Supporting Information

A self-healing and recyclable polyurethane-urea Diels-Alder adduct synthesized from carbon dioxide and furfuryl amine

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Synthesis of diglycidyl furfuryl amine (DGFA)

Diglycidyl furfuryl amine was synthesized according to reported procedures.[1] The detailed experiment process was as follows: epichlorohydrin (40 g, 0.4324 mol) and tetrabutylammonium bromide 3.5 g were placed into a 500 mL round-bottom flask in an ice bath, and then furfuryl amine (20 g, 0.2062 mol) was slowly added dropwise while stirring. The reaction was continued for 12 h at room temperature. After the reaction, 60 mL of aqueous sodium hydroxide (40% w/w) was poured into the reaction mixture and it was stirred at room temperature for 4 h. Finally, the product was extracted with ethyl acetate (200 ml) and washed with water three times. The organic layer was collected, dried with magnesium sulfate, and ethyl acetate was removed using a rotary evaporator. The crude product so obtained was purified by distillation. The final product diglycidyl furfuryl amine (DGFA), a yellow liquid, was obtained with a total yield of 50% based on furfuryl amine.
^{1}H NMR (400 MHz, Chloroform-d) δ 7.29 (d, J = 2.2 Hz, 1H), 6.24 (dd, J = 3.4, 1.8 Hz, 1H), 6.16 (d, J = 3.2 Hz, 1H), 3.88 (dd, J = 14.9, 2.4 Hz, 1H), 3.79 (s, 1H), 3.74 – 3.65 (m, 1H), 3.03 (dh, J = 6.6, 3.2 Hz, 2H), 2.96 (dd, J = 13.8, 3.0 Hz, 1H), 2.83 (dd, J = 14.0, 3.5 Hz, 1H), 2.69 (t, J = 4.6 Hz, 2H), 2.55 (dd, J = 13.9, 6.4 Hz, 1H), 2.44 (ddd, J = 8.0, 5.0, 2.7 Hz, 2H), 2.31 (dd, J = 13.9, 6.8 Hz, 1H).

Synthesis of bis(cyclic carbonate) furfuryl amine (BCCFA)

Bis(cyclic carbonate) furfuryl amine was synthesized according to reported procedures.[1] The detailed experiment process was as follows: diglycidyl furfuryl amine (10.45 g, 0.05 mol), lithium bromide 0.217 g and DMF 30 mL were poured into a 50 mL stainless-steel autoclave and it was sealed and purged with N_2 three times to remove air. Then, the autoclave was heated to 100 ºC and CO_2 was introduced up to 5 MPa. The reaction was run at a stirring speed of 800 rpm for 4 h. After the reaction was finished, the autoclave was cooled to ambient temperature and CO_2 was vented slowly. DMF was removed by distillation under vacuum and the product was extracted with ethyl acetate (100 ml) and washed with water three times to remove lithium bromide. The organic layer was then collected, dried with magnesium sulfate, and ethyl acetate was removed using a rotary evaporator. A dark viscous liquid bis(cyclic carbonate) furfuryl amine (BCCFA) was obtained with a 95% yield based on diglycidyl furfuryl amine.
^{1}H NMR (400 MHz, Chloroform-d) δ 7.32 (d, J = 1.8 Hz, 1H), 6.27 (t, J = 2.5 Hz, 1H), 6.19 (d, J = 3.2 Hz, 1H), 4.70 (ttd, J = 7.9, 5.1, 2.8 Hz, 2H), 4.42 (td, J = 8.4, 2.3 Hz, 2H), 4.05 (ddd, J = 8.7, 7.1, 5.6 Hz, 2H), 3.82 – 3.68 (m, 2H), 2.89 (q, J = 4.3, 3.3 Hz, 4H).

Table S1 List of abbreviations used in this work.

Chemical, Compound, Material	Abbreviation
4,7,10-Trioxa-1,13-tridecanediamine	TTD
Epichlorohydrin	ECH
Tetrabutylammonium bromide	TBAB
Lithium bromide	LiBr
4,4-Bismaleimidodiphenylmethane	BIM
Poly(propylene glycol) bis(2-aminopropyl ether)	PEA
N,N-Dimethylformamide	DMF
Furfuryl amine	FA
Diglycidyl furfuryl amine	DGFA
Bis(cyclic carbonate) furfuryl amine	BCCFA
Oligourea	OUa
Polyurea	PUa
Polyurethane-urea	PUUa
Polyurethane-urea Diels-Alder adduct	PUUa-DA
Poly(propylene glycol) bis(2-aminopropyl ether) Diels-Alder adduct	PEA-DA
4,7,10-Trioxa-1,13-tridecanediamine Diels-Alder adduct	TTD-DA

Table S2 Thermal properties determined by DSC, TGA.

Entry	Sample[a)]	DSC				TGA
		T_{m1} (ºC)[b)]	T_{m2} (ºC)[b)]	T_c (ºC)[b)]	T_g (ºC)[b)]	$T_{d,5\%}$ (ºC)[c)]
1	OUa	79	107	55	-26	221
2	PUa	90	116	54	-20	292
3	PUUa	84	102	--	-14	225
4	PUUa-DA	--	--	--	-8	226
5	PUUa-DA [d)]	66	80	/	--	226
6	TTD-DA	/	/	/	/	100
7	PEA-DA	--	--	--	--	273

[a)] Heating/cooling/heating thermal cycles at 10 ºC/min, values determined from second heating scans to eliminate heating history. The abbreviations are listed in Table S1 [b)] T_{m1} and T_{m2} are melting temperature and T_g is glass transition temperature, which are measured as the peak temperature in the endotherm. T_c is crystallization temperature measured as the peak temperature in the exotherm. [c)] $T_{d,5\%}$ is the initial decomposition temperature (the temperature of 5% weight loss). [d)] Values determined from first heating scans. -- Not detected, / Not tested.

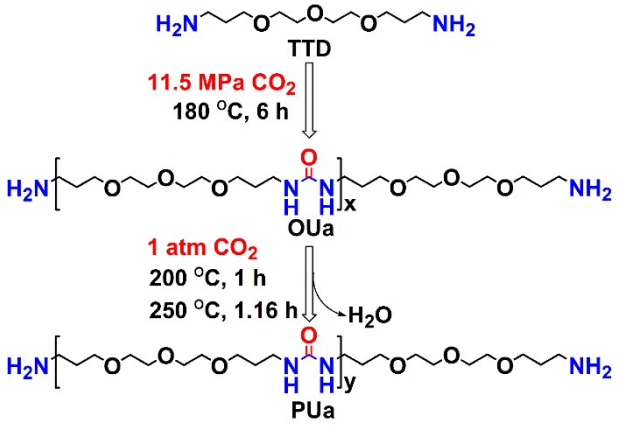
Table S3 Mechanical properties of polyurea (PUa), polyurethane urea (PUUa), polyurethane-urea Diels-Alder adduct (PUUa-DA) and poly(propylene glycol) bis(2-aminopropyl ether) Diels-Alder adduct (PEA-DA).

Sample	Tensile stress (MPa)	Elongation at break (%)	Young's modulus (MPa)
PUa	15.2 ± 1.0	3.4 ± 0.4	527 ± 57
PUUa	15.9 ± 0.3	46 ± 8	206 ± 8
PUUa-DA	18.5 ± 0.9	136 ± 20	151 ± 5
PEA-DA	0.085 ± 0.015	58 ± 5	0.21 ± 0.02

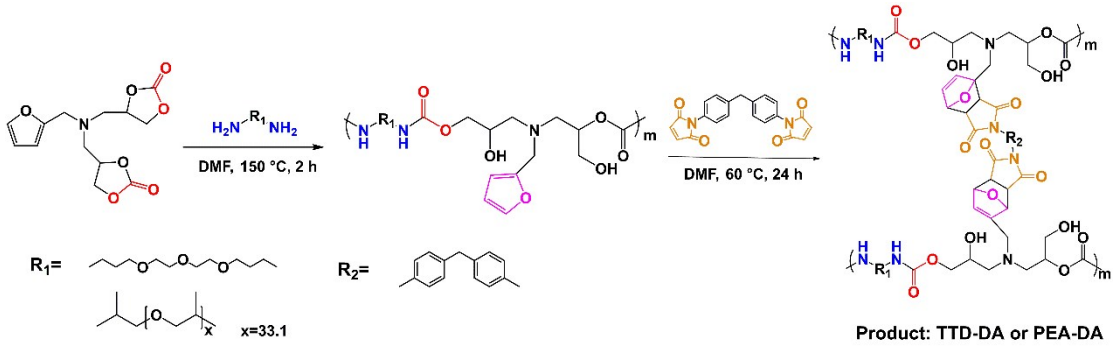
Table S4 Mechanical properties and healing efficiency of polyurethane-urea Diels-Alder adduct (PUUa-DA) and healed PUUa-DA.

Healed conditions	Tensile stress (MPa)	Elongation at break (%)	Toughness (MJ/m^{-3})	Healing efficiency [a] (%)
Original specimen	18.5 ± 0.9	136 ± 20	21.1 ± 3.9	/
120 ºC, 10 min; 60 ºC, 24 h	16.6 ± 0.3	140 ± 22	19.9 ± 2.5	94
60 ºC, 24 h	11.7 ± 0.9	88 ± 14	8.3 ± 1.7	39
120 ºC, 10 min	17.5 ± 0.3	27 ± 0.1	4.9 ± 0.1	23

[a] The healing efficiency was calculated by the ratio of the toughness of the healed specimen against the original one.



Scheme S1 Synthesis of non-isocyanate oligourea (OUa) and polyurea (PUa) from CO_2.



Scheme S2 Synthesis of 4,7,10-Trioxa-1,13-tridecanediamine Diels-Alder adduct (TTD-DA) and poly(propylene glycol) bis(2-aminopropyl ether) Diels-Alder adduct (PEA-DA).

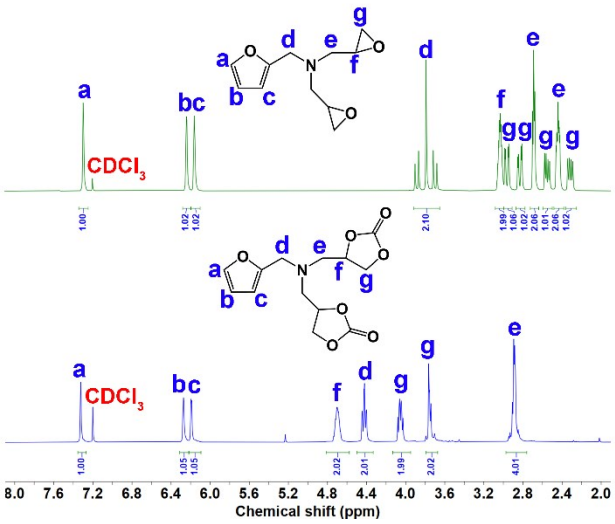


Fig. S1 ^{1}H NMR of diglycidyl furfuryl amine (DGFA) (top), bis(cyclic carbonate) furfuryl amine (BCCFA) (bottom).

The signals of protons between 2.3 and 3.1 ppm ascribed to DGFA oxirane groups indicated DGFA was produced from furfurylamine, these signals disappeared after reacting with CO_2, and the signals at 4.7, 4.1, and 3.7 ppm ascribed to cyclic carbonate group appeared. Moreover, a signal at 7.4 ppm characterized a position proton of the furan ring, and the ratio between integrations of ***a*** and ***f*** position protons was 1:2, confirming that the difunctional cyclic carbonate group belonging to BCCFA was formed and the purity was good.

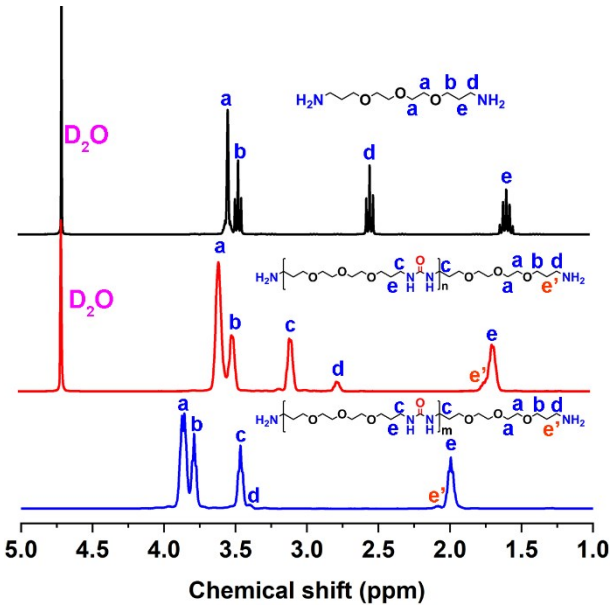


Fig. S2 ^{1}H NMR of 4,7,10-trioxa-1,13-tridecanediamine (top), oligourea (medium) and polyurea (bottom). 4,7,10-trioxa-1,13-tridecanediamine and oligourea were dissolved in D_2O and polyurea was dissolved in TFA-*d* for ^{1}H NMR measurement.

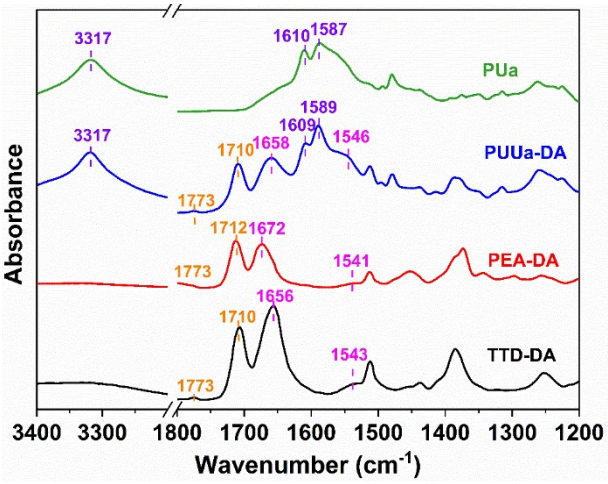


Fig. S3 FTIR spectra of polyurea (PUa), polyurethane-urea Diels-Alder adduct (PUUa-DA), poly(propylene glycol) bis(2-aminopropyl ether) Diels-Alder adduct (PEA-DA) and 4,7,10-Trioxa-1,13-tridecanediamine Diels-Alder adduct (TTD-DA).

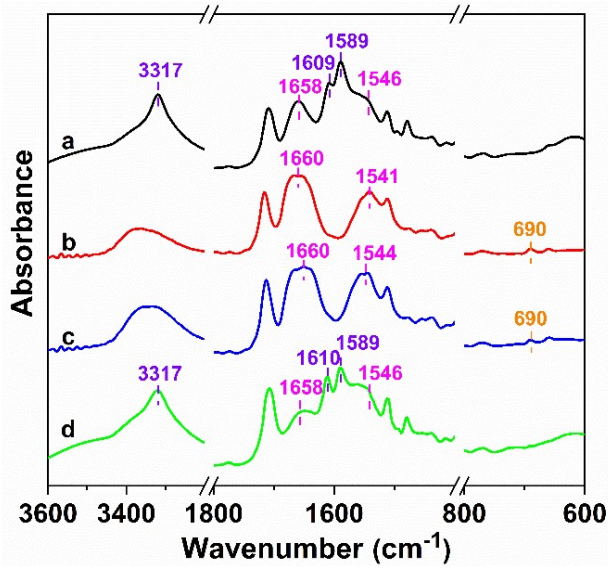


Fig. S4 FTIR spectra of polyurethane-urea Diels-Alder adduct (PUUa-DA) (a) at 30 ºC, (b) heating up to 120 ºC, (c) cooling down to 30 ºC and (d) cooling down to 30 ºC and then staying at 30 ºC for 24 h.

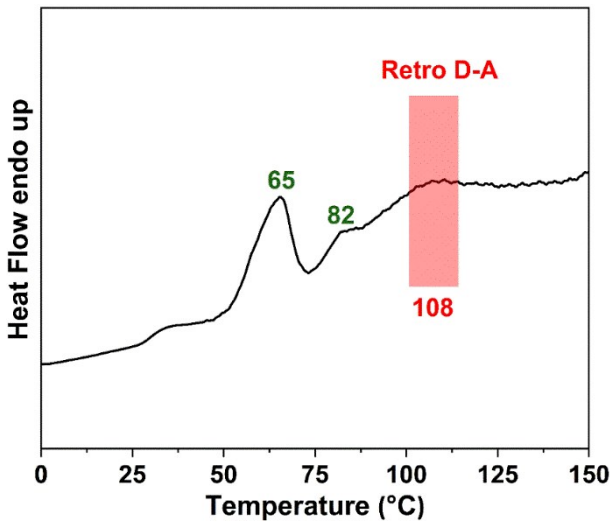


Fig. S5 DSC curve of polyurethane-urea Diels-Alder adduct (PUUa-DA) from first heating scan.

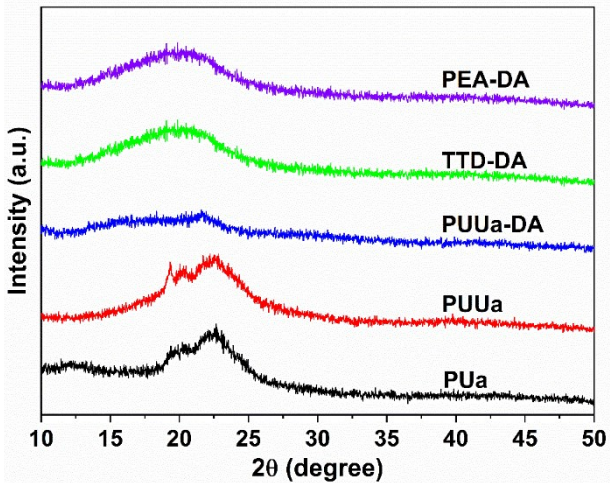


Fig. S6 XRD curves of polyurea (PUa), polyurethane-urea (PUUa), polyurethane-urea Diels-Alder adduct (PUUa-DA), 4,7,10-Trioxa-1,13-tridecanediamine Diels-Alder adduct (TTD-DA) and poly(propylene glycol) bis(2-aminopropyl ether) Diels-Alder adduct (PEA-DA).

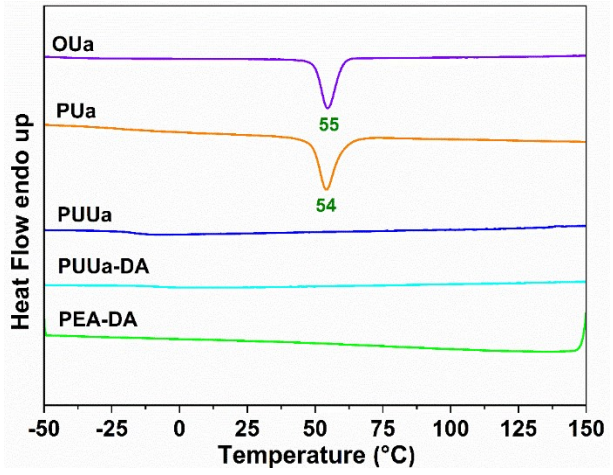
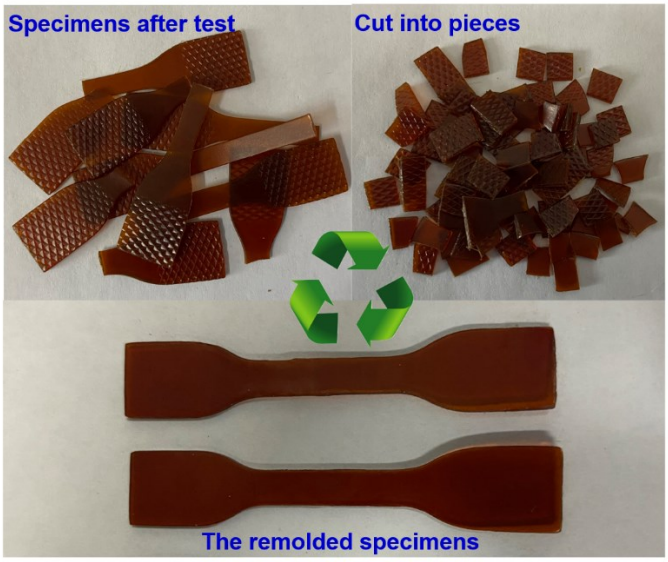


Fig. S7 DSC curves of oligourea (OUa), polyurea (PUa), polyurethane-urea (PUUa), polyurethane-urea Diels-Alder adduct (PUUa-DA) and poly(propylene glycol) bis(2-aminopropyl ether) Diels-Alder adduct (PEA-DA) from cooling scan.



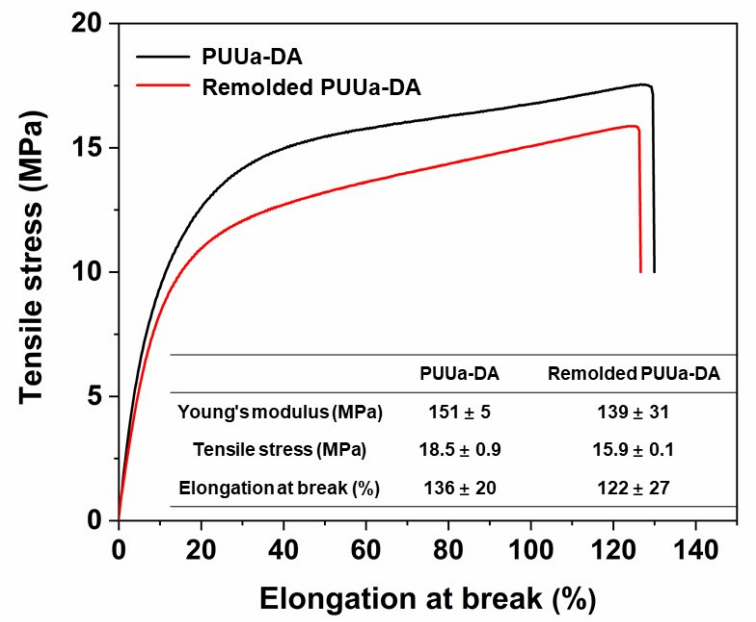


Fig. S8 Recyclability of polyurethane-urea Diels-Alder adduct (PUUa-DA) through the hot-press molding.

Reference

1 E. Dolci, V. Froidevaux, G. Michaud, F. Simon, R. Auvergne, S. Fouquay and S. Caillol, J. Appl. Polym. Sci., 2017, **134**, 44408.