

Supporting Information for

Natural-silk-inspired design provides ultra-tough biobased structural adhesives with supercold tolerance

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Experimental

Synthesis procedures of monomers. HD was synthesized from commercially available castor oil-derived methyl 10-undecenoate by the previously reported procedures. Briefly, HD (4.23 g, 10 mmol of hydroxyl units), succinic anhydride (1.2 g, 12 mmol), DMAP (0.04 g, 0.1 mmol), and anhydrous THF (10 mL) were placed into a 100-mL flame-dried round-bottom flask with stirring at 65 °C under an N₂ atmosphere. The reaction was continued for 24 h and then quenched using deionized water (2 mL) and THF (8 mL). After cooling the reaction solution, an appropriate amount of ultrapure water was added, followed by extraction with DCM five times (25 mL each time). The solution was diluted with DCM (25 mL) and washed thrice with aqueous solutions of NaHCO₃ and NaCl (25 mL each time), followed by drying overnight with anhydrous magnesium sulfate to obtain a white color solid MD monomer. BD was synthesized by following the same procedure of the synthesis of MD as depicted in the reaction scheme (**Fig. S1**). ¹H NMR spectra of all target products are given in **Fig. S3**.

Calculation of the actual molar fraction of MD. The actual molar fraction of MD in each component was obtained by integrating the characteristic peaks at 2.274 ppm, 3.742 ppm and 4.481 ppm in the ¹H NMR spectra of the copolymers (**Fig. S4**).

$$MD \text{ content} = \frac{I_{4.841} - I_{2.274}/2}{I_{4.841} + I_{3.742}} \quad \text{eq. S1}$$

Where, 4.841 ppm is attributed to the sum of -CH- beside the ester group in BD and MD, 3.742 ppm is attributed to -CH- beside the ester group in HD and 2.274 ppm is attributed to -CH₂- beside the ester group in BD.

Samples for peeling test. Peeling adhesive strength was performed on a SUNS UTM2502 electronic test instrument (SUNS, China) at a 180° peeling angle and 240 mm min⁻¹ speed under ambient conditions. Dry copolymer was first dissolved in anhydrous THF (5 wt%) and coated on a plasma-cleaned polyethylene terephthalate (PET) film. A 120 mm × 20 mm × 100 μm substrate was used for peel test of each sample. The sample was cured for 10 min at 20 °C and then tested with the universal testing machines. At least six measurements of testing were performed for each sample.

Table S1. Composition, number average molecular weight (M_n , GPC), polydispersity index (\mathcal{D}), glass transition temperature (T_g), and melting temperature (T_m) for cPAs copolymers.

Polymer	Monomer (HD:BD:MD) feed ratio (mol%)	Actual mole fraction of MD (%)	M_n (g mol ⁻¹)	T_g (°C)	T_m (°C)	
cPA0	40: 60: 0	-	37400	1.9	-6.7	94.5
cPA1	40: 55: 5	6.3	34700	1.8	-5.8	93.2
cPA2	40: 52: 8	8.4	40200	2.1	-6.6	92.1
cPA3	40: 45: 15	14.75	33500	1.9	-0.7	95.5
NE-cPA	40: 52: 8 ^{a)}	7.6	31800	1.9	-5.2	93.1

Note: polymerization of HD, BD, and MD with 1,8-octanedithiol in place of an ether-containing dithiol. The actual mole fraction of MD was determined by ¹H NMR.

Table S2. Mechanical properties of cPA0~3 and NE-cPA.

Entry	Tensile strength (MPa)	Strain (%)	Toughness (MJ m⁻³)
cPA0	20.5±0.3	660.4±11.1	112.1±2.6
cPA1	23.5±0.2	825.1±15.1	113.5±2.1
cPA2	27.2±0.1	819.2±6.8	128.8±1.9
cPA3	29.5±0.3	706.6±2.8	123.6±2.1
NE-cPA	25.9±0.5	745.2±14.7	113.8±2.9

Table S3. Mechanical properties of cPA2 and NE-cPA samples tested at different temperatures in air for 24 h.

Entry	temperature	Tensile strength (MPa)	Strain (%)	Toughness (MJ m⁻³)
cPA2	LN ^[a]	36.3±0.5	610.9±17.4	143.2±3.4
	-60 °C	33.5±0.7	668.1±12.9	122.0±2.7
	0 °C	29.4±0.2	833.9±5.7	127.2±2.9
	25 °C	27.2±0.1	819.2±6.8	128.8±1.9
NE-cPA	LN	29.3±0.6	309.4±18.6	61.8±4.5
	-60 °C	24.8±0.7	334.9±20.1	51.6±3.7
	0 °C	23.7±0.9	586.8±16.3	91.2±3.9
	25 °C	25.9±0.5	745.2±14.7	113.8±2.9

[a] “LN” means the operation in liquid nitrogen temperature (-196 °C).

Table S4. A rough comparison of the overall performance between this work and recently reported typical elastomeric adhesive materials.

Elastomeric adhesives	Adhesion strengths			Mechanical properties			Underwater adhesion stability (MPa)	Recyclability	Ref.
	RT (MPa)	LT (MPa)	Test method	Strength (MPa)	Strain (%)	Toughness (MJ m ⁻³)			
cPA	12.3	17.4 (LN)	lap-shear	27.2	819.2	128.8	5.8 (3 weeks)	10	This work
PFPU-1.5	-[a]	-	-	16	50	-	-	-	[S1]
polymeric ion liquids	5.3	4.8 (LN)	lap-shear	-	-	-	2.1 (2 weeks)	8	[S2]
PC ₁₀ -W ₁	2.3	1.2 (LN)	lap-shear	-	-	-	-	10	[S3]
polydisulfide-CNC	2.8	-	lap-shear	-	-	-	-	6	[S4]
DESPs	1.4	1.3 (-80 °C)	lap-shear	-	-	-	2.4	-	[S5]
fluorine-pIG	3.4	-	lap-shear	12.4	29	-	5.2	-	[S6]
LMWMs	4.2	1.0 (-18 °C)	lap-shear	-	-	-	3.2 (12 months)	10	[S7]
PEG-TA	8.8	1.1 (LN)	lap-shear	-	-	-	-	8	[S8]
TC7-water	4.2	2 (-20 °C)	Pull-off	-	-	-	-	10	[S9]
DESSs	4.4	1.5 (-80 °C)	Pull-off	-	-	-	2.2 (21 days)	-	[S10]
CEP144	22.3	21.5 (LN)	lap-shear	-	-	-	1.1 (1 hour)	-	[S11]

[a] “RT”, “LT”, and “LN” mean that tests were conducted at room temperatures (20–30 °C), low temperatures (below 20 °C), and liquid N₂ (-196 °C), respectively.

Macroscopic adhesion on the lap shear strength study using steel substrates. “-” means that data was not mentioned or tested. [b] Mechanical characterization of samples

at

110

°C.

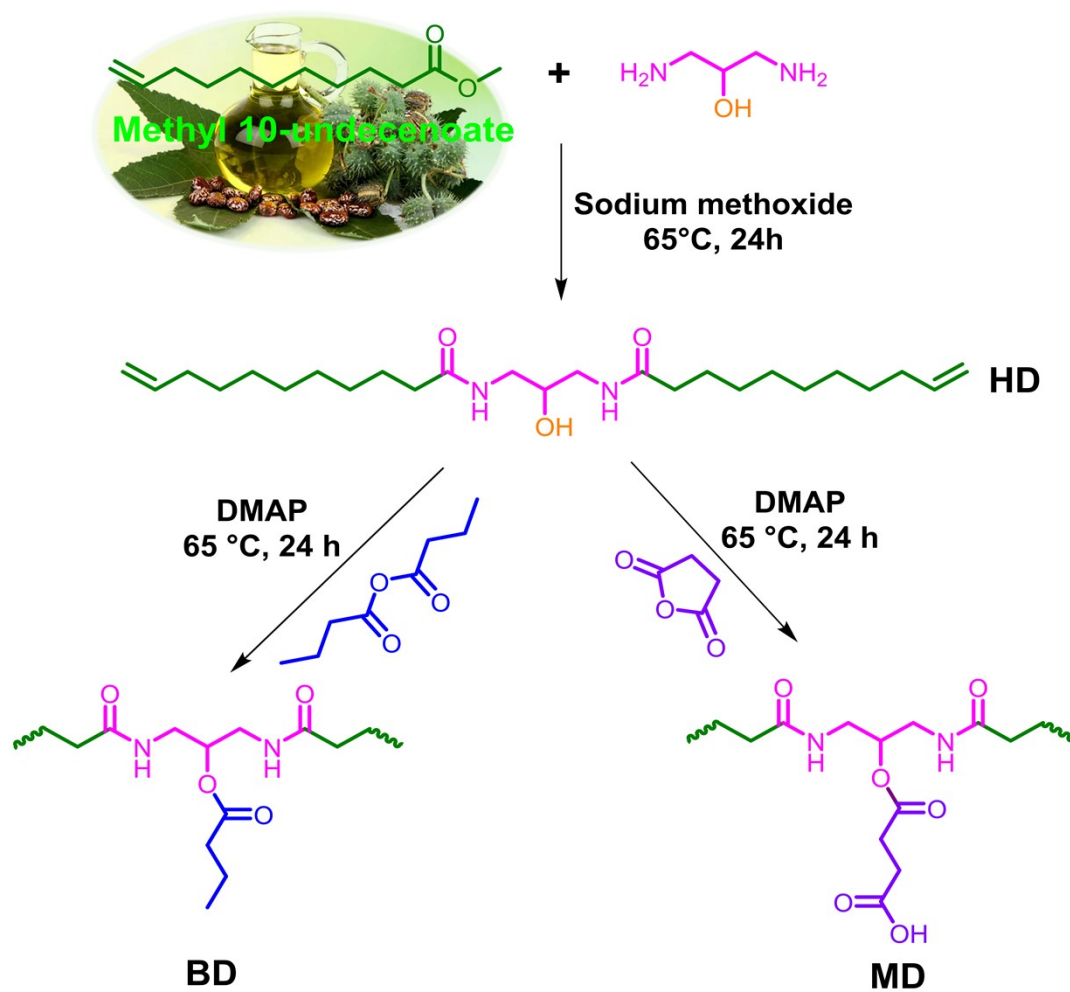


Fig. S1. Synthetic route of compounds HD, BD, and MD.

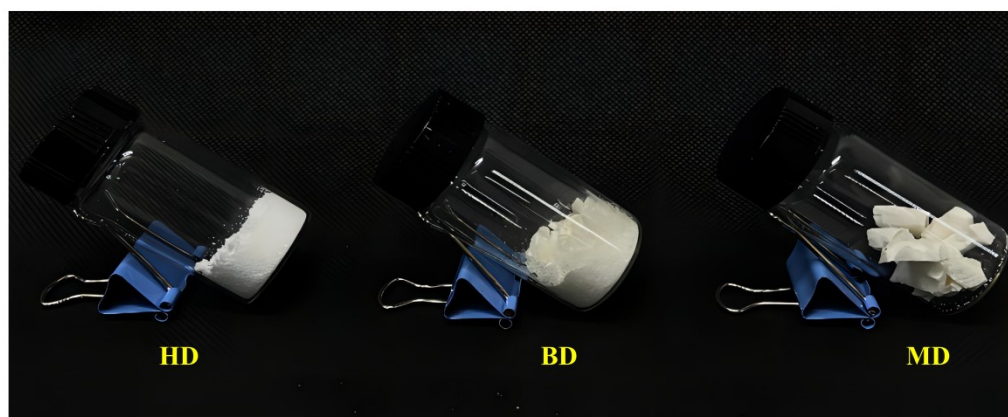


Fig. S2. Photographs of the obtained compounds.

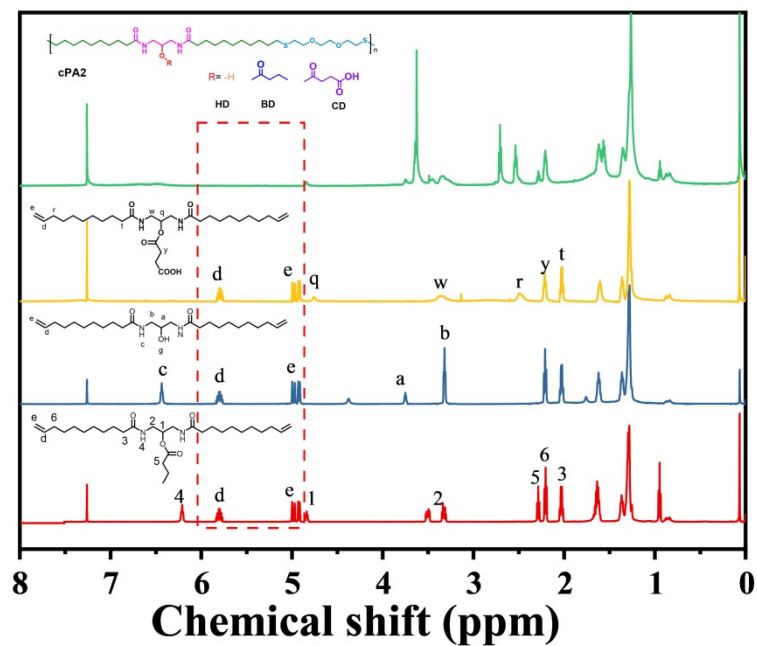


Fig. S3. ^1H NMR spectra of compounds HD, BD, and MD; copolymer cPA2.

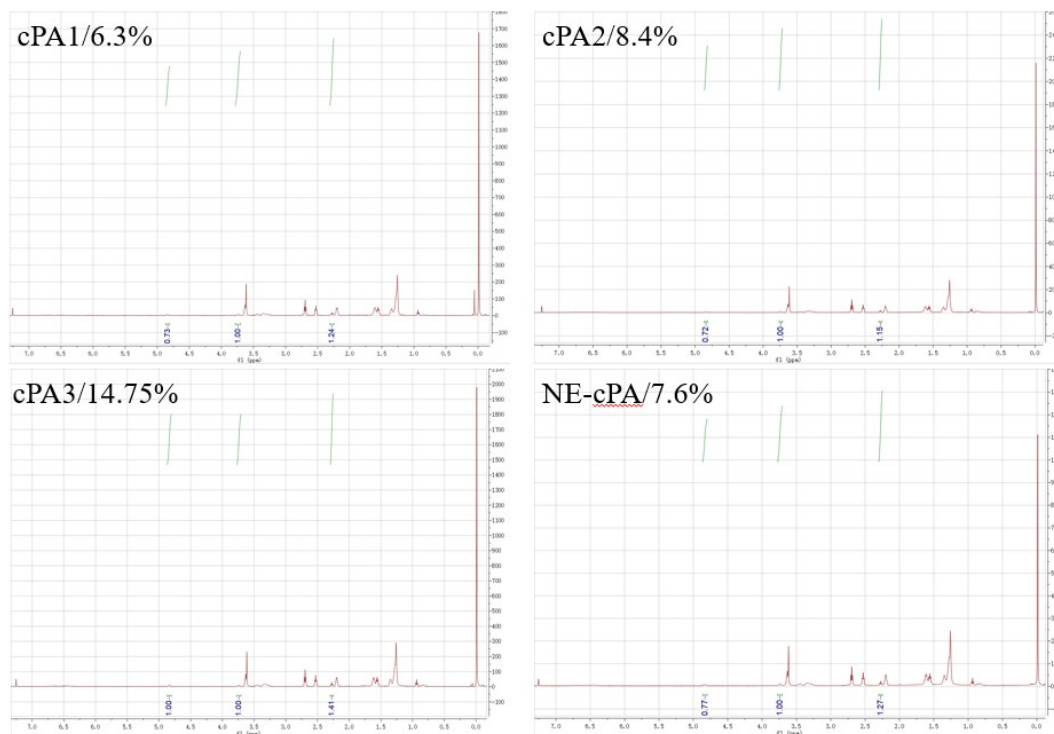


Fig. S4. ^1H NMR integration graphs of CAP1~3 and NE-cPA were used to verify the actual molar fractions of MD in the different components.

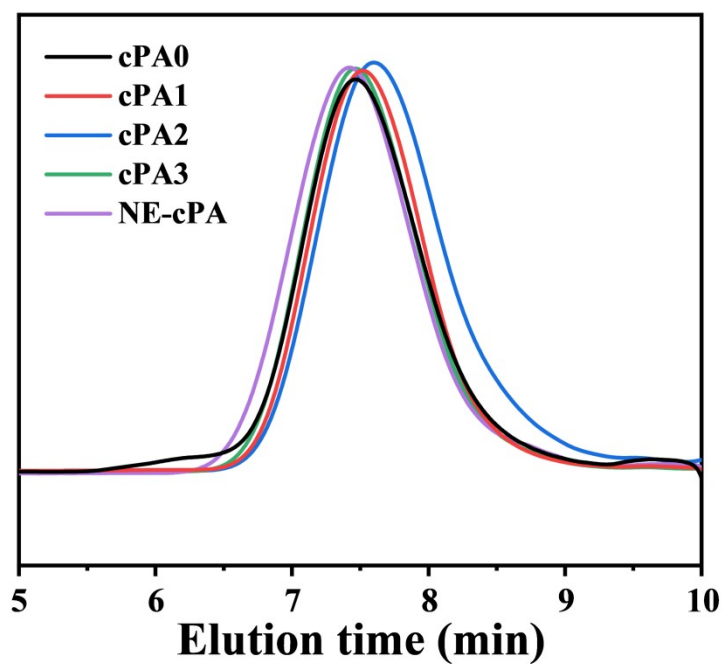


Fig. S5. GPC elution curves of all cPAs samples with DMF as eluent.

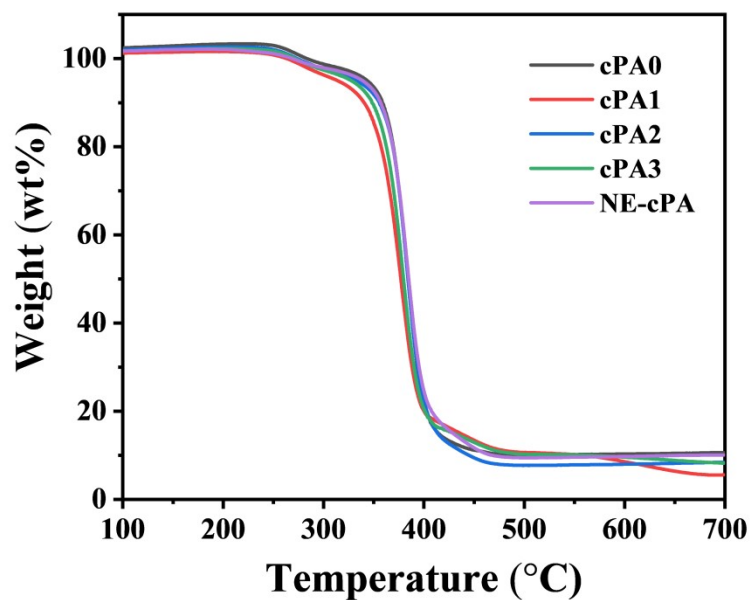


Fig. S6. TGA traces of cPA0~3 and NE-cPA samples.

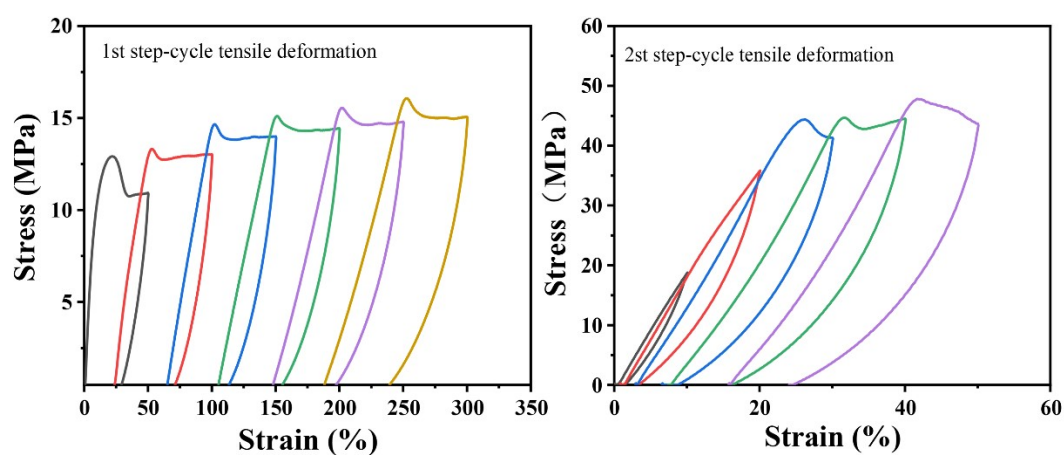


Fig. S7. First and second step-cycle tensile deformation of cPA2.

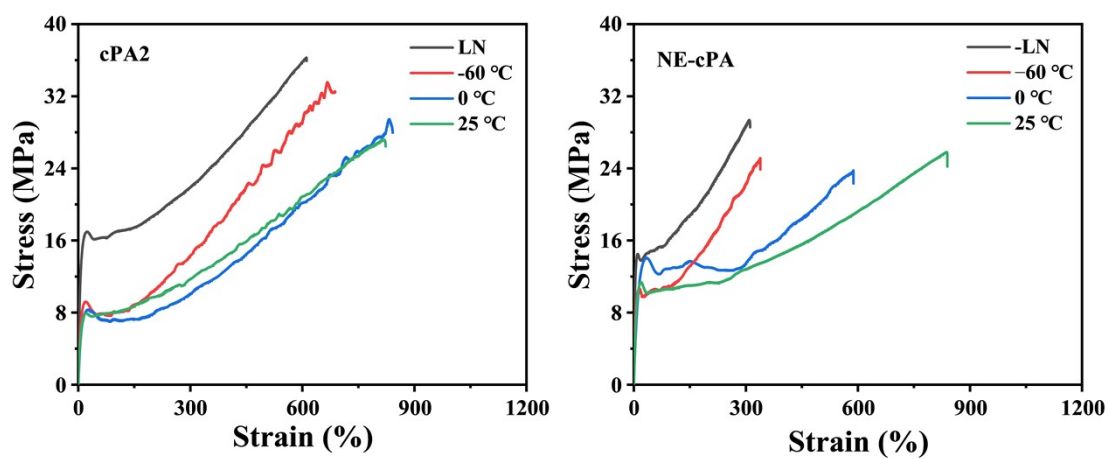


Fig. S8. Representative stress-strain curves of cPA2 and NE-cPA samples tested at different temperatures for 24 h.

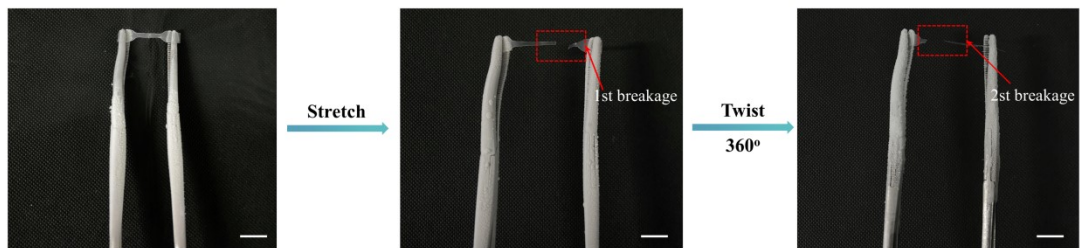


Fig. S9. The optical photographs of NE-cPA film during stretching and twisting operations in liquid nitrogen.

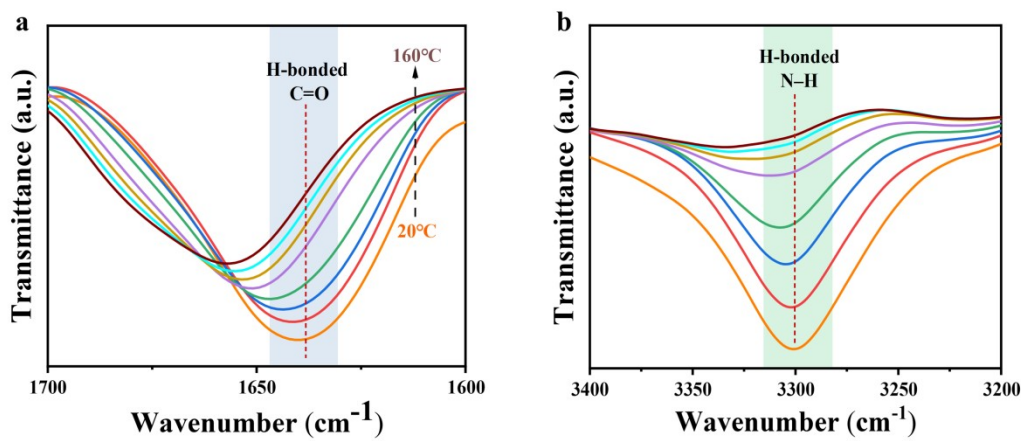


Fig. S10. In situ ATR-FTIR spectra of cPA2 upon heating from 20 to 160 °C. 1700–1600 cm⁻¹ (left, a), 3400–3200 cm⁻¹ (right, b).

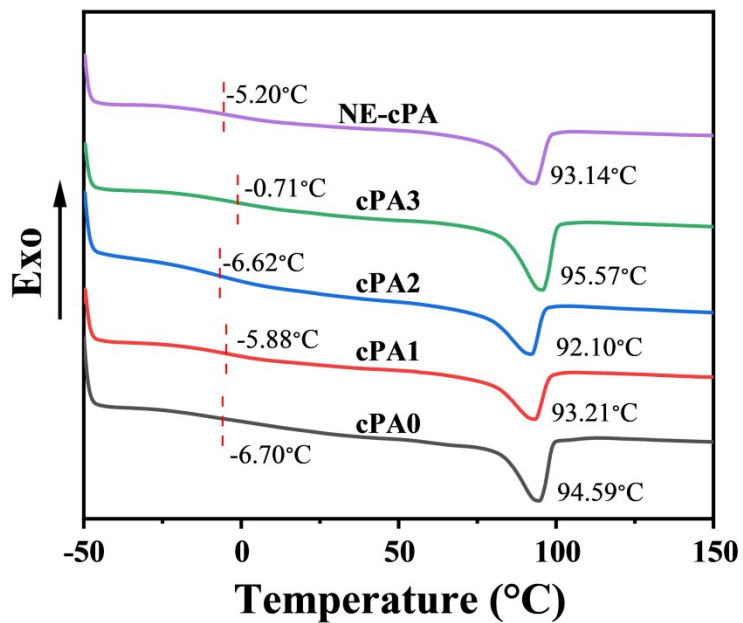


Fig. S11. DSC traces of cPA0~3 and NE-cPA samples.

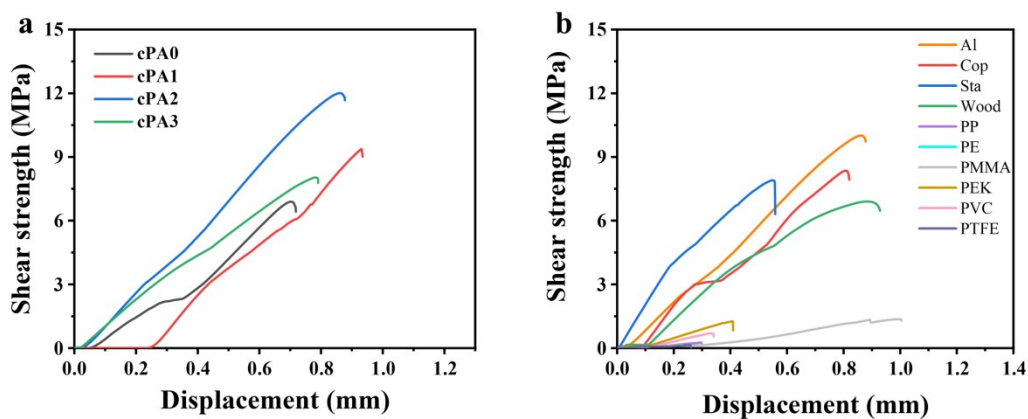


Fig. S12. a) Shear strengths of the copolymer for different MD-to-cPAs molar ratios on steel slices. b) Shear strengths of cPA2 adhesive on different substrates.

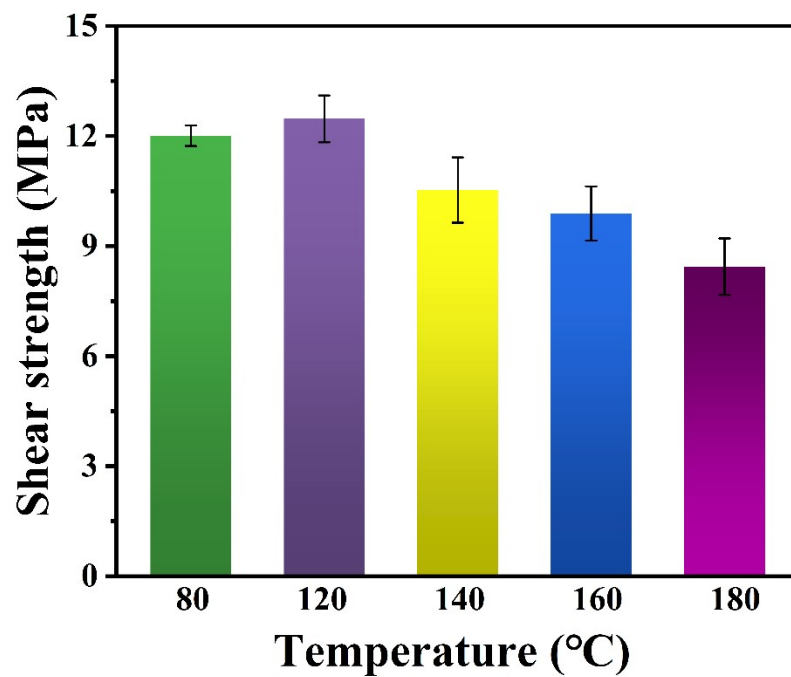


Fig. S13. Lap-shear strength of cPA2 at different serving temperatures.

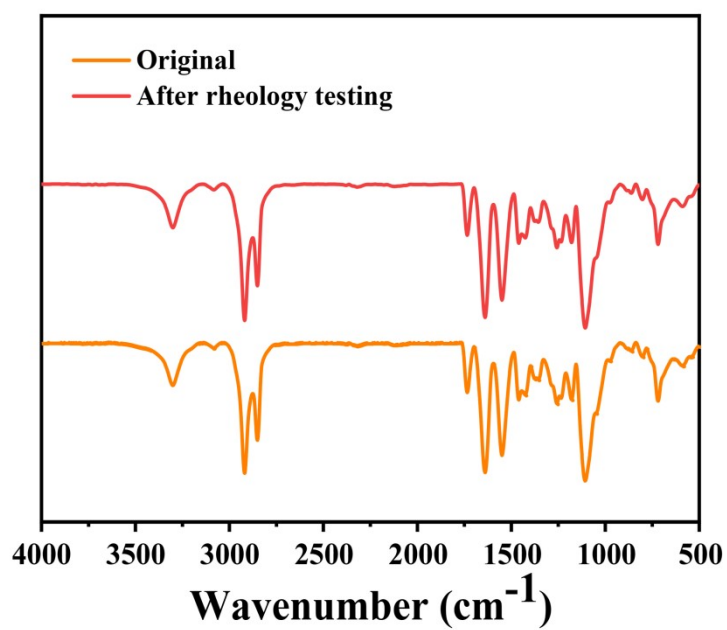


Fig. S14. FTIR spectra of cPA2 adhesive before and after rheology tests.

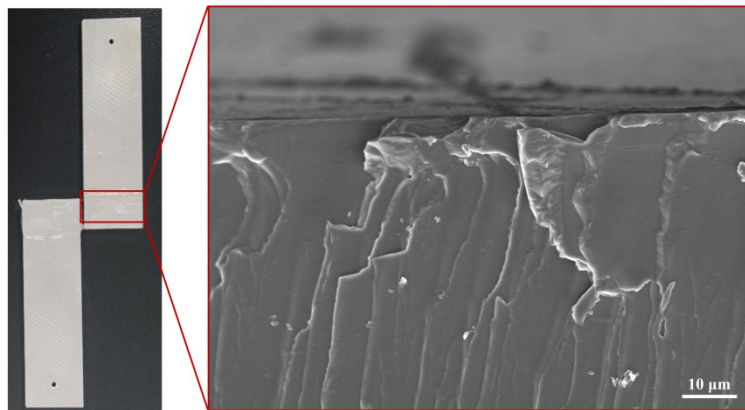


Fig. S15. SEM image of the fracture surface of NE-cPA bonded steel sheets observed after lap-shear tests in liquid nitrogen.

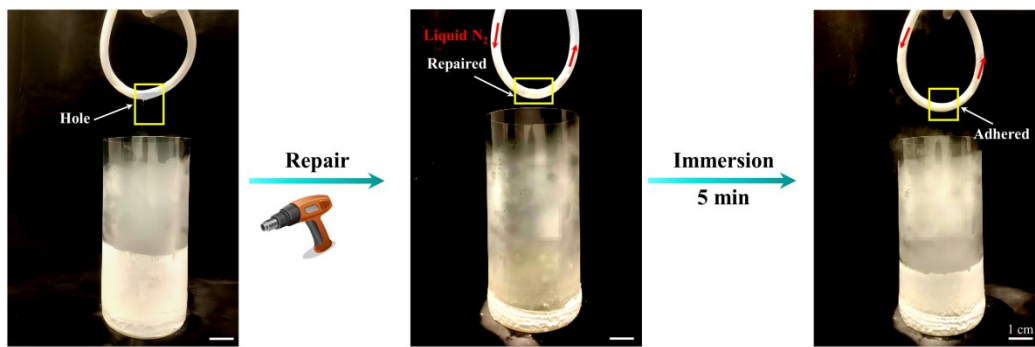


Fig. S16. The cPA2 adhesive for repairing broken PVC tubes against leakage of the internal liquid nitrogen.

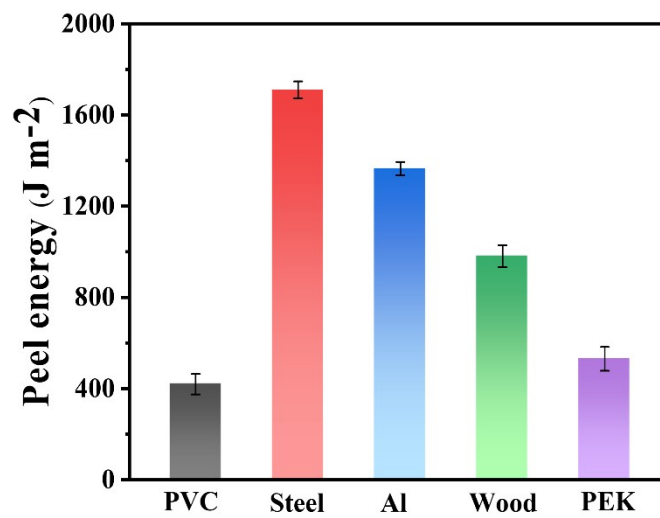


Fig. S17. Peel test results of cPA2 elastomers on various substrates.

Supplementary videos captions

Movie S1. Test process of macroscopic adhesion behavior of cPA2 adhesive in liquid N₂. Before: adhesion strength before LN treatment; After: adhesion strength after 24 h liquid N₂ treatment.

Movie S2. The videos showed the test process of reliable adhesion behavior of cPA2 label on PVC tubes when suffering from splashing in liquid N₂.

References

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