Supplementary Information (SI) for Materials Chemistry Frontiers.

Fully Recyclable and Regeneratable Plant-based Adhesives

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Table of contents

Experimental Methods

Materials. Ethanol (99.8%) and β-cyclodextrin (β-CD, 98%) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Tannic acid (TA, >99.5%) was purchased from Sigma-Aldrich, Inc. Ecoflex 00-30 was purchased from Smooth-On, Inc. Deuterium oxide (D_2O, >99.99%) and hexadeuterodimethyl sulfoxide (DMSO-*d*6, 99.9%) were purchased from Shanghai Macklin Biochemical Co., Ltd. All chemicals were used as received without further purification.

Preparation of the recyclable and regeneratable plant-based adhesive (RRPA). The RRPA precursor solution was obtained by mixing β-CD and TA with different molar ratios in deionized (DI) water. Detailed formulations can be found in Table S1**.** For 1:3-RRPA, 1.00 g (0.88 mmol) β-CD and 4.496 g (2.64 mmol) TA were dissolved in 10 mL DI water at 80 °C under stirring. The precursor solution then heated in an oven at 65 °C to evaporate the excess amount of water, and the RRPA was obtained by cooling of the concentrated precursor solution at room temperature. The remaining water content in RRPA was determined gravimetrically by subtracting the total mass of solids (β-CD and TA) from the mass of the final RRPA sample.

Adhesion strength tests.

The adhesion strength of RRPA were tested by the CMT6103 electronic universal testing machine (Shenzhen SANS Testing Machine Co., Ltd, China). For the lap shear test, the RRPA was casted on the surface of substrates including stainless steel (2 mm), wood (2 mm), glass (2 mm) PTFE (1.25 mm), PET (1.25 mm), PI (1.25 mm) and Cu (2 mm), then covered and pressed a new substrate above it. The two plates adhered immediately and firmly together. The adhered thickness was 0.1 mm. RRPA was sandwiched between the substrates with an overlapping area of 10 × 20 mm^2. After pressing with 5 kg weight for 8 h, the adhesive-substrate systems were used for lap-shear tests. For each test, the amount of adhesive coated on surfaces was ~10 mg cm^{-2}. For temperature- or relative humidity (RH)-dependent adhesion tests, the adhered plates were stored at different temperature or RH for two hours before testing. Stress-strain curves were obtained by uniaxial stretching of the RRPA at a speed of 50 mm min^{-1}.

Molecular simulation.

Molecular simulation was conducted to explore the combination of β-cyclodextrin, tannic acid, cellulose, and water. The Forcite module of Materials Studio was employed for interaction energy calculations. To ensure the accuracy and consistency of our calculations, we set the tolerance at 2.0×10^{-5} kcal/mol for energy, 0.001 kcal/mol/Å for force, and 1.0×10^{-5} Å for displacement. The COMPASSII force field was utilized for modeling van der Waals interactions with a cutoff distance of 15 Å. Electrostatic interactions were treated using the Ewald summation method.

The interaction energy was obtained by calculating the energy difference between the individual components and the combinations:

$$\Delta E = E_{AB} - E_A - E_B$$

To determine the combinations' Gibbs free energy, all models underwent optimization using the Forcite module, followed by frequency calculations using the DMol3 module. Density functional theory (DFT) was employed, utilizing the Perdew-Burke-Ernzerhof (PBE) and Becke-Lee-Yang-Parr (BLYP) functionals. The Grimme method was applied for DFT-D correction. A self-consistent field (SCF) tolerance of 1.0×10^{-5} and a smearing of 5.0×10^{-2} Ha were implemented to ensure calculation convergence.

The correction term for the total energy (E_{Tcorr}) was calculated as the total energy (E_{Total}) plus the finite temperature corrections at 298.15 K for standard thermodynamic quantities (entropy, heat capacity, enthalpy, and free energy):

$$E_{Tcorr} = E_{Total} + G_{Total(298.15K)}$$

These corrections include the zero-point vibrational energy (ZPVE). The Gibbs free energy for the combination was determined by calculating the correction term for the total energy:

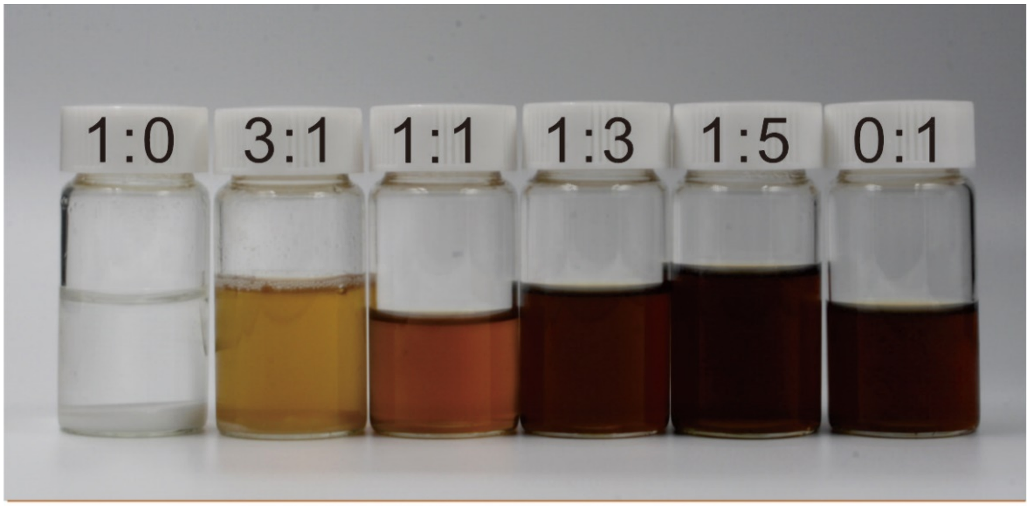
$$\Delta G_{combination} = E_{Tcorr(AB)} - E_{Tcorr(A)} - E_{Tcorr(B)}$$

Characterization

Fourier-transform IR (FT-IR) spectra were collected by a Bruker Vertex 70 FT-IR spectrophotometer. Thermogravimetric analysis (TGA) was carried out by using a TGA5500 with a heating rate was 10 ℃ min^{-1} from 25 to 600 ℃ in nitrogen atmosphere. Differential Scanning Calorimeter (DSC) measurements were carried out by using a TAQ 200 with a heating rate of 10 ℃·min^{-1} from 25 to 600 ℃ in nitrogen atmosphere. Scanning electron microscopy (SEM) images were obtained by the APREO S SEM (ThermoFisher Scientific).

Recycling

The recycling process involves adding an appropriate amount of DI water to the previous used RRPA, followed by heating at 60 ℃ for 5 min. The mixture was then concentrated to a viscous solution of 15 wt% water content by using a rotary evaporator. The recycled RRPA was obtained for performing a lap-shear test. This recycling process is conducted 1, 2, 10, 50, 100 and 200 times to compare the adhesion strength differences between RRPA samples with differing recycling times.



β-CD:TA Molar Ratio	1:0	3:1	1:1	1:3	1:5	0:1
Dissolution time	Partially soluble	12 h	1 h	10 min	30 min	8 min

Fig. S1 RRPA precursor solutions with different β-CD:TA molar ratios.

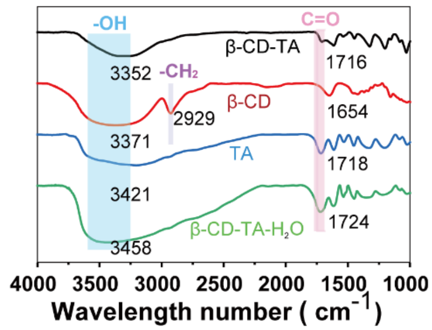


Fig. S2 FT-IR spectra of β-CD, TA, β-CD-TA mixture, and β-CD-TA-H_2O mixture.

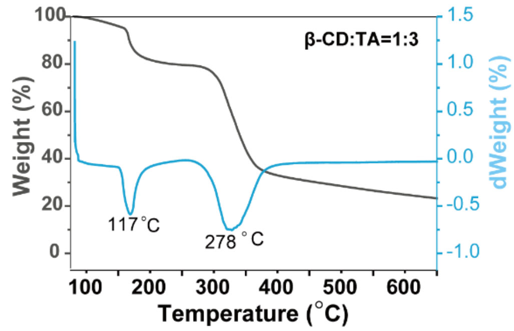


Fig. S3 TGA curves of 1:3-RRPA.

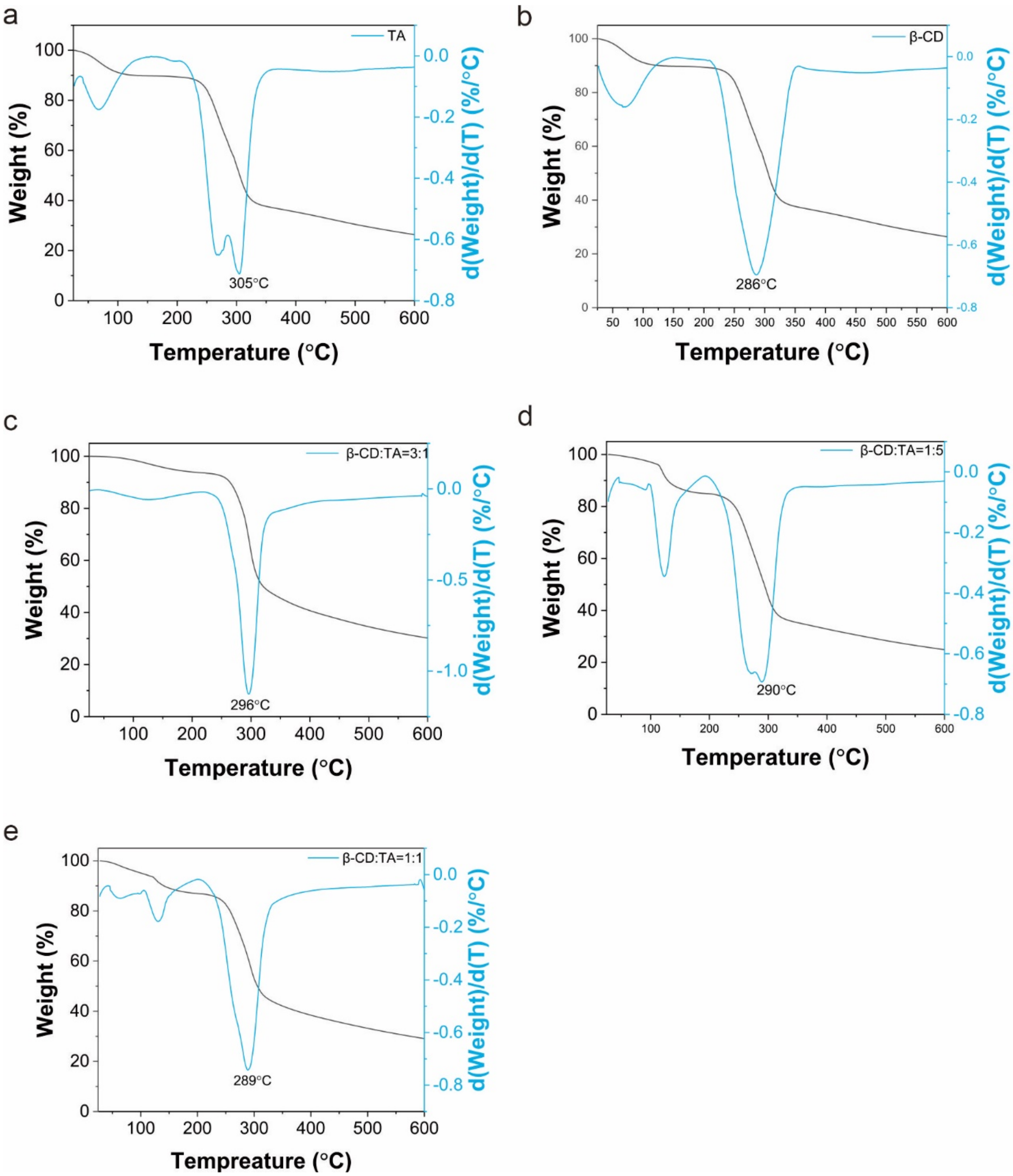


Fig. S4 TGA curves of 1) TA powder, b) β-CD powder, c) RRPA-3:1, d) RRPA-1:5, and e) RRPA-1:1.

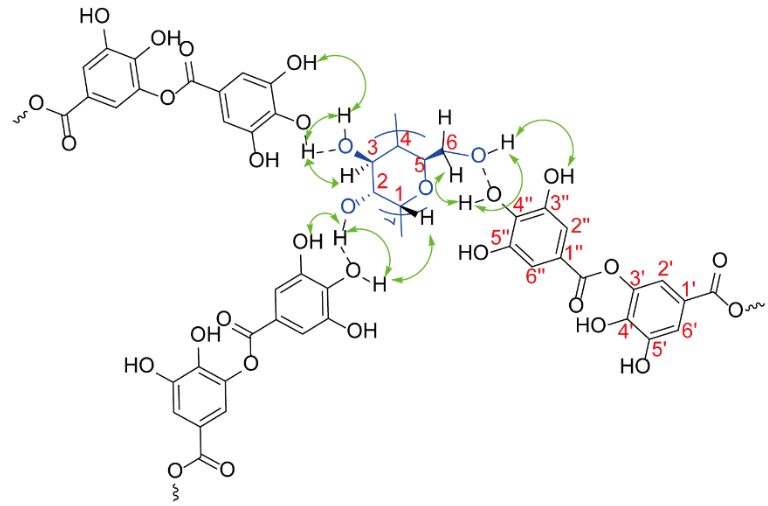


Fig. S5 Labelled hydrogen atoms of β-CD and TA relevant to intermolecular hydrogen bonds.

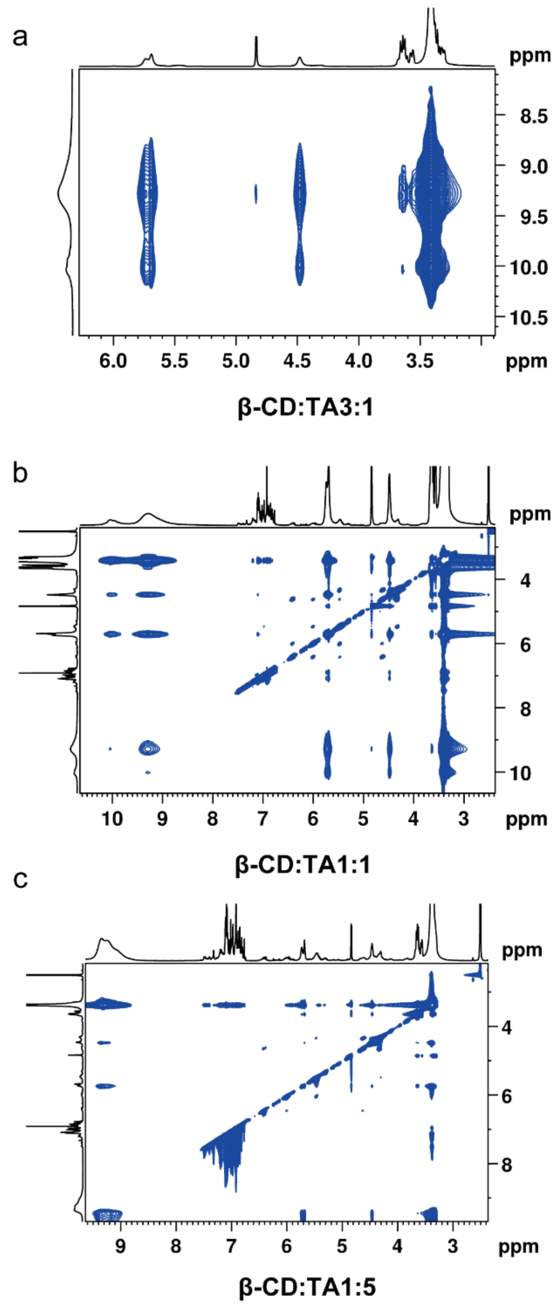


Fig. S6 2D NOESY NMR spectra of RRPAs with β-CD:TA molar ratios of a) 3:1, b) 1:1, and c) 1:5.

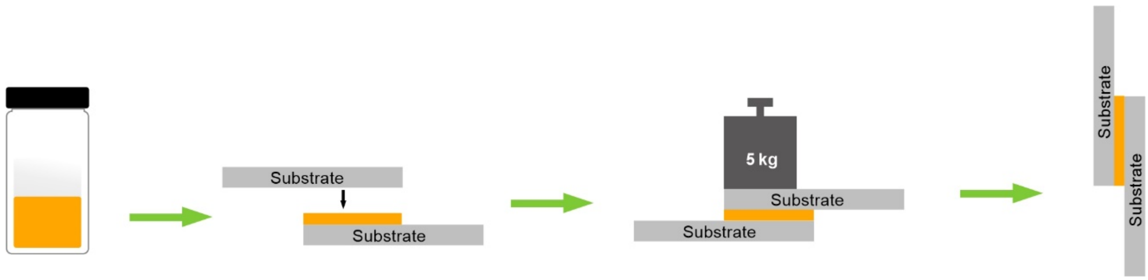


Fig. S7 Procedures for lap shear adhesion test.

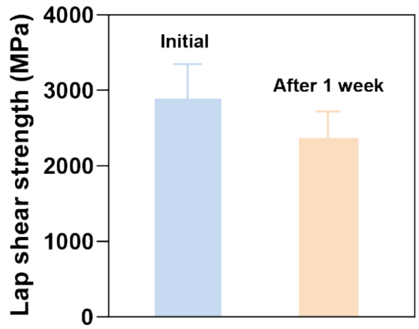


Fig. S8 Strength retention after conditioning at 85% RH, 25 °C, for 24 h, 1 week.

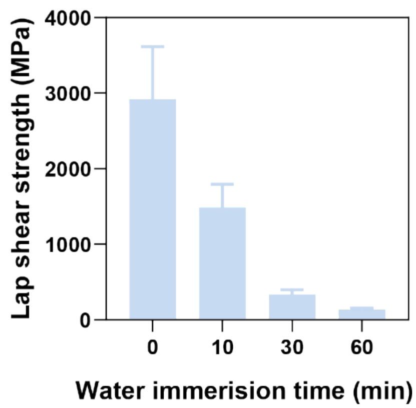


Fig. S9 lap-shear strength retention after immersion in water for 1min,10min,30min,1h.

Table S1. Formulation and Moisture Control for RRPH Adhesive at Various β-CD-TA Molar Ratios.

β-CD−TA Content	Solvent (DI water) for Precursor Solution (g)	Total Water Mass (g)	Residual Water Content (%)	Bound Water (g)
1 g−0.500 g (3-1)	10	5.158	50	0.158
	10	3.158	30	
	10	2.158	20	
	10	1.615	15	
	10	1.158	10	
1 g−1.499 g (1-1)	10	5.235	50	0.235
	10	3.235	30	
	10	2.235	20	
	10	1.735	15	
	10	1.235	10	
1 g−4.496 g (1-3)	10	5.464	50	0.464
	10	3.464	30	
	10	2.464	20	
	10	1.964	15	
	10	1.464	10	
1 g−7.796 g (1-5)	10	5.694	50	0.694
	10	3.694	30	
	10	2.694	20	
	10	2.194	15	
	10	1.694	10	

Notes for Table S1:

- **"Residual water"**, refers to the mass fraction of added water (as the solvent for precursor solution) remaining in the final sample after the drying process**.**
- "**Bound water**", refers to the mass of inherent moisture in the raw materials (β-cyclodextrin and tannic acid powders) as determined by thermogravimetric analysis (TGA).

- **“Total water mass”** is defined as the sum of “residual water” and “bound water,” representing the total mass fraction of water in the final adhesive.

Table S2. Lap-shear strength comparison of fully recyclable/natural adhesives.

Type/Name	lap-shear strength (kPa)	Components	synthesis method	Reference
RRPH	3100	β-CD，TA, H_2O	One-pot	This work
D-SMGs	40	Achatina fulica，Helix lucorum	freeze-dried	*Nature Communications*, 2023, 14, 396.
CS-BA-ERA	2700	Rosin acid, chitosan, boric acid	One-pot	*Green Chemistry,* 2025, 27, 12319-12332.
TF-P	3800	Tannin, Furfuryl alcohol, phytic acid	One-pot	*Journal of Cleaner Production,* 2024, 538, 147440.
UBSA-PAA	104.5	unfolded bovine serum albumin, polyacrylic acid	One-pot	*Advanced Materials,* 2025. https://doi.org/10.1002/adma.202511921
PD-L	1000.48	N-hydroxy succinimide, Pectin, Dopa	One-pot	*International Journal of Molecular Sciences,* 2023, 24, 9987.
LNIPU	3009	Lignin, Isocyanate-free polyol	Microwave and ultrasound	*Green Chemistry,* 2025, 27, 13577-13606.
PATO	2210	Thioctic acid	polymerization-crystallization	*Materials Today*, 2025, 92, 326-338.
LPF	1200	Lignin, phenol, formaldehyde resin	One-pot	*Nature Protocols,* 2026. https://doi.org/10.1038/s41596-025-01316-8