A Strong, Healable, Recyclable Bio-Based Adhesive via a Bone-Inspired Triple Network

Jiarong Huang [a,*], Hanbo Zhang [a], Zhenze Yang [a], Lingcao Tan [a], Wenhua Xu [a,b], Baiping Xu [a]

a. School of Mechanical and Automation Engineering, Jiangmen Key Laboratory of Polymer Intelligent Manufacturing, Wuyi University, Jiangmen, 529020, China

b. Key Laboratory of Polymer Processing Engineering (South China University of Technology), Ministry of Education, Guangzhou, 510640, China

Corresponding Author: Jiarong Huang (hjr@wyu.edu.cn)

Table S1. The formulations of ESO-TA-CA adhesive

Samples ESO-TA-CA	ESO (g)	TA (g)	CA (g)	Industrial alcohol (ml)
1-0.4-0.4	1	0.4	0.4	10
1-0.4-0.5	1	0.4	0.5	10
1-0.5-0.4	1	0.5	0.4	10
1-0.5-0.5	1	0.5	0.5	10
1-0.5-0.6	1	0.5	0.6	10
1-0.6-0.4	1	0.6	0.4	10

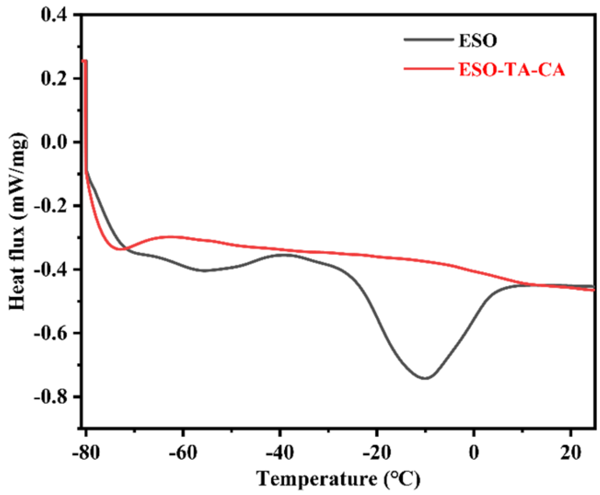

Figure S1. DSC of ESO and ESO/TA/CA adhesive before curing.

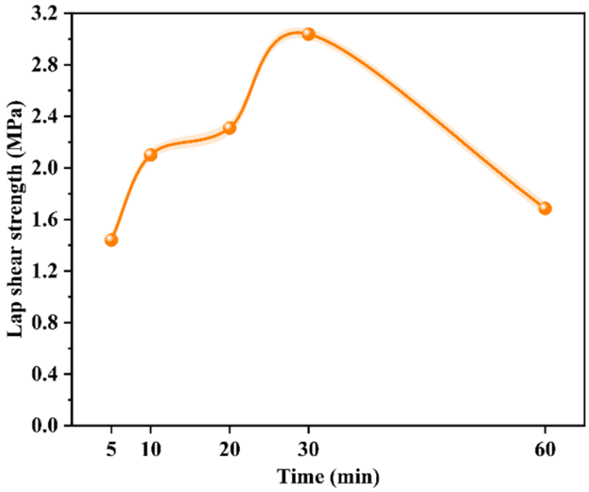

Figure S2. Lap shear strength of ESO/TA/CA adhesive with different curing times.

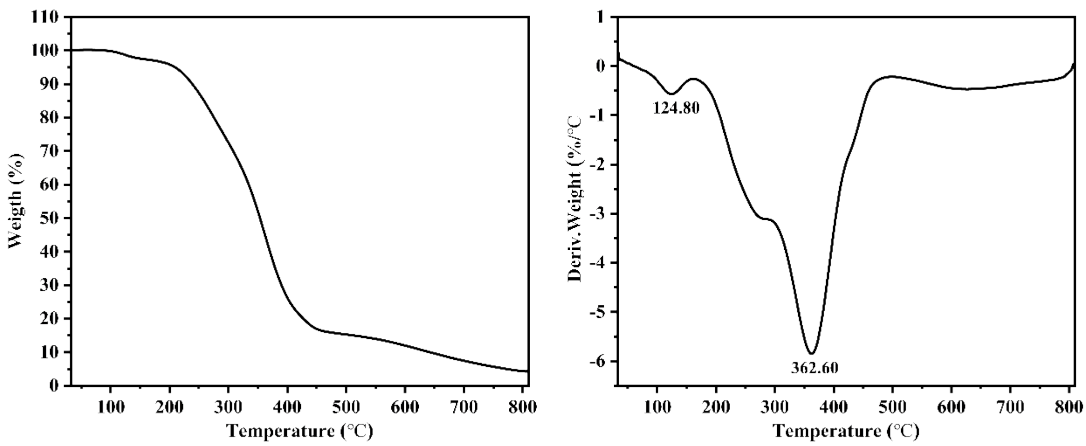

Figure S3. TG and TGA curves of the ESO/TA/CA adhesive (1:0.5:0.5)

Thermogravimetric analysis (TGA) was conducted on a NETZSCH STA 2500 instrument to evaluate the thermal stability of the ESO/TA/CA adhesive. Measurements were performed under a nitrogen atmosphere at a heating rate of 10 °C/min over a temperature range of 40 to 800 °C.

Table S2. Interfacial interactions for different substrates.

Substrate	Interfacial interaction
Aluminum	Coordination interaction/Hydrogen bonding
Steel	Coordination interaction/Hydrogen bonding
Wood	Hydrogen bonding
PET	Van der Waals interactions/Hydrogen bonding

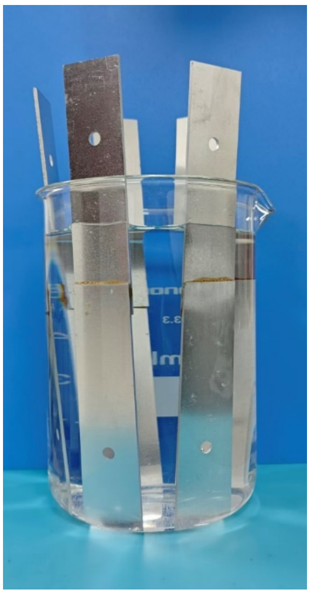

Figure S4. Photos of the water resistance test of the adhesive

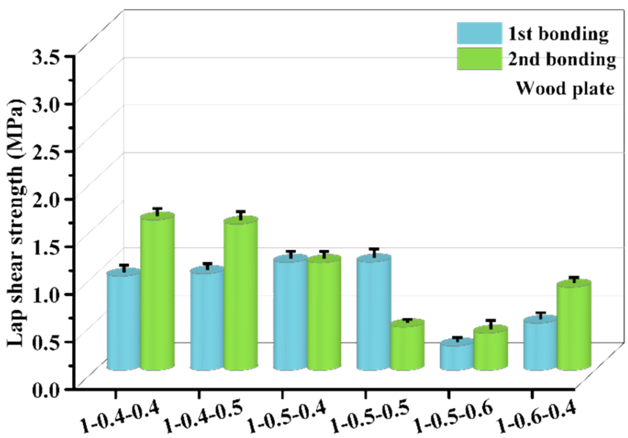

Figure S5. Reusability of the biomimetic adhesive on a wood plate

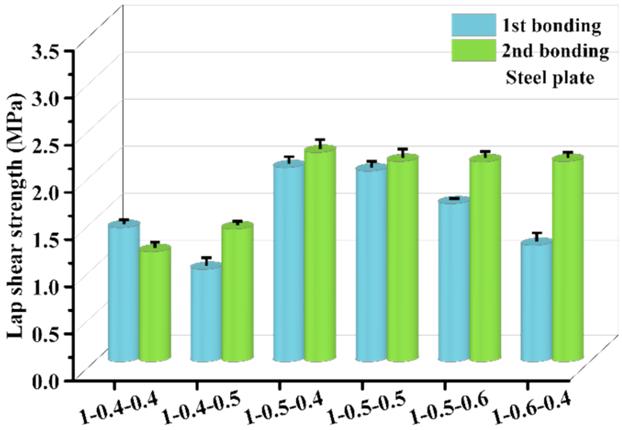

Figure S6. Reusability of the biomimetic adhesive on a steel plate

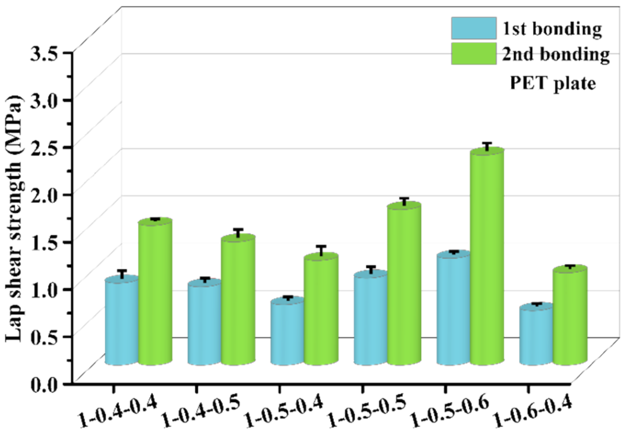

Figure S7. Reusability of the biomimetic adhesive on a PET plate

Table S3. Multi-parameter performance comparison between the ESO/TA/CA adhesive and reported reversible adhesives.

Literatures	Lap shear strength (MPa)	Residual ratio (%)	Main synthetic raw materials	Healable / Healing efficiency (%)	Recyclable / Recycling method	Raw material cost / Sustainability	Environmentally friendly
This work	3.04	95	Epoxidized soybean oil (ESO), Tannic acid (TA), Citric acid (CA)	Yes/93	Yes/Solvent evaporation recovery	Low cost, high sustainability	Yes
J. Mater. Chem. A 2025, 13(26), 21035-21047. Ref. [16]	1.3	95	Epoxidized soybean oil (ESO), Epoxy-functionalized polyolefin elastomer (EP-POE)	Yes/86	Yes / Hot pressing at 130 °C, 15 MPa for 5 min	High cost, low sustainability	Relatively good
Adv. Mater. 2021, 33(42), 2103674. Ref. [42]	1	95	Cellulose nanocrystals (CNC), Poly (vinyl alcohol) (PA)	Yes/101	Yes / Water spraying at the bonding interface	Low cost, good sustainability	Yes
Angew. Chem. 2021, 133(21), 12189-12196. Ref. [43]	0.6	94	Chitosan (CS), Poly(N-isopropylacrylamide) copolymer (CS-g-PNIPAM)	Yes/99	Yes / Cooling below 4 °C	Relatively low cost, good sustainability	Yes
Ind. Crops Prod. 2025, 235, 121712. Ref. [44]	1.59	72	Oil tea cake protein (COP), Glyoxal (G), Melamine (M)	No	No	Low cost, high sustainability	Yes
Int. J. Biol. Macromol. 2025, 145929. Ref. [45]	2.31	75	Soy protein isolate (SPI), Sodium Carboxymethyl Cellulose (CMCNa), Lauroyl Arginine Ethyl Ester Hydrochloride (LAE), Triglycidylamine (TGA), Epichlorohydrin (ECH)	No	No	Low cost, good sustainability	Yes
Compos. Part B: Eng. 2025, 298, 112374. Ref. [46]	1.64	90	Chitosan (CS), Tannic acid (TA), Nano-hydroxyapatite(n-HA), Tris(2-carboxyethyl) isocyanurate(TCI)	No	No	Relatively low cost, good sustainability	Yes

Colloids Surf. A 2023, 671, 131722. Ref. [47]	2.22	85	Chitosan (CS), Gallic acid (GA)	No	No	Low cost, high sustainability	Yes
Int. J. Biol. Macromol. 2023, 242, 125095. Ref. [48]	2.78	43	Soybean meal powder (SM), Silk fibroin (SF), Tannic acid (TA)	No	No	Relatively low cost, high sustainability	Yes
Int. J. Biol. Macromol. 2023, 253, 127135. Ref. [49]	1.65	96	Soy protein isolate (SPI), Citric acid (CA)	No	No	Low cost, high sustainability	Yes
Chem. Eng. J. 2023, 465, 142888. Ref. [50]	2.05	61	Aldehyde/Aminated nanocellulose (DNC/A-NC)	No	No	Relatively high cost, high sustainability	Yes
Chem. Eng. J. 2023, 453, 139761. Ref. [51]	2.1	55	Soy protein isolate (SPI), Functionalized nanomaterials (f-NM)	No	No	Low cost, high sustainability	Yes

Table S4. Healing efficiency of the adhesive with different healing durations.

Healing time (min)	Healing efficiency (%)
5	8.55
10	55.09
15	76.19
20	88.65

The healing efficiencies were calculated according to the following equation:

$$\text{Healing efficiency} = (\gamma - \beta) / (\alpha - \beta) \times 100\%$$

where α is the stress or strain of the original plywood, β is the stress or strain of the damaged sample, γ is the stress or strain of the healed sample.

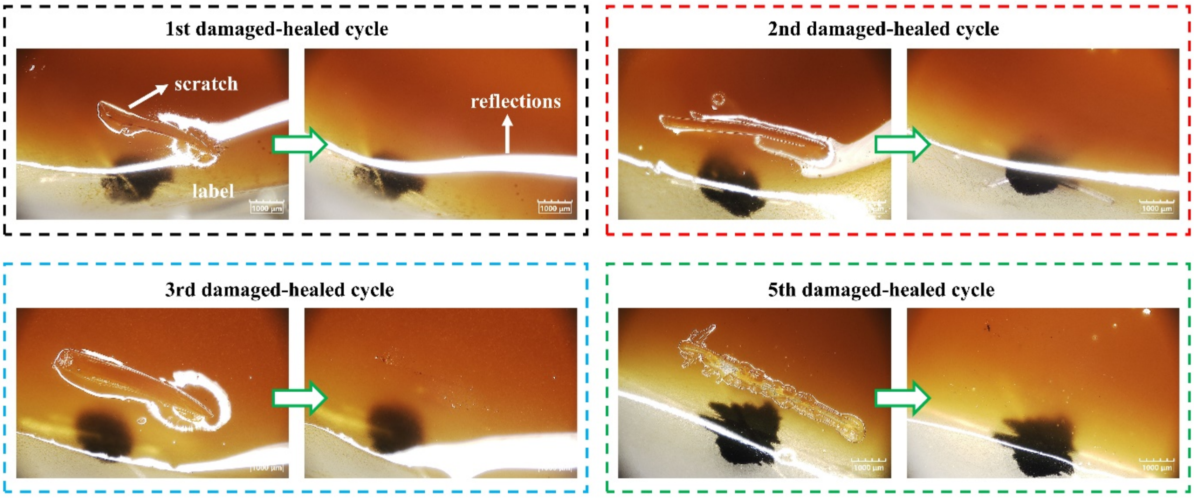

Figure S8. Surface morphology of the adhesive after multiple damage-healing cycles.

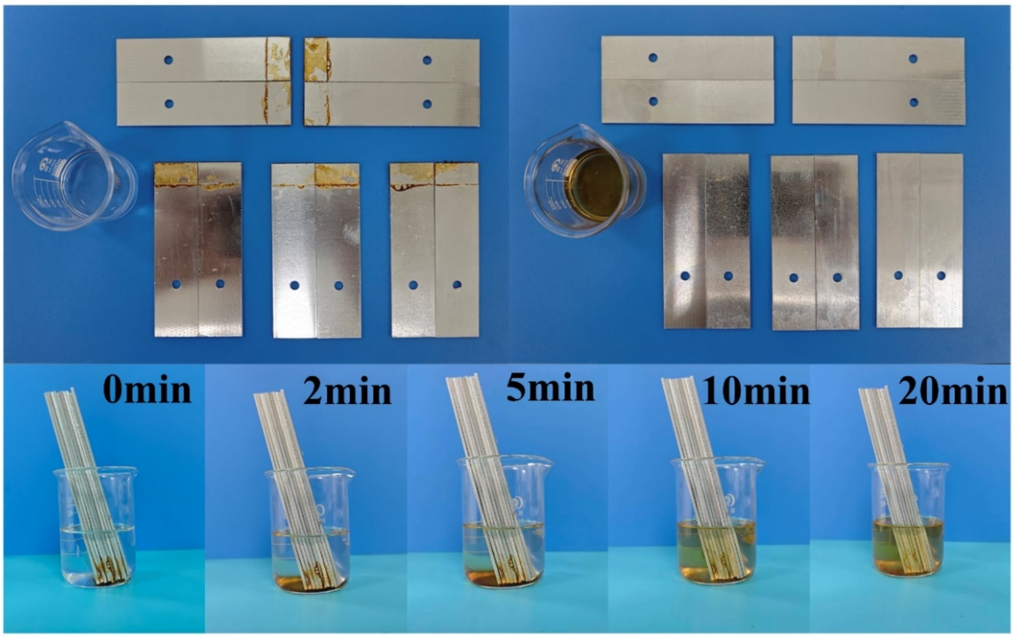

Figure S9. Digital photo of recycled ESO/TA/CA adhesive on the aluminum substrate

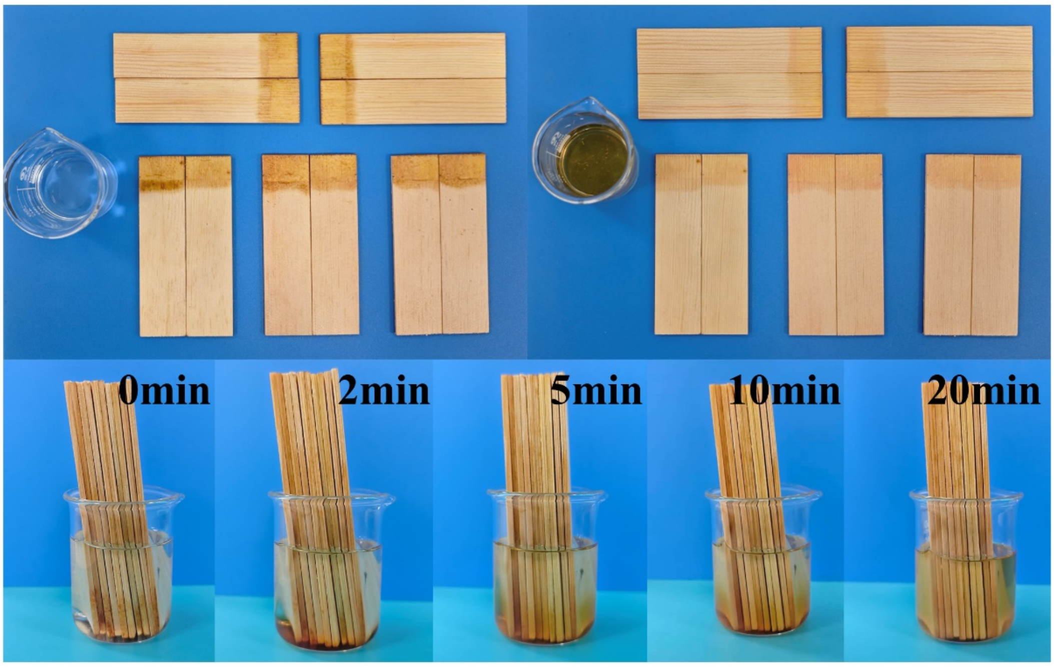

Figure S10. Digital photo of recycled ESO/TA/CA adhesive on the wood substrate

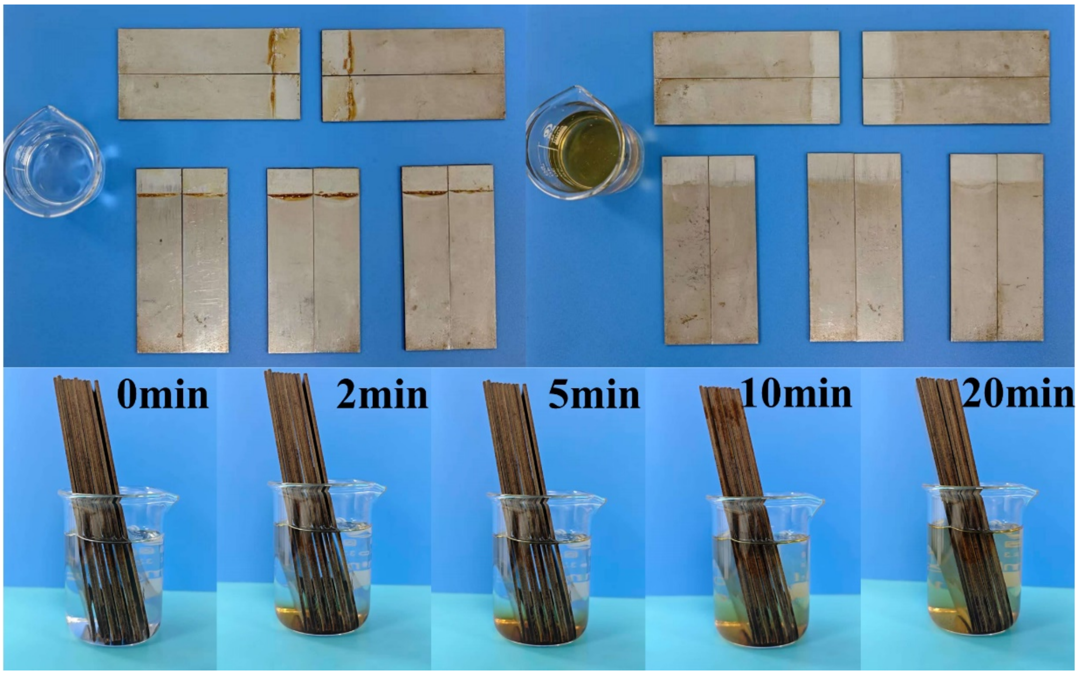

Figure S11. Digital photo of recycled ESO/TA/CA adhesive on the steel substrate

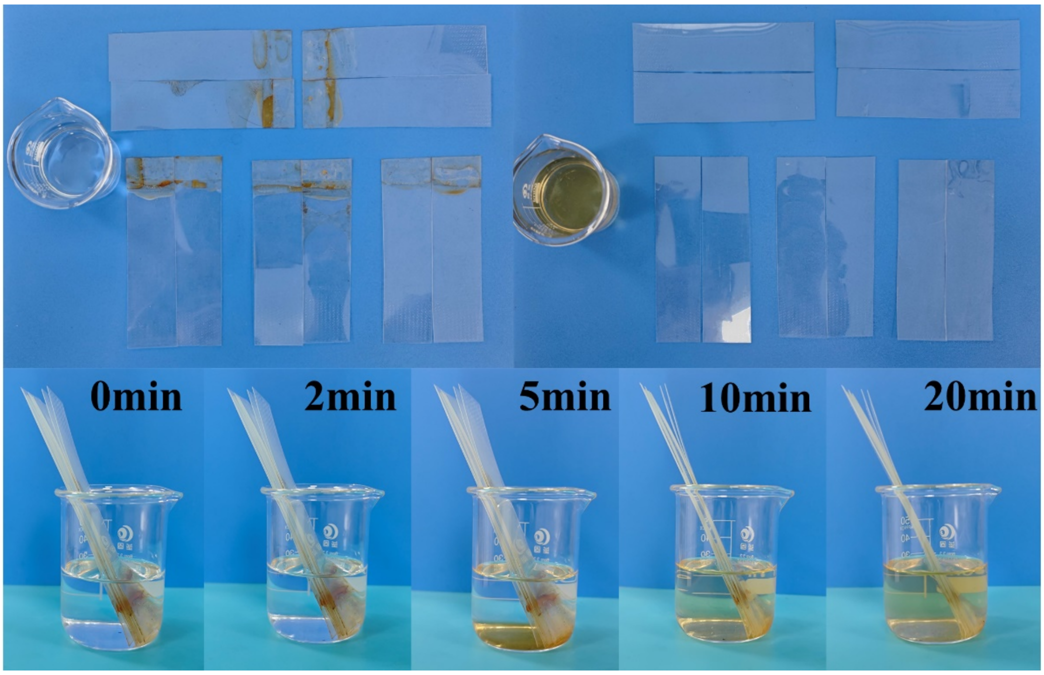

Figure S12. Digital photo of recycled ESO/TA/CA adhesive on the PET substrate

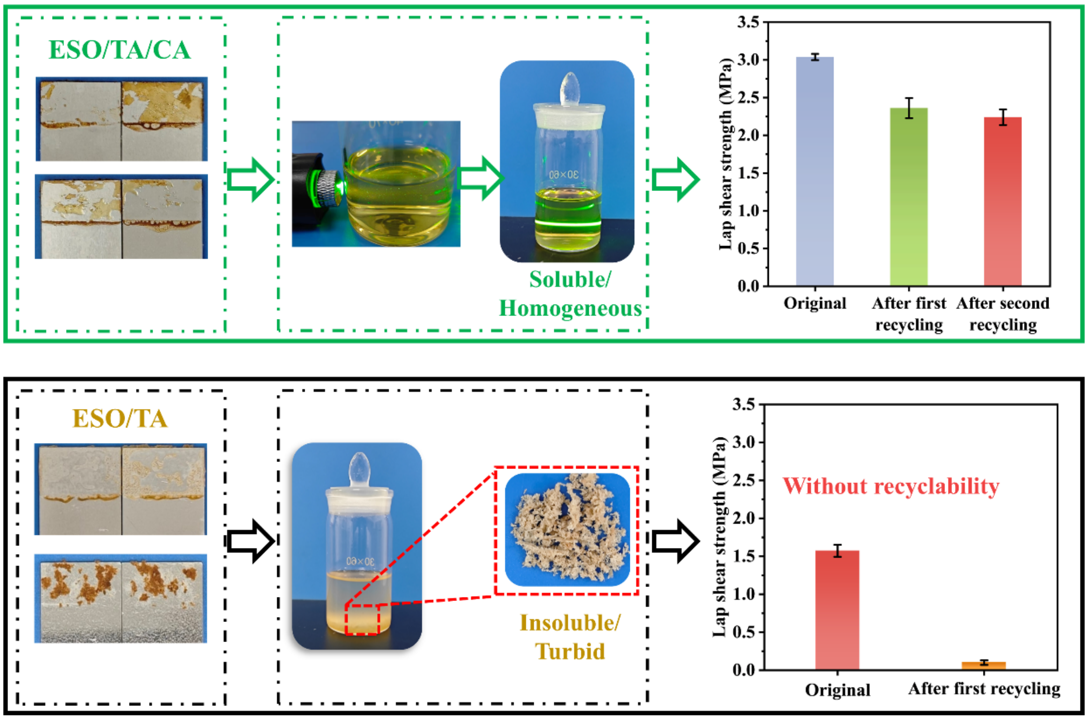

Figure S13. Comparison of the recycling processes of different adhesive systems.

Table S5. Comparison of reusability and recyclability pathways for the ESO/TA/CA adhesive.

	Reusability	Recyclability
Definition	Thermally triggered re-bonding of the same adhesive piece after debonding	Dissolution of the cured adhesive in ethanol and re-casting into a new entity
Process	Hot-pressing	Ethanol dissolution & Hot-pressing
Mechanism	In-situ rearrangement of dynamic covalent with minimal topological change	Disassembly and reconstitution of the network with a more disruptive process
Mechanical Retention	~95%	~79%
Primary Advantage	Suitable for efficient in-situ repair, simple operation with high property recovery	Enables complete green life-cycle management of the material, true chemical recycling