

Supplementary Information

Table S1. Mole feed amounts of reactants for PU samples.

Sample	T5000 (mmol)	D2000 (mmol)	D230 (mmol)	UPy-NCO (mmol)	HDI (mmol)
PU0	1.0	0.0	0.0	2.1	7.95
PU1	1.0	8.0	1.0	2.1	7.95
PU2	1.0	7.5	1.5	2.1	7.95
PU3	1.0	7.0	2.0	2.1	7.95
PU4	1.0	6.0	3.0	2.1	7.95

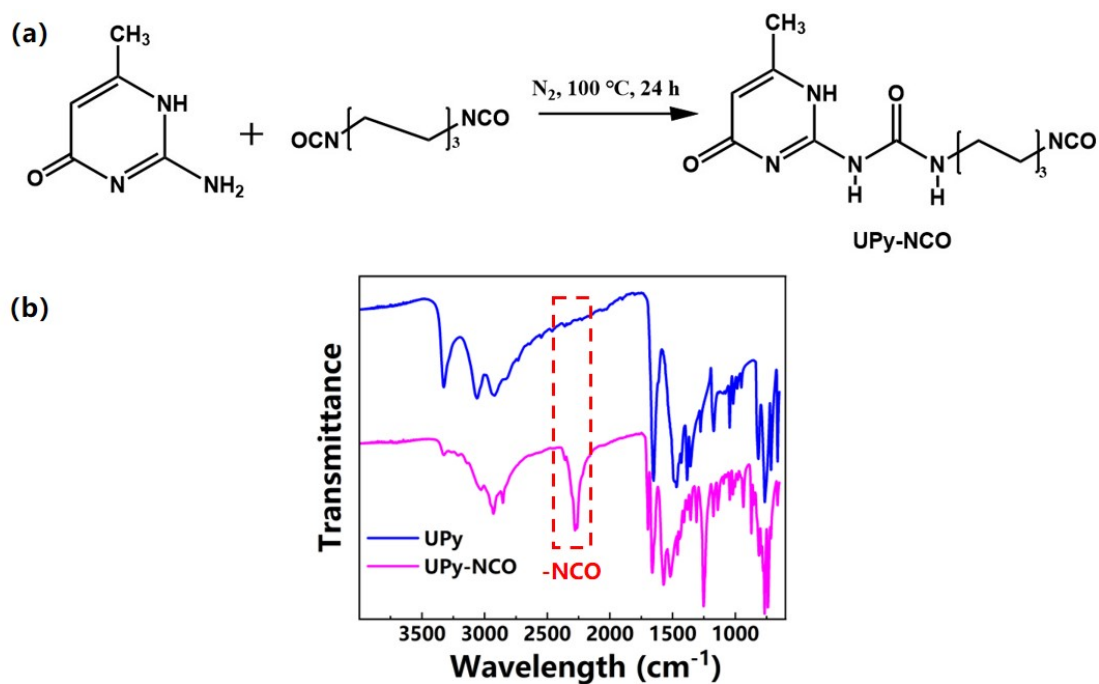


Figure S1. (a) Synthesis process of UPy-NCO. (b) FTIR spectra of UPy and UPy-NCO samples

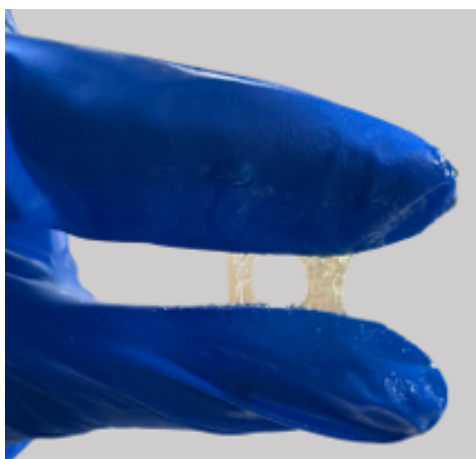


Figure S2. The viscous-flow state of PU0 at room temperature

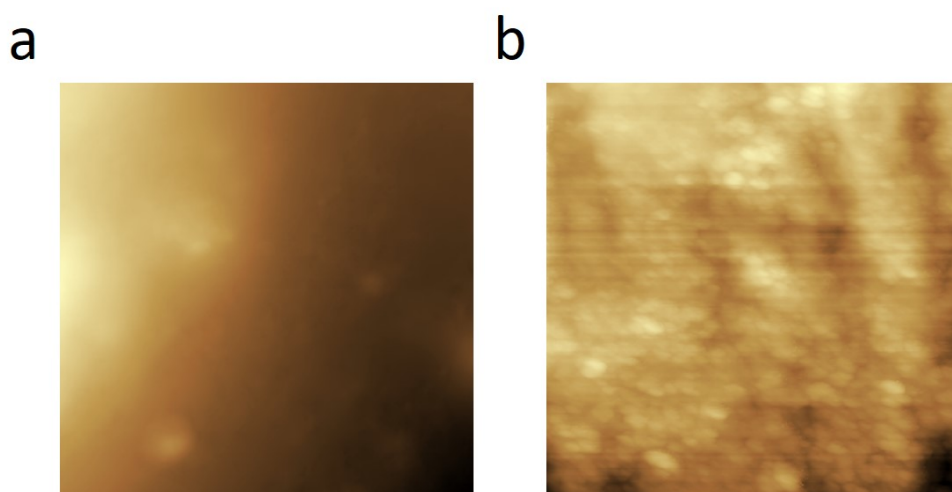


Figure S3. AFM images of ion-milled samples (a)PU3 and PU4

Table S2. q_{max} and its corresponding interdomain spacing (d) of PU samples

Sample	PU1	PU2	PU3	PU4
q_{max} (nm ⁻¹)	1.09	1.11	1.14	1.17
d (nm)	5.76	5.65	5.51	5.36
S	2.2	2.2	2.4	2.6

Table S3. DSC Data of PU samples

Temperature (°C)	PU1	PU2	PU3	PU4
Tg(h)	38.8	50.1	59.1	65.5
ΔT_g	97.6	108.9	117.9	124.3

Table S4. Summary of mechanical properties of PU

Sample	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (MJ·m ⁻³)	Elastic recovery (%)	
					2nd	5st
PU1	0.63 ± 0.19	5.5 ± 0.98	403.3 ± 17.7	2.46 ± 0.67	44.1	29.1
PU2	1.16 ± 0.28	9.9 ± 1.62	318.5 ± 21.5	3.44 ± 0.82	32.3	21.2
PU3	1.85 ± 0.23	24.2 ± 2.55	290.1 ± 10.3	4.96 ± 1.13	30.4	19.1
PU4	2.55 ± 0.27	42.3 ± 2.11	268.4 ± 28.8	6.21 ± 1.22	29	19.2

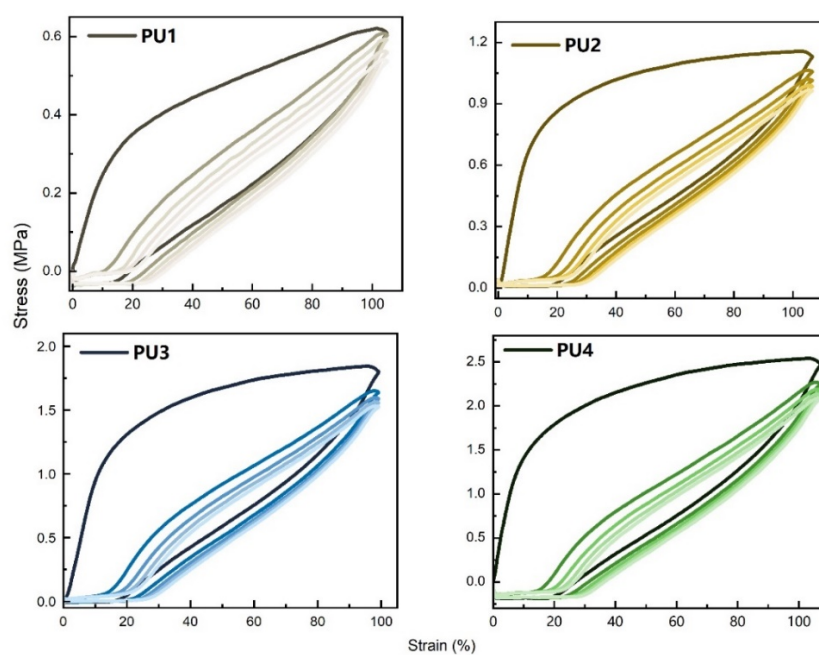
**Figure S4.** The cyclic stress-strain curve of different PUs.

Table S5. Summary of self-healing efficiencies of PU for in original state and after 8 h at 60 °C.

Samples		Tensile strength (MPa)	Young's modulus (MPa)	Elongation (%)
PU1	origin	0.63 ± 0.19	5.5 ± 0.98	402.3 ± 17.7
	8 h	0.61 ± 0.22	5.3 ± 1.27	372.9 ± 24.3
	η (%)	96.8 ± 5.1	96.3 ± 4.7	92.7 ± 2.5
PU2	origin	1.16 ± 0.28	9.91 ± 1.62	318.5 ± 21.5
	8 h	1.13 ± 0.17	7.78 ± 2.74	319.9 ± 17.8
	η (%)	97.4 ± 11	78.6 ± 29.1	100 ± 6.3
PU3	origin	1.85 ± 0.23	24.2 ± 2.55	290.6 ± 10.3
	8 h	1.51 ± 0.21	22.3 ± 2.31	258.7 ± 8.8
	η (%)	81.1 ± 11.8	92.1 ± 8.8	89.1 ± 2.95
PU4	origin	2.55 ± 0.27	42.3 ± 2.11	268.4 ± 28.8
	8 h	1.41 ± 0.18	38.0 ± 4.02	96.1 ± 21.5
	η (%)	55.2 ± 6.9	89.8 ± 9.5	36.3 ± 7.5

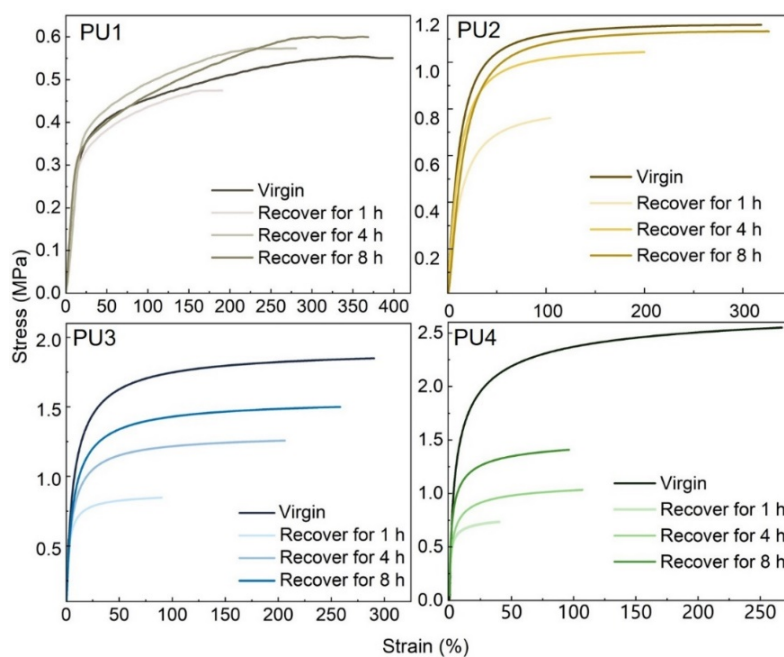


Figure S5. The stress-strain curves for PU in original state and heated at 60 °C with different time;

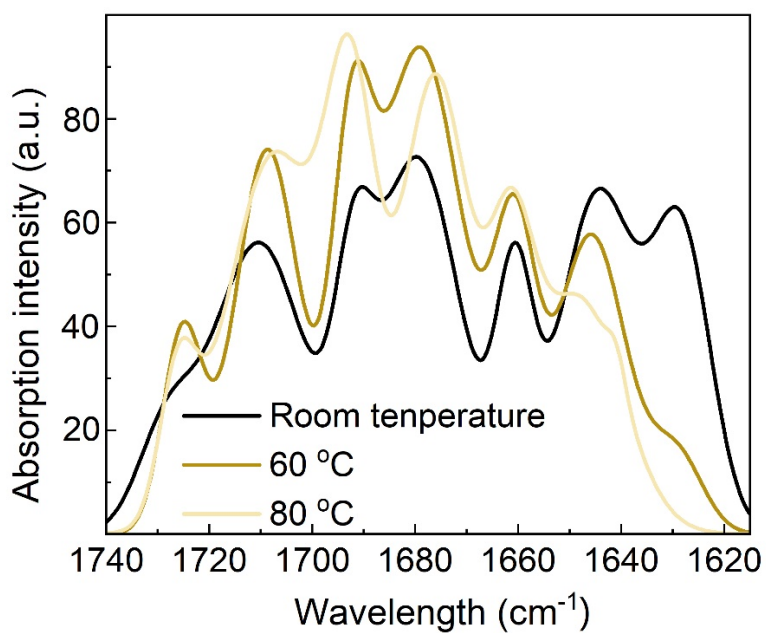


Figure S6. In situ variable temperature infrared of PU2 at 25 °C, 60 °C and 80 °C

Table S6. Summary of the assignment of the deconvoluted subpeaks in the FTIR -C=O absorption bands for the PU3.

Assignment		Wavenumber (cm ⁻¹)			Area (%)		
		25°C	60°C	80°C	25°C	60°C	80°C
(C=O) urea amide	Free	1722	1723	1724	2.6	2.9	4.4
	H-bonded (disorder)	1689	1690	1690	10.1	11.8	19.3
	H-bonded (disorder)	1676	1676	1677	7.7	11.8	3.4
	H-bonded (disorder)	1653	1655	1656	29.9	23.3	52.6
	H-bonded (Order)	1636	1639	1641	29.2	31.4	6.1
(C=O) amide	Free	1709	1708	1707	5.5	9.1	13.0
	H-bonded (Order)	1626	1627	1629	14.9	9.6	1.3

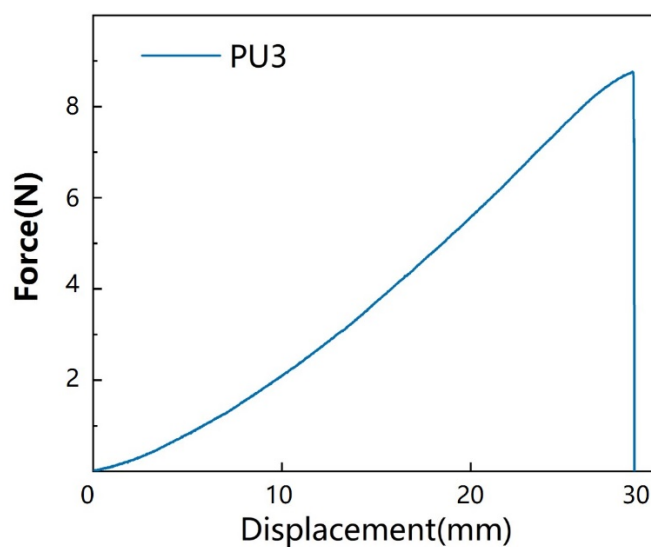


Figure S7. Puncture force of PU3

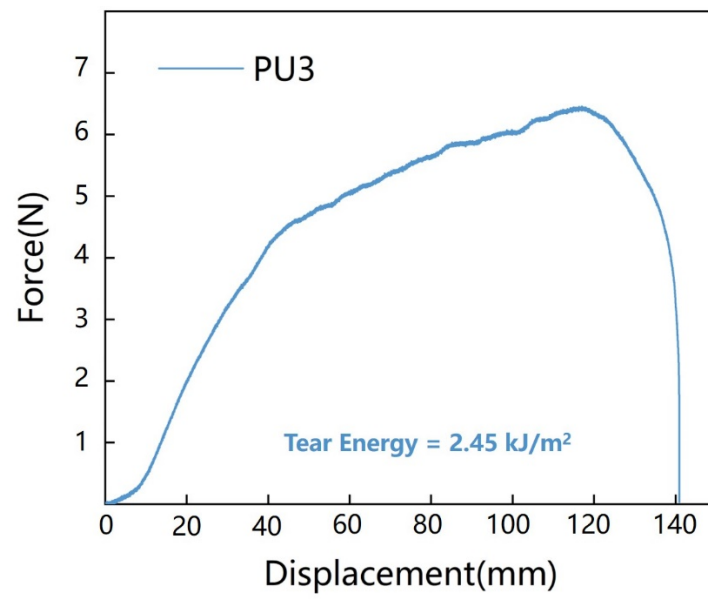


Figure S8. Tear energy of PU3