

## **Supplementary Information**

Preparation of tough, antioxidant and antibacterial bioplastic for sustainable packaging through an in-situ phenolization strategy

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### The calculation method for the hydroxyl content of lignin

The aliphatic hydroxyl group, phenolic hydroxyl group and carboxyl group of lignin are quantitatively analyzed using nuclear magnetic resonance phosphorus spectroscopy ( $^{31}\text{P}$  NMR). Cholesterol has proved to be one of the most effective internal standards (ISs) in  $^{31}\text{P}$  NMR analysis of lignin, its integral in  $\delta$  145 is used as the baseline for hydroxyl quantitative analysis.

(1) Calculate the mole quantity of IS (Cholesterol, with a purity of 99%) in IS solution:

$$\text{Cholesterol in IS solution (mmol)} = \frac{\text{Mass of Cholesterol (g)}}{386.65 \text{ (g/mol)}} \times 99\% \times 1000$$

(2) Calculate the mole quantity of IS (Cholesterol) in the NMR sample:

$$\begin{aligned} \text{Cholesterol in the NMR sample (mmol)} \\ = \frac{\text{Cholesterol in IS solution (mmol)}}{\text{Total mass of IS solution (g)}} \times \\ \text{Mass of 0.1 ml of IS solution (g)} \end{aligned}$$

(3) Calculate the ratio (R) of the integration of the spectral region of interest (IOH) over the IS region (I Cholesterol):

$$R = \frac{\text{Integration of the spectral region of interest}}{\text{Integration of Cholesterol region}}$$

(4) Calculate the amount of different hydroxyl groups in lignin samples, that is, mmol OH/g lignin:

$$\begin{aligned} \text{mmol of different types of OH per g of lignin} \\ = \frac{R \times \text{mmol of cholesterol in NMR sample (mmol)}}{\text{Dry weight of lignin (g)}} \end{aligned}$$

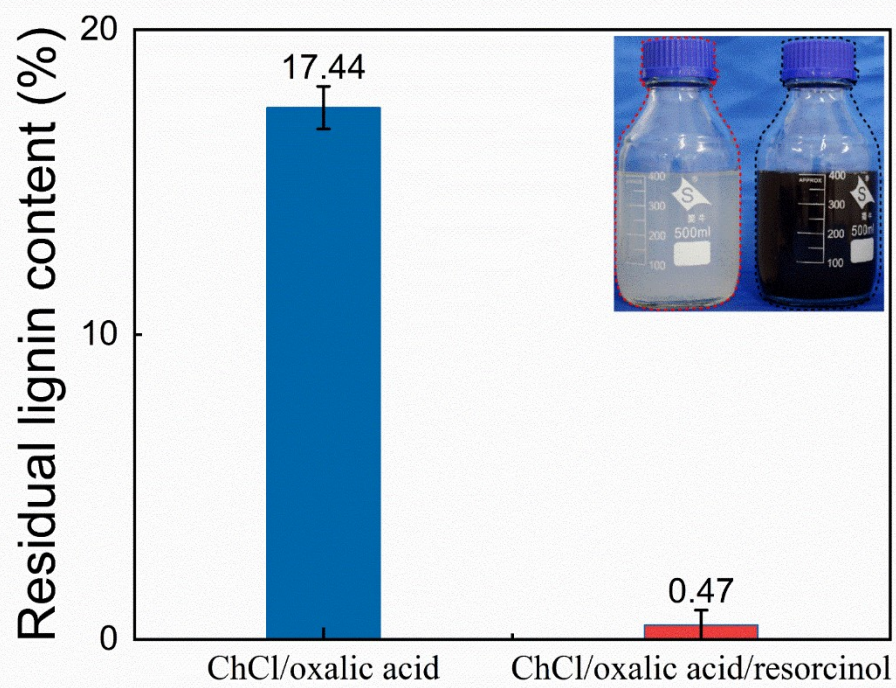


Fig. S1. The residual lignin content in cellulose treated by ChCl/oxalic acid and ChCl/oxalic acid/resorcinol.

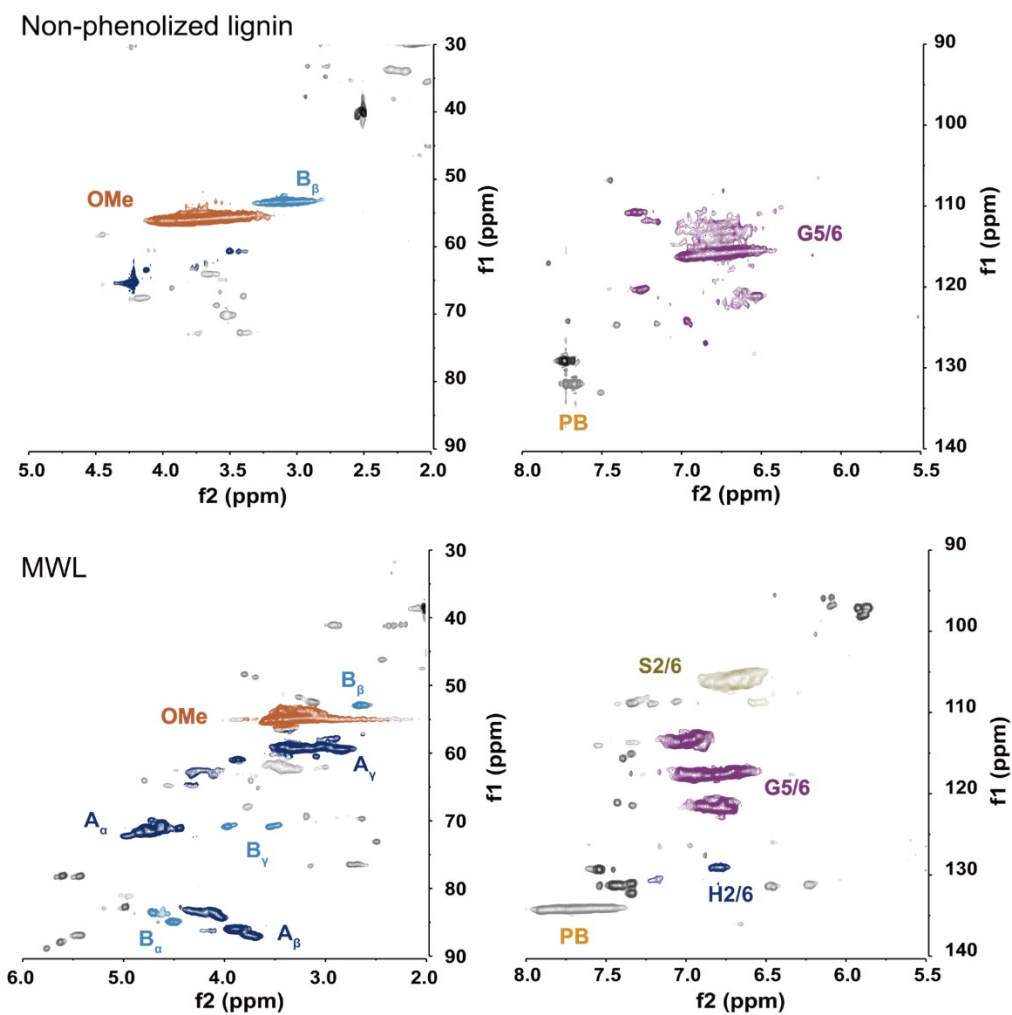


Fig. S2. The 2D-HSQC NMR spectra of non-phenolized lignin obtained by DES (ChCl/oxalic acid) treatment and milled wood lignin (MWL).

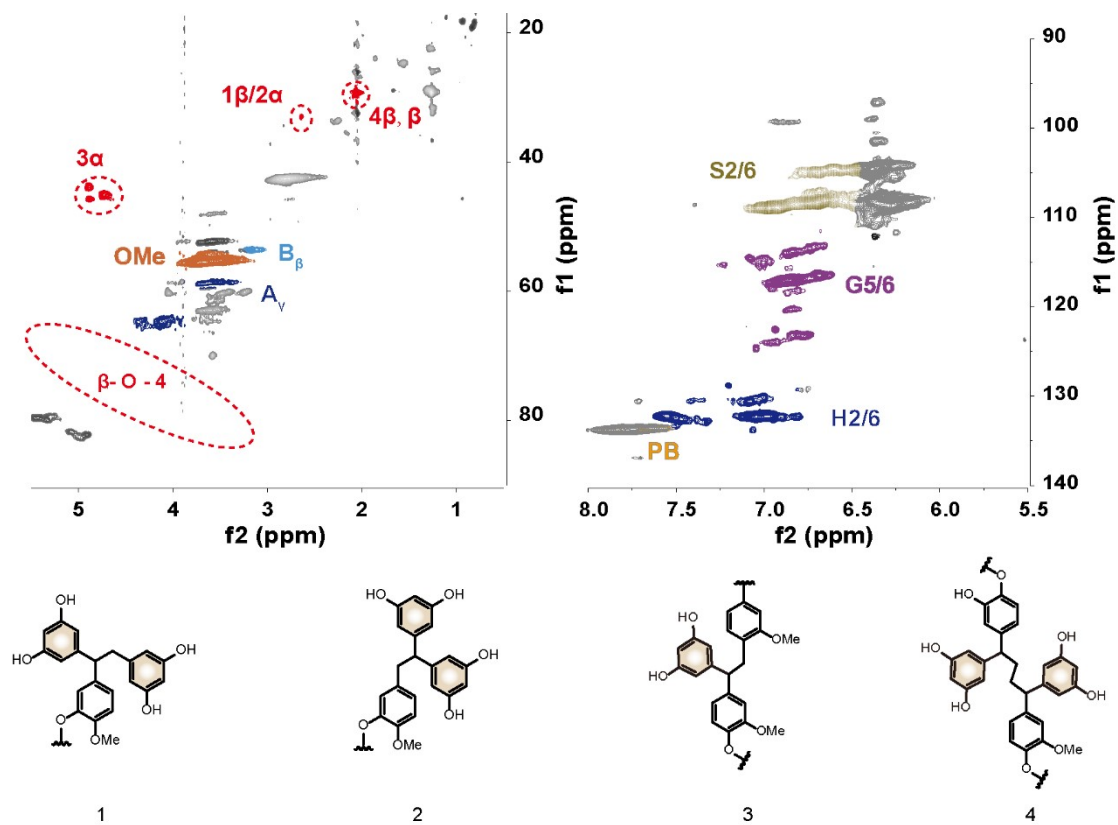


Fig. S3. The 2D-HSQC NMR spectra of phenolized lignin obtained by DES (ChCl/citric acid/resorcinol) treatment.

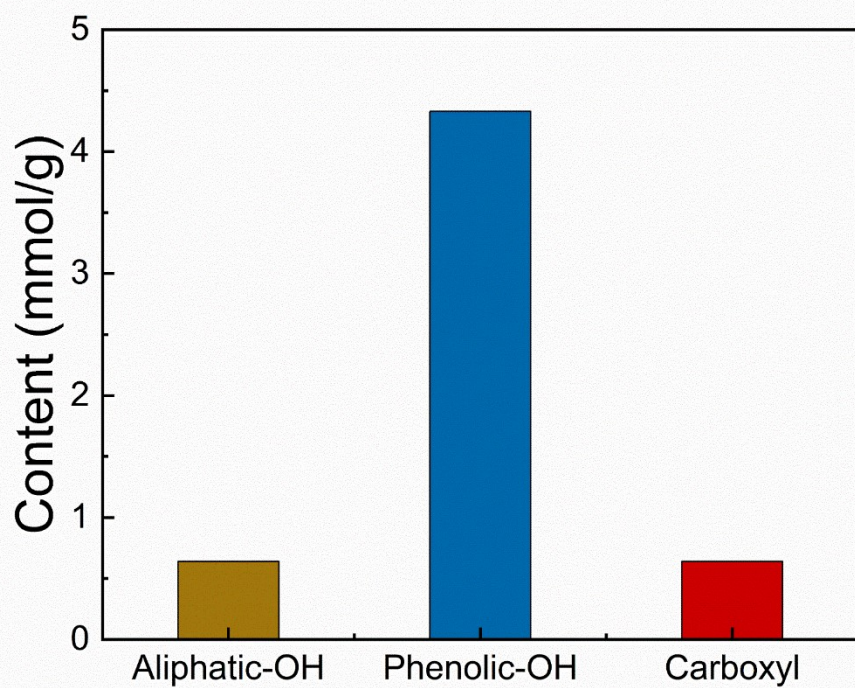


Fig. S4. The content of aliphatic hydroxyl, phenolic hydroxyl, and carboxyl groups in phenolized lignin obtained by DES (ChCl/citric acid/resorcinol) treatment.

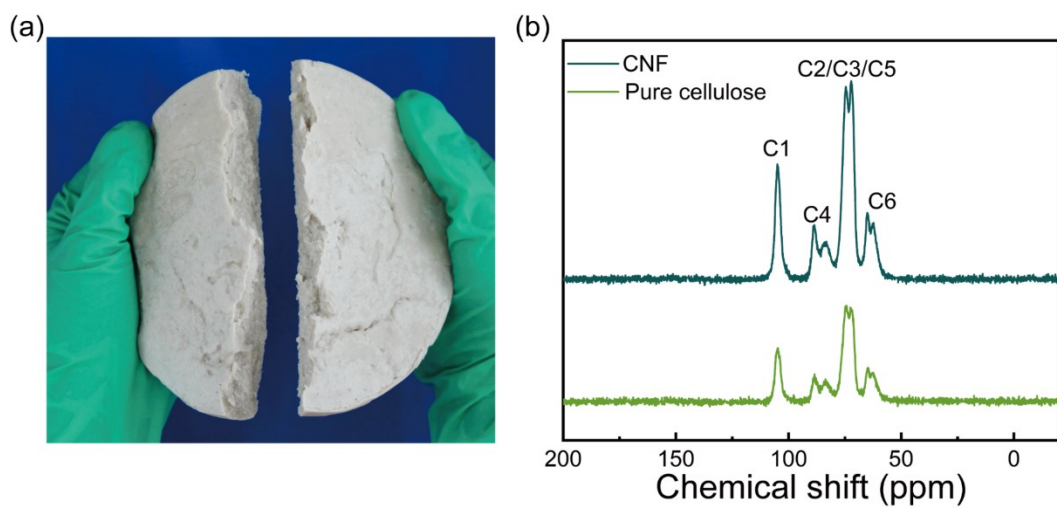


Fig. S5. (a) Cellulose obtained by DES (ChCl/oxalic acid/resorcinol) treatment; (b) Solid-state  $^{13}\text{C}$  NMR spectra of CNF obtained by DES (ChCl/oxalic acid/resorcinol) and pure cellulose.

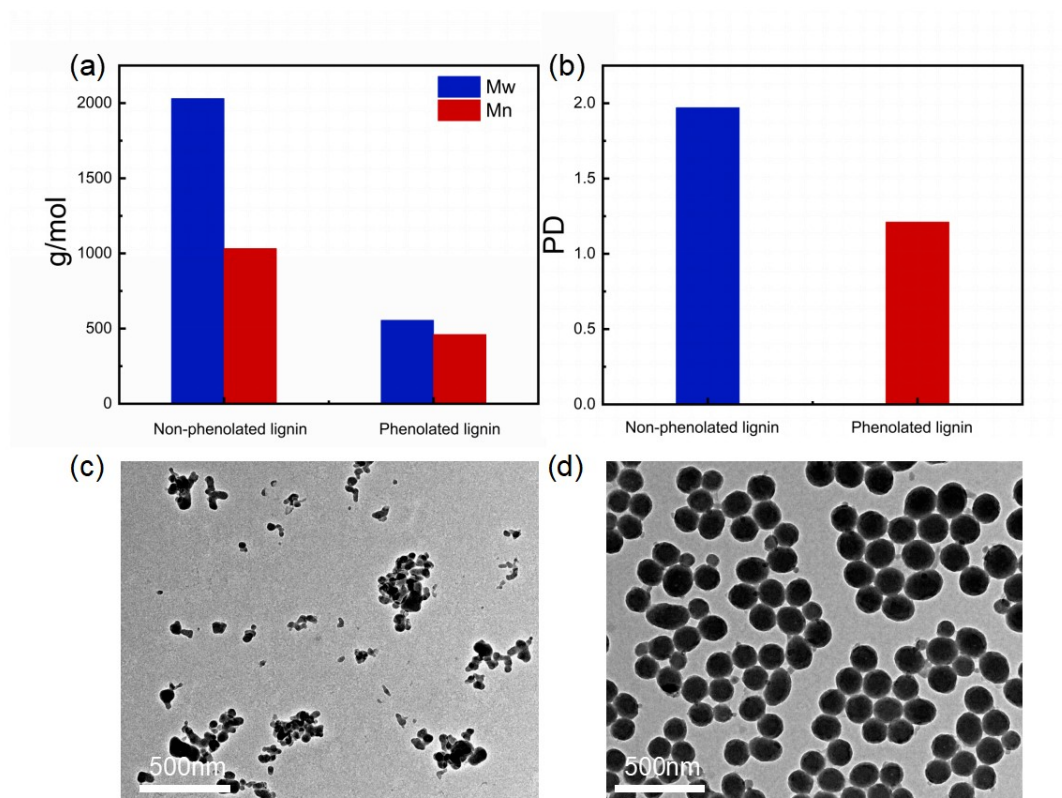


Fig. S6. (a) The Mw and Mn of non-phenolized lignin and phenolized lignin. (b) The PD of non-phenolized lignin and phenolized lignin. TEM images of (c) non-phenolized lignin nanospheres and (d) phenolized lignin nanospheres.



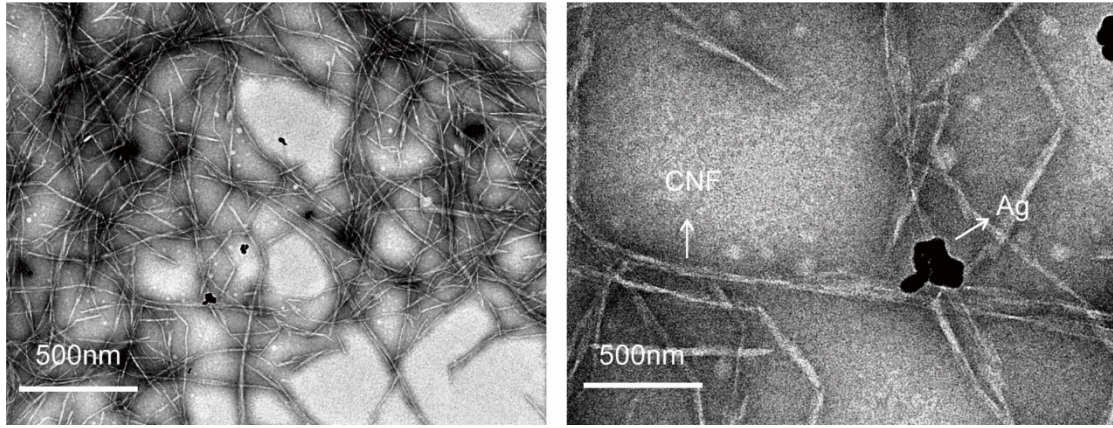


Fig. S7. Transmission electron microscope (TEM) images of cellulose-based bioplastic.

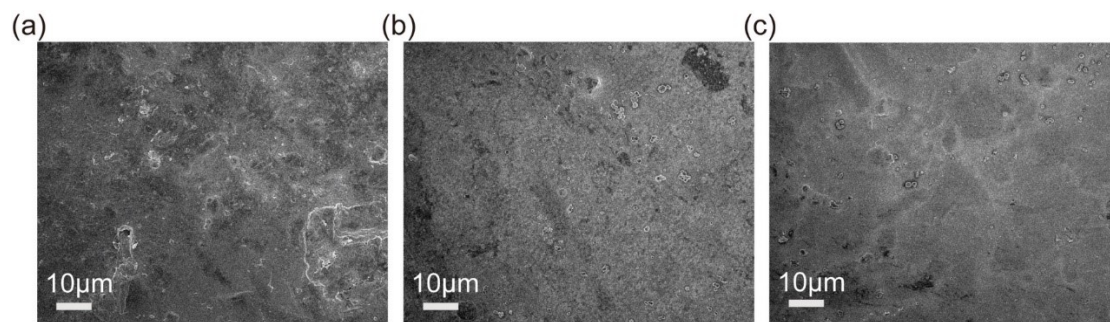
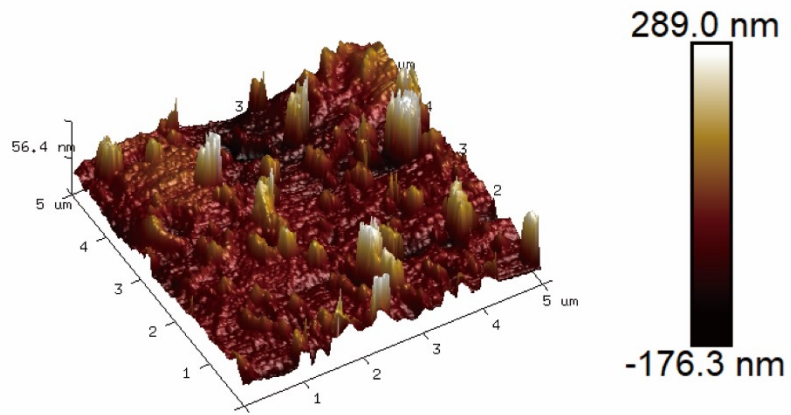


Fig. S8. SEM images of (a) cellulose-based bioplastic, (b) non-phenolized bioplastic and (c) Ph-bioplastic.



Height Sensor

Ra=50.7nm

Fig. S9. Atomic Force Microscope (AFM) images of cellulose-based bioplastic.

**Both DES dissolution and acid-catalyzed phenol modification effectively increase the phenolic hydroxyl content in lignin.** We selected DES-separated lignin<sup>[1]</sup> (denoted as PL1) and the phenol-modified lignin<sup>[2]</sup> (denoted as PL2), and applied the same preparation method used for Ph-bioplastic to prepare PL1-bioplastic and PL2-bioplastic, respectively.

**DES-separated lignin (PL1) <sup>[1]</sup>:**

Glycerol and choline chloride were combined in a molar ratio of 2:1 with water at a ratio of 6:1 (The ratio is the mass ratio of DES to water), with the addition of 2% concentrated sulfuric acid was added to form an acidic binary solvent system. The sifted poplar powder was blended with the prepared solvent system in a mass ratio of 1:10 and subsequently stirred at 140 °C for 3 hours. After the reaction is completed, an appropriate amount of water is added, and then the solid-liquid separation is carried out by suction filtration. The obtained filtrate was diluted with deionized water to induce the precipitation of lignin solid and dried in a 60 °C oven for 12 hours to obtain the final product of lignin.

**Phenol-modified lignin (PL2) <sup>[2]</sup>:**

100 mg of sulfate lignin was dissolved in 300 mg phenol. 2.73  $\mu$ L of concentrated H<sub>2</sub>SO<sub>4</sub> (98 wt%) was added to the mixture and the reaction was carried out in a pressurized reactor at 105 °C for 1 h. The reaction was cooled to room temperature and dissolved with 5 mL of acetone/water (9:1, v/v) was added. The acetone solution was slowly dripped into 100 mL of deionized water while stirring. The precipitate was washed with deionized water to neutral, and dried in a 60 °C oven for 12 hours to obtain the final product of phenolated lignin.

The phenolic hydroxyl content of lignin obtained using our method is higher than other phenolized method (PL1: 1.72 mmol/g; PL2: 7.28 mmol/g). The abundant phenolic hydroxyl groups enable the lignin to strongly adhere to cellulose nanofibers through robust hydrogen bonds. Ph-bioplastic features a dense and uniform structure, while the surface of PL1-bioplastic and PL2-bioplastic are loose and rough (Fig. S10a, b, c). This further proves that lignin can better connect with cellulose to form a dense structure though in situ phenolation strategy. We evaluated the mechanical performance of Ph-bioplastic, PL1-bioplastic, and PL2-bioplastic and found that Ph-bioplastic exhibited higher tensile strength and tensile strain compared to both PL1-bioplastic and PL2-bioplastic in Fig. S10d. The toughness of Ph-bioplastics reaches 20 MJ/m<sup>3</sup>, approximately 5 times that of PL1-bioplastic and 2 times that of PL2-bioplastic (Fig. S10e), indicating that in situ phenolation strategy effectively improves the mechanical properties of bioplastic.

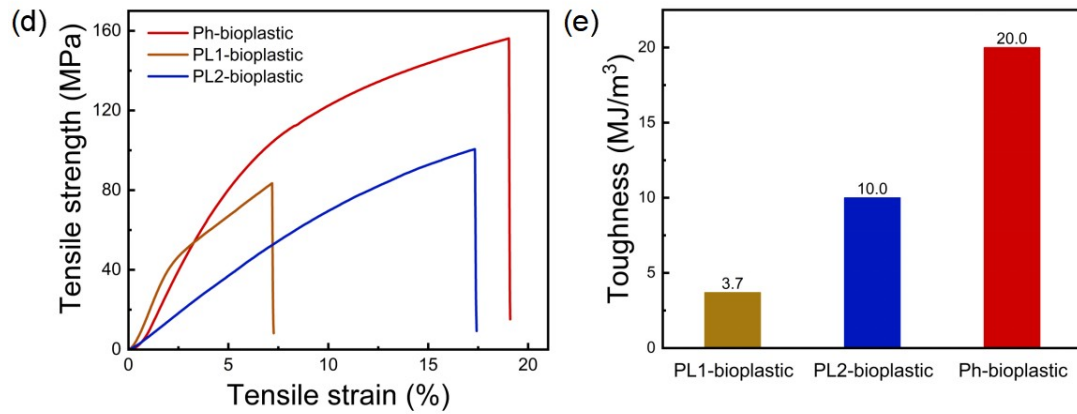
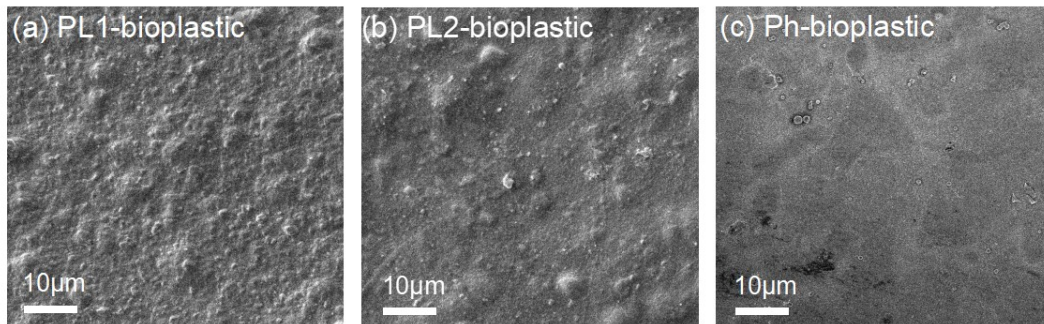


Fig. S10. SEM images of (a) PL1-bioplastic, (b) PL2-bioplastic, and (c) Ph-bioplastic. (d) The tensile stress-strain curves and (e) toughness of the PL1-bioplastic, PL2-bioplastic and Ph-bioplastic.

The maximum thermal degradation temperature of phenolized lignin (294 °C) was lower than that of non-phenolized lignin (368 °C), which may be attributed to the self-condensation of non-phenolized lignin through stronger C-C bond formation. This difference in lignin thermal stability directly influences the thermal stability of the corresponding bioplastics. The maximum thermal degradation temperature of Ph-bioplastic (357 °C), prepared by phenolized lignin, is slightly lower than that of non-phenolized bioplastic (364 °C); The glass transition temperature of phenolized lignin (112.5 °C) is higher than that of non-phenolized lignin (101.9 °C), which may be due to high phenolic hydroxyl group enhancing the intermolecular force of phenolized lignin, thereby limiting intermolecular mobility. Moreover, high phenolic hydroxyl group contribute to the formation of robust hydrogen bonds between phenolized lignin and cellulose. Therefore, phenolized bioplastic has a higher glass transition temperature (135.4 °C) compared to non-phenolized bioplastic (108 °C).

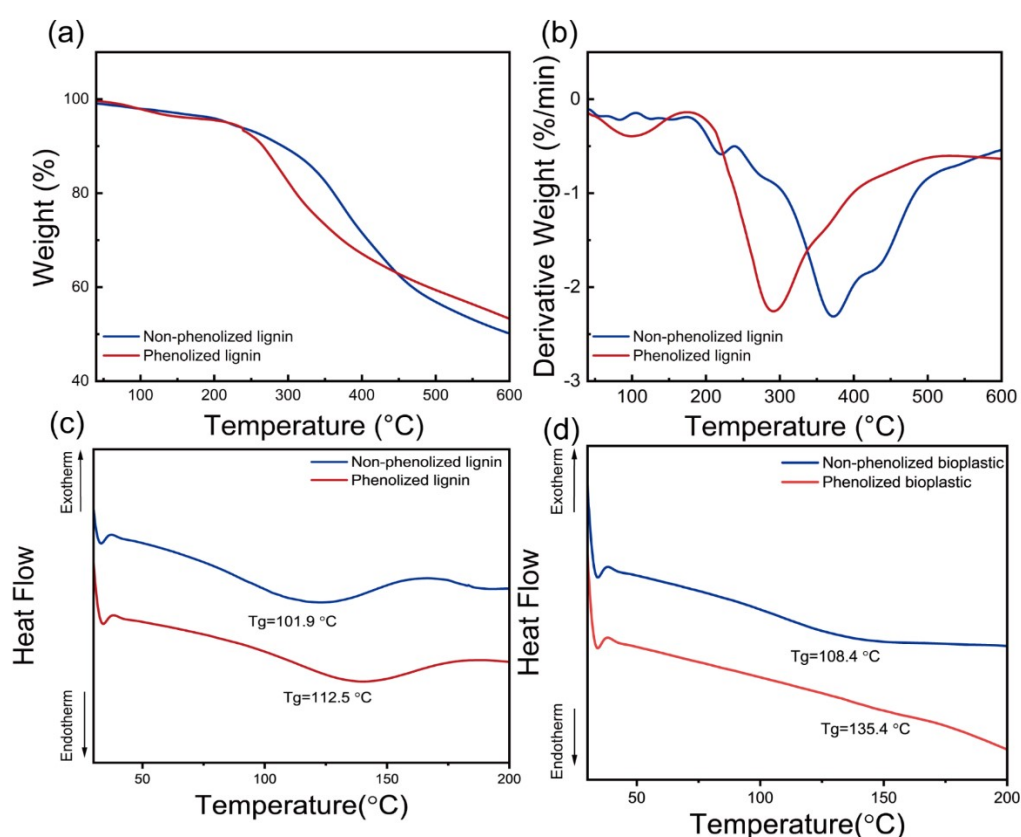


Fig. S11. (a) TGA and (b) DTG of non-phenolized lignin and phenolized lignin. (c) DSC of non-phenolized lignin and phenolized lignin. (d) DSC of non-phenolized bioplastic and Ph-bioplastic.

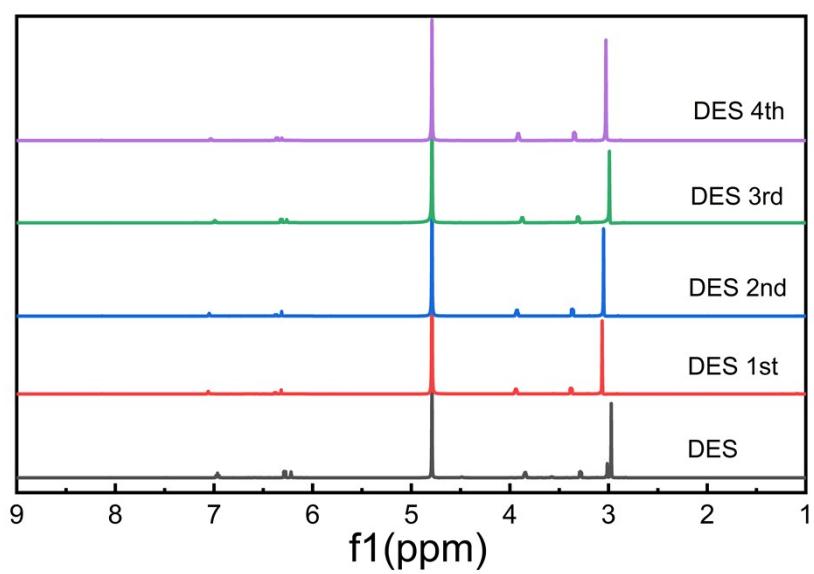


Fig. S12. <sup>1</sup>H NMR spectra of the phenolic DES was reused four times.

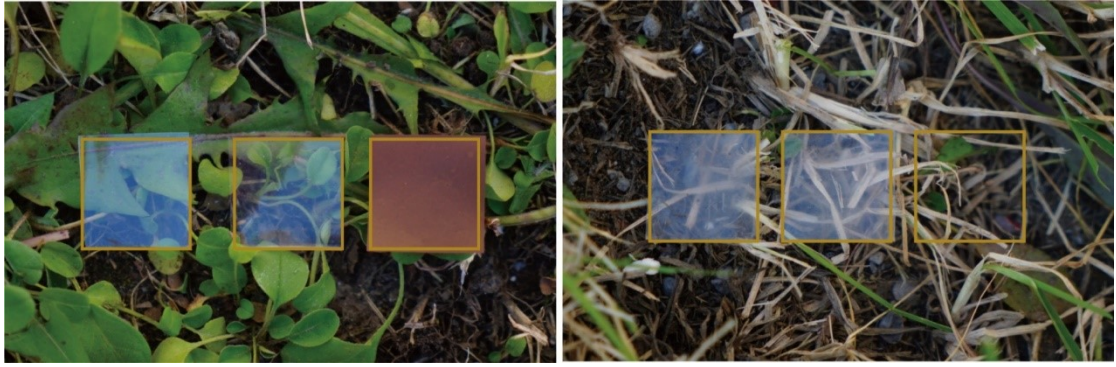


Fig. S13. The degradability tests of PE, PLA, and Ph-bioplastic under moist soil.



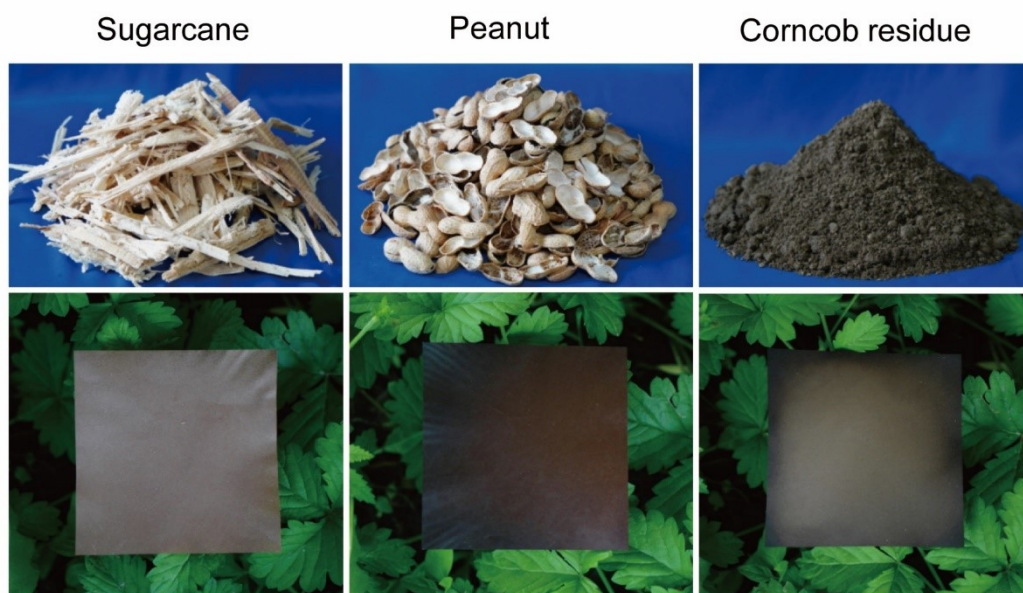


Fig. S14. The universality of lignin in situ phenolization strategy. Ph-bioplactic can be extracted from various biomass sources, including wood, sugarcane, peanut and corn cob residue.

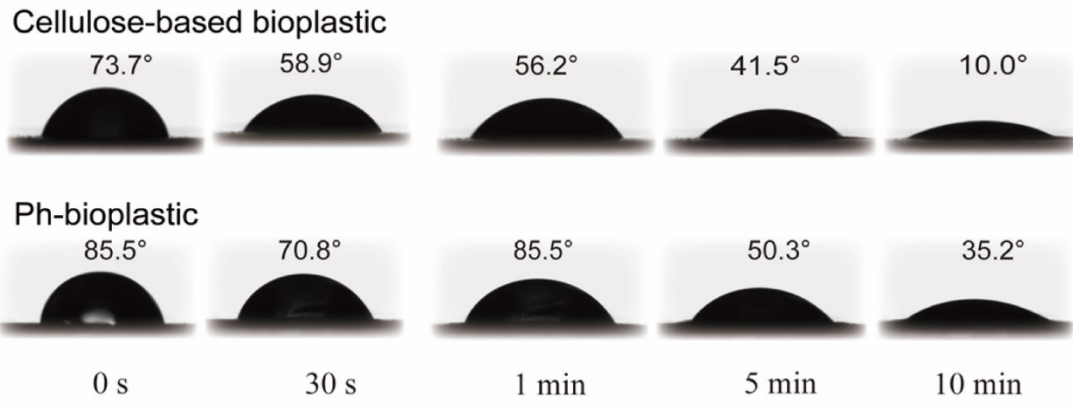


Fig. S15. Photographs of water droplets on the cellulose-based and Ph-bioplactic surface over time (0-10 min).

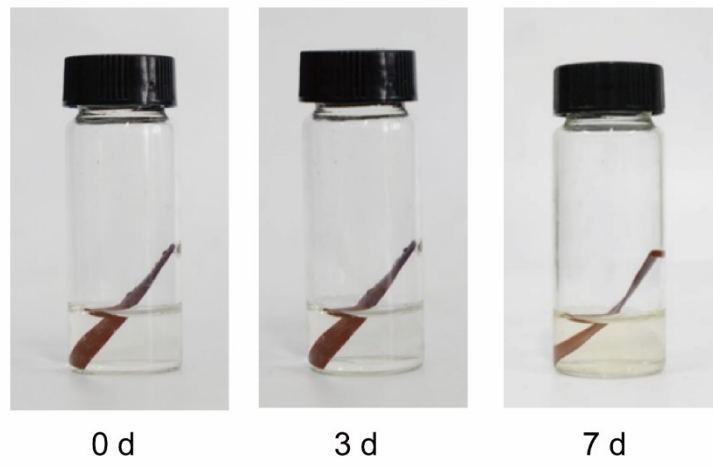


Fig. S16. Water stability test of cellulose film and Ph-bioplastic in water for 7 days.

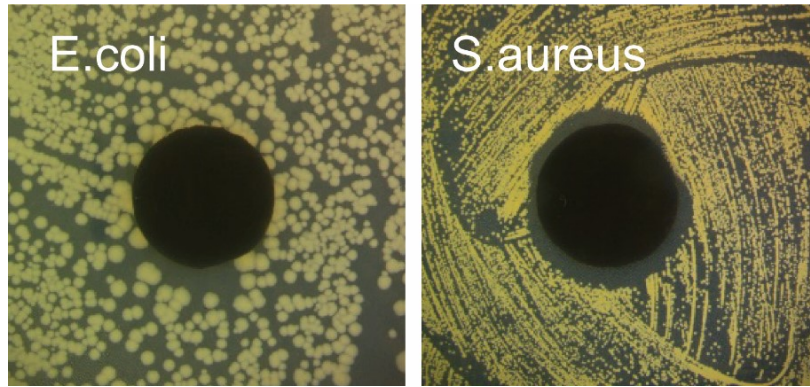


Fig. S17. Assessment of antibacterial properties of non-phenolized bioplastic.

Table S1. Detailed costs of processing 1 ton of poplar wood powder to prepare Ph-bioplastic.

| Raw material   | Quantity | Unit | Price        |
|--|----------|------|--------------|
| <b>Step 1: Preparation of phenolic DES</b>                     |          |      |              |
| Poplar powder  | 1        | ton  | 34.4 \$/ton  |
| Choline chloride   | 5.5      | ton  | 382.9 \$/ton |
| Oxalic acid dihydrate  | 10.5     | ton  | 247.9 \$/ton |
| Resorcinol   | 4.0      | ton  | 407.0 \$/ton |
| Energy (Heat treatment)  | 0.5      | kWh  | 0.06 \$/kwh  |
| <b>Cost:</b> 1274 \$/ton. The phenolic DES was cycled 4 times. |          |      |              |
| <b>Step 2: Poplar powder for phenolic DES treatment</b>        |          |      |              |
| Ethanol  | 7        | ton  | 220 \$/ton   |
| Water  | 10       | ton  | 14.5 \$/ton  |
| Energy (Heat treatment)  | 12       | kWh  | 0.06 \$/kwh  |
| Energy (solvent recovery)                                      | 27       | kWh  | 0.06 \$/kwh  |
| <b>Cost:</b> 171 \$/ton. Ethanol and water was cycled 9 times. |          |      |              |
| <b>Step 3: Preparation of Ph-bioplastic</b>                    |          |      |              |
| AgNO <sub>3</sub>  | 3.8      | kg   | 80 \$/ kg    |
| Energy (UV light)  | 1        | kWh  | 0.06 \$/kwh  |
| <b>Cost:</b> 304 \$/ton  |          |      |              |
| <b>All-in Cost:</b> 1749 \$/ton (1.7 \$/kg)                    |          |      |              |

The price is calculated based on the treatment of 1 ton of poplar wood powder. The price of resorcinol comes from Xinyuansheng Chemical Co., Ltd., and the price of other reagents is sourced from Alibaba. The price of industrial water in China is 14.5 \$/ton, while the price of industrial electricity in Harbin is 0.06 \$/kwh.

Table S2. Water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) of cellulose-based bioplastic and Ph-bioplastic.

| Sample                     | WVTR (g/(m <sup>2</sup> •day)) | OTR (cc/(m <sup>2</sup> •day)) |
|----------------------------|--------------------------------|--------------------------------|
| Cellulose-based bioplastic | 561.15                         | <0.05                          |
| Ph-bioplastic              | 528.85                         | <0.05                          |

#### References

- (1) L. Zhang, C. Zhang, Y. Ma, X. Zhao and X. Zhang, *Industrial Crops and Products*, 2024, **211**.
- (2) J. Ou, S. Li, W. Li, C. Liu, J. Ren and F. Yue, *ACS Sustainable Chemistry & Engineering*, 2022, **10**, 14845-14854.