ADVANCED MATERIALS

Supporting Information

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Malleable and Recyclable Poly(urea-urethane) Thermosets bearing Hindered Urea Bonds

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Malleable and Recyclable Poly(urea-urethane)Thermoset via Hindered Urea Bond

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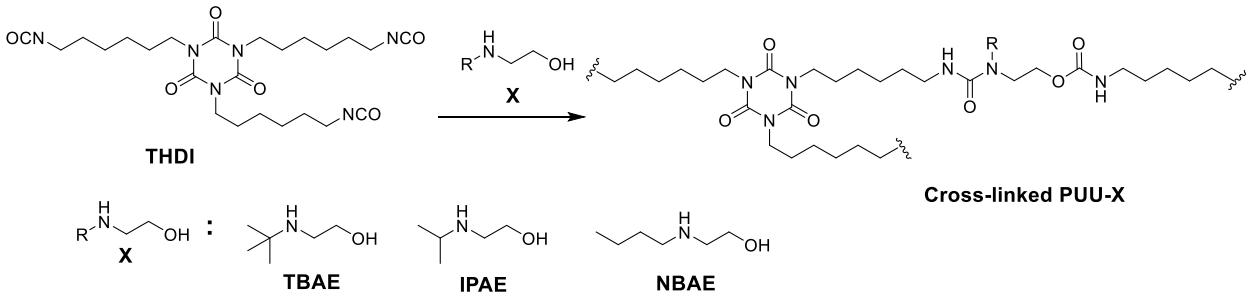
Experimental section

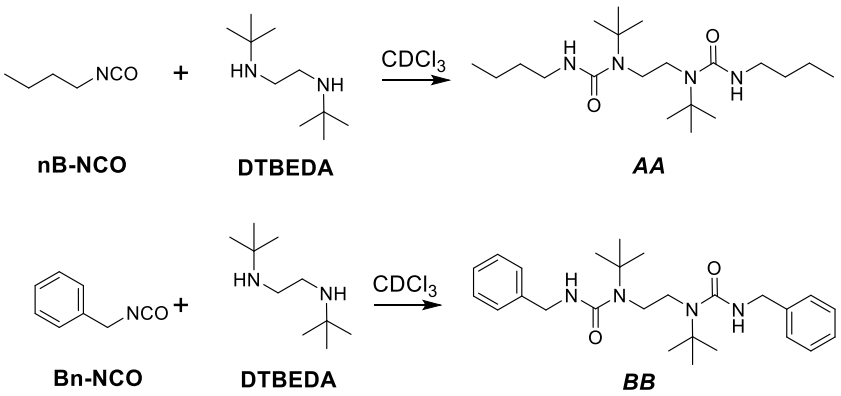


Scheme S1. Chemical route for preparation of PUU-TBAE, PUU-IPAE, and PUU-NBAE thermosets.

Synthesis of PUU-TBAE. TBAE (10.0 g, 85.5 mmol) and THDI (28.1 g, 55.9 mmol) were mixed in 50 mL centrifuge tube and heated up to 60 ºC. After the dispersion turned to homogeneous and viscous solution, DBTDL (100 μL, 0.17 mmol) was added into the mixture. Then the mixture was incubated at 60 ºC for 12 h, and then cooled down to room temperature. The bulk materials were subsequently ground into fine powders by pulverization machine (38.1 g, yield 100%). ^{13}C NMR ($CDCl_3$, 500 MHz): δ 158.7, 149.6, 64.9, 56.4, 43.5, 30.1, 27.4.

0.1 wt% Rhodamine 6G was added in the synthesis of stained PUU-TBAE sample.

PUU-IPAE and PUU-NBAE were synthesized with the same procedure except for the different amine monomers used (IPAE and NBAE instead of TBAE, Scheme S1).



Scheme S2. Synthesis of model compounds AA and BB.

Synthesis of model compounds AA and BB. The model compounds AA and BB were synthesized by mixing n-butyl isocyanate (or benzyl isocyanate, 1 mmol) and *N, N'*-di-tert-butylethylenediamine (DTBEDA, 0.5 mmol) in $CDCl_3$ (1 mL). The mixtures were stirred at room temperature for 2 h then diluted with $CDCl_3$ for NMR and ESI-MS analysis. Compound AA: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.97 (q, J = 5.3 Hz, 2H), 3.35 – 3.17 (m, 8H), 1.58 – 1.46 (m, 4H), 1.47 – 1.31 (m, 18H), 0.99 – 0.89 (m, 6H). ^{13}C NMR ($CDCl_3$, 500 MHz): δ 160.3, 77.6, 77.3, 55.1, 47.3, 40.7, 32.4, 29.8, 20.4, 14.0. ESI-MS (low resolution, positive mode): calculated for $C_{20}H_{43}N_4O_2$, *m/z*, 371.3 $[M + H]^+$; found 371.6 $[M + H]^+$.

Compound BB: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.42 – 7.21 (m, 10H), 6.35 (q, *J* = 7.2, 5.7 Hz, 2H), 4.37 (t, *J* = 5.9 Hz, 4H), 3.41 – 3.32 (m, 4H), 1.52 – 1.33 (m, 18H). ^{13}C NMR ($CDCl_3$, 500 MHz): δ 160.1, 140.1, 128.6, 128.0, 127.2, 77.7, 77.4, 55.4, 47.5, 44.9, 29.7. ESI-MS (low resolution, positive mode): calculated for $C_{26}H_{39}N_4O_2$, *m/z*, 439.3 $[M + H]^+$; found 439.5 $[M + H]^+$.

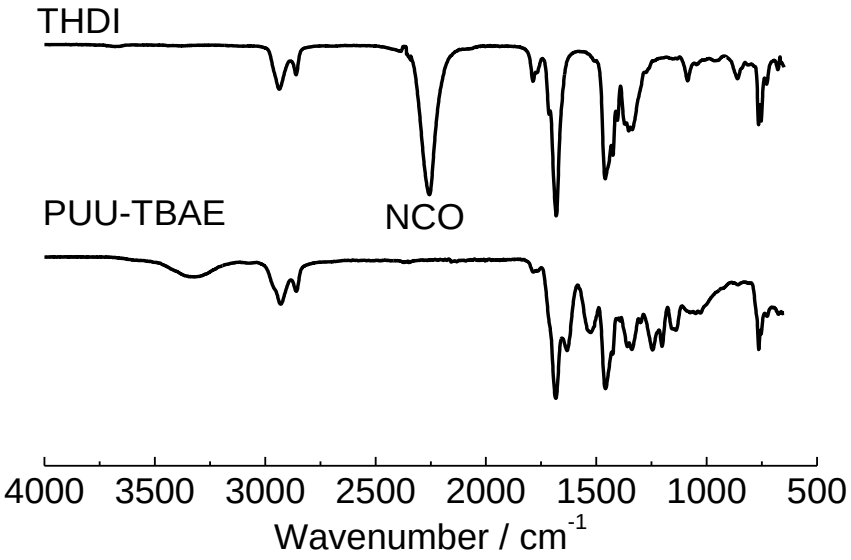


Figure S1. ATR FT-IR spectra of THDI and PUU-TBAE.

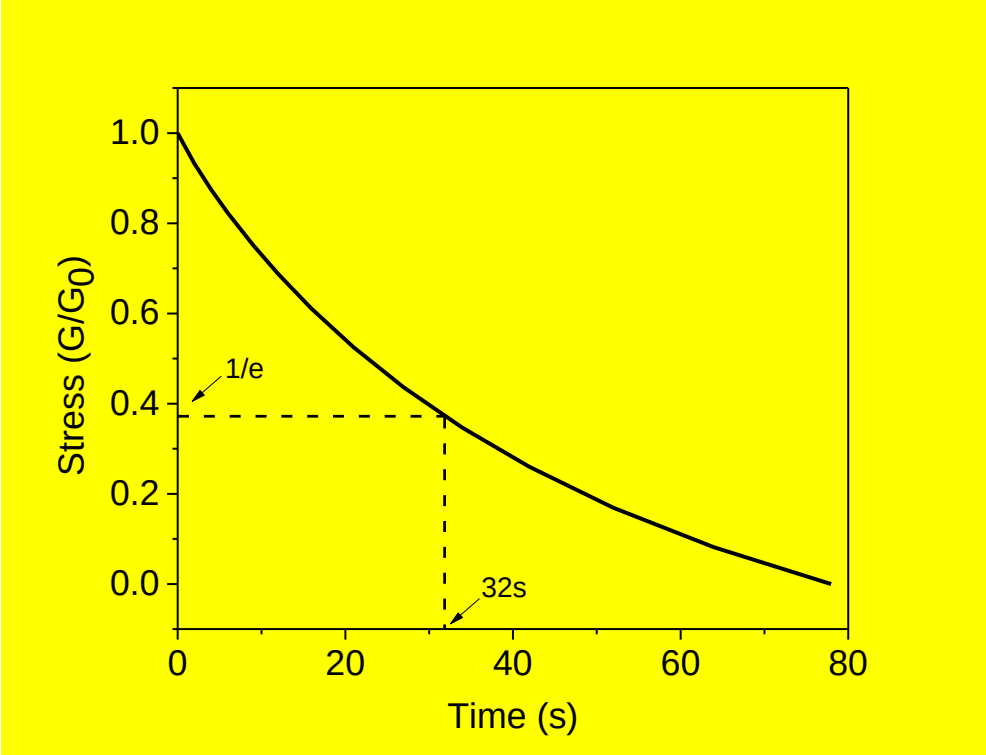
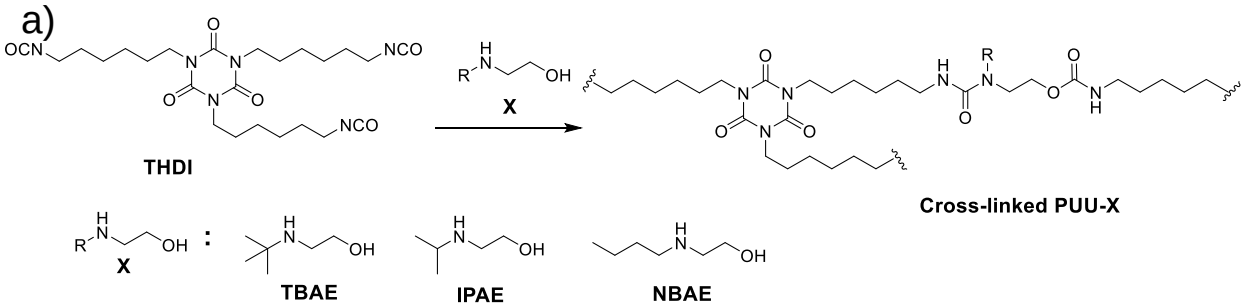


Figure S2. Stress-relaxation curve of PUU-TBAE at 100 ºC (strain = 5%, the characteristic relaxation time was calculated as 32 s)

a)



b)

Sample	**X**	Ration of **X**/THDI	Temperature (^{o}C)	Time (h)	T_g (^{o}C)
PUU-TBAE	TBAE	1.1/0.67	60	12	53
PUU-IPAE	IPAE	1.1/0.67	60	12	45
PUU-NBAE	NBAE	1.1/0.67	60	12	61

Figure S3. (a) Synthetic routes of PUUs thermosets. (b) Synthetic conditions and T_g characterizations of PUUs thermosets.

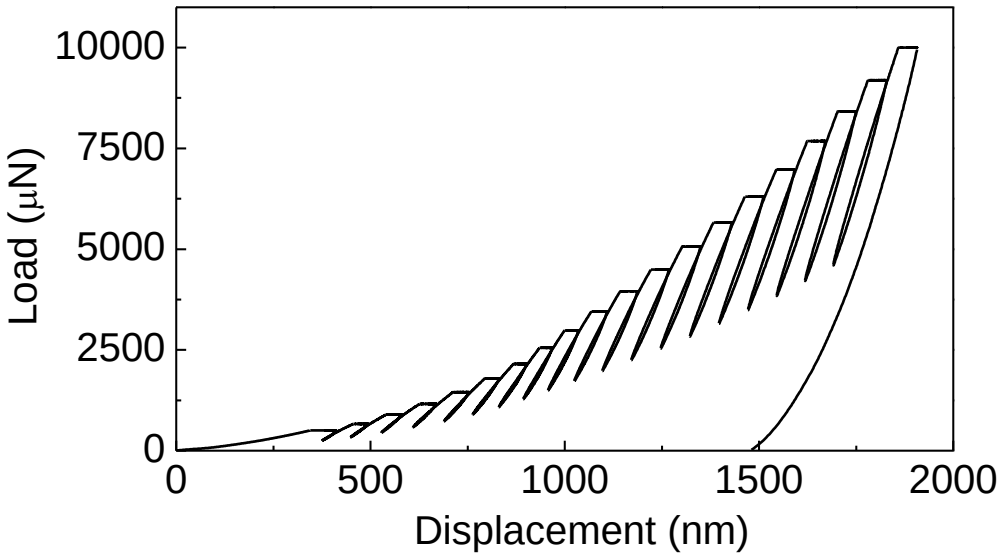
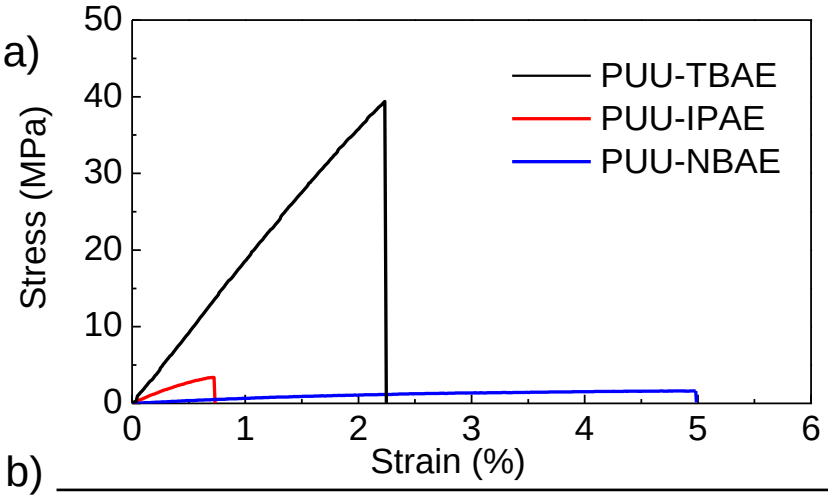


Figure S4. Force vs. displacement curves for PUU-TBAE films.

a)



b)

Sample	Modulus (GPa)	Breaking Strength (MPa)
PUU-TBAE	1.87 ± 0.32	39.5 ± 9.3
PUU-IPAE	0.58 ± 0.15	3.4 ± 2.1
PUU-NBAE	0.07 ± 0.02	1.8 ± 0.6

Figure S5. (a) Stress–strain curves for the dog bone shaped PUU-TBAE, PUU-IPAE, and PUU-NBAE samples after remolded via hot press (100 ^{o}C, 300 kPa for 20 min). (b) The Young's modulus and breaking strength of dog bone shaped PUU-TBAE, PUU-IPAE, and PUU-NBAE solid after processing.

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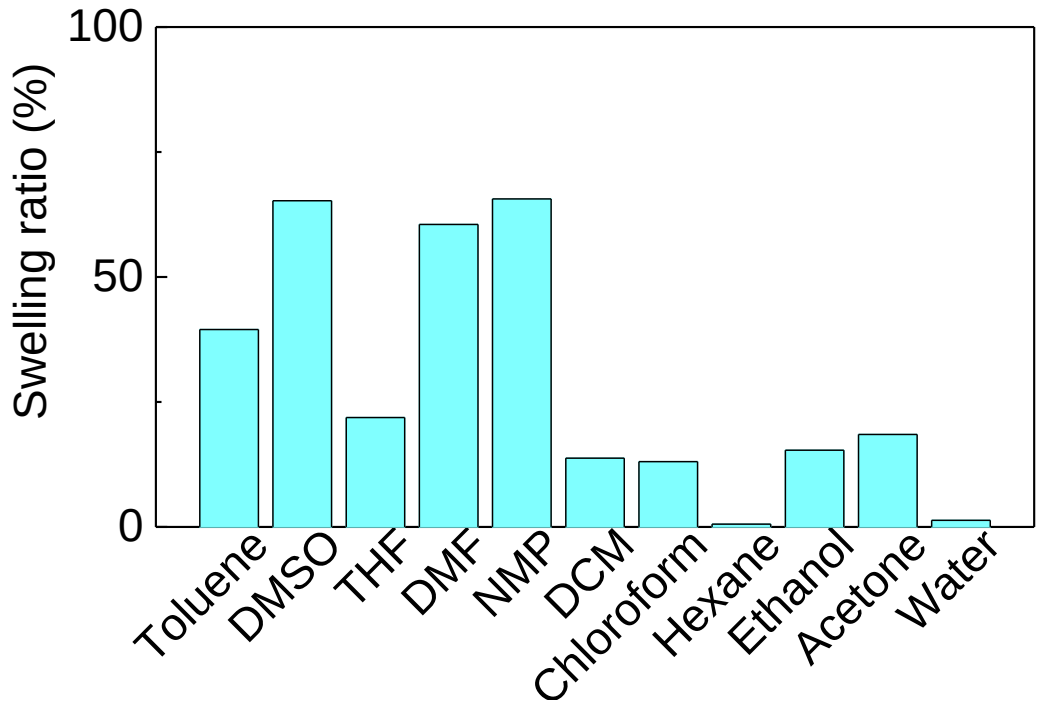

Figure S6. Swelling ratios of PUU-TBAE thermoset in different solvents for 48 h at room temperature.

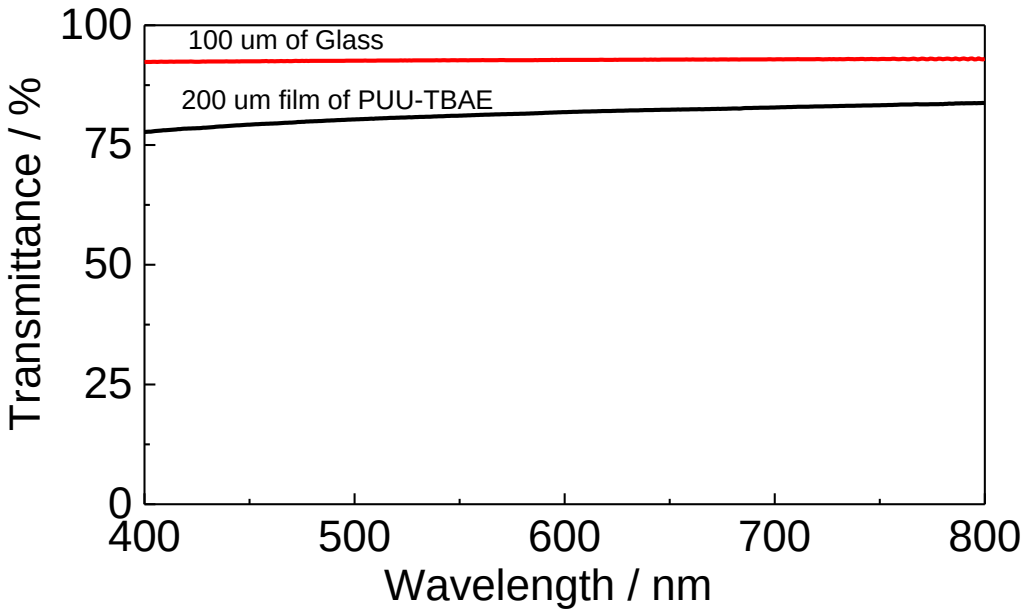

Figure S7. The UV-Vis absorption spectra of glass and PUU-TBAE films.

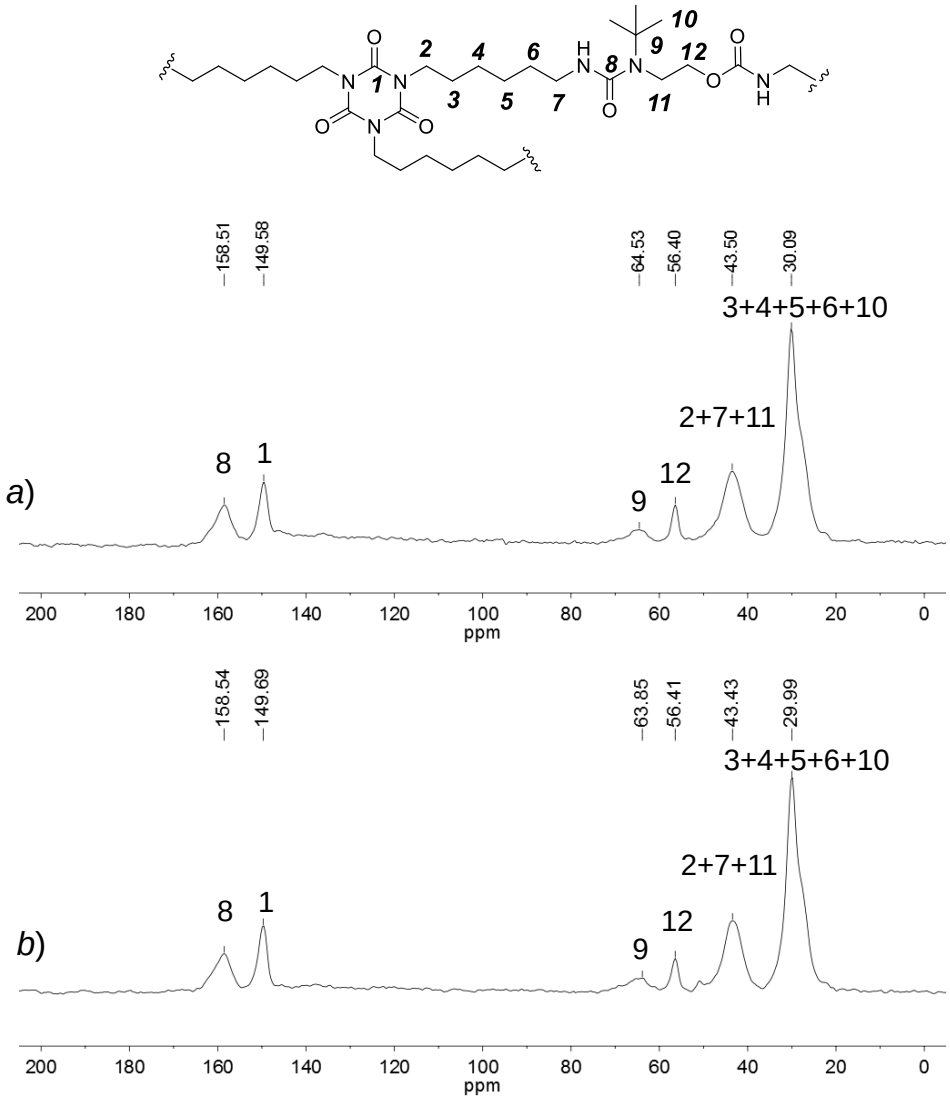

Figure S8. Solid ^{13}C NMR spectra of PUU-TBAE as prepared (a) and after 5 generations of hot press.

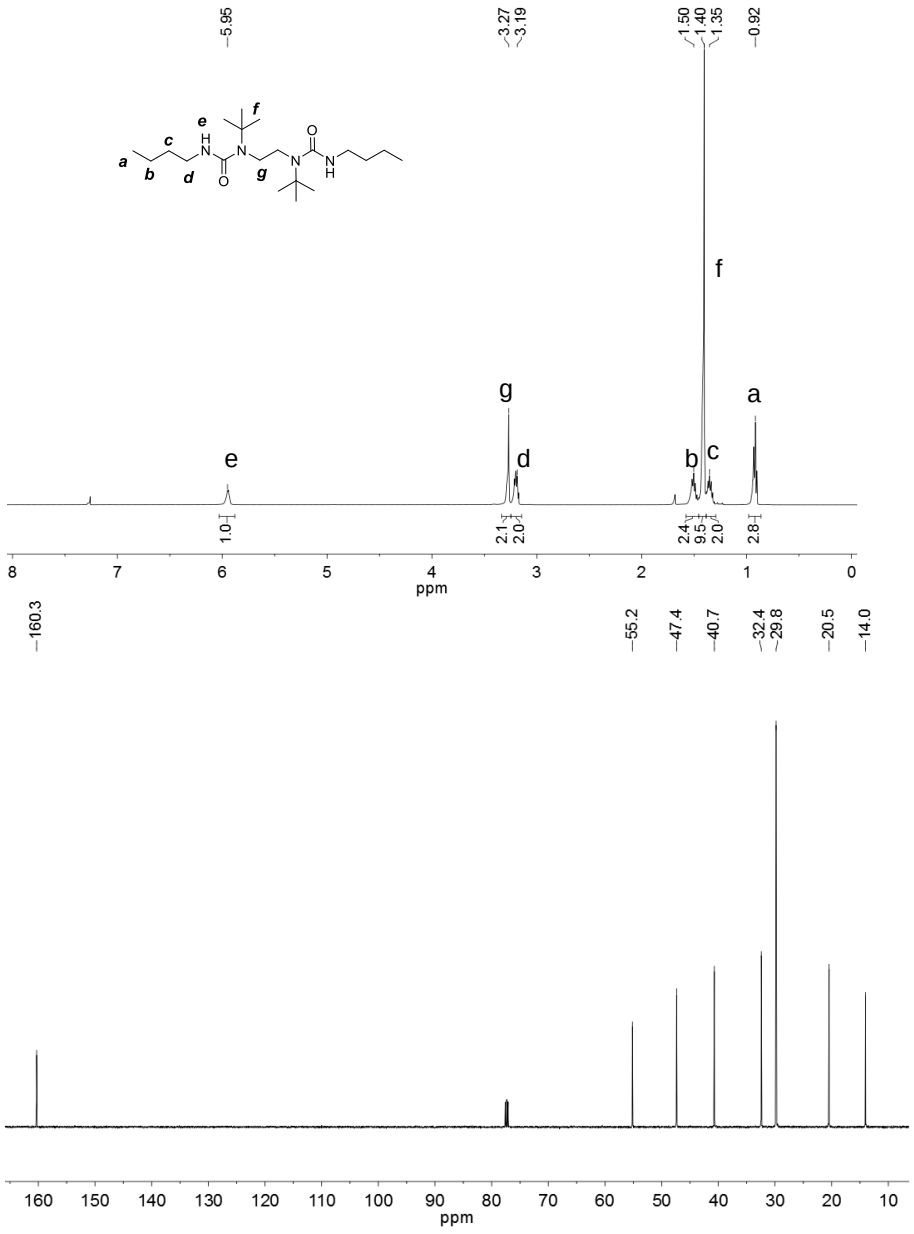

Figure S9. ^{1}H and ^{13}C NMR spectra of model compound AA.

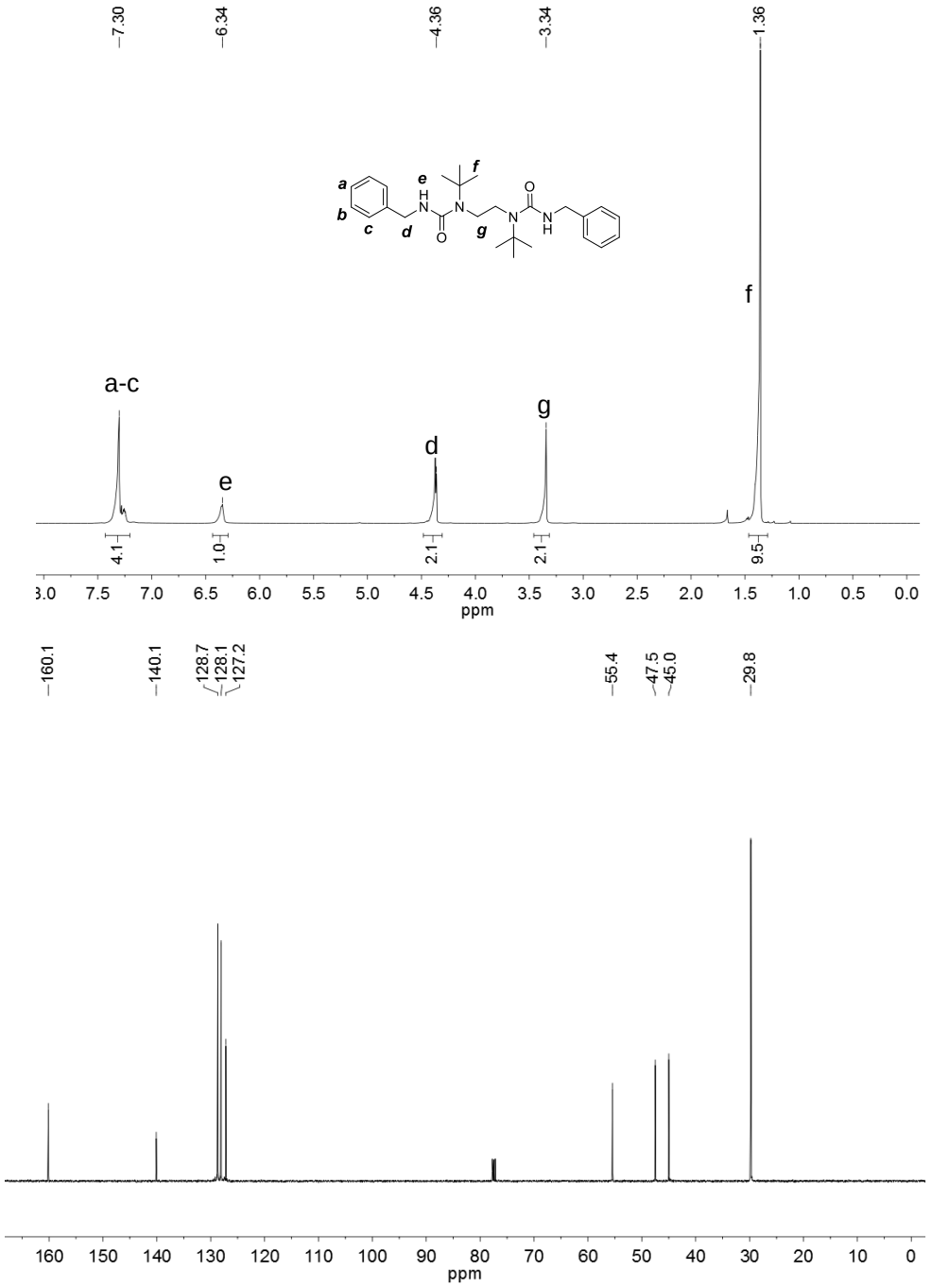

Figure S10. ^{1}H and ^{13}C NMR spectra of model compound BB.

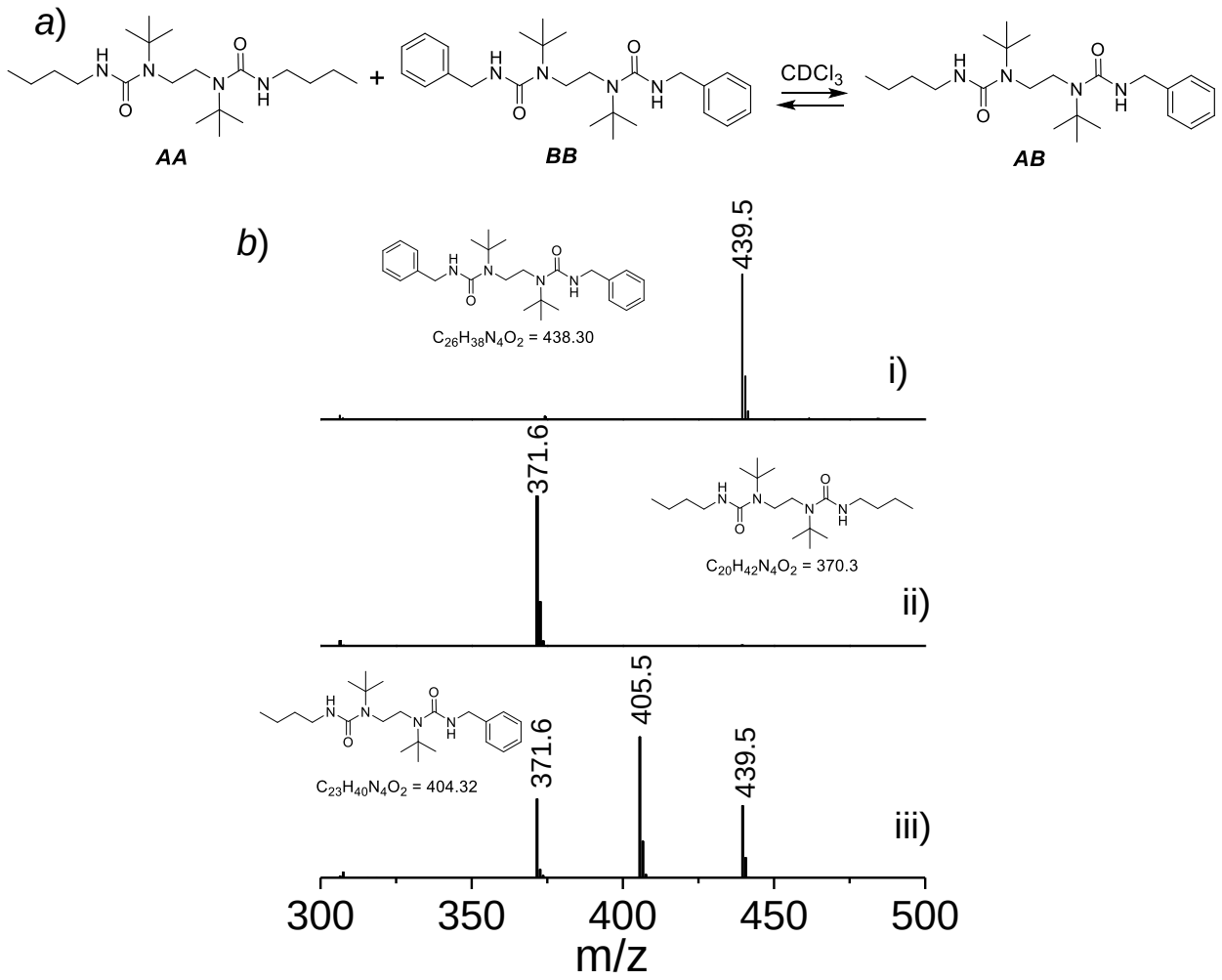

Figure S11. (a) Chemical structures of model compounds (AA, BB, and AB). (b) ESI-MS spectra of AA (i) BB (ii) and a mixture of AA and BB (iii) at 60 ^{o}C for 24 h.

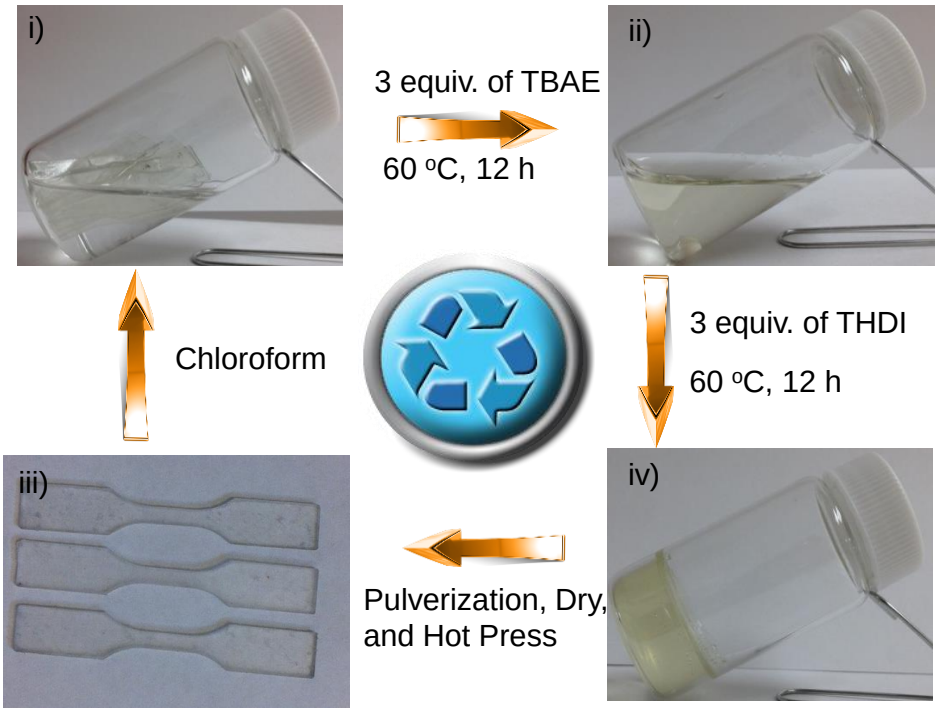

Figure S12. Recycling of PUU-TBAE thermoset. (a) Chemical route for dissolve the cross-linked PUU-TBAE thermoset by adding of access of TBAE and reform the cross-linked PUU-TBAE thermoset by adding of THDI. (b) the processing of recycling of PUU-TBAE thermoset by chemical and physical treatments. (i) PUU-TBAE thermoset in chloroform; (ii) PUU-TBAE thermoset was dissolved in chloroform by adding of 3 equiv. of TBAE at 60 °C for 12 h. (iii) PUU-TBAE based organogel was formed by adding of 3 equiv. of THDI at 60 °C for 12 h. (iv) Dog bone shaped solids were prepared via heat press of dry powders from PUU-TBAE based organogel after pulverization and vacuum-dry treatment.

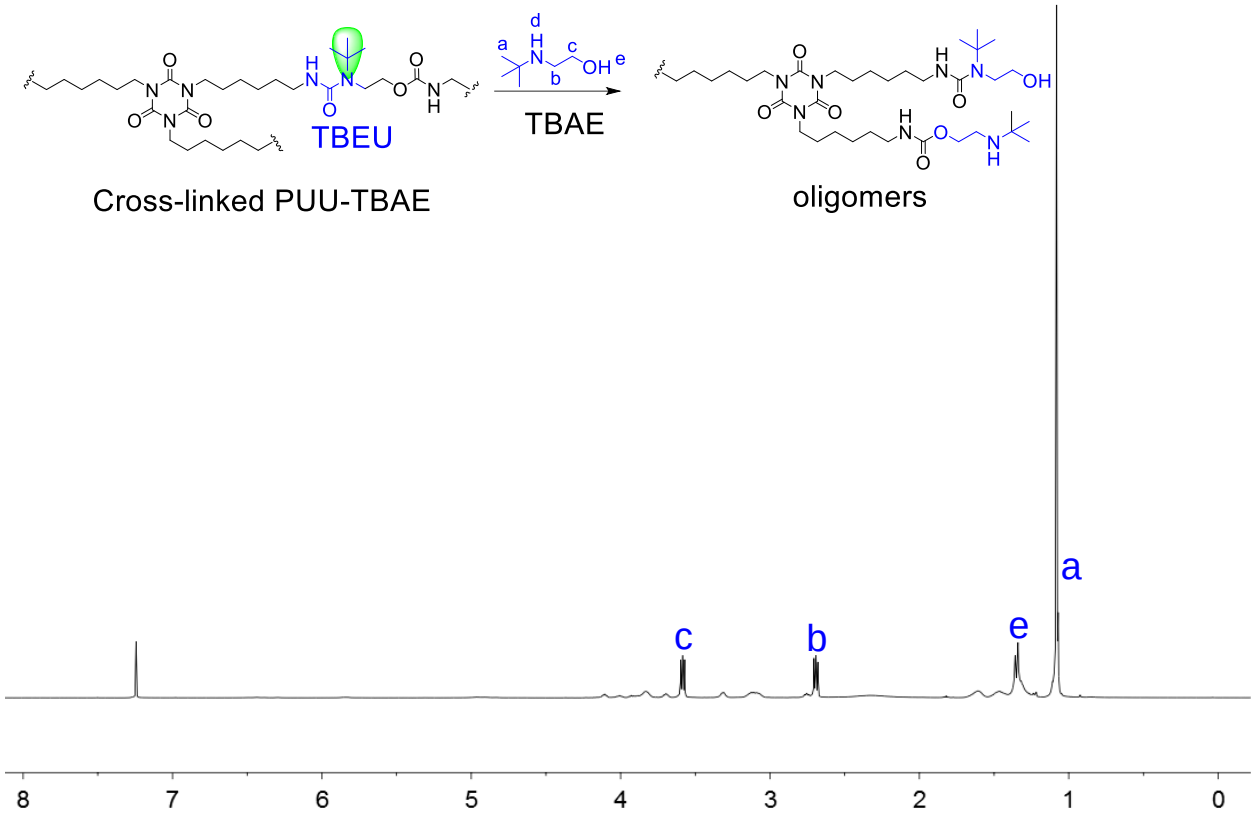

Figure S13. ^{1}H NMR spectrum of $CDCl_3$ solution with dissolved PUU-TBAE in 3 equiv. of TBAE. Sharp and labeled peaks were assigned to the excess TBAE, and the broad peaks were oligomers mixture from degraded PUU-TBAE.

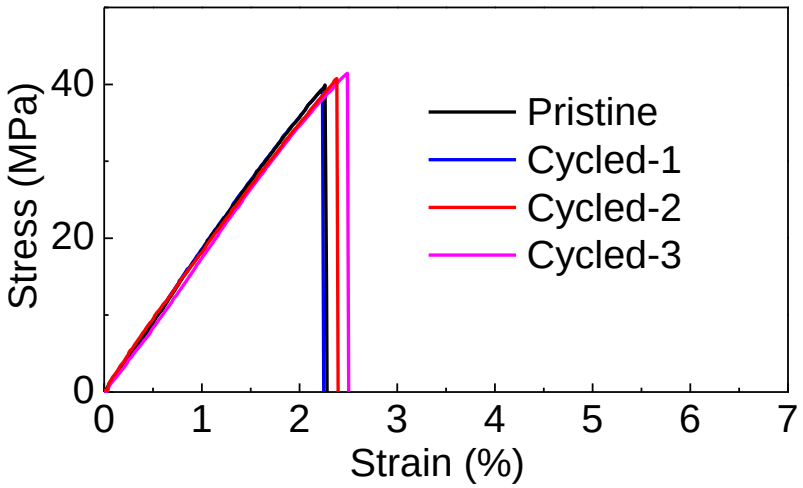

Figure S14. Tensile stress–strain curves for the pristine and recycled dog bone shaped PUU-TBAE samples.

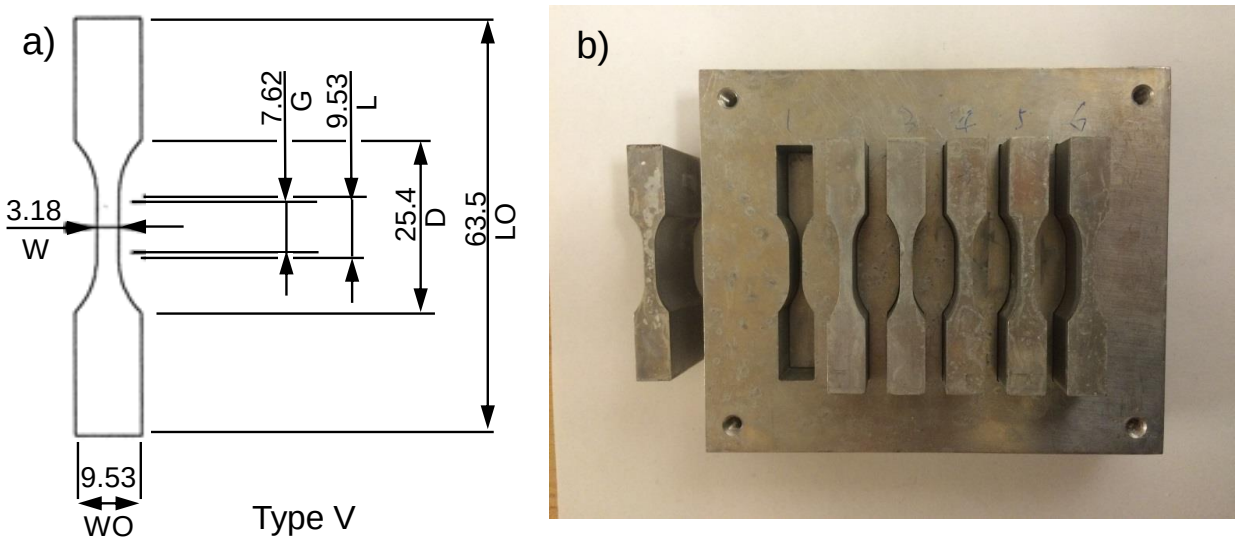

Figure S15. (a) Geometry of Type V standard dog-bone shaped sample. All dimensions in mm. (b) The aluminum mold for preparation of Type V standard dog-bone shaped samples via hot-press processing.

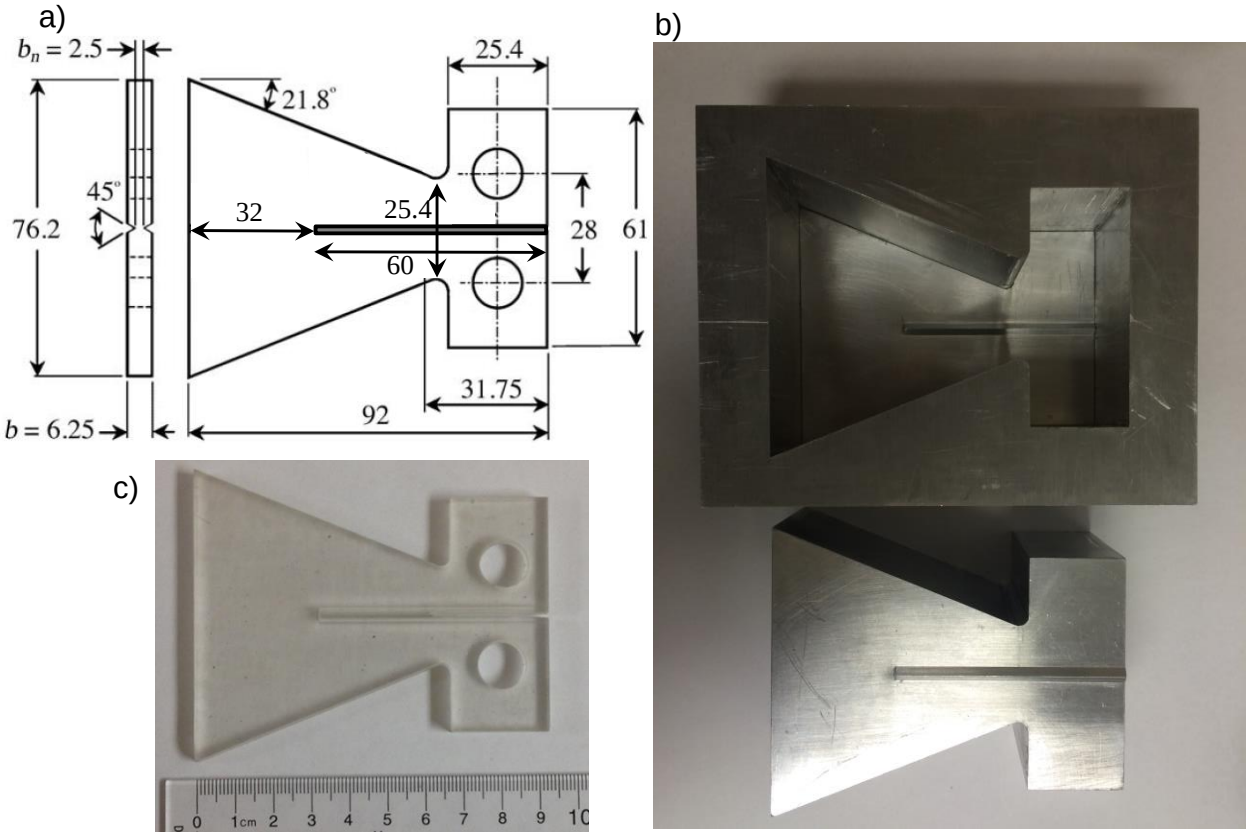

Figure S16. (a) Geometry of Tapered-double-cantilever-beam (TDCB) sample. All dimensions in mm. (b) The aluminum mold for preparation of TDCB shaped samples via hot-press processing. (c) An example of TDCB shaped sample of PUU-TBAE via hot-press processing.