Supporting information

A room temperature dissolution solvent and mechanism for natural biopolymers: hydrogen bonding interaction investigation

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Notes

Note S1. Calculation of dissolution ratio.

The dissolution ratio (wt%) is the weight percentage of dissolved biopolymers to the sum of dissolved biopolymers and total solvent.

Dissolution ratio (wt%) = mass of dissolved biopolymers / (mass of dissolved biopolymers + mass of solvent) × 100%

Note S2. Calculation of Huggins constant [1-2]**.**

From the perspective of thermodynamic, intrinsic viscosity [η] is one of the important parameters to reflect the solubility of a solvent, and its value can be calculated by equations (1) and (2):

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s} \quad (1) \qquad [\eta] = lim(\frac{\eta_{sp}}{C})_{c\to 0} \quad (2)$$

Where η_{sp} and η are the specific viscosity and viscosity of solutions, and η_s is the viscosity of the pure solvent. C is the concentration of solution.

The Huggins-equation is a truncated version of equation (3) and is defined as follows:

$$\eta_{sp} = C\cdot[\eta] + K_H\cdot(C\cdot[\eta])^2 + A\cdot(C\cdot[\eta])^n \quad (3)$$

Where K_H is the Huggins constant, A and n are obtained from the non-linear regression.

Note S3. Determination content of formyl group and degree of substitution of the regenerated biopolymers.

The contents of formyl group in regenerated biopolymers were measured according to the calcium acetate method [2-3]. Firstly, 50 grams of deionized water and 30 grams of 0.25 M calcium acetate solution were mixed in a flask and then 0.5 gram regenerated cellulose was added. After reaction for 12 hours with continuously shaking, 30 grams of the dispersion liquid was titrated with 0.01 M sodium hydroxide using a phenolphthalein indicator. Then, the formyl contents were calculated according to the formula (4):

$$Formyl\ content\ (mmol/g) = \frac{\frac{50+30+0.5}{30} \times 0.01 \times V_{NaOH}}{m} \quad (4)$$

Where 0.01 is the molar concentration (mol/L) of NaOH, V_{NaOH} is the volume (mL) of NaOH solution used for titration, and m is the weight (gram) of regenerated biopolymers sample.

Note S4. The process of regenerating biopolymers and recycling solvent.

Water was added to the dissolved biopolymers mixture solution (20:1), and the mixture was stirred for around twenty minutes. The precipitated biopolymers were filtrated and putted it into a vacuum drying oven 60 ℃ for 12 hours. The excess water was removed using rotary evaporator. Finally, we obtain the regenerated biopolymers and regenerated DES. In consideration of formic acid (FA) tends to be evaporated with water, the loss of FA is approximate 2-3 grams, so pristine solvent (DES) is used to make up for it.

Note S5. The process of preparation of regenerated biopolymer materials

The dissolved solutions of biopolymers were centrifuged at 7000 rpm for 5-20 minutes to remove the bubbles. The cellulose dissolved solution was evenly poured into petri dish, then 30 wt% calcium chloride aqueous solution was added and soaked for about 5 hours. Take out the sample and then soak it in ethanol for about 2 hours to obtain the regenerated hydrogel. Next, the ions and ethanol in hydrogel were removed by water and the gel was placed in a vacuum drying oven to obtain a transparent film material. Besides, the solution was uniformly injected into syringe and a piston was pushed to squeeze the solution into a petri dish of calcium chloride, which solidified the filament. Subsequently, the filament sample was immersed in ethanol for 10 minutes and removed all the ions and impurities with water. Drying the sample to get the strong filament material.

The starch dissolved solution was uniformly poured into petri dish, then 50 wt% glutaraldehyde aqueous solution was added and used for ambient crosslinking about 48 hours. Take out the sample and soak it in ethanol for about 5 hours to obtain the regenerated hydrogel. Next, the ions and ethanol in hydrogel were removed by water and the gel was placed in a vacuum drying oven to obtain the film material. The dissolved solution of chitin and silk were uniformly poured into petri dish, then ethanol was added to soak the samples for

12 hours and obtain the white gels. Next, the ions and ethanol in gels were removed by water and the gels were placed in a vacuum drying oven to obtain the white film materials.

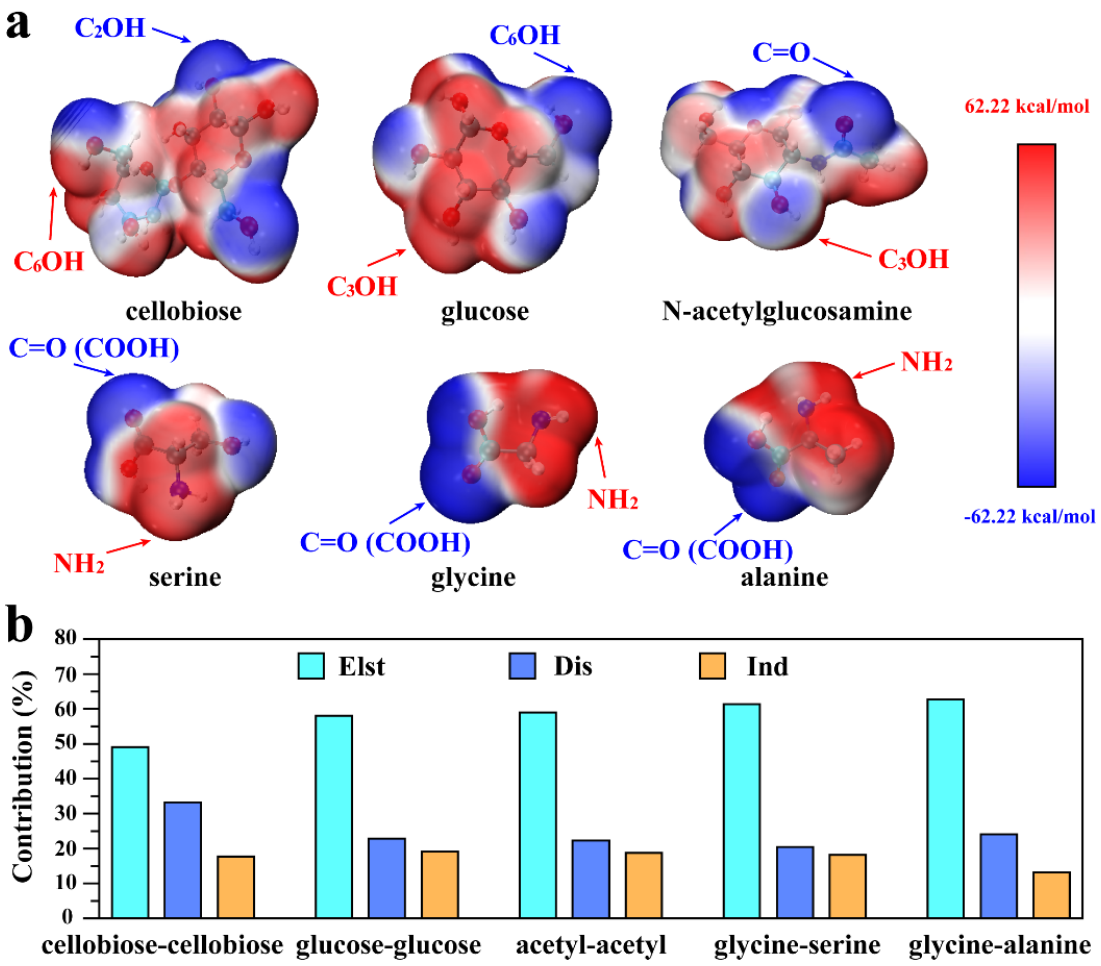

Figure S1 (a) The electrostatic surface potential (ESP) plots of natural biopolymers models. The red (or blue) area is where the positive (or negative) potential is intensive. (b) Contribution percentage diagram of electrostatic, dispersion and induction interactions for biopolymers.

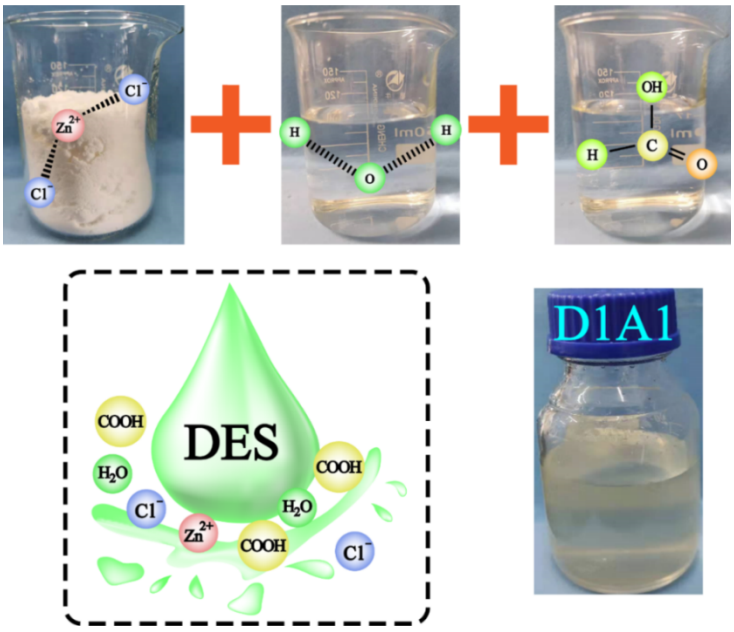

Figure S2 Illustration of the synthesis of deep eutectic solvent (DES).

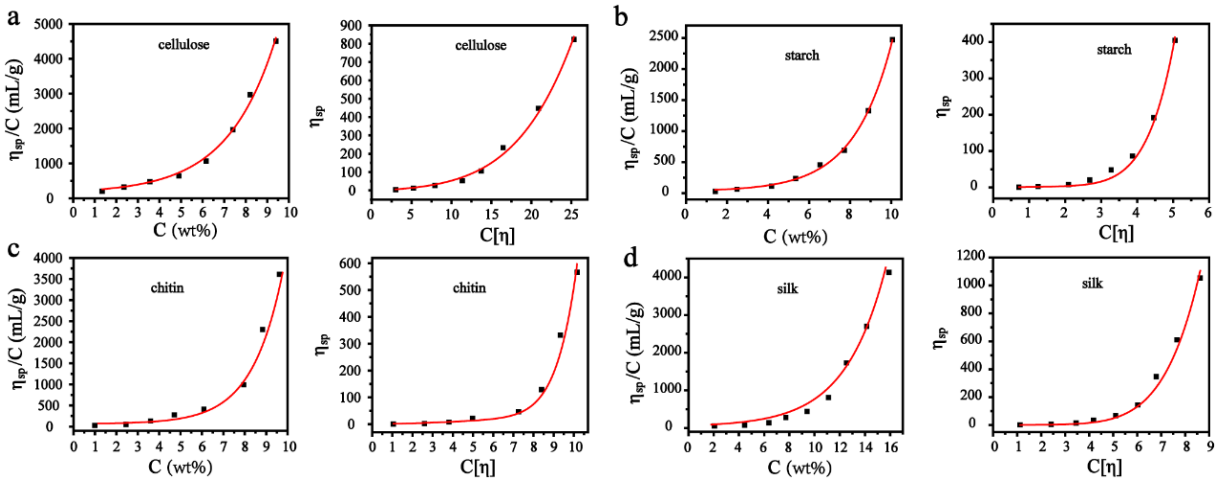

Figure S3 (a) and (b) Concentration dependence of η_{sp}/C for biopolymers/DES solutions at room temperature. (c) and (d) The specific viscosity (η_{sp}), as a function of C[η] for biopolymers/DES solutions at room temperature.

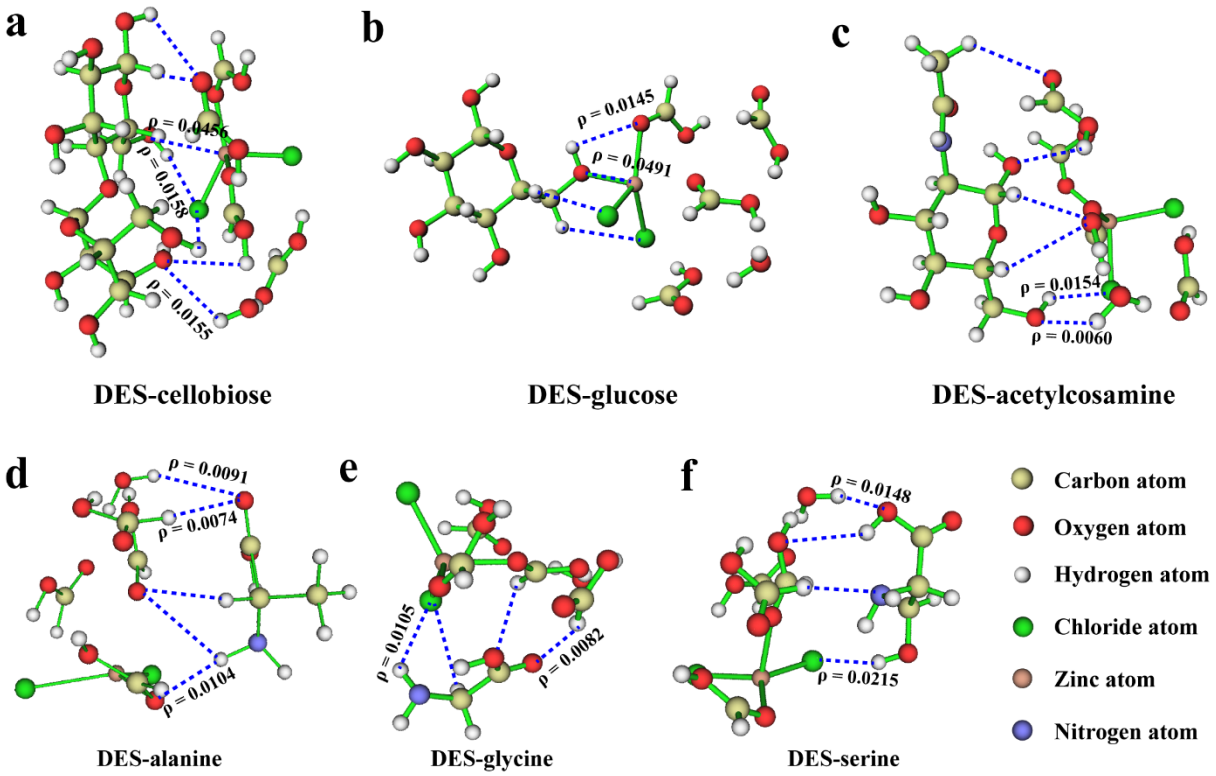

Figure S4 The topological diagram of hydrogen bonding networks between biopolymers and solvent for (a) DES-cellobiose, (b) DES-glucose, (c) DES-acetylglucosamine, (d) DES-alanine, (e) DES-glycine, (f) DES-serine.

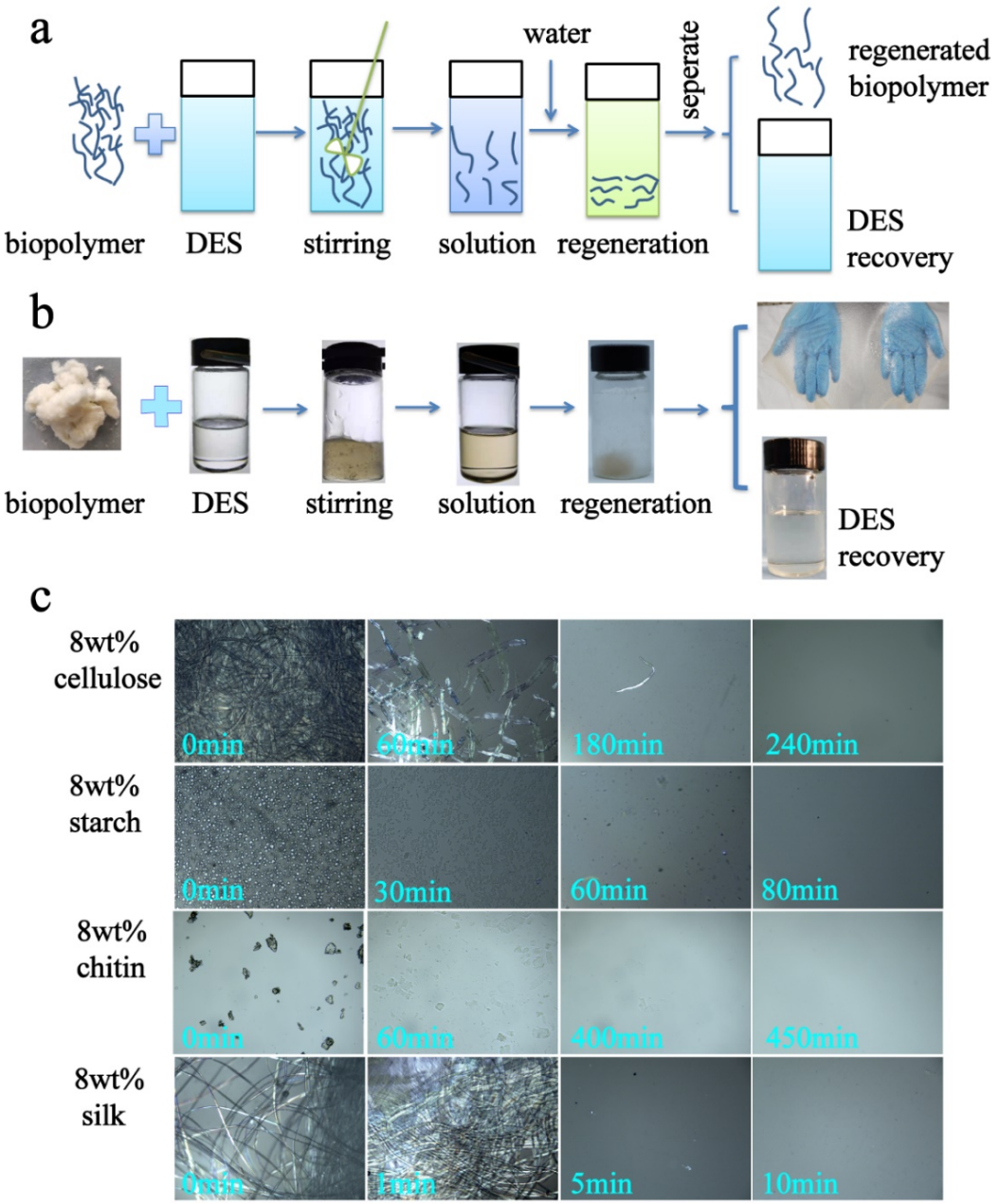

Figure S5 (a) Flow chart and (b) photographic images of the dissolving biopolymers process using DES and regenerating biopolymers using water. (c) Micrographs of cellulose, starch, chitin, and silk dissolved by DES at room temperature.

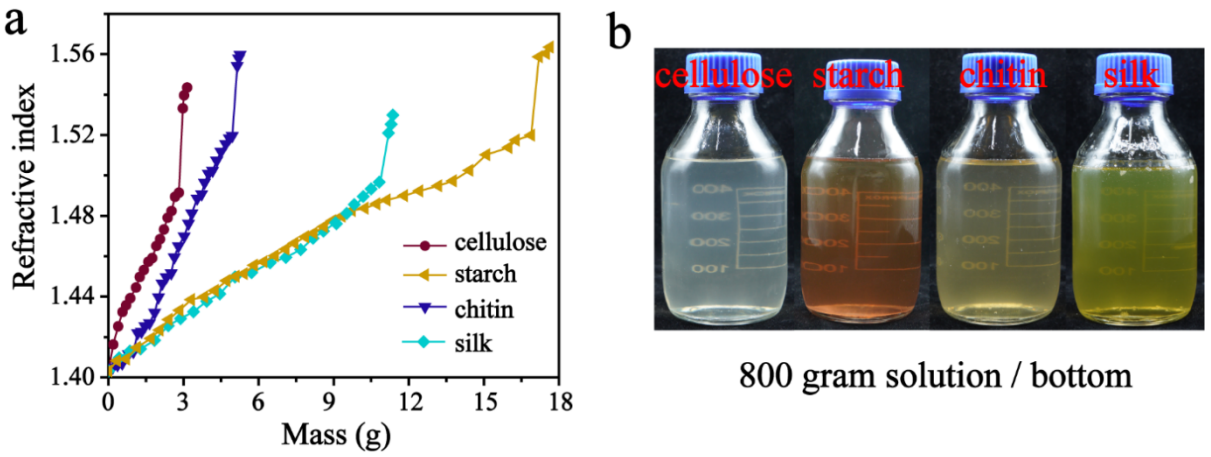

Figure S6 (a) Refractive index of biopolymers sources using the DES at room temperature. (b) The photographic images for the 8 wt% dissolved solutions of biopolymers incorporated cellulose, starch, chitin, and silk.

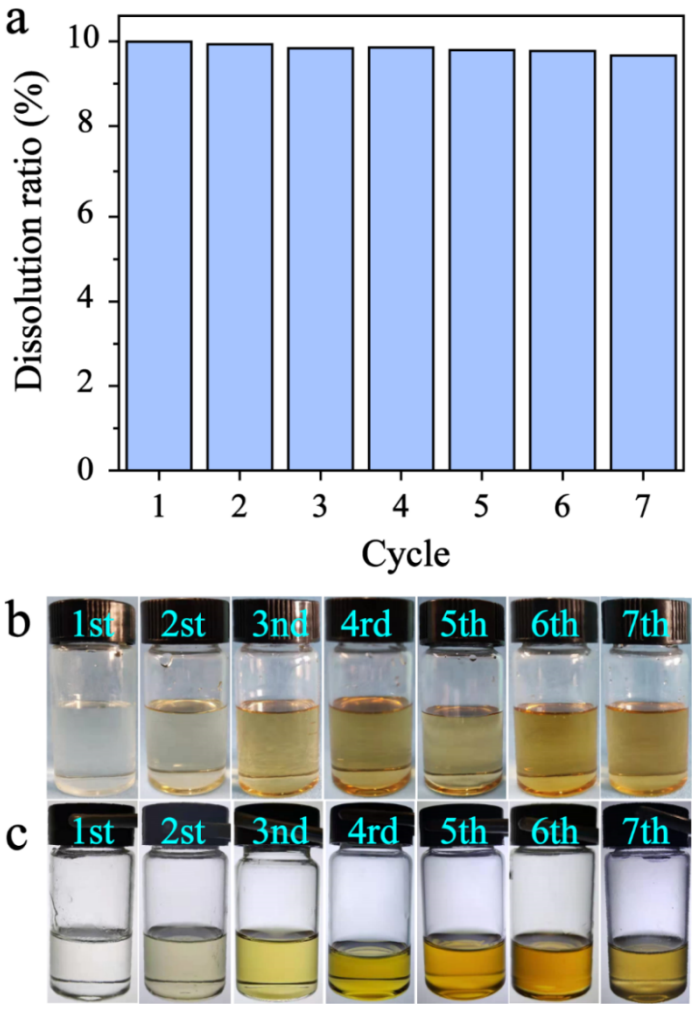

Figure S7 (a) Dissolving capacity of DES during seven successive reuses for cellulose dissolution at room temperature. Photographic pictures of (b) the DES solvent after seven successive recycles and (c) their corresponding dissolved cellulose solutions.

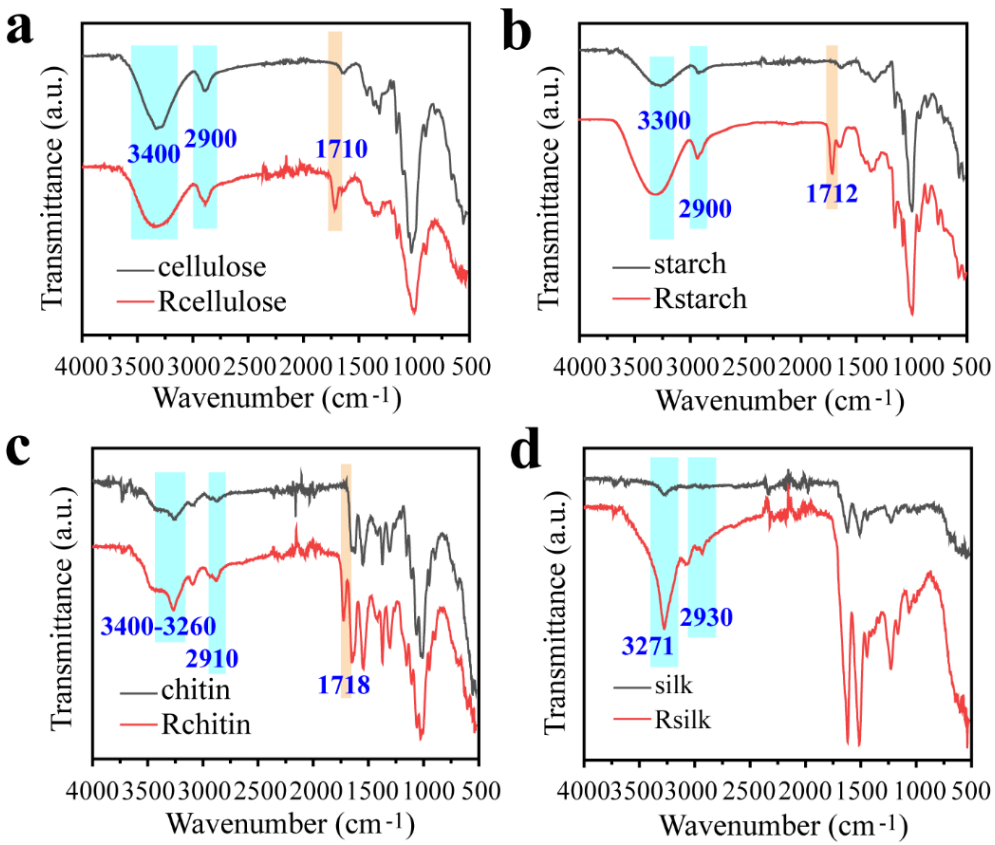

Figure S8 FTIR spectra for biopolymers and the corresponding regeneration products.

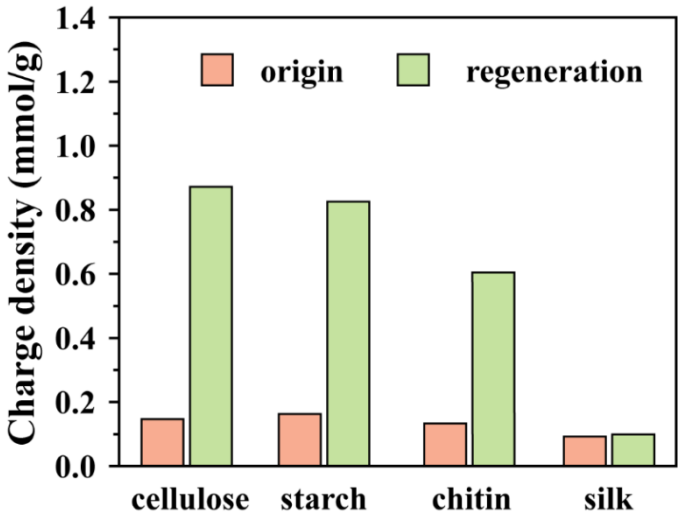

Figure S9 The values of charge density of biopolymers and the corresponding regeneration products.

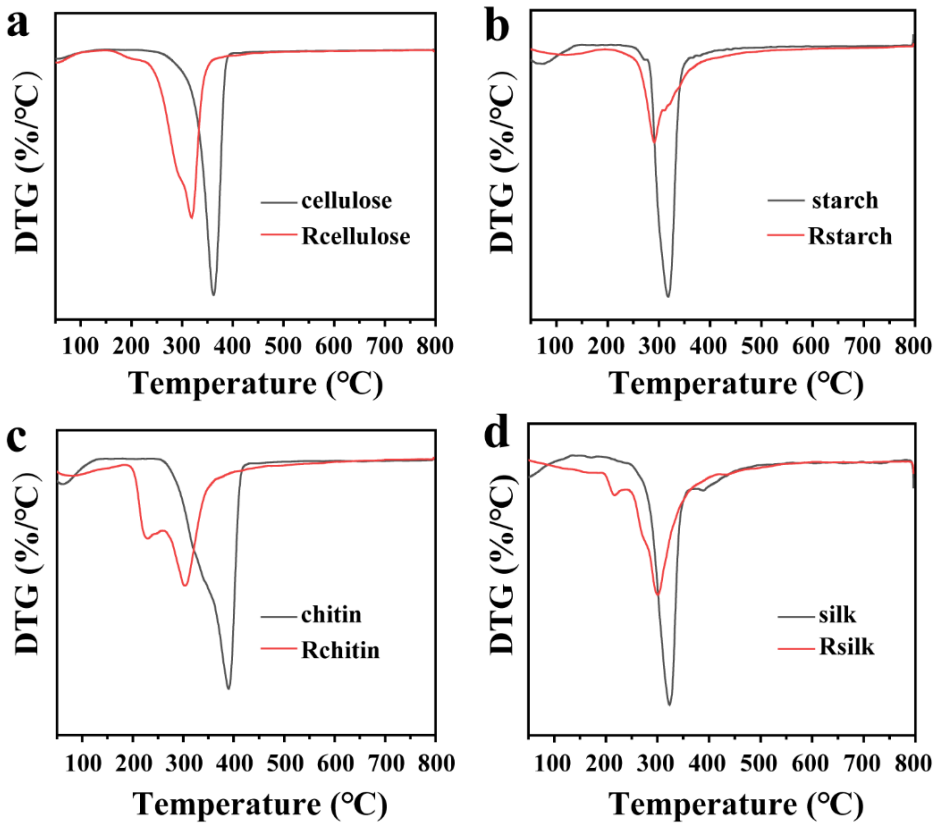

Figure S10 Differential thermogravimetry (DTG) data acquired from biopolymers feedstocks and regenerated biopolymers materials.

Table S1 The electron density (ρ) and Laplacian ($^{\nabla 2}\rho$) values for biopolymers itself at the bond critical points as calculated at the M062X/6-311++G** level.

System	Interaction	Sort	Length (Å)	ρ (0.002-0.035)	$^{\nabla 2}\rho$ (0.024-0.139)
cel-cel	OH···O	$C_6OH\cdots C_2'OH$	2.956	0.0261	0.0990
	O···HO	$C_3OH\cdots C_6'OH$	2.245	0.0255	0.1055
	O···HO	$C_2OH\cdots C_6'OH$	1.847	0.0301	0.1159
glu-glu	OH···O	$C_1OH\cdots C_2'OH$	1.836	0.0312	0.1165
	O···OH	$O_5\cdots C_1'OH$	1.839	0.0295	0.1186
	OH···O	$C_6OH\cdots O'_5$	1.913	0.0260	0.1026
ace-ace	O···NH	$C_1OH\cdots NH$	1.964	0.0225	0.0929
	O···OH	$O_5\cdots C_3'OH$	1.869	0.0288	0.1119
	OH···O	$C_6OH\cdots C_3'OH$	2.427	0.0110	0.0407
	O···OH	$C_6OH\cdots C_4'OH$	1.856	0.0292	0.1121
gly-ala	O···NH	C=O···HN	2.381	0.0097	0.0370
	NH···O	NH···O=C	2.432	0.0105	0.0398
gly-ser	O···CH	OH···CH	2.837	0.0051	0.0172
	O···OH	C=O···HO	1.874	0.0273	0.1076
	NH···O	NH···O=C	2.829	0.0086	0.0335

Table S2 Density functional theory (DFT) and PSI4 calculations of binding energies (BEs).

Parameters	BE (DFT) kcal mol^{-1}	BE (PSI4) kcal mol^{-1}	E_{elst} kcal mol^{-1}	E_{exch} kcal mol^{-1}	E_{ind} kcal mol^{-1}	E_{dis} kcal mol^{-1}
cel-cel	-18.28	-20.97	-30.67	41.36	-11.07	-20.79
glu-glu	-15.91	-17.44	-30.93	35.52	-10.17	-12.18
ace-ace	-10.86	-10.15	-15.83	16.54	-5.03	-5.98
gly-ser	-7.27	-8.85	-10.89	8.83	-3.22	-3.63
gly-ala	-4.87	-4.98	-8.60	8.81	-1.81	-3.30
DES-cel	-20.09	-21.28	-14.67	30.45	-9.19	-27.36
DES-glu	-18.04	-20.51	-12.88	43.31	-12.51	-38.43
DES-ace	-11.19	-13.80	-14.33	23.24	-5.43	-17.36
DES-ser	-8.10	-10.09	-8.85	14.44	-3.63	-12.11
DES-gly	-7.57	-10.27	-10.06	9.01	-2.38	-6.28
DES-ala	-7.60	-7.04	-8.24	10.08	-3.28	-5.68

Table S3 The electron density (ρ) and Laplacian ($^{\nabla 2}\rho$) values for DES-biopolymer systems at the bond critical points as calculated at the M062X/6-311++G** level.

System	Interaction	Sort	Length (Å)	ρ (0.002-0.035)	$^{\nabla 2}\rho$ (0.024-0.139)
DES-cel	C=O···OH	FA···C_1-OH	3.463	0.0068	0.0250
	C=O···CH	FA···C_1H	2.904	0.0034	0.0143
	Cl···HO	**Cl^-···HO-C_6**	**2.406**	**0.0158**	**0.0529**
	Zn···OH	**Zn^{2+}···OH-C_6**	**2.208**	**0.0456**	**0.0208**
	Cl···HC	Cl^-···HC_6	3.067	0.0113	0.0376
	Cl···HO	Cl^-···HO-C_6'	2.967	0.0128	0.0420
	HOH···O	**water···OH-C_3'**	**2.597**	**0.0155**	**0.0496**
	OH···O	FA···OH-C_3'	3.275	0.0034	0.0124
DES-glu	**Zn···OH**	**Zn^{2+}···OH-C_6**	**2.162**	**0.0491**	**0.2305**
	Cl···HC	Cl^-···HC_6	3.029	0.0062	0.0203
	C=O···OH	**FA···HO-C_6**	**2.629**	**0.0145**	**0.0506**
	Cl···HO	Cl^-···HC_5	2.682	0.0107	0.0336
DES-ace	C=O···CH	FA···CH_3	3.014	0.0073	0.0325
	OH···O	FA···OH-C_1	3.314	0.0032	0.0121
	OH···O	FA···OH-C_1	2.588	0.0077	0.0245
	HO···HC	FA···HC_5	3.105	0.0032	0.0115
	Cl···HO	**Cl^-···HO-C_6**	**2.406**	**0.0154**	**0.0532**
	HOH···O	water···OH-C_6	3.319	0.0060	0.0214
DES-ala	O=C···NH	FA···NH_2	2.369	0.0104	0.0378
	O=C···NH	FA···NH_2	2.703	0.0064	0.0235
	O=C···CH	FA···CH	2.764	0.0114	0.0375
	CH···O=C	FA···HOOC	2.335	0.0074	0.0273
	HOH···O=C	water···HOOC	3.055	0.0091	0.0349
DES-gly	Cl···HN	Cl^-···HN_2	2.670	0.0105	0.0352
	Cl···HN	Cl^-···HC	3.005	0.0084	0.0292
	CH···O	FA···COOH	3.009	0.0082	0.0274
	CH···O	FA···COOH	3.413	0.0050	0.0163
DES-ser	**Cl···HO**	**Cl^-···HO**	**2.242**	**0.0215**	**0.0677**
	HOH···OH	**water···COOH**	**2.163**	**0.0148**	**0.0586**
	CH···N	FA···N	2.968	0.0036	0.0108
	O···HO	FA···COOH	2.633	0.0056	0.0210

Table S4 The scaling theory predictions for the structures of dissolved solutions.

Parameters	slope	C_1	C_2
cellulose	1.03, 1.45, 4.04	2.35	6.17
starch	1.02, 2.36, 4.73	1.94	7.95
chitin	0.87, 1.14, 3.39	2.48	5.34
silk	0.82, 1.58, 3.27	1.87	5.86

Reference

[S1] W. M. Kulicke, R. Kniewske, *Rheol. Acta*, 1984, **23**, 75-83.

[S2] Z. Tong, W. Wang, S. Zeng, Y. Sun, J. Meng, Q. Xia, H. Yu, *Green Chem.*, 2022, **24**, 8760-8769.

[S3] Y. Zhang, J. Wang, C. Liu, Y. Liu, Y. Li, M. Wu, Z. Li, B. Lin, *Int. J. Biol. Macromol.*, 2021, **170**, 397-405.