Supplementary Information

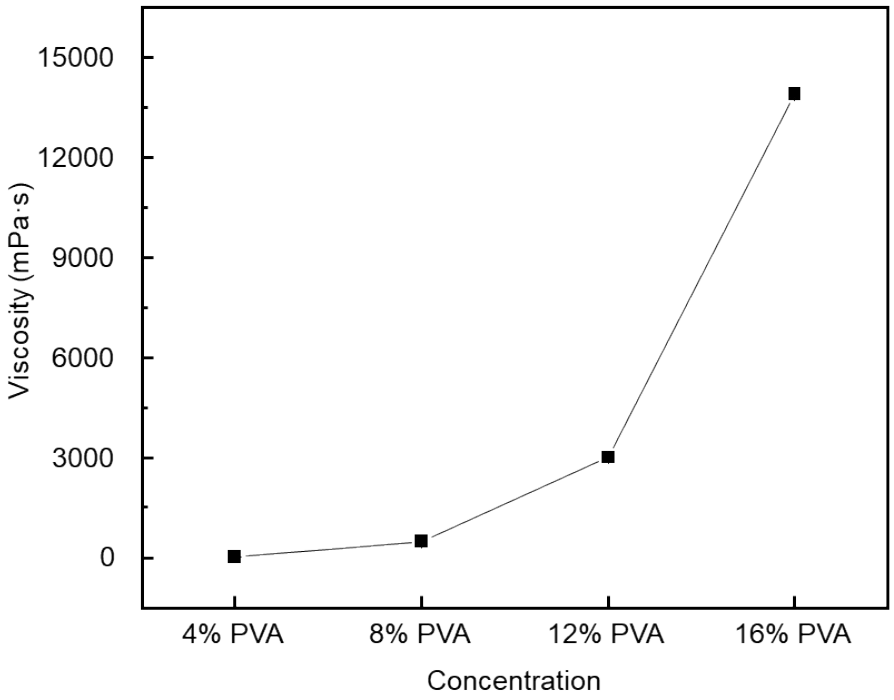
Polyvinyl Alcohol Solvent-free Adhesives for Biomass Bonding via Rapid Water Activation and Heat Treatment

Liangxian Liu[1,2], Ming Wei[2,3], Haiyu Li[1], Yutong Chen[1], Yuyan Jiang[1], Tian Ju[1], Zetan Lu[1], Guoqing Mu[1], Lijian Cai[1], Dexiu Min[3], Yanjun Xie[2], Jian Li*[1,2], Shaoliang Xiao*[1,2]

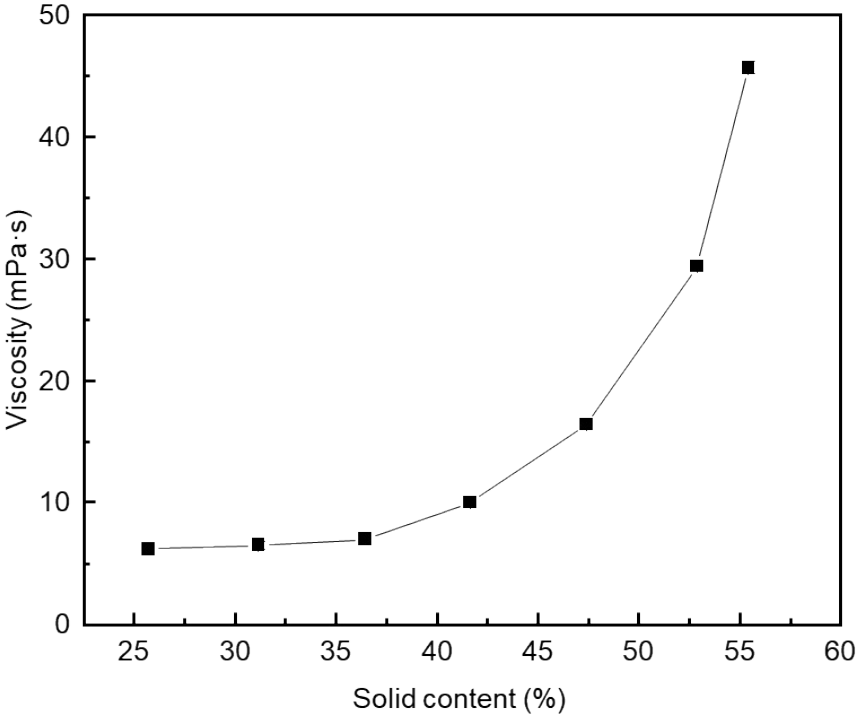
1. Key Laboratory of Bio-based Material Science & Technology (Ministry of Education), Northeast Forestry University, Harbin, P.R. China
2. Engineering Research Center of Advanced Wooden Materials (Ministry of Education), Northeast Forestry University, Harbin, P.R. China
3. Shandong Xingang Enterprise Group Co., Ltd, Shandong，P.R. China

* Email: shaoliangxiao@nefu.edu.cn

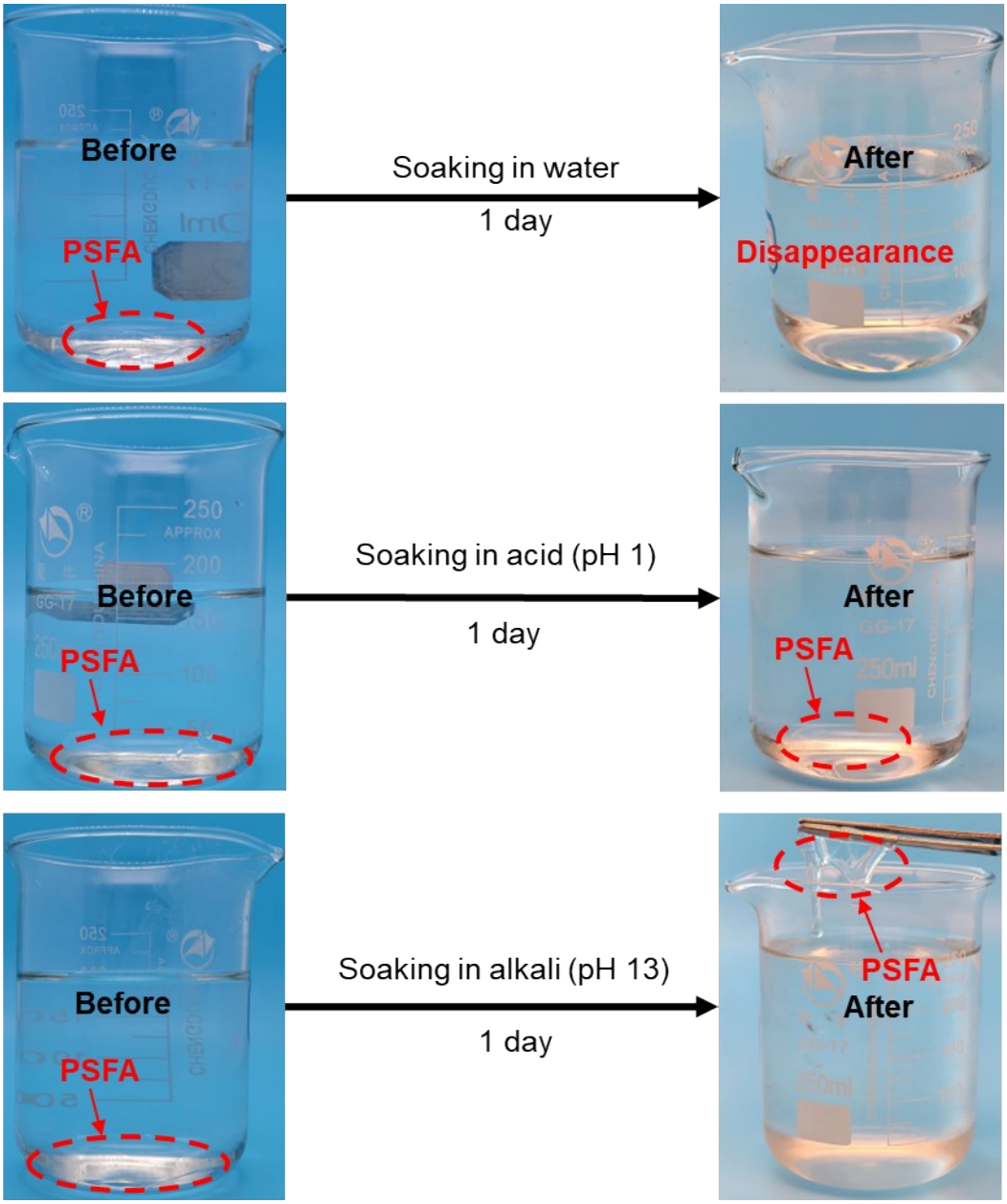
* Email: nefulijian@163.com



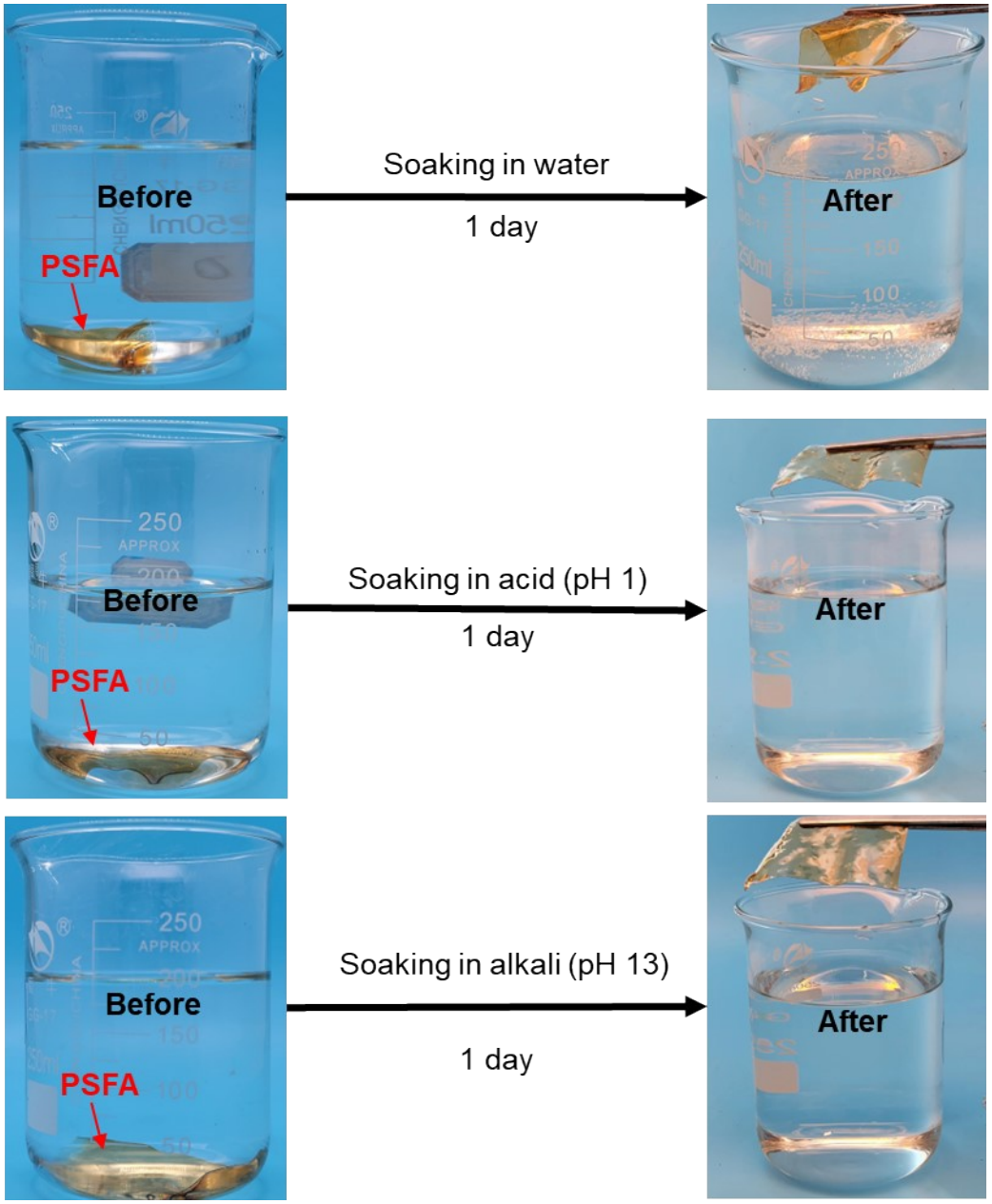
Supplementary Fig. 1 Influence of PVA solution of different solids content on viscosity at 25 ℃.



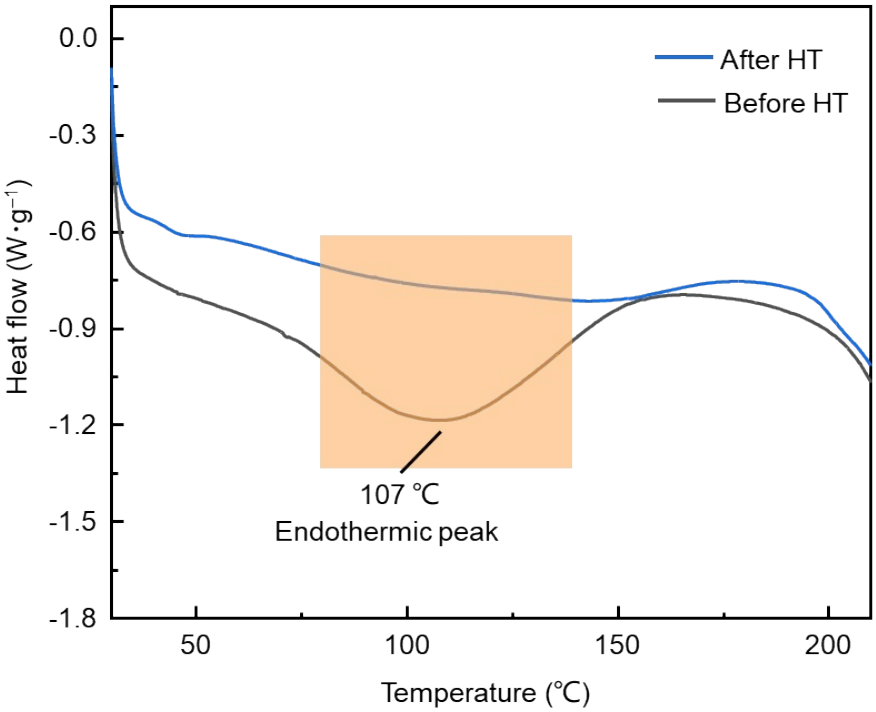
Supplementary Fig. 2 Influence of UF adhesive of different solids content on viscosity at 25 ℃.



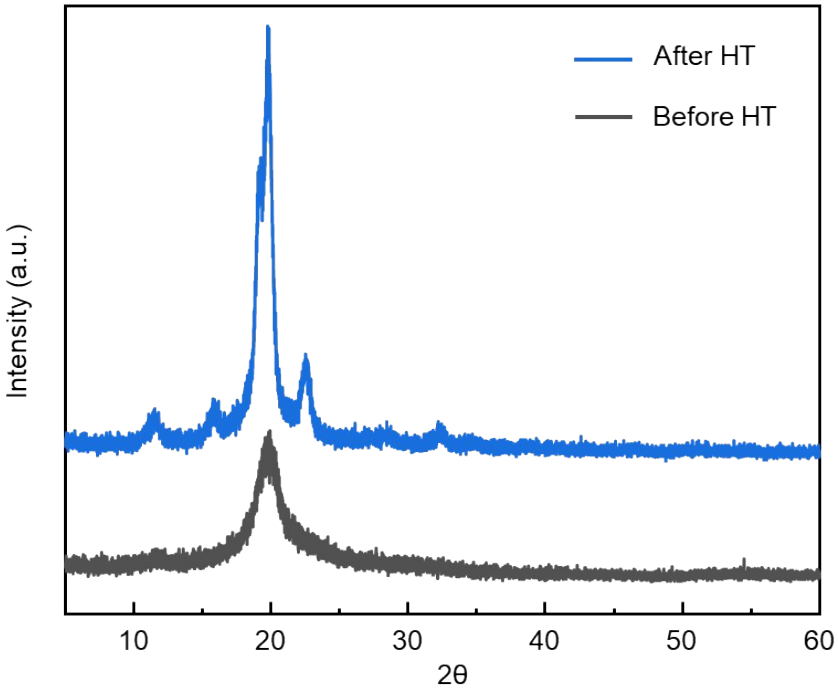
Supplementary Fig. 3 Photographs of the insolubility rate of PSFA after soaking in water, acid (pH 1) and alkali (pH 13) for one day before heat treatment.



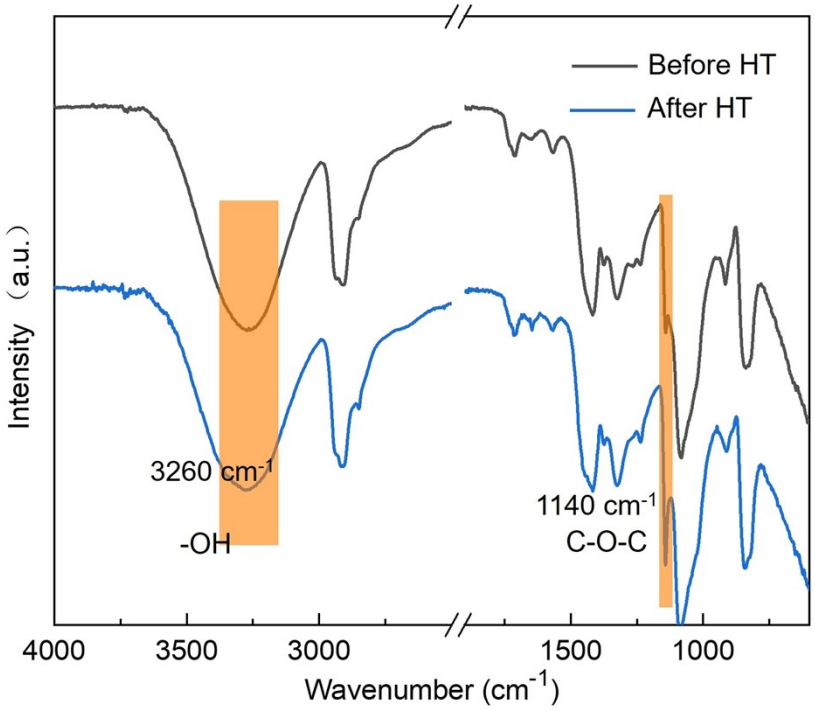
Supplementary Fig. 4 Photographs of the insolubility rate of PSFA after soaking in water, acid (pH 1) and alkali (pH 13) for one day after heat treatment.



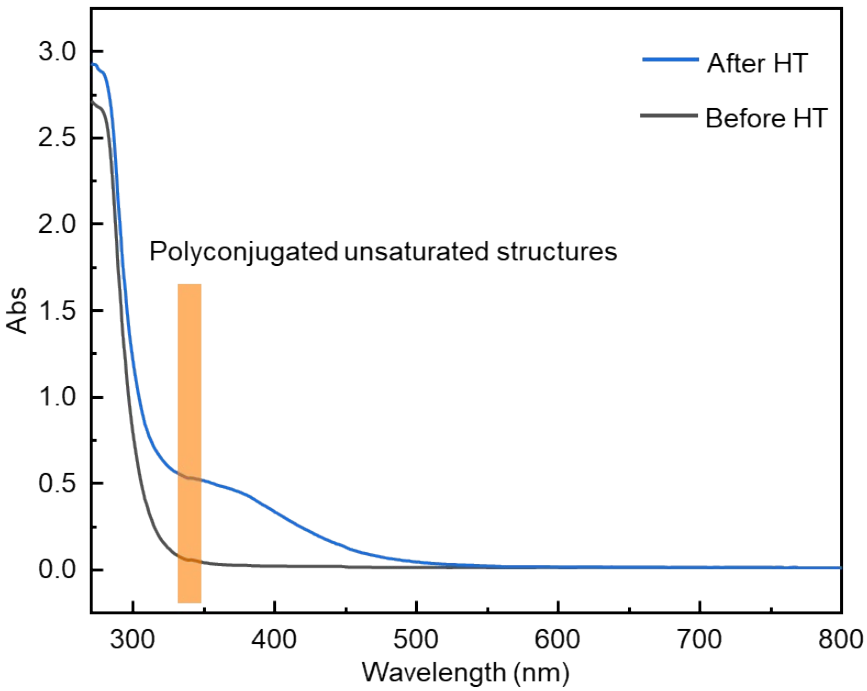
Supplementary Fig. 5 DSC curves of PSFA before and after heat treatment.



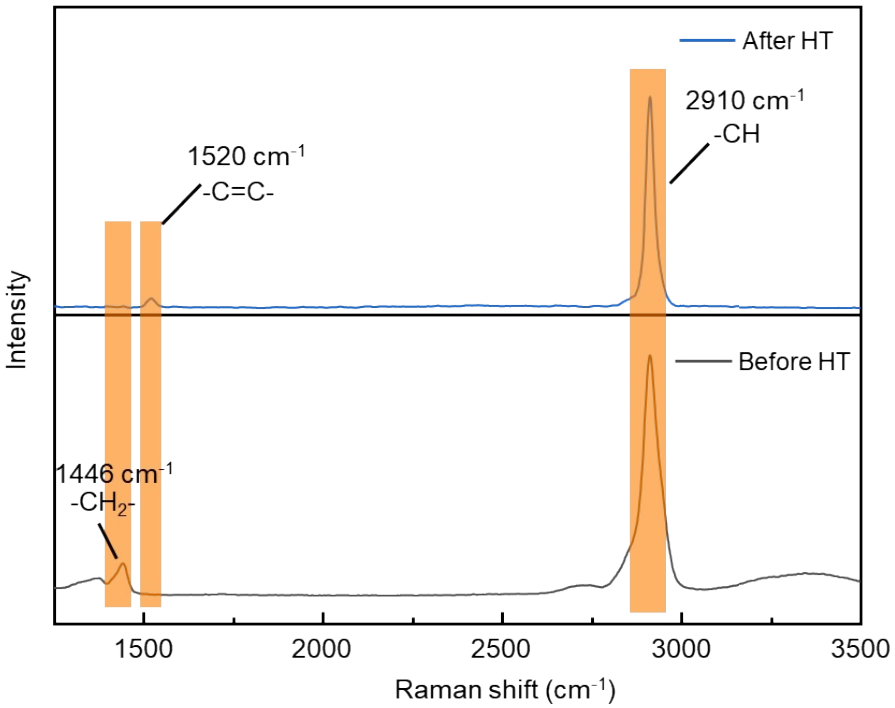
Supplementary Fig. 6 XRD patterns of PSFA before and after heat treatment.



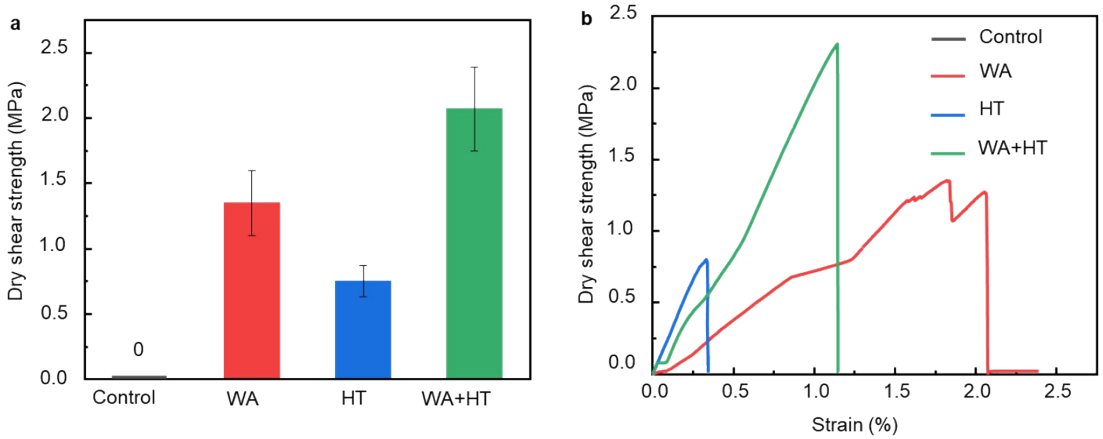
Supplementary Fig. 7 FTIR spectra of PSFA before and after heat treatment.



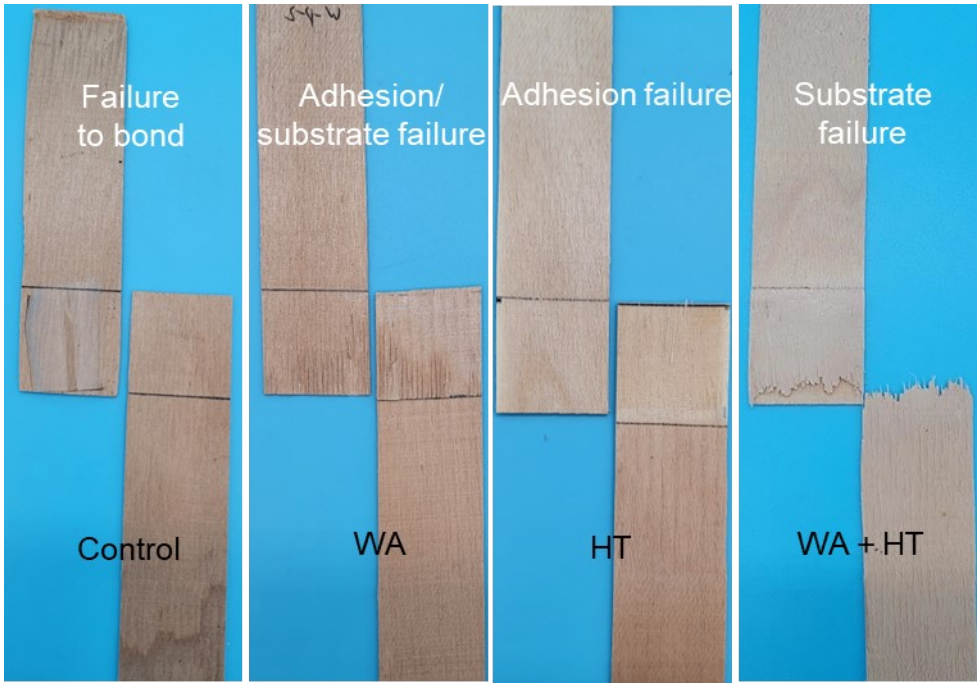
Supplementary Fig. 8 UV-vis spectra of PSFA before and after heat treatment.



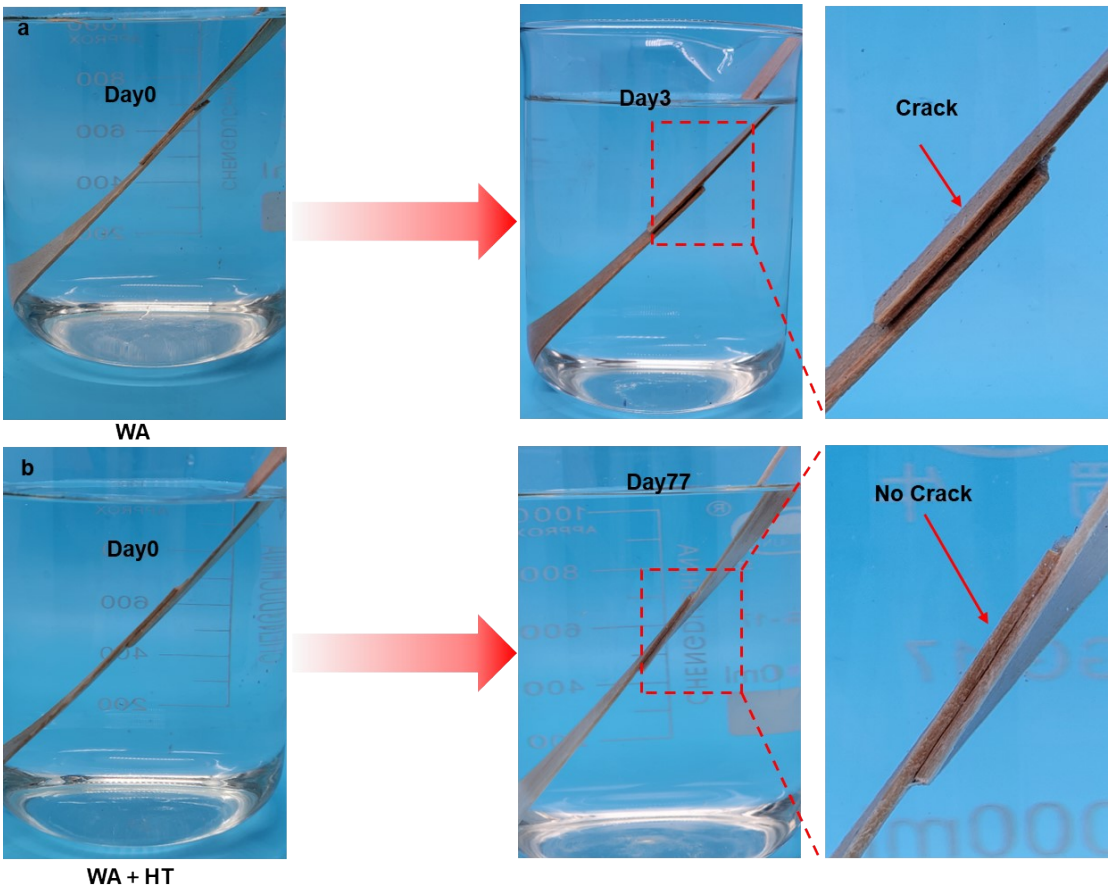
Supplementary Fig. 9 Raman spectra of PSFA before and after heat treatment.



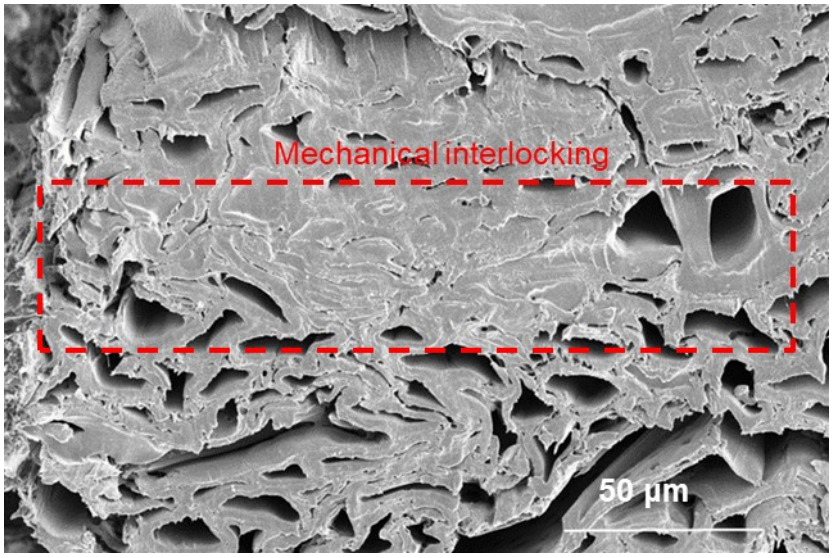
Supplementary Fig. 10 (a) Dry shear strength of single-lap joints using PSFA by different treatments. (b) Stress-strain curves of single-lap joints using PSFA by different treatments.



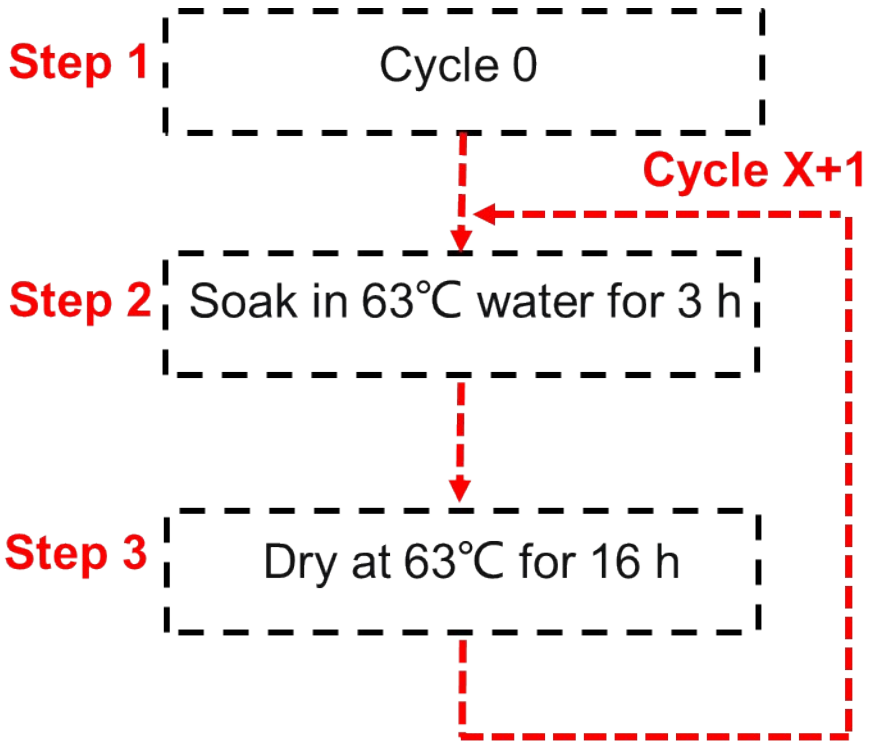
Supplementary Fig. 11 Photographs of dry single-lap joints failure of PSFA under different treatment conditions.



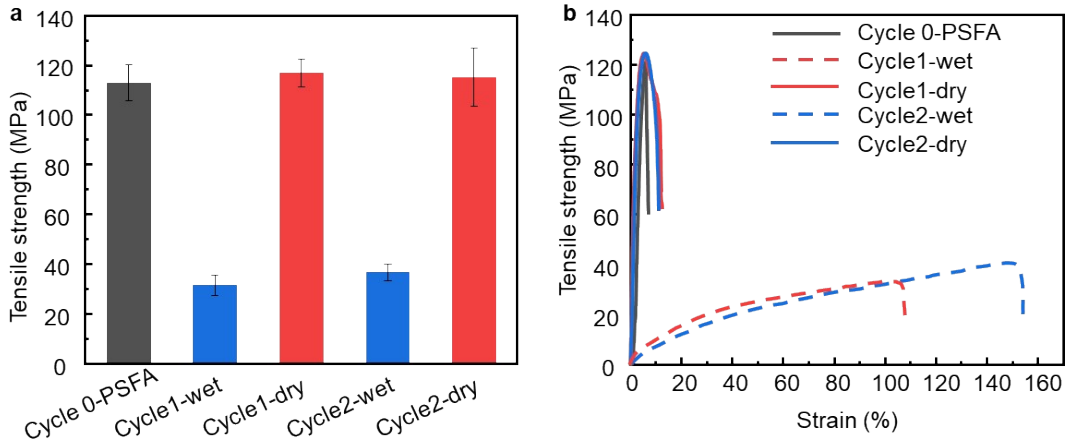
Supplementary Fig. 12 (a) Photographs of PSFA single-lap joint treated with WA immersed in cold water. (b) Photographs of PSFA single-lap joint treated with WA+HT immersed in cold water.



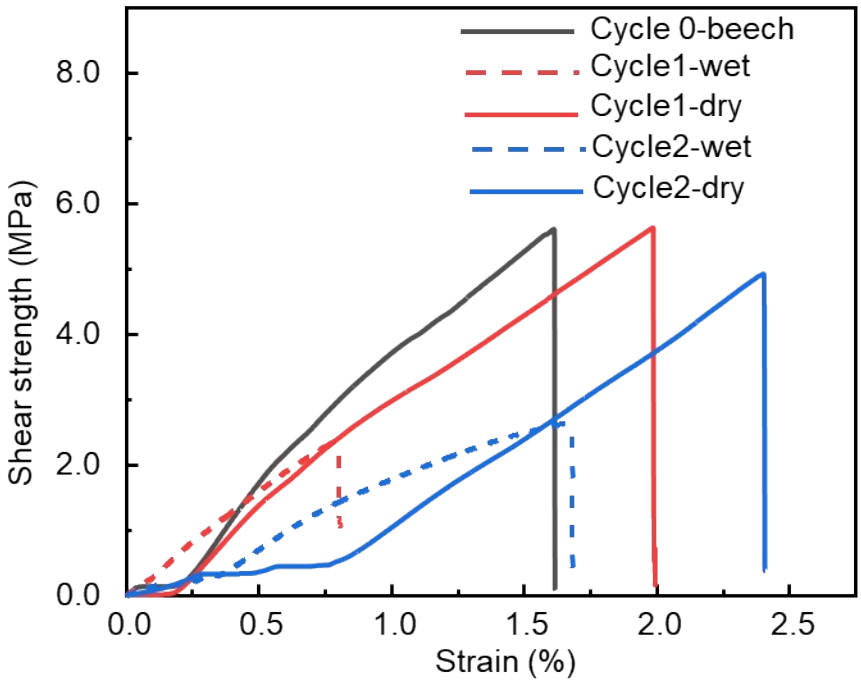
Supplementary Fig. 13 SEM photographs of poplar dry lap sample.



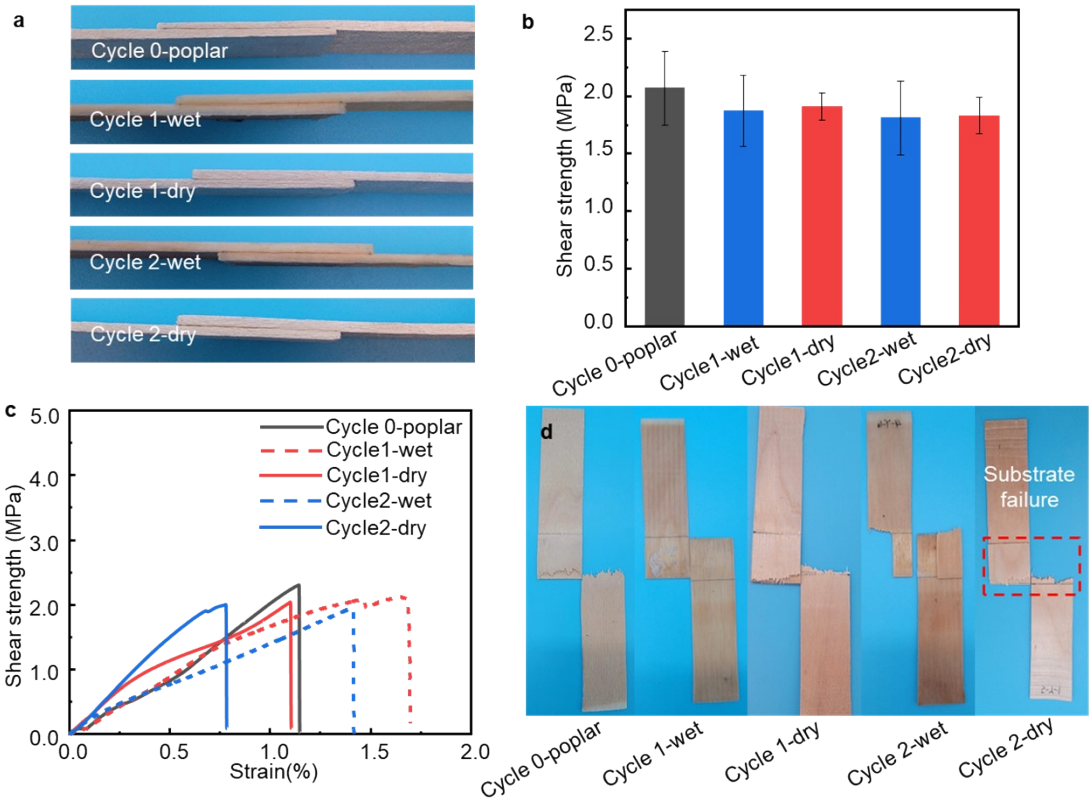
Supplementary Fig. 14 Flowchart of the cyclic testing procedure.



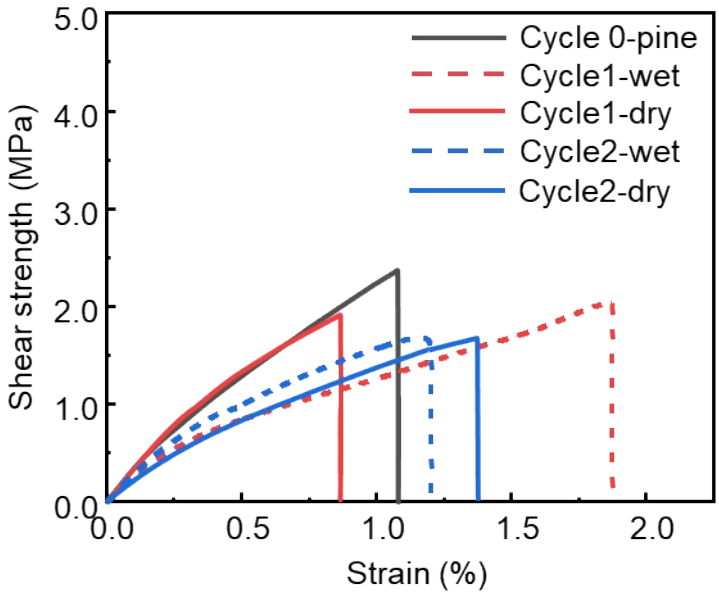
Supplementary Fig. 15 (a) Tensile strength of PSFA. (b) Stress-strain curve of PSFA.



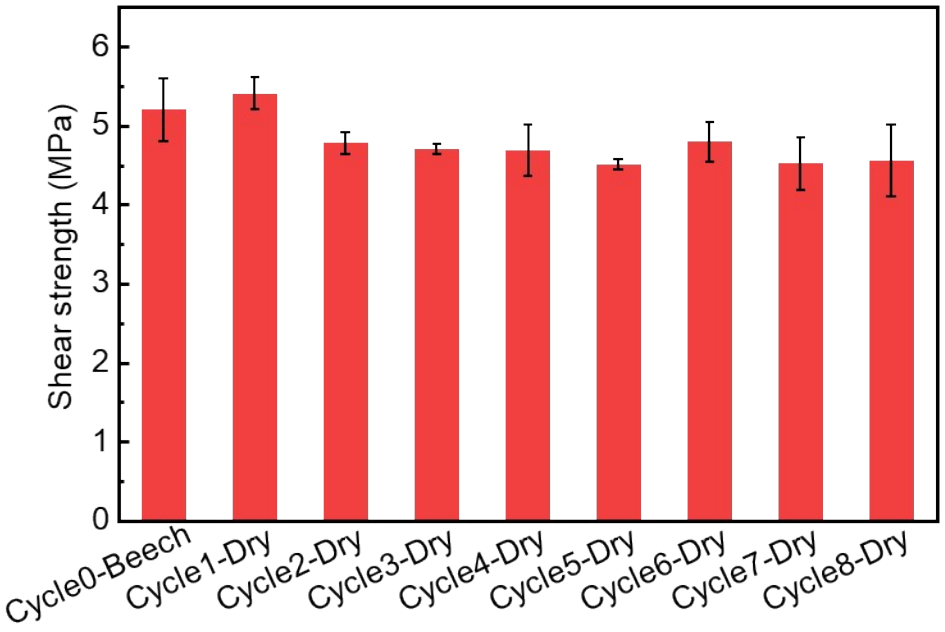
Supplementary Fig. 16 Stress-strain curves of beech single-lap joints.



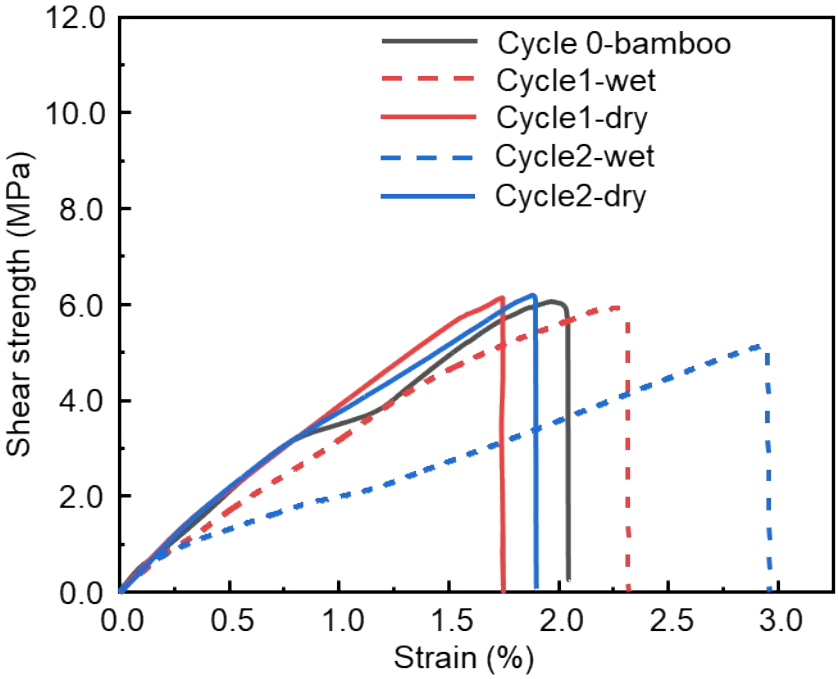
Supplementary Fig. 17 (a) Photographs of poplar single-lap joints during cyclic testing. (b) Bonding performance of poplar single-lap joints. (c) Stress-strain curves of poplar single-lap joints. (d) Failure modes of poplar single-lap joints.



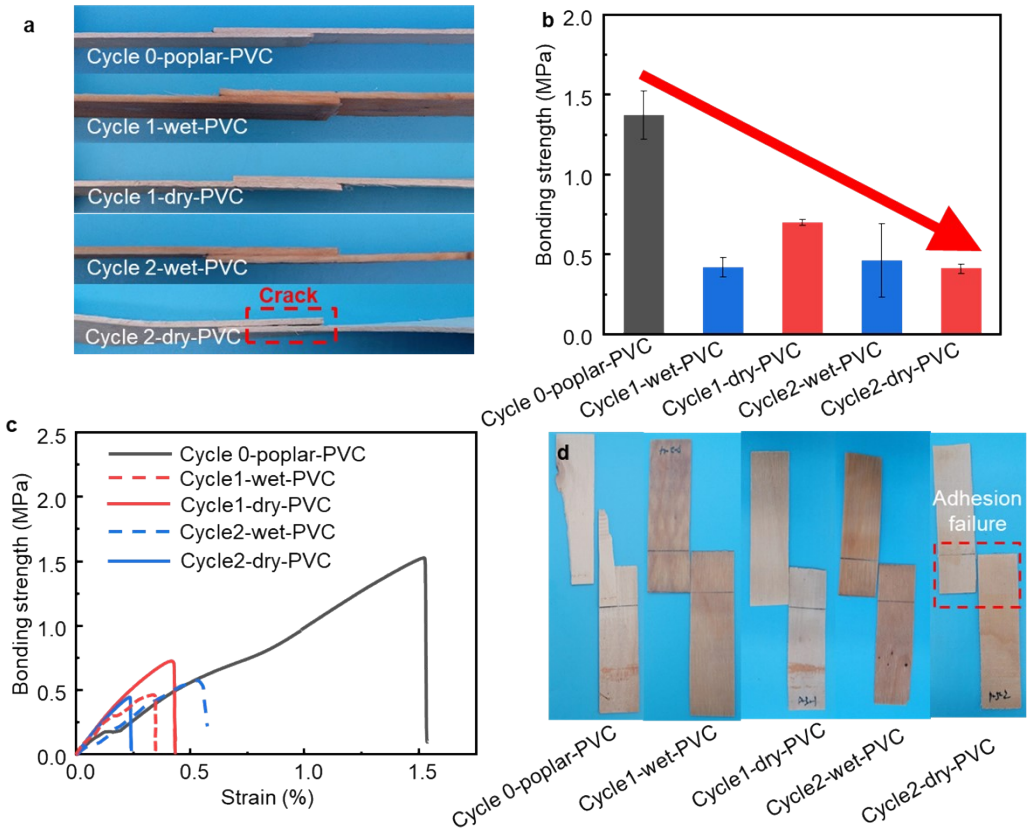
Supplementary Fig. 18 Stress-strain curves of pine single-lap joints.



Supplementary Fig. 19 Shear strength of beech single-lap joints under multiple "soaking in hot water-drying" cycling tests.

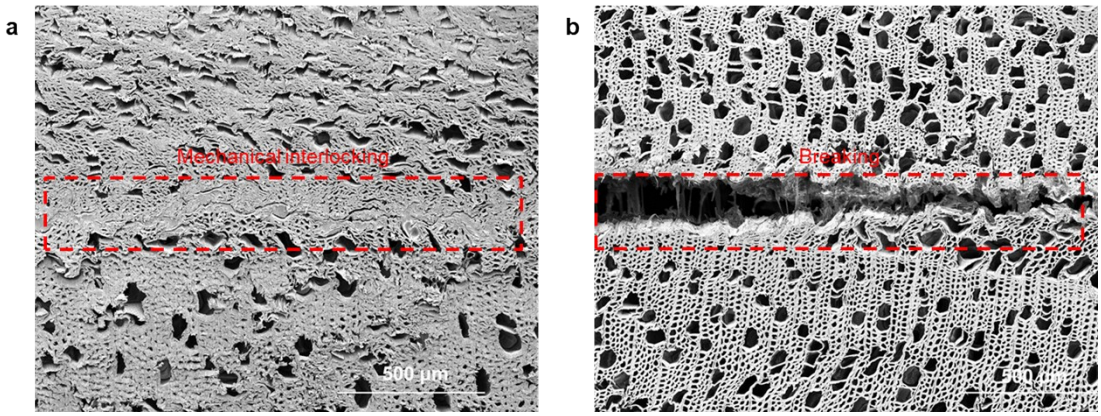


Supplementary Fig. 20 Stress-strain curves of bamboo single-lap joints.

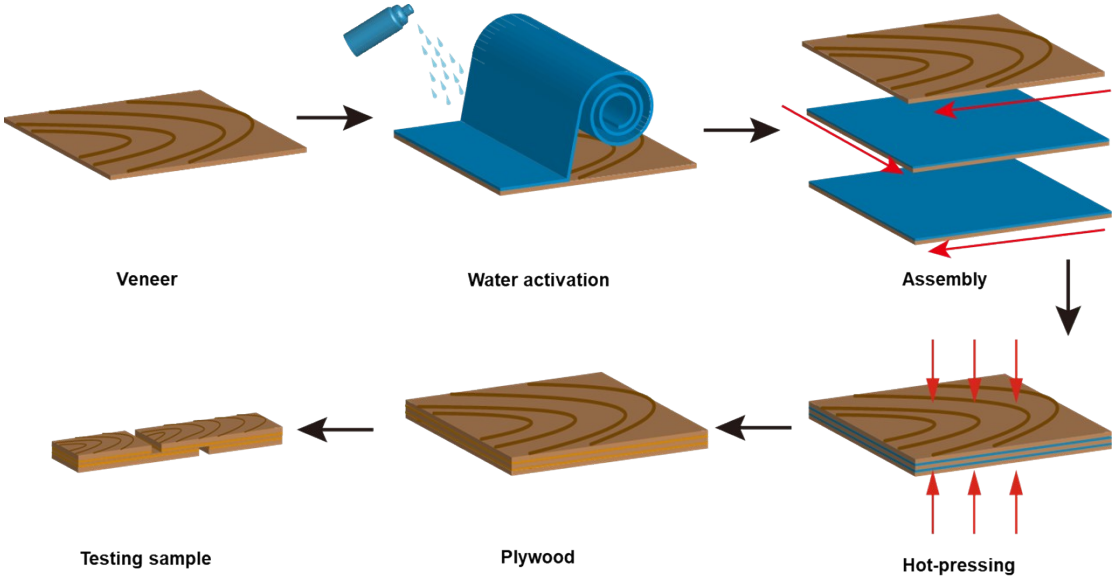


Supplementary Fig. 21 (a) Photographs of poplar single-lap joints using PVC. (b) Bonding performance of poplar single-lap joints using PVC. (c) Stress-strain curves of poplar single-lap joints using PVC. (d) Photographs of failure of poplar single-lap joints using PVC.

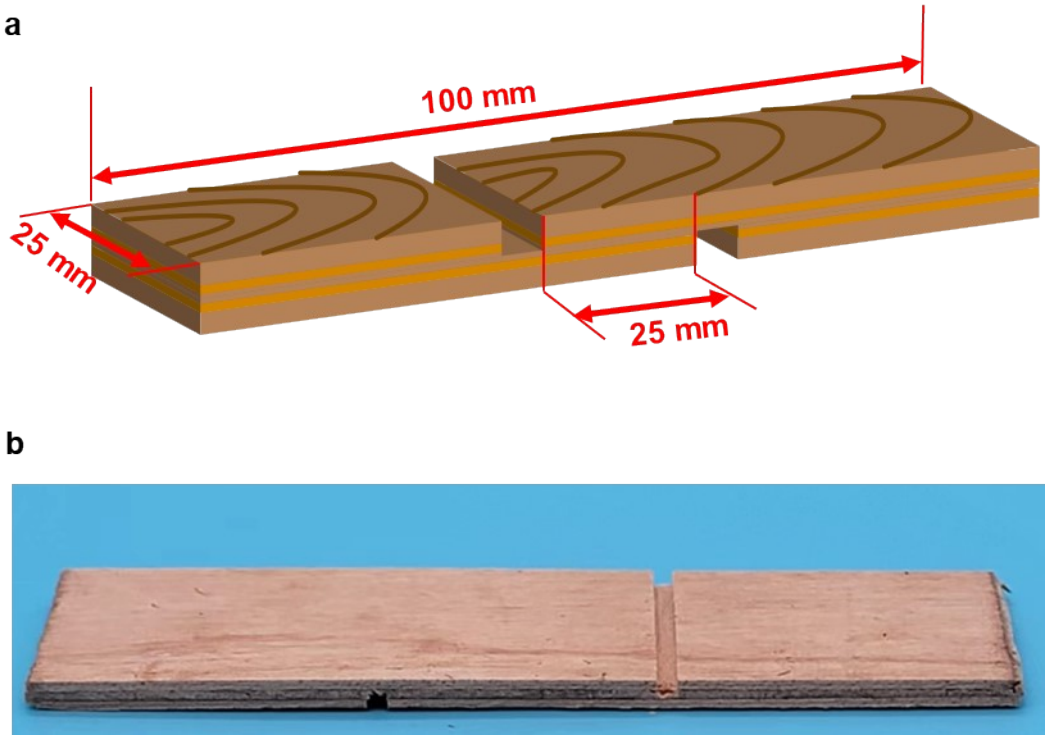
Supplementary Fig. 22 Photos of PVC after water activation.



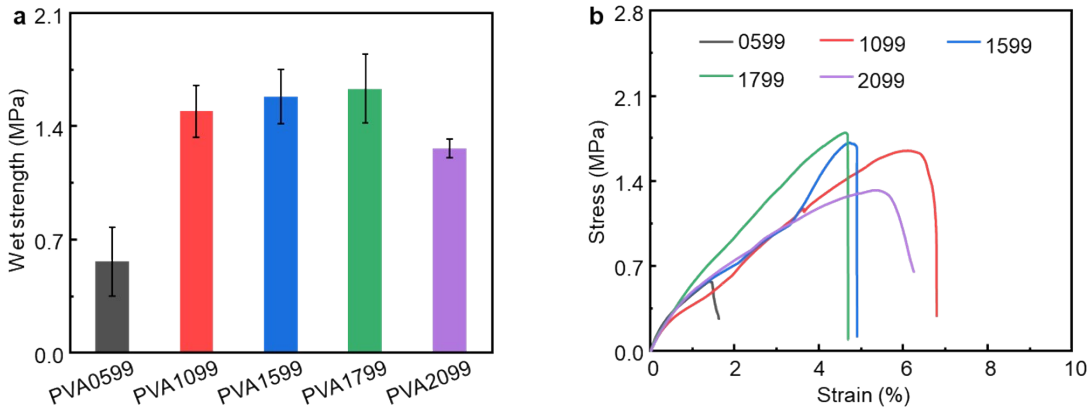
Supplementary Fig. 23 SEM photographs of poplar dry lap sample (a) and wet lap sample (b) using PVC.



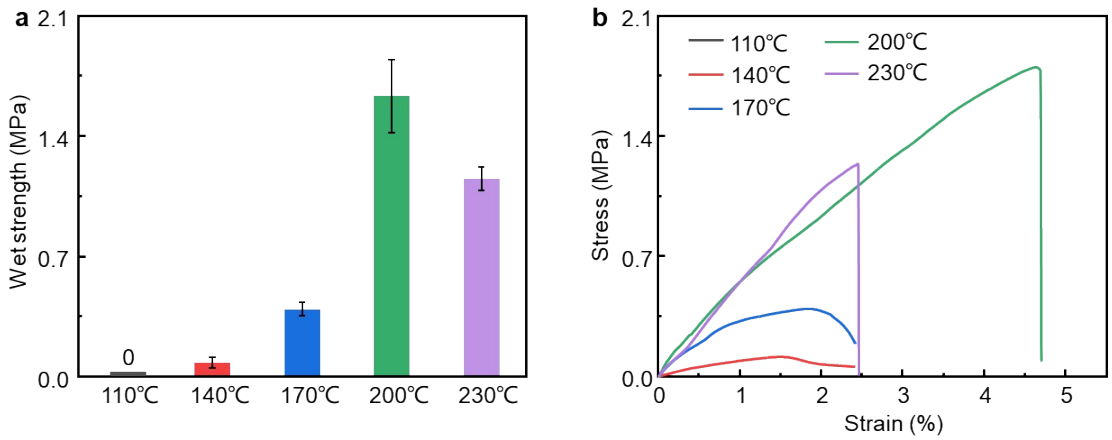
Supplementary Fig. 24 Schematic illustration of the preparation process for plywood testing samples using PSFA.



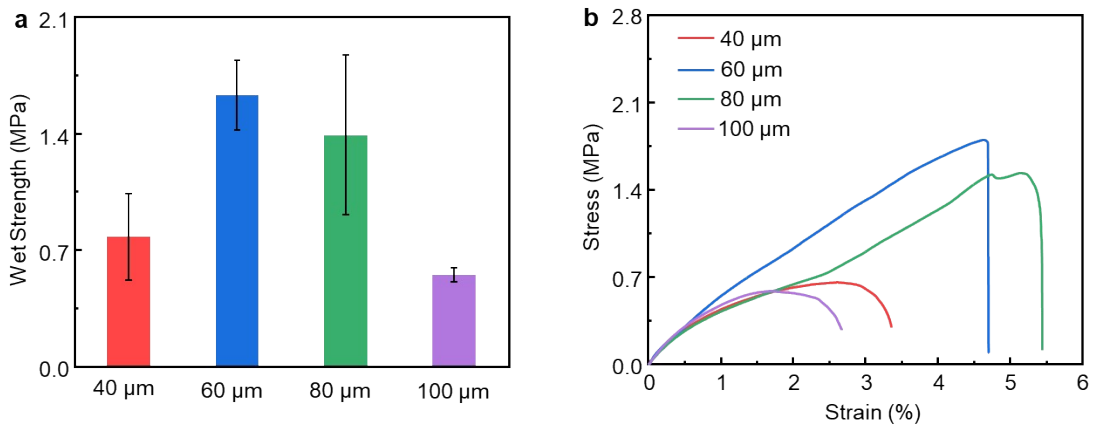
Supplementary Fig. 25 (a) Dimensions of plywood shear strength test samples. (b) Photo of testing sample of plywood.



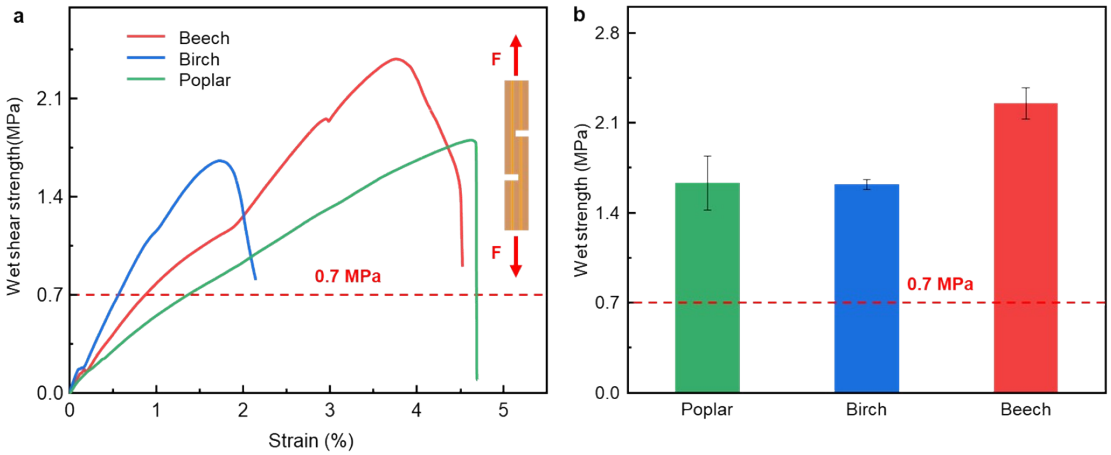
Supplementary Fig. 26 (a) Wet bonding performance and (b) Stress-strain curves of PSFAs under different PVA molecular weight. PVA 0599 (Mw = 20,000–25,000), PVA 1099 (Mw = 40,000–50,000), PVA 1599 (Mw = 60,000–70,000), PVA 1799 (Mw = 70,000–80,000), and PVA 2099 (Mw = 85,000–95,000). The wet strengths of PVA 0599, PVA 1099, PVA 1599, PVA 1799, and PVA 2099 are 0.56±0.21 MPa, 1.49±0.16 MPa, 1.58±0.17 MPa, 1.63±0.21 MPa, and 1.26±0.06 MPa, respectively.



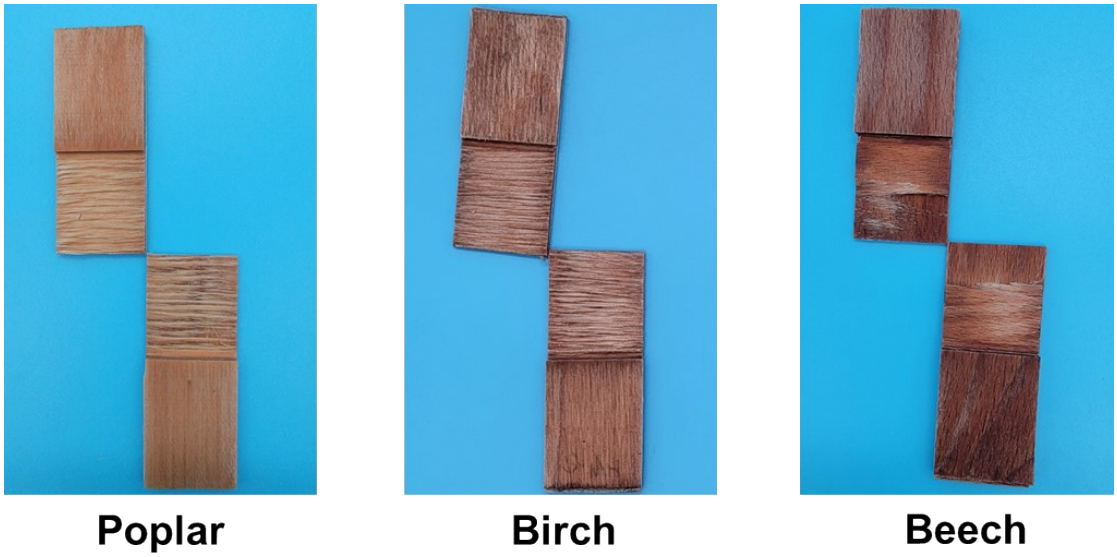
Supplementary Fig. 27 (a) Wet bonding performance and (b) Stress-strain curves of PSFAs under different hot-pressing temperatures. The wet strengths of PSFA at hot-pressing temperatures of 110°C, 140°C, 170°C, 200°C, and 230°C are 0 MPa, 0.08±0.03 MPa, 0.39±0.04 MPa, 1.63±0.21 MPa, and 1.15±0.07 MPa, respectively.



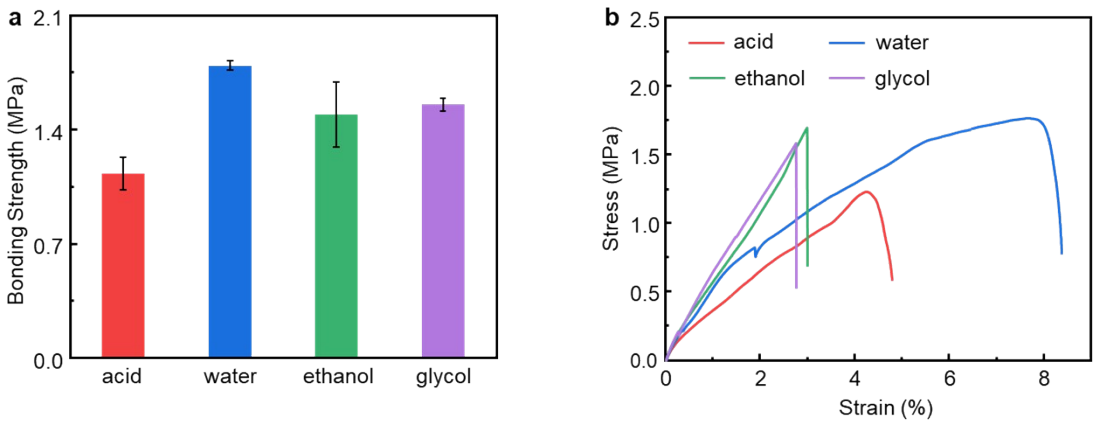
Supplementary Fig. 28 (a) Wet bonding performance and (b) Stress-strain curves of PSFAs with different thickness. The wet strengths of PSFAs with thicknesses of 40μm, 60μm, 80μm, and 100μm are 0.78±0.26 MPa, 1.63±0.21 MPa, 1.39±0.48 MPa, and 0.55±0.04 MPa, respectively.



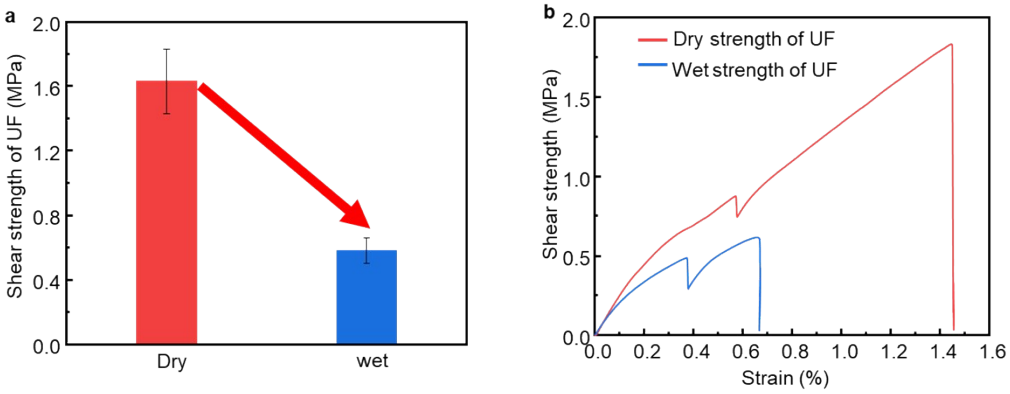
Supplementary Fig. 29 (a) Stress-strain curves of wet bonding performance of plywood. (b) Wet bonding performance of plywood.



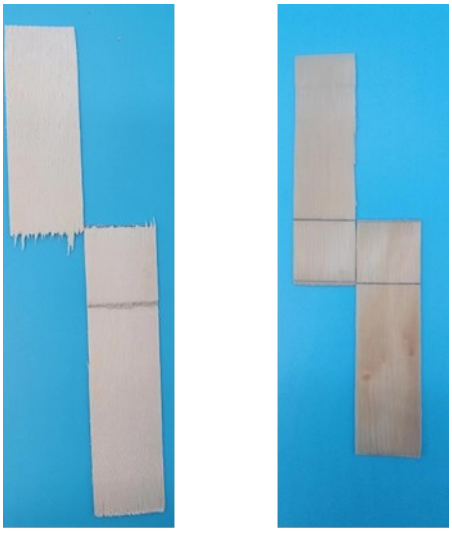
Supplementary Fig. 30 Photo of wood breakage rate of wet shear strength of plywood.



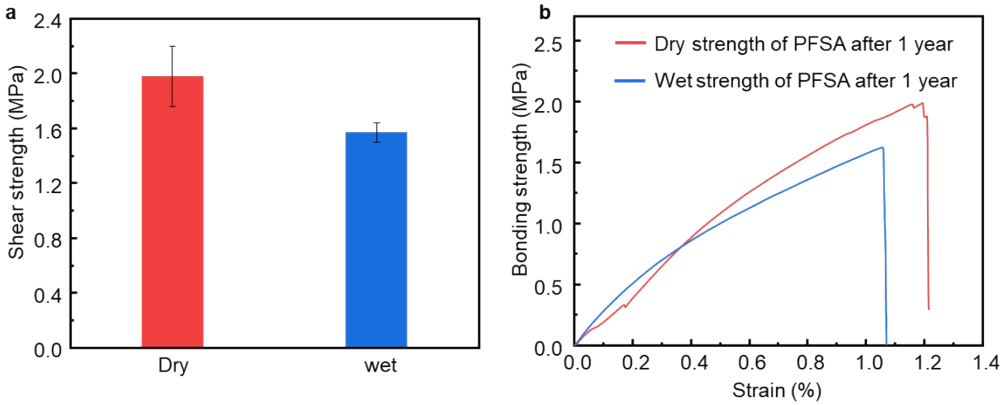
Supplementary Fig. 31 (a) Bonding performance and (b) Stress-strain curves of PSFAs bonding performance after soaking in different solvents for one day. The bonding strengths of PSFAs after soaking in acid, water, ethanol and glycol for one day were 1.13±0.10 MPa, 1.79±0.03 MPa, 1.49±0.20 MPa, and 1.55±0.04 MPa, respectively.



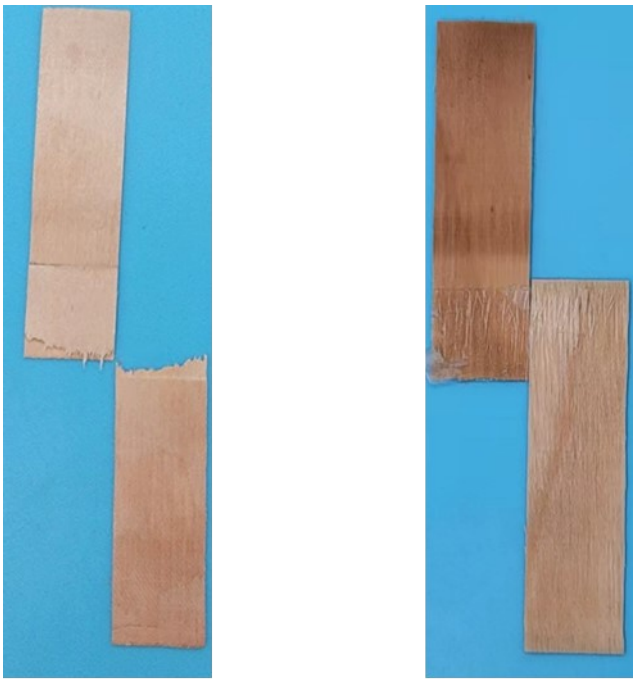
Supplementary Fig. 32 (a) Bonding performance of UF. (b) Stress-strain curves of UF bonding performance.



Supplementary Fig. 33 Failure mode of poplar single-lap joints using UF.



Supplementary Fig. 34 (a) Bonding performance of PSFA after storage for 1 year. (b) Stress-strain curves of PSFA bonding performance after storage for 1 year.



Supplementary Fig. 35 Failure mode of poplar single-lap joints using PFSA after storage for 1 year.

Supplementary Table 1. Different treatment of PSFA and their corresponding names.

	Without water activation	**With water activation**
Without heat treatment	**Control**	**WA**
With heat treatment	**HT**	**WA+HT**

Supplementary Table 2. Wet shear strength comparison of PSFA with other reported green biomass adhesives.

Adhesive type	Adhesive name	Wet shear strength (MPa)	Refs.
Soybean adhesive	SM-20%PM	1.02 ± 0.02	1
	SM/PAE/SD/Zn	1.09 ± 0.05	2
	SM/BEP-10	0.89 ± 0.04	3
Lignin adhesive	EPL/SM	1.02 ± 0.07	4
	SPI–MAL2.0%-Cu	1.29 ± 0.09	5
	FPL	1.20 ± 0.05	6
Starch adhesive	SWA-N	1.10 ± 0.21	7
	GMA graft starch adhesive	1.00 ± 0.09	8
	SCA-50%	0.83 ± 0.14	9
Solvent-free adhesive	WPUG1.5	1.06	10
	HDPE film	1.46 ± 0.11	11
	EVA film	0.91 ± 0.08	12
	PSFA	2.25 ± 0.12	This study

Supplementary Table 3. Comparison of PSFAs with UF resins and MDI adhesives in terms of green advancement.

	PSFAs	UF	MDI
Resources	**Biomass**	**Fossil fuels**	**Fossil fuels**
Starting materials	**Bioethanol**	**Urea and Formaldehyde**	**Aniline, Phosgene, and Formaldehyde**
Toxicity	**Nontoxic**	**Toxic**	**Toxic**
Biodegradability	**Biodegradable**	**Non-biodegradable**	**Non-biodegradable**
Biocompatibility	**Biocompatible**	**Non-Biocompatible**	**Non-Biocompatible**

Supplementary Table 4. Cost comparison of PSFA with UF (Urea-formaldehyde adhesive), MDI (Methylene diphenyl diisocyanate) and SB (Soybean adhesive).

Adhesive	Price ($USD \cdot ton^{-1}$)	Amounts ($g \cdot m^{-2}$)	Cost ($USD \cdot m^{-2}$)
PSFA	**1300**[13]	**70**	**0.09**
UF	**200**[14]	**320**	**0.06**
MDI	**2000**[15]	**200**	**0.40**
SB	**560**[16]	**350**	**0.20**

Supplementary Table 5. Comparison of transportation cost and safety between PSFA and existing commercial biomass adhesives.

Adhesive	Solid content (%)	Transportation cost (Relative ratio, %)	Safety
PSFA	**100**	**100**	**Safe**
UF	**50–60**	**167–200**	**Unsafe**
MDI	**100**	**100**	**Unsafe**
SB	**15–40**	**250–667**	**Safe**

Supplementary Table 6. Comparison of storage time between PSFA and existing commercial biomass adhesives.

Adhesive	Storage time
PSFA	**＞365 days (＞1 year)**
UF	**10–30 days**
MDI	**120–180 days (3–6 months)**
SB	**＜30 days**

References:

1. X. Li, F. Zhang, J. Li, C. Xia and J. Li, *Polymer Testing*, 2022, **109**, 107543.
2. X. Huang, Y. Chen, J. Li, J. Li, Q. Gao and X. Zhan, *Materials & Design*, 2022, **223**, 111163.
3. J. Luo, Y. Zhou, Q. Gao, J. Li and N. Yan, *ACS Sustainable Chemistry & Engineering*, 2020, **8**, 10767-10773.
4. S. Chen, H. Chen, S. Yang and D. Fan, *Industrial Crops and Products*, 2021, **170**, 113795.
5. Z. Liu, T. Liu, Y. Li, X. Zhang, Y. Xu, J. Li and Q. Gao, *Journal of Cleaner Production*, 2022, **366**, 132906.
6. G. Yang, Z. Gong, X. Luo, L. Chen and L. Shuai, *Nature*, 2023, **621**, 511-515.
7. Y. Gu, L. Cheng, Z. Gu, Y. Hong, Z. Li and C. Li, *Int J Biol Macromol*, 2019, **134**, 247-254.
8. X. Chen, C. Sun, Q. Wang, H. Tan and Y. Zhang, *Int J Biol Macromol*, 2022, **194**, 954-961.
9. H. Yin, P. Zheng, E. Zhang, J. Rao, Q. Lin, M. Fan, Z. Zhu, Q. Zeng and N. Chen, *Carbohydr Polym*, 2020, **250**, 116884.
10. M. Yang, Y. Li and X. Dang, *Environ Res*, 2022, **206**, 112266.
11. L. Fang, L. Chang, W.-j. Guo, Y.-p. Ren and Z. Wang, *European Journal of Wood and Wood Products*, 2013, **71**, 739-746.
12. Y. Zhang, Y. He, J. Yu, Y. Lu, X. Zhang and L. Fang, *Polymers (Basel)*, 2023, **15**, 1834.
13. PVA 1799, https://www.alibaba.com/product-detail/High-quality-Poly-vinyl-alcohol-PVA_1600985574787.html?spm=a2700.galleryofferlist.normal_offer.d_title.41904550BZDOJY), (accessed January 10, 2024).
14. UF adhesive, https://yurunchemical.en.made-in-china.com/product/zFXtLpRcXOUl/China-Urea-Formaldehyde-Liquid.html, (accessed January 10, 2024).
15. MDI, https://www.alibaba.com/product-detail/Mdi-Mdi-Hot-Sale-Methyl-Diphenylene_1600978169045.html?spm=a2700.galleryofferlist.p_offer.d_title.26e227e1Ymut0x&s=p, (accessed January 10, 2024).
16. SB adhesive, https://www.china.cn/zhiwujiao/5041309196.html, (accessed January 10, 2024).