after chopping into small pieces and molded at 95 ^{o}C for 20 min into a whole piece.

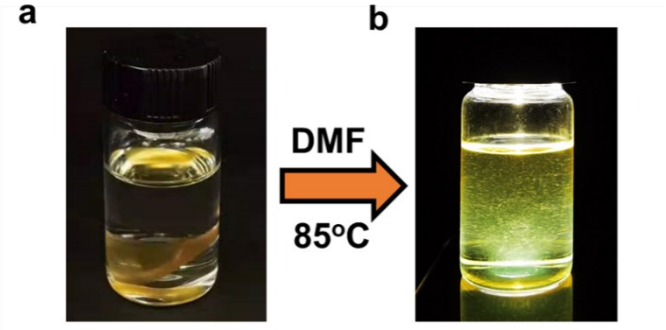


Figure S10. GAPUV P40-90 was degraded in DMF solvent at 85 °C for 5 h.

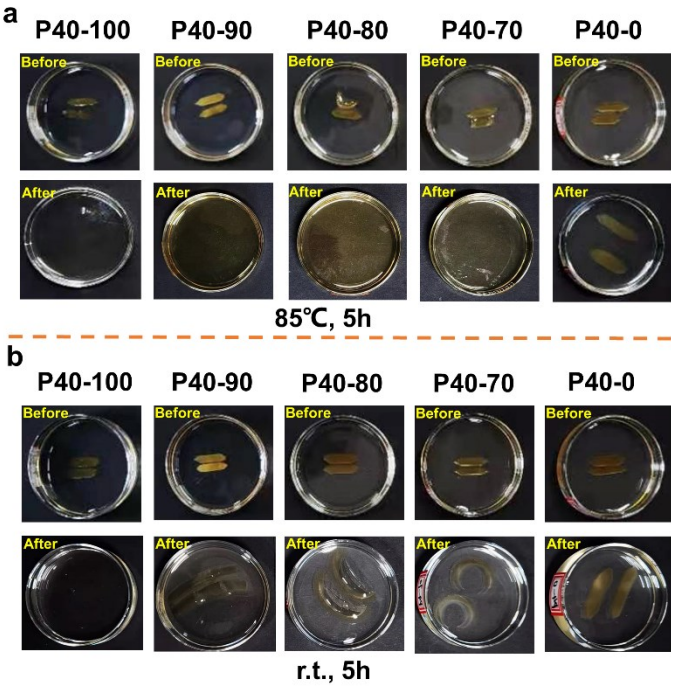


Figure S11. Optical pictures of the P40-100, P40-90, P40-80, P40-70 and P40-0 samples (a) before dipping into solvent, heated in DMF at 85 °C for 5 h (top), (b) dipped in DMF at r.t. for 5 h (bottom).

Sample	100	90	80	70	0
P30-T_2/ms	1.292	1.097	0.983	0.904	0.792
P40-T_2/ms	1.085	0.994	0.897	0.749	0.673
P50-T_2/ms	0.932	0.798	0.693	0.626	0.572

Table S1. The data of inversion curves of GAPUVs.

Wavenumber (cm^{-1})	Assignment
3339	υ (NH)
2924	υ_a (CH_2)
2857	υ_s (CH_2)
2100	υ (N_3)
1700	υ (C=O)
1520	H-bond υ (C-N) + δ (N-H) amide
1446/1275	Free υ (C-N) + δ (N-H) amide
1086	υ (C-O-C)

Table S2. The assignment of the FT-IR peaks of GAPUVs samples.

subscript a = antisymmetric, subscript s = symmetric[1]

Sample	P30				
	100	**90**	**80**	**70**	**0**
T_{d1}/°C	226.7	227.5	228.7	229.3	232.7
T_{d2}/°C	232.9	240	241.3	241.9	270.4
T_g/°C	-30.6	-35.4	-36.9	-36.0	-34.5
Sample	**P40**				
	100	**90**	**80**	**70**	**0**
T_{d1}/°C	230.3	231.0	231.1	231.9	235.8
T_{d2}/°C	241.1	241.7	242.3	244.5	276.9
T_g/°C	-30.3	-34.8	-35.1	-34.7	-33.2
Sample	**P50**				
	100	**90**	**80**	**70**	**0**
T_{d1}/°C	230.6	232.9	233.1	233.4	239.2
T_{d2}/°C	243.6	244.3	246.9	248.4	279.1
T_g/°C	-29.7	-31.5	-34.1	-33.6	-32.9

Table S3. The data of TGA and DSC for GAPUVs.

Sample	P30				
	100	**90**	**80**	**70**	**0**
σ / MPa	1.33±0.08	2.76±0.10	3.03±0.09	2.87±0.05	3.99±0.08
ε / %	1120±14	692±11	549±15	476±9	152±10
Toughness / MJ m^{-3}	7.60±0.35	8.88±0.40	8.17±0.39	7.03±0.30	3.76±0.32
Young's Modulus / MPa	0.34±0.09	0.56±0.28	1.03±0.51	1.12±0.98	11.39±2.04
Sample	**P40**				
	100	**90**	**80**	**70**	**0**
σ / MPa	3.78±0.11	4.70±0.17	7.58±0.19	6.21±0.15	9.17±0.14
ε / %	730±18	590±16	474±17	347±13	111±9
Toughness / MJ m^{-3}	18.67±0.69	19.48±0.64	21.66±0.72	14.18±0.59	6.65±0.51
Young's Modulus / MPa	2.85±1.17	4.28±1.43	6.21±1.98	9.13±2.16	20.69±3.87
Sample	**P50**				
	100	**90**	**80**	**70**	**0**
σ / MPa	8.12±0.24	9.36±0.21	16.29±0.57	15.30±0.46	24.28±1.99
ε / %	438±9	377±7	360±15	282±14	63±8
Toughness / MJ m^{-3}	27.56±0.71	28.34±0.68	39.99±1.98	32.15±1.37	10.34±1.76
Young's Modulus / MPa	10.54±1.08	14.99±1.69	37.32±2.12	53.86±3.48	75.96±4.22

Table S4. The σ, ε, toughness and Young's Modulus of different GAPUV samples.

P40-90	σ / MPa	ε / %
Cycle1	1.99	100
Cycle2	1.79	100
Cycle3	1.94	100

Table S5. The data of stress-strain cycle curves of P40-90.

P40-90	σ / MPa	ε / %	Toughness / MJ m^{-3}
Pristine	4.70±0.17	590±16	19.48±0.64
6 h	2.88±0.13	256±14	4.99±0.42
12 h	3.93±0.11	453±17	12.21±0.51
24 h	4.73±0.19	575±18	18.74±0.70

Table S6. The σ, ε and toughness of P40-90 with different healing time at 85°C.

P40-90	σ / MPa	ε / %	Toughness / MJ m^{-3}
Pristine	4.70±0.17	590±16	19.48±0.64
70 °C	3.75±0.21	470±13	11.98±0.68
75 °C	4.03±0.19	519±21	14.53±0.81
80 °C	4.26±0.11	541±17	16.16±0.59
85 °C	4.73±0.19	575±18	18.74±0.70
90 °C	4.62±0.18	608±20	19.99±0.75

Table S7. The σ, ε and toughness of P40-90 after 24 h of healing at different temperatures.

Sample		σ / MPa	ε / %	Toughness / MJ m^{-3}
P30-100	**Pristine**	1.33±0.08	1120±14	7.60±0.35
	Cut	0.29±0.04	290±11	0.49±0.21
	Healed	1.23±0.07	1120±17	7.35±0.40
	Recycled	1.11±0.10	1113±14	7.39±0.39
P30-90	**Pristine**	2.76±0.10	692±11	8.88±0.40
	Cut	0.56±0.06	189±16	0.67±0.31
	Healed	2.56±0.11	675±19	8.41±0.45
	Recycled	1.85±0.12	629±17	6.47±0.42
P30-80	**Pristine**	3.03±0.09	549±15	8.17±0.39
	Cut	0.64±0.04	128±9	0.46±0.09
	Healed	2.65±0.18	518±15	7.27±0.45
	Recycled	2.32±0.13	538±18	6.84±0.41
P30-70	**Pristine**	2.87±0.05	476±9	7.03±0.30
	Cut	0.63±0.10	108±12	0.43±0.11
	Healed	2.41±0.18	465±18	6.24±0.59
	Recycled	1.96±0.15	395±16	4.46±0.43
P30-0	**Pristine**	3.99±0.08	152±10	3.76±0.32
	Cut	1.19±0.09	54±13	0.42±0.08
	Healed	1.18±0.16	59±11	0.48±0.11

Table S8. The σ, ε and toughness of pristine, cut, healed, and recycled P30 samples.

Sample		σ / MPa	ε / %	Toughness / MJ m^{-3}
P40-100	**Pristine**	3.78±0.11	730±18	18.67±0.69
	Cut	0.89±0.18	117±5	0.72±0.14
	Healed	3.76±0.31	713±14	18.14±0.88
	Recycled	3.71±0.22	658±20	15.02±1.21
P40-90	**Pristine**	4.70±0.17	590±16	19.48±0.64
	Cut	1.69±0.27	157±12	1.96±0.68
	Healed	4.73±0.19	575±18	18.74±0.70
	Recycled	4.81±0.30	542±14	16.80±0.81
P40-80	**Pristine**	7.58±0.19	474±17	21.66±0.72
	Cut	1.83±0.08	117±19	1.53±0.99
	Healed	6.99±0.38	452±21	19.37±0.91
	Recycled	5.45±0.26	403±11	14.62±0.66
P40-70	**Pristine**	6.21±0.15	347±13	14.18±0.59
	Cut	1.55±0.27	83±16	0.96±0.12
	Healed	5.42±0.39	298±14	10.78±0.89
	Recycled	3.93±0.31	248±19	6.84±0.85
P40-0	**Pristine**	9.17±0.14	111±9	6.65±0.51
	Cut	3.32±0.38	24±7	0.51±0.33
	Healed	3.78±0.41	27±9	0.63±0.38

Table S9. The σ, ε and toughness of pristine, cut, healed, and recycled P40 samples.

Sample		σ / MPa	ε / %	Toughness / MJ m^{-3}
P50-100	**Pristine**	8.11±0.24	438±9	28.41±0.71
	Cut	2.78±0.21	55±7	1.19±0.32
	Healed	8.12±0.17	436±13	27.55±0.56
	Recycled	6.98±0.42	410±16	23.43±0.98
P50-90	**Pristine**	9.36±0.21	377±7	28.34±0.68
	Cut	4.03±0.11	135±9	3.22±0.53
	Healed	9.01±0.62	345±11	24.89±1.13
	Recycled	7.54±0.78	246±16	11.86±1.28
P50-80	**Pristine**	16.29±0.57	360±15	39.99±1.98
	Cut	4.42±0.09	98±10	3.43±0.29
	Healed	13.79±0.68	340±16	34.91±2.09
	Recycled	9.60±0.66	261±21	20.67±2.14
P50-70	**Pristine**	15.30±0.46	282±14	32.15±1.37
	Cut	5.64±0.17	53±6	2.33±0.12
	Healed	12.89±0.37	251±13	24.40±1.18
	Recycled	9.27±0.22	153±18	11.84±1.06
P50-0	**Pristine**	24.28±1.99	63±8	10.34±1.76
	Cut	2.88±0.72	9±6	0.51±0.28
	Healed	2.51±0.61	11±4	0.55±0.23

Table S10. The σ, ε and toughness of pristine, cut, healed, and recycled P50 samples.

Sample	P30				
	100	**90**	**80**	**70**	**0**
Pristine toughness / MJ m^{-3}	7.60±0.35	8.88±0.40	8.17±0.39	7.03±0.30	3.76±0.32
Healing toughness / MJ m^{-3}	7.35±0.40	8.41±0.45	7.27±0.45	6.24±0.59	0.48±0.11
Recycling toughness / MJ m^{-3}	7.39±0.39	7.46±0.42	6.84±0.41	4.46±0.43	-
η_h (%)	96.71±1.41	94.71±0.98	88.98±1.17	88.76±1.49	12.76±1.98
η_r (%)	97.24±1.38	84.01±1.29	83.72±1.67	63.44±1.94	-
Sample	**P40**				
	100	**90**	**80**	**70**	**0**
Pristine toughness / MJ m^{-3}	18.67±0.69	19.48±0.64	21.66±0.72	14.18±0.59	6.65±0.51
Healing toughness / MJ m^{-3}	18.14±0.88	18.74±0.70	19.37±0.91	10.78±0.89	0.63±0.38
Recycling toughness / MJ m^{-3}	15.02±1.21	16.80±0.81	14.62±0.66	6.84±0.85	-
η_h (%)	97.16±1.34	96.20±0.86	89.42±1.57	76.02±0.99	9.47±0.93
η_r (%)	80.44±1.61	86.24±1.34	67.49±1.82	48.24±2.01	-
Sample	**P50**				
	100	**90**	**80**	**70**	**0**
Pristine toughness / MJ m^{-3}	28.41±0.71	28.34±0.68	39.99±1.98	32.15±1.37	10.34±1.76
Healing toughness / MJ m^{-3}	27.55±0.56	24.89±1.13	34.91±2.09	24.40±1.18	0.55±0.23
Recycling toughness / MJ m^{-3}	23.44±0.98	11.86±1.28	20.67±2.14	11.84±1.06	-
η_h / %	96.97±1.55	87.83±1.96	87.29±1.74	75.89±1.28	5.32±1.47

η_r / %	82.51±1.18	41.85±1.47	51.69±1.26	36.83±1.68	-

Table S11. The healing and recycling efficiency of GAPUVs.

P40-90	σ / MPa	ε / %	Toughness / MJ m^{-3}
Pristine	4.76±0.16	119±18	4.22±0.89
Healing	4.62±0.12	116±10	4.15±0.77
η_h (%)	-	-	98.34±0.91

Table S12. The σ, ε and toughness of composite material in pristine, cut and healing.

References:

1. Y. Lai, X. Kuang, P. Zhu, M. Huang, X. Dong and D. Wang, *Adv. Mater.*, 2018, **30**, 1802556.