Supporting information

Polyphenol-Metal Ion Redox-Induced Gelation System for Constructing Plant Protein Adhesives with Excellent Fluidity and Cold-Pressing Adhesion

Huiwen Pang[a], Qian Yan[a], Chao Ma[a], Shifeng Zhang[a], Zhenhua Gao[b]**

[a] MOE Key Laboratory of Wooden Material Science and Application and Key Laboratory of Wood Science and Engineering, Beijing Forestry University, Beijing 100083, P.R. China

[b] MOE Key Laboratory of Bio-based Material Science and Technology, Northeast Forestry University, Harbin 150040, P.R. China

* Corresponding author: shifeng.zhang@bjfu.edu.cn (*Shifeng Zhang*); gaozh1976@163.com (Zhenhua Gao)

Introduction

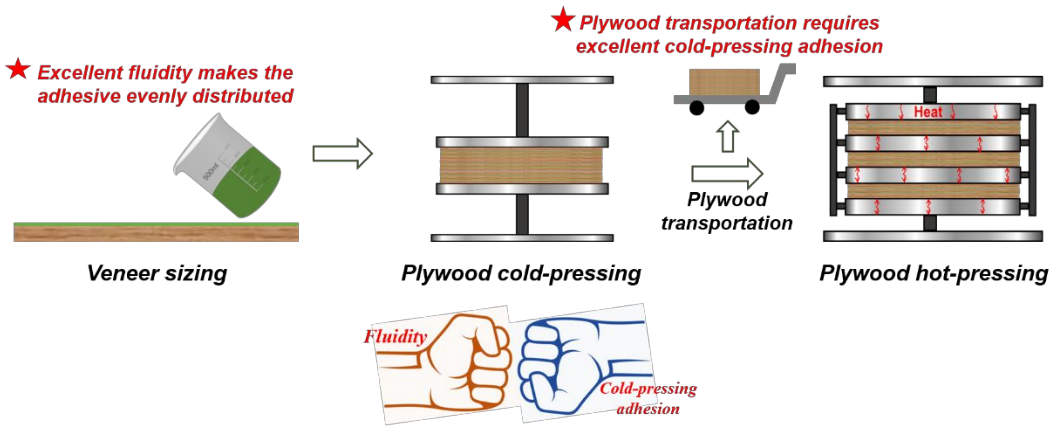
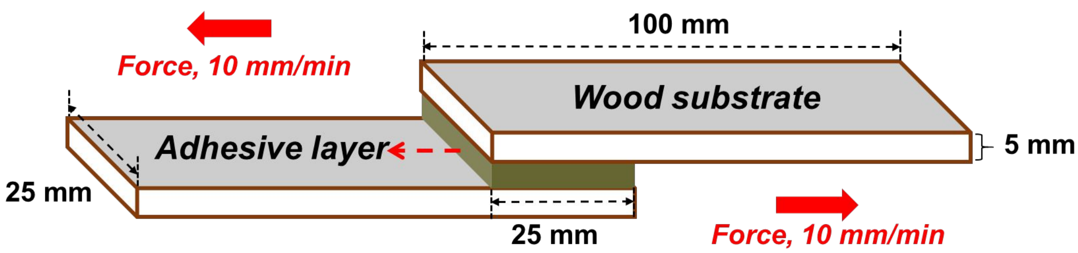


Figure S1. The practical production problems of the plywood bonded by the SP adhesive.

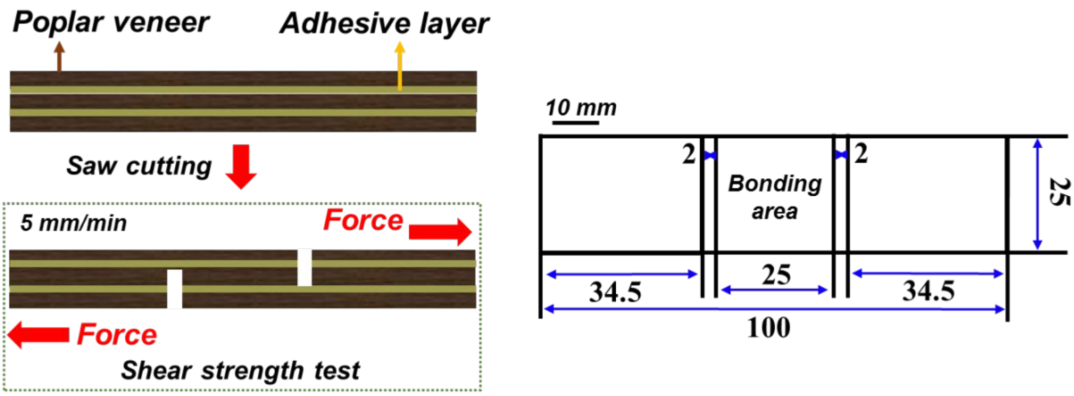
Experimental Procedures

Cold-pressing bonding strength of adhesives



Scheme S1. Detailed test process of lap shear strength.

Hot-pressing bonding strength of adhesives



Scheme S2. Detailed dimensions of the plywood specimens.

Characterization

The ultraviolet-visible (UV-Vis) spectra of samples were measured with a UV-Vis spectrophotometer (TU-1901, Purkinje General, China) from 300 to 600 nm. The morphologies of the cured SP-based adhesives were observed by scanning electron microscopy (SEM) (Hitachi Ltd., Tokyo, Japan) coupled with energy-dispersive X-ray spectroscopy (EDX) at an acceleration voltage of 5 kV. The cured SP-based adhesives were analyzed by Fourier transform infrared (FT-IR) spectroscopy using the attenuated total reflection (ATR) sampling technique performed on a Thermo Scientific Nicolet 6700 spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) over a spectral range of 600–4,000 cm^{-1} with 4 cm^{-1} resolution. The internal structure of the cured SP-based adhesives was examined by X-ray photoelectron spectroscopy (XPS) (Thermo Escalab 250, Thermo Fisher Scientific Inc.) with Al Kα radiation. Thermogravimetric analysis (TGA) was performed using an A TA Q50 thermogravimetric analyzer (Waters Corporation, Milford, MA, USA) to measure changes in the weight of the plywood samples over the temperature range of 10-250°C at a heating rate of 10°C/min. The tensile strength of the adhesive hydrogels and the bonding strength of the adhesives using a Shimadzu AGS-X tensile tester (Shimadzu Scientific Instruments Inc., Columbus, MD, USA), and the tensile strength of the adhesive hydrogels (100 mm × 25 mm) was tested at a crosshead speed of 1 mm/min. The rheological behavior of the SP-based adhesive gels was investigated on an Anton Paar MCR 302 rheometer (Anton Paar GmbH, Graz, Austria) equipped with a flat parallel plate. An oscillatory sweep was used over a frequency range from 0.1 to 100 rad/s at γ = 1% of the fixed strain amplitude. A FLIR T540 handheld thermal imaging camera (FLIR Systems Inc., Wilsonville, OR, USA) was used to record the temperature changes during SP-based adhesive gelation. The electron paramagnetic resonance (EPR) spectra were acquired on a Bruker EMX plus 10/12 spectrometer (Bruker Biospin GmbH, Rheinstetten, Germany) to observe the mechanism of the TA-Fe^{3+}/persulfate system. Reaction conditions were m(TA) = 0.01 g, m($FeCl_3$) = 0.3 g, m(APS) = 0.75 g, m(water) = 17.5 g. TA, $FeCl_3$, with APS mixed firstly and DMPO added to the mixture.

Results and discussion

TA@Fe^{3+} complex-induced in-situ gelation of SP-based adhesives

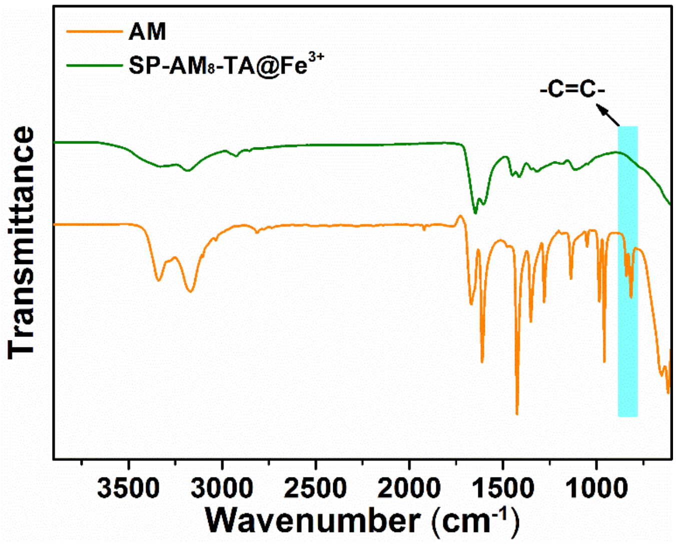


Figure S2. FTIR spectra of the AM and SP-AM_8-TA@Fe^{3+}adhesives.

Cold-pressing bonding strength of SP-based adhesives

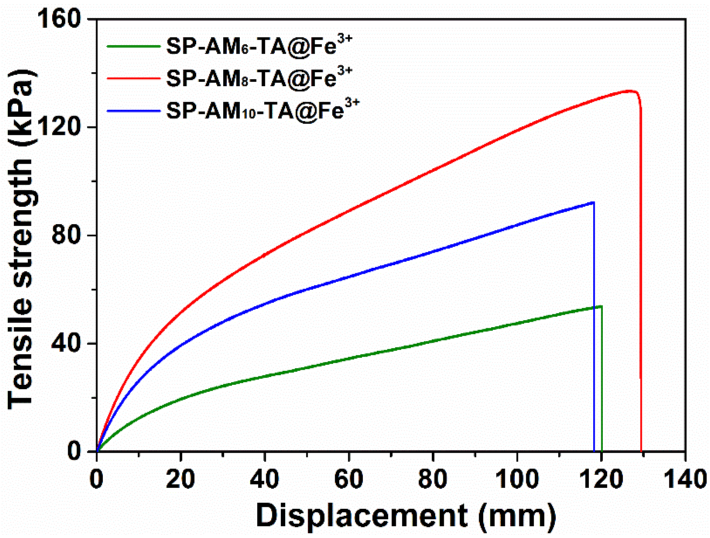


Figure S3. Tensile strength of the SP-AM-TA@Fe^{3+} adhesive hydrogels.

Investigation of SP-based adhesive bonding mechanism

Table S1. Content of atoms of SP-based adhesives

Sample	Content of atoms (%)		
	C	**O**	**N**

SP	72.42	22.64	4.94
SP-AM	70.99	23.18	5.83
SP-AM-TA@Fe^{3+}	74.13	24.63	1.24

Hot-pressing bonding strength of SP-based adhesives

Table S2. Comparison of hot-pressing bonding strength between the three-ply plywood bonded by the adhesives prepared in this work and that bonded by other reported adhesive samples.

Sample	Dry bonding strength (MPa)	Wet bonding strength (MPa)	Reference
UF	1.80	1.02	[1]
SP-MG-EPR	2.16	0.91	[2]
SF-WPU	1.66	1.10	[3]
SP/TCA-HBSi	3.77	1.45	[4]
SM/AC@CNF-PA	1.80	1.19	[5]
SP-HBPE-SB	1.94	0.90	[6]
SP-PUSD	3.03	1.74	[7]
SPI/TGA/A-SSPS	1.78	1.07	[8]
SP-AM-TA@Fe^{3+}	1.40	1.28	This work

Mildew resistance and biodegradability of SP-based adhesives

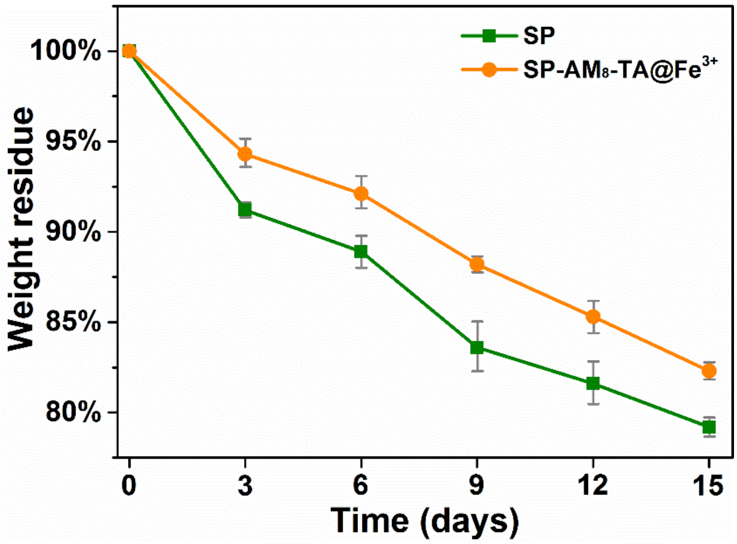


Figure S4. The biodegradation rates of the SP and SP-AM_8-TA@Fe^{3+}adhesive.

Reference

1. Han-Seung Yang, D.-J. K., Hyun-Joong Kim, Rice Straw–Wood Particle Composite for Sound Absorbing Wooden Construction Materials. *Bioresource Technology* **2003,** *86* (2), 117-121.
2. Wu, Z.; Lei, H.; Cao, M.; Xi, X.; Liang, J.; Du, G., Soy-Based Adhesive Cross-linked by Melamine–Glyoxal and Epoxy Resin. *Journal of Adhesion Science and Technology* **2016,** *30* (19), 2120-2129.
3. Wang, Y.; Fan, Y.; Deng, L.; Li, Z.; Chen, Z., Properties of Soy-Based Wood Adhesives Enhanced by Waterborne Polyurethane Modification. *Journal of Biobased Materials and Bioenergy* **2017,** *11* (4), 330-335.
4. Wang, Z.; Zhao, S.; Pang, H.; Zhang, W.; Zhang, S.; Li, J., Developing Eco-friendly High-Strength Soy Adhesives with Improved Ductility through Multiphase Core–Shell Hyperbranched Polysiloxane. *ACS Sustainable Chemistry & Engineering* **2019,** *7* (8), 7784-7794.
5. Jin, S.; Li, K.; Zhang, X.; Gao, Q.; Zeng, L.; Shi, S. Q.; Li, J., Phytic Acid-Assisted Fabrication for Soybean Meal/Nanofiber Composite Adhesive via Bioinspired Chelation Reinforcement Strategy. *J Hazard Mater* **2020,** *399*, 123064.
6. Gu, W. D.; Li, F.; Liu, X. R.; Gao, Q.; Gong, S. S.; Li, J. Z.; Shi, S. Q. Q., Borate Chemistry Inspired by Cell Walls Converts Soy Protein into High-Strength, Antibacterial, Flame-Retardant Adhesive. *Green Chemistry* **2020,** *22* (4), 1319-1328.
7. Zhao, S.; Pang, H.; Li, Z.; Wang, Z.; Kang, H.; Zhang, W.; Zhang, S.; Li, J.; Li, L., Polyurethane as High-Functionality Crosslinker for Constructing Thermally Driven Dual-Crosslinking Plant Protein Adhesion System with Integrated Strength and Ductility. *Chemical Engineering Journal* **2021,** *422*, 130152.
8. Zhang, Y.; Zhang, M.; Chen, M.; Luo, J.; Li, X.; Gao, Q.; Li, J., Preparation and Characterization of a Soy Protein-Based High-Performance Adhesive with a Hyperbranched Cross-linked Structure. *Chemical Engineering Journal* **2018,** *354*, 1032-1041.