Supporting Information

Water-mediated fabrication of reprocessable and self-healing cellulose-based polyimine plastics

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Includes,

1. Supplementary methods

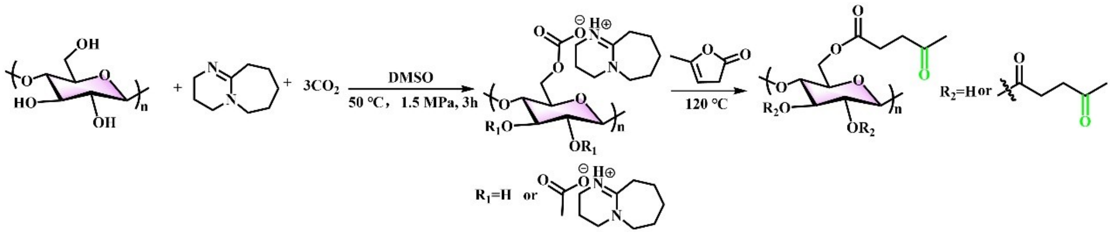
2. Supplementary figures and tables (Fig. S1-S4 and Tables S1-S13)

3. Supplementary references

1. Supplementary methods

(1) The preparation of CLE

Cellulose levulinate ester (CLE) was prepared following our prior work.[1] Typically, following a specific ratio, MCC (10 g, 0.185 mol OH), DMSO (154 g) and DBU (28 g, 0.184 mol) were weighed and added to a 400 mL high-pressure reaction vessel. CO_2 was slowly introduced until reaching 1 MPa, followed by a gradual release. This process was repeated three times to exchange gases in both the reaction vessel and the solution. Finally, CO_2 was introduced until the pressure stabilized at 1.5 MPa. The reaction solution was heated to 50 ^{o}C and mechanically stirred for 3 h to obtain a 5 wt% homogeneous and transparent cellulose solution. Next, α-AL (45.4 g, 0.463 mol, molar ratio: -OH/α-AL = 1/2.5) was slowly added into the 5 wt% cellulose solution in a flask, the reaction solution was heated up to 120 °C for 1 h under mechanical stirring. After completion of the reaction, the reaction solution was slowly poured into isopropanol (400 mL) to precipitate the product. The product was collected by filtration and repeatedly washed with isopropanol (100 mL × 2). Finally, the obtained CLE (DS = 0.63) was dried under vacuum at 60 °C for 48 h, affording 12.5 g of product.



Scheme S1. The preparation process of CLE (DS = 0.63).

The DS of CLE was calculated according to the following equation:

$$DS = \frac{I_{Methyl} \times 7}{I_{AGU} \times 3} \#(1)$$

Where I_{Methyl} represents the integration value of the terminal methyl group and I_{AGU} represents the integration value of the cellulose structural units.

(2) Preparation of regenerated cellulose film

MCC (5 g, 0.093 mol OH), DMSO (77 g) and DBU (14 g, 0.092 mol) were weighed accurately and sequentially transferred into a high-pressure vessel equipped with mechanical stirring and temperature control. The vessel was purged with CO_2 by three pressurization and vent cycles to remove air, then pressurized with CO_2 to 1.5 MPa and held at this pressure. The mixture was heated to 50 °C and stirred for 3 h until a clear cellulose solution with a concentration of 5 wt% was obtained. The homogeneous cellulose solution was uniformly cast onto a 60 mm glass Petri dish and immediately immersed in ethanol to form a hydrogel film, followed by washing with ethanol to remove residual solvent. The gel films were dried in an oven at 30 °C to obtain regenerated cellulose films.

(3) Self-healing of the CPP

The surface of CPP-Ph was first scratched by a metal blade and hot-pressed at 180 °C and 15 MPa for 60 minutes when sandwiched between two pieces of polyimide membrane.

(4) Reprocessing process of the CPP

The CPP-Ph was ground into powder and sandwiched between two pieces of polyimide membrane. After the hot-pressing at 130 °C and 15 MPa for 30 minutes, the remolded CPP-Ph was obtained.

(5) Water contact angle, hygroscopicity and durability tests

First, 5 μL of pure water was dropped on the surface of CPP and regenerated cellulose film, then the contact angle changing with time was recorded. The hygroscopicity of the samples was determined by immersing them in water for predetermined durations and subsequently measuring the weight gain. For the durability test, the CPP-Ph were immersed into water and various organic solvents for a month to observe their shape stability. The detailed materials and methods for regenerating cellulose film are available in the Supplementary Materials.

(6) Chemical degradability and biodegradability tests

An amine-catalyzed degradation method was employed to evaluate chemical degradability. Specifically, CPP-Ph film (20 × 5 mm) was immersed in 6 mL of a 5 wt% aqueous solution of 1,3-bis(aminomethyl)benzene with magnetic stirring at 80 °C for 10 h. For the biodegradability test, CPP-Ph films were cut into 15 × 15 mm square pieces and buried in natural soil at a depth of 10 cm. The samples were periodically retrieved for observation, and their weight changes over time were recorded.

(7) Green chemistry metrics

The green chemistry metrics were evaluated based on the following parameters.

(a) Atom economy (AE)

AE is a measure of the efficiency of a chemical reaction, indicating the extent to which atoms from the reactants are incorporated into the desired product.[2, 3] The ideal value of AE factor is 100% (all atoms from the starting materials reside in the product). The atom economy values of CLE and CPP samples were calculated according to the equation (2):

$$\mathrm{AE}\ (\%) = \frac{\text{Molecular weight of the product}}{\sum \text{Molecular weight of reactants}} \times 100 \qquad (2)$$

The diamine monomers used for preparing CPP-Ph, CPP-C5, and CPP-C10 were 1,3-bis(aminomethyl)benzene (136.19 g/mol), 1,5-diaminopentane (102.18 g/mol), and 1,10-diaminodecane (172.31 g/mol), respectively.

(b) Environmental factor (*E*-factor) and process mass intensity (PMI) analysis

R. A. Sheldon has proposed the *E*-factor to quantify the sustainability of a process.[4-6] The *E*-factor was calculated based on the mass of waste generated, with recovery rates of 87.0% for DBU, 96.2% for DMSO, and 92.4% for i-PrOH adopted from a related DBU/DMSO/CO_2 solvent system.[7] The *E*-factors of the CPP samples were calculated according to the equation (3):

$$E\text{ - factor} = \frac{\sum \mathrm{m}\ (\text{raw materials}) + \sum \mathrm{m}\ (\text{spent reagents}) + \sum \mathrm{m}\ (\text{solvent losses}) - \mathrm{m}}{\mathrm{m}\ (\text{product})}$$

PMI is defined as the total mass of all materials used in a process divided by the mass of the product.[8, 9] The PMI values of the CPPs were calculated according to the equation (4):

$$\mathrm{PMI} = \frac{\sum \mathrm{m}\ (\text{raw materials}) + \sum \mathrm{m}\ (\text{reagents}) + \sum \mathrm{m}\ (\text{solvent})}{\mathrm{m}\ (\text{product})} \qquad (4)$$

The amount of CO_2 in step 1 was estimated using the ideal gas law:

$$\mathrm{n}\left(\mathrm{CO_2}\right) \approx 3 \times \frac{P_1 V}{RT} + \frac{P_2 V}{RT} \qquad (5)$$

Where P_1 is 1 MPa, P_2 is 1.5 MPa, V is 400 mL, R is 8.314 J $\mathrm{mol^{-1}}$ $\mathrm{K^{-1}}$, and T is 298.15 K. The calculation was based on a representative batch using 10 g of MCC. For other batch sizes, the CO_2 amount was scaled proportionally according to the MCC mass.

(c) Biorenewable carbon (BRC) content

BRC content refers to the percentage of carbon derived from biorenewable resources relative to the total carbon content of the material.[10, 11] The BRC values of the CPP samples were calculated according to the equation (6):

$$\mathrm{BRC}\ (\%) = \frac{\text{Biosourced carbon}}{\text{Biosourced carbon} + \text{Fossil carbon}} \times 100 \qquad (6)$$

In this calculation, 1,5-diaminopentane and 1,10-diaminodecane were treated as bio-based, whereas 1,3-bis(aminomethyl)benzene was treated as fossil-based.

(d) Energy consumption

The energy consumption of each processing step was estimated based on the rated power of the laboratory equipment and the corresponding operating time,[12, 13] as follows:

$$E = \sum (P_i \times t_i) \qquad (7)$$

Where E is the total energy consumption, P_i is the rated power of each laboratory device, and t_i is the corresponding operating time. The reported values are laboratory-scale estimates based on a representative batch using 10 g of cellulose as the starting material and were not normalized to the mass of the final product, because such normalization would substantially overestimate the specific energy consumption under low equipment loading conditions, particularly during the prolonged oven-drying step.

2. Supplementary figures and tables

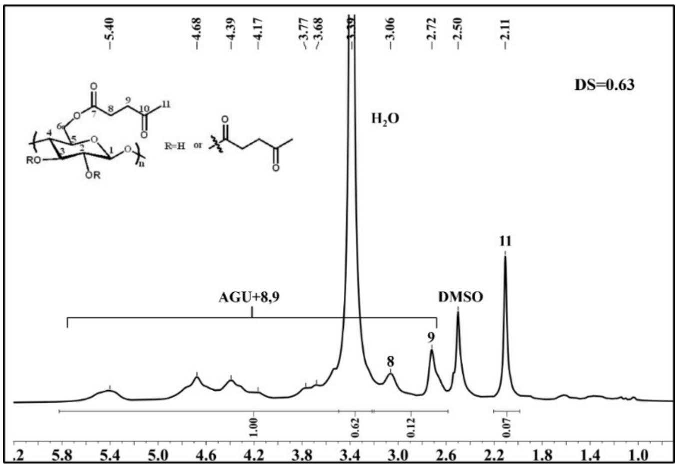


Fig. S1 ^{1}H-NMR of CLE (DS = 0.63).

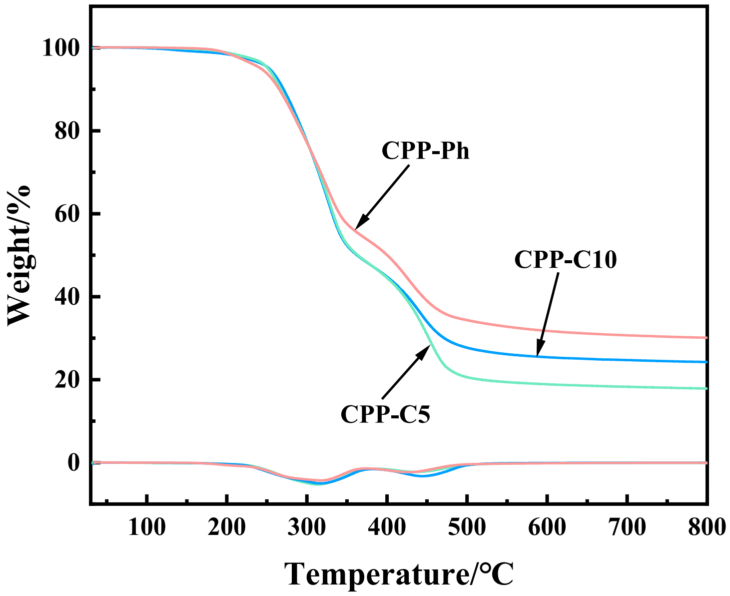


Fig. S2 TGA Spectra of CPP-Ph, CPP-C5, CPP-C10.

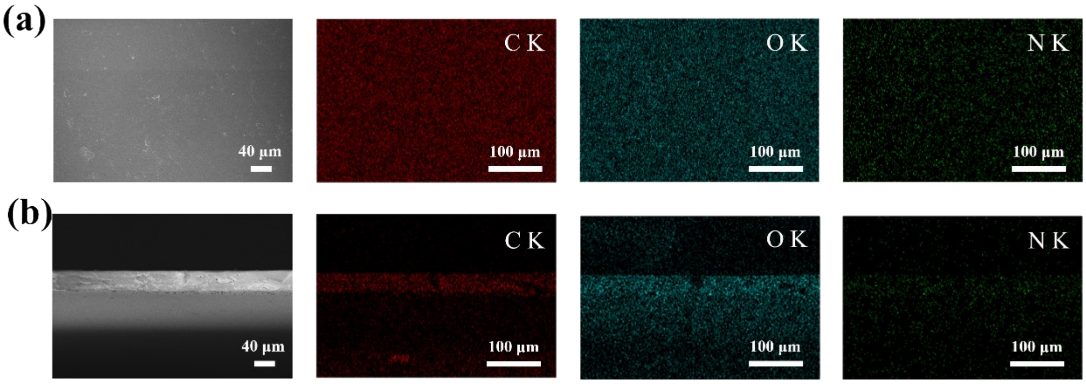


Fig. S3 (a) SEM images of the surface and EDS mapping images of C, O, N element at the surface for CPP-Ph film, (b) SEM images of the cross section and EDS mapping images of C, O, N element at the cross section for CPP-Ph film.

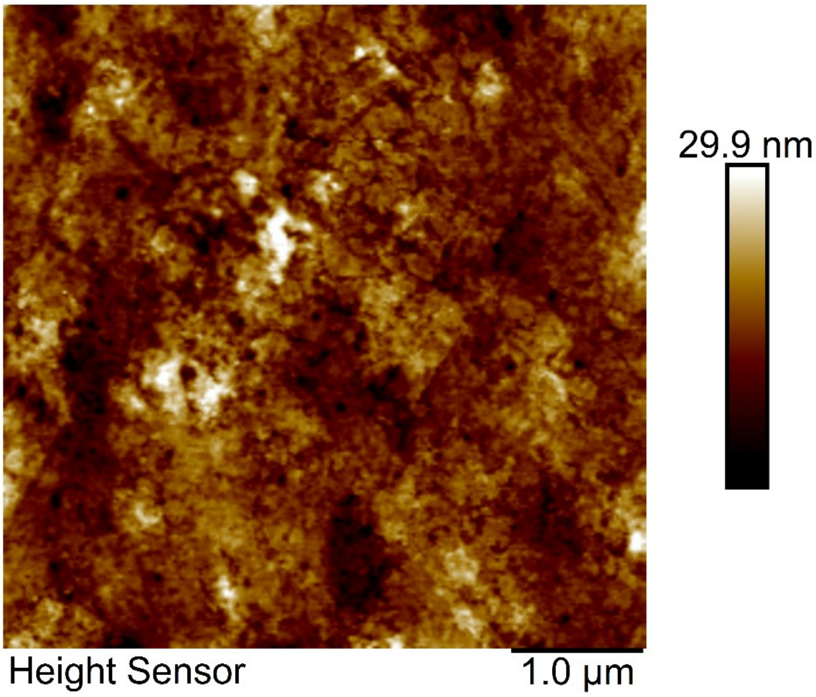
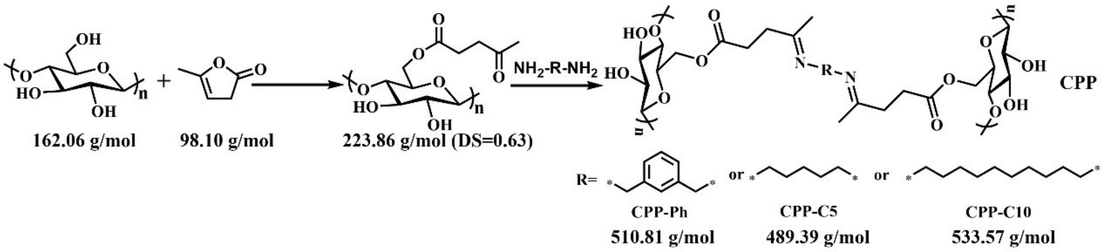


Fig. S4 2D AFM image of CPP-Ph film surface.

Table S1 Comparison of the tensile strength and Young's modulus of CPP-Ph with other biomass plastics and representative commercial plastics.

Plastics	**Tensile strength (MPa)**	**Young's modulus (GPa)**	**References**
PLA	50.0	2.5	[14]
PET	70.0	3.1	[15]
PHB	49.2	2.1	[16]
PP	28.7	1.6	[17]
AC-TPA	67.0	3.2	[18]
PPC	71.0	3.2	[19]
CNF-imine	57.8	3.5	[20]
RM paper-20	47.9	2.3	[21]
LEHL-D	79.1	1.9	[22]
EN-PL20SA80	66.9	2.0	[23]
KL-70	45.2	2.3	[24]
Lignin@TN	74.9	1.3	[25]
PGCS-100	56.5	0.4	[26]
CP1-40%	47.0	2.9	[27]
CS-PI	38.4	2.8	[28]
CFP/TAV-PI	57.9	1.3	[29]
CPP-Ph	84.5	3.7	This work

Table S2. Theoretical atom economy of CLE and CPP.



Step	**Product**	**Reactants MW [a] (g/mol)**	**Product MW [b] (g/mol)**	**AE (%)**
1	CLE	223.86	223.86	100.00
2	CPP-Ph	533.52	510.81	95.74
2	CPP-C5	512.09	489.39	95.57
2	CPP-C10	556.28	533.57	95.92
Overall	CPP-Ph	533.52	510.81	95.74
Overall	CPP-C5	512.09	489.39	95.57
Overall	CPP-C10	556.28	533.57	95.92

a. The α-AL contribution in the reactants molecular weight was calculated as $\mathrm{DS} \times M_{\alpha\text{-AL}}$, where DS = 0.63.

b. For CPP, the diamine contribution was calculated as $\mathrm{DS} \times M_{\mathrm{diamine}}$, and the product molecular weight was obtained after subtracting $2 \times \mathrm{DS} \times M_{H_2O}$.

Table S3. Material input-output table for the process toward CPP-Ph.

Step	Input material	Input type	Output material	MW (g/mol)	Density (g/mL)	Equiv.	Input mol	Input weight (kg)	Output weight (kg)
1	MCC	Raw material		162.06		1.00	4.548	0.737	
	DBU	Reagent		152.24		3.00	13.643	2.077	
	DMSO	Solvent		78.13				11.350	
	CO_2	Reagent		44.01			53.433	2.352	
	α-AL	Raw material		98.10		-OH/α-AL=1/2.5	34.108	3.346	
	i-PrOH	Solvent			0.78			34.492	
			CLE (DS=0.63)	223.86					0.921
2	CLE (DS=0.63)	Intermediate		223.86		1	4.114	0.921	
	1,3-bis(aminomethyl)benzene	Raw material		136.19		0.5	1.296	0.176	
	H_2O	Solvent		18.00	1			8.289	
			CPP-Ph	510.81					1

The material inputs were estimated based on a representative CLE preparation batch. CO_2 and H_2O were included for PMI calculation but excluded from the total *E*-factor calculation. At larger scales, the used CO_2 could potentially be recycled, as it is released during the derivatization reaction. H_2O was used as a processing solvent and removed by evaporation during film formation. The treatment of CO_2 and H_2O described above also applies to the following tables.

Table S4. *E*-factor analysis of the process toward CPP-Ph.

Step	Raw material (kg)	Spent reagent (excl. CO_2) (kg)	Solvent losses (excl. water) (kg)	Product (kg)	*E*-factor contribution (kg waste/kg final product)
1	4.083	0.270	3.053	0.921	6.485
2	1.097			1.00	0.097
Total				1.00	6.582

Table S5. PMI analysis of the process toward CPP-Ph.

Entry	Raw material (kg)	Reagent (kg)	Solvent (kg)	Product (kg)	PMI (kg/kg)
Overall	4.259	4.429	54.131	1.00	62.819

Table S6. Material input-output table for the process toward CPP-C5.

Step	Input material	Input type	Output material	MW (g/mol)	Density (g/mL)	Equiv.	Input mol	Input weight (kg)	Output weight (kg)
1	MCC	Raw material		162.06		1.00	4.745	0.769	
	DBU	Reagent		152.24		3.00	14.235	2.167	
	DMSO	Solvent		78.13				11.843	
	CO_2	Reagent		44.01			55.753	2.454	
	α-AL	Raw material		98.10		-OH/α-AL=1/2.5	35.589	3.491	
	i-PrOH	Solvent			0.78			35.989	
			CLE (DS=0.63)	223.86					0.961
2	CLE (DS=0.63)	Intermediate		223.86		1	4.293	0.961	
	1,5-diaminopentane	Raw material		102.18		0.5	1.352	0.138	
	H_2O	Solvent		18.00	1			8.649	
			CPP-C5	489.39					1

Table S7. *E*-factor analysis of the process toward CPP-C5.

Step	Raw material (kg)	Spent reagent (excl. CO_2) (kg)	Solvent losses (excl. water) (kg)	Product (kg)	*E*-factor contribution (kg waste/kg final product)
1	4.260	0.282	3.185	0.961	6.766
2	1.099			1.000	0.099
Total				1.000	6.865

Table S8. PMI analysis of the process toward CPP-C5.

Entry	Raw material (kg)	Reagent (kg)	Solvent (kg)	Product (kg)	PMI (kg/kg)
Overall	4.398	4.621	56.481	1.00	65.500

Table S9. Material input-output table for the process toward CPP-C10.

Step	Input material	Input type	Output material	MW (g/mol)	Density (g/mL)	Equiv.	Input mol	Input weight (kg)	Output weight (kg)
1	MCC	Raw material		162.06		1.00	4.350	0.705	
	DBU	Reagent		152.24		3.00	13.051	1.987	
	DMSO	Solvent		78.13				10.857	
	CO_2	Reagent		44.01			51.113	2.249	
	α-AL	Raw material		98.10		-OH/α-AL=1/2.5	32.627	3.201	
	i-PrOH	Solvent			0.78			32.994	
			CLE (DS=0.63)	223.86					0.881
2	CLE (DS=0.63)	Intermediate		223.86		1	3.935	0.881	
	1,10-decanediamine	Raw material		172.31		0.5	1.240	0.214	
	H_2O	Solvent		18.00	1			7.929	
			CPP-C10	533.57					1

Table S10. *E*-factor analysis of the process toward CPP-C10.

Step	Raw material (kg)	Spent reagent (excl. CO_2) (kg)	Solvent losses (excl. water) (kg)	Product (kg)	***E*-factor contribution (kg waste/kg final product)**
1	3.906	0.258	2.920	0.881	6.203
2	1.095			1.000	0.095
Total				1.000	6.298

Table S11. PMI analysis of the process toward CPP-C10.

Entry	**Raw material (kg)**	**Reagent (kg)**	**Solvent (kg)**	**Product (kg)**	**PMI (kg/kg)**
Overall	4.120	4.236	51.780	1.00	60.136

Table S12. Carbon-source composition and BRC values of CPP.

Sample	**MCC-derived carbon**	**α-AL-derived carbon** [a]	**Diamine-derived carbon** [b]	**Bio-based carbon**	**Fossil-based carbon**	**Total carbon**	**BRC%**
CPP-Ph	12.00	6.30	5.04	18.30	5.04	23.34	78.40
CPP-C5	12.00	6.30	3.15	21.45	0.00	21.45	100.00
CPP-C10	12.00	6.30	6.30	24.60	0.00	24.60	100.00

DS represents the degree of substitution of CLE, which was determined to be 0.63.

a. α-AL-derived carbon was calculated as 2 × 5 × DS, where 5 is the number of carbon atoms introduced by α-AL.

b. Diamine-derived carbon was calculated as n × DS, where n is the number of carbon atoms in the diamine.

Table S13. Estimated energy consumption of each processing step for CPP preparation.

Step	**Process**	**Equipment**	**Rated power, *P* (kW)**	**Operation time, *t* (h)**	**Energy consumption, *E* (kWh)**
1	Dissolution of cellulose	Reactor	1.000	3.000	3.000
	Stirring during dissolution	Mechanical stirrer	0.025	3.000	0.075
	Transesterification	Reactor	1.000	1.000	1.000
	Stirring during transesterification	Mechanical stirrer	0.025	1.000	0.025
	Vacuum filtration	Vacuum pump	0.180	0.500	0.090
	Vacuum drying	Vacuum oven	0.800	48.000	38.400
2	Dissolution/mixing of CLE and diamine	Stirrer	0.005	0.200	0.001
	Vacuum drying	Vacuum oven	0.800	6.000	4.800
Total					47.391

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