

## Supporting information for

### **Borate chemistry inspired by cell walls converts soy protein into high-strength, antibacterial, flame-retardant adhesive**

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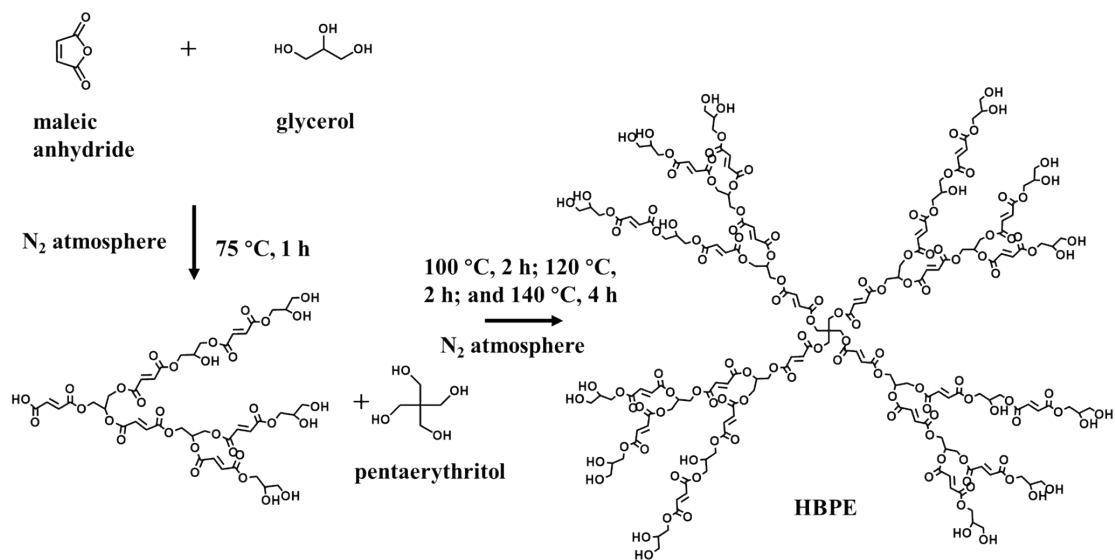
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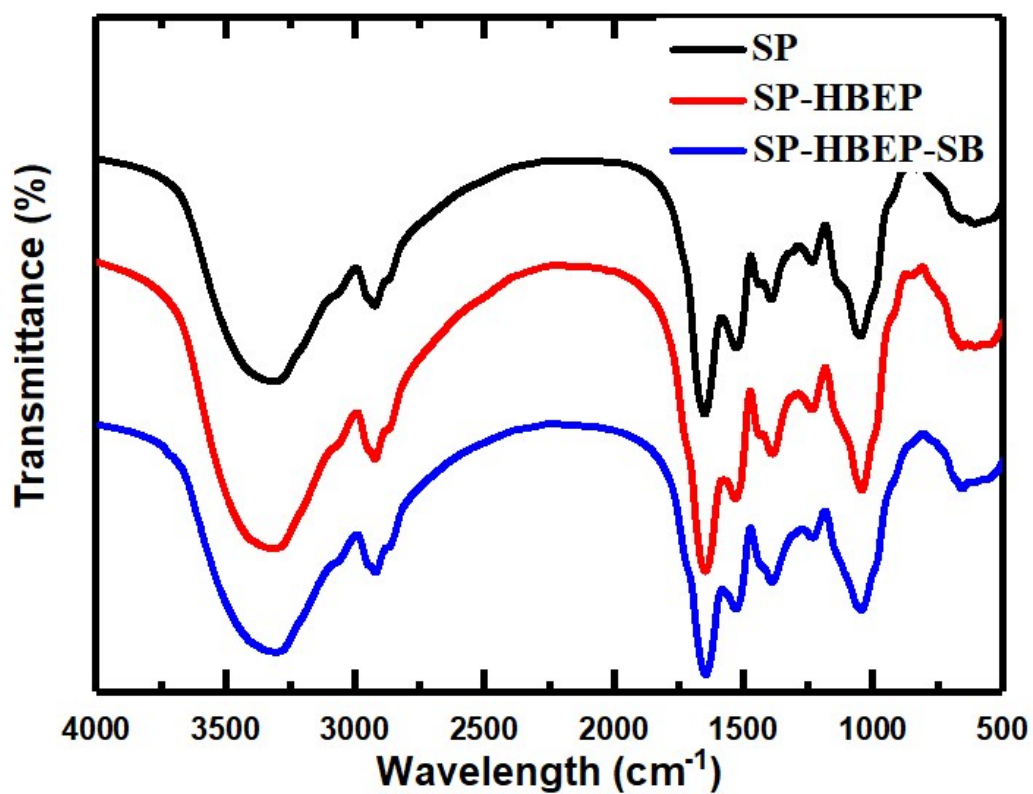
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## **Synthesis of water-soluble HBPE**

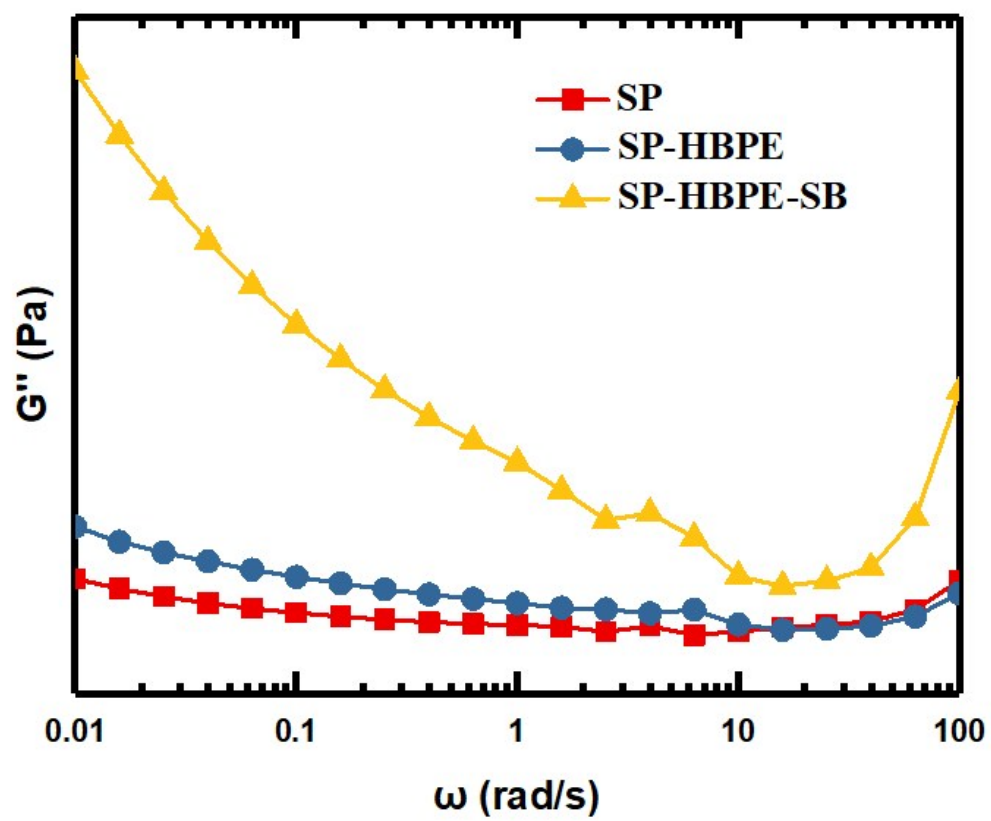
We synthesized HBPE according to previously reported methods.<sup>1-2</sup> First, glycerol (46 g, 0.5 mol) and maleic anhydride (49 g, 0.5 mol) were continuously stirred at 75 °C for 1 h under a nitrogen (N<sub>2</sub>) atmosphere. Pentaerythritol (0.454 g, 0.005 mol) was added and then reacted with the residual maleic anhydride by heating the mixture at 100 °C for 2 h, 120 °C for 2 h, and then 140 °C for 4 h. After the polymerization reaction was complete, the HBPE was purified by column chromatography using silica gel as the fixed phase and ethanol as the mobile phase.



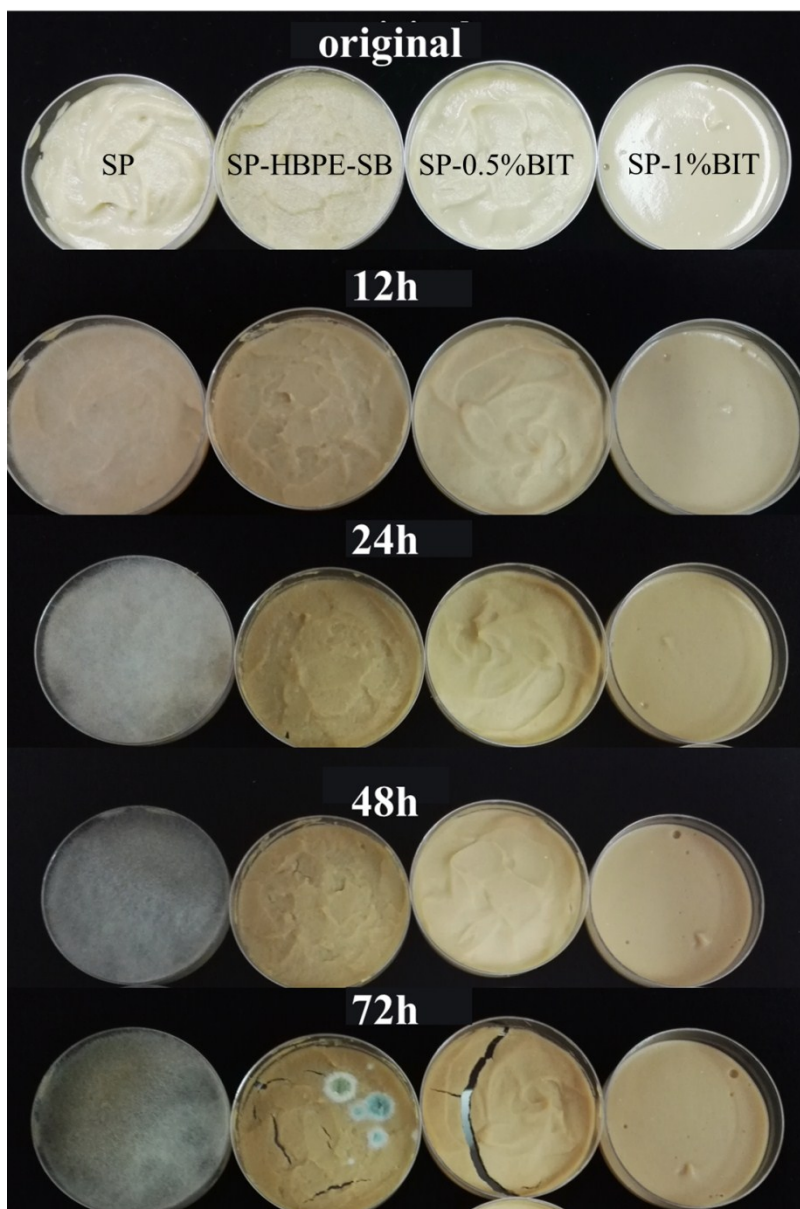
**Figure S1.** The synthesis of the HBPE



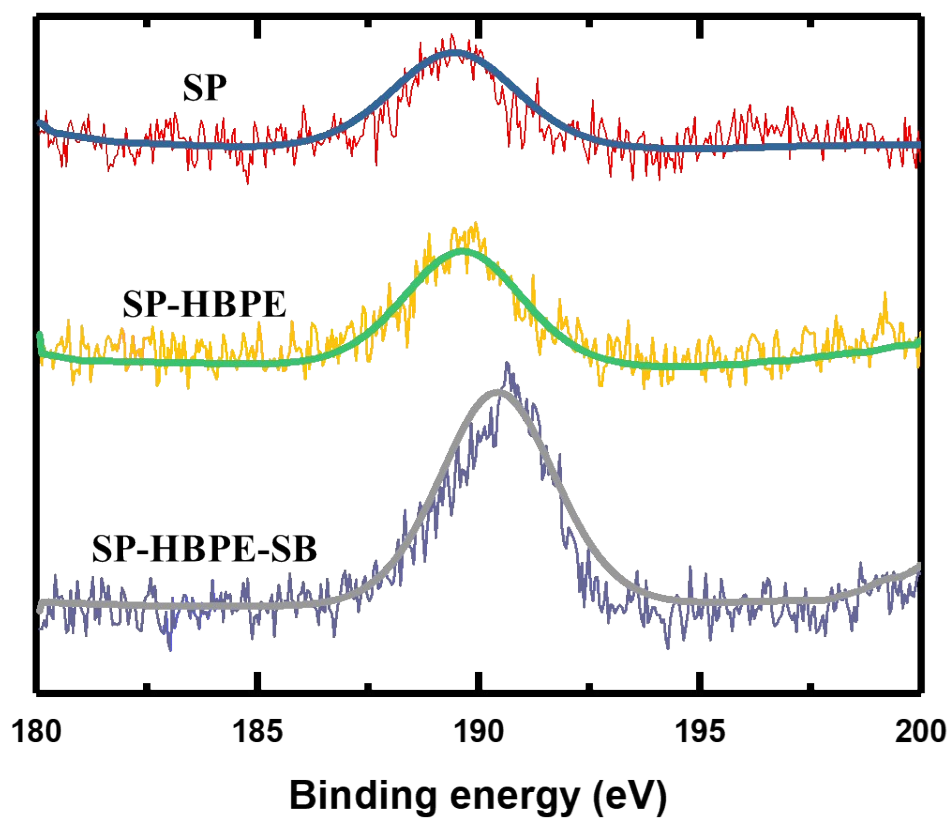
**Figure S2.** FTIR spectra of SP, SP-HBPE, and SP-HBPE-SB adhesives.



**Figure S3.** Loss modulus ( $G''$ ) of SP, SP-HBPE, and SP-HBPE-SB adhesives.



**Figure S4.** Photographs of SP, SP-HBPE-SB, SP-0.05%BIT, and SP-1%BIT adhesives before and after storage at 40 °C and 100% relative humidity for 72 h, respectively (BIT= 1,2-Benzisothiazol-3(2H)-one).



**Figure S5.** B 1s peak of the SP, SP-HBPE, and SP-HBPE-SB adhesives.

**Table S1.** The characteristics of different adhesives.

Types	Additive	Strength	References
Soy protein	Ascorbic acid	1.0 MPa <sup>a</sup>	3
Soy protein	Hyperbranched aminated polysaccharide and triglycidylamine	1.07 MPa <sup>b</sup>	4
Soy protein	Pickering emulsion and nanocrystals	1.21 MPa <sup>b</sup>	5
Soy protein	2-octen-1-ylsuccinic anhydride	3.2 MPa <sup>a</sup>	6
Soy protein	Montmorillonite and polyisocyanate	0.64 MPa <sup>c</sup>	7
Soy protein	Sorghum lignin	3.32 MPa <sup>a</sup>	8
Soy protein	Aspergillus niger	1.45 MPa <sup>b</sup>	9
Soy protein	Hyperbranched polysiloxane	1.45 MPa <sup>b</sup>	10
Tannin	Soy protein	1.03 MPa <sup>b</sup>	11
Soy protein	Tannin and poly(ethyleneimine)	1.05 MPa <sup>b</sup>	12
Lignin	Glycerol diglycidyl ether	2.2 MPa <sup>a</sup>	13
Phenolic resin	Bioethanol fermentation residues	1.07 MPa <sup>b</sup>	14
Starch	Acetylation	0.12 MPa <sup>a</sup>	15

<sup>a</sup> ASTM Standard Method D2339-98, <sup>b</sup> China National Standard GB/T 17657, <sup>c</sup> JIS K6806-2003.



1. Zhao, X.; Liu, L.; Dai, H.; Ma, C.; Tan, X.; Yu, R., Synthesis and application of water-soluble hyperbranched poly(ester)s from maleic anhydride and glycerol. *J. Appl. Polym. Sci.* **2009**, *113* (5), 3376-3381.
2. Gu, W.; Liu, X.; Li, F.; Shi, S. Q.; Xia, C.; Zhou, W.; Zhang, D.; Gong, S.; Li, J., Tough, strong, and biodegradable composite film with excellent UV barrier performance comprising soy protein isolate, hyperbranched polyester, and cardanol derivative. *Green Chem.* **2019**, *21* (13), 3651-3665.
3. Roman, J. K.; Wilker, J. J., Cooking Chemistry Transforms Proteins into High-Strength Adhesives. *J Am Chem Soc* **2019**, *141* (3), 1359-1365.
4. 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. *Chem. Eng. J.* **2018**, *354*, 1032-1041.
5. Zhao, S.; Wang, Z.; Kang, H.; Zhang, W.; Li, J.; Zhang, S.; Li, L.; Huang, A., Construction of bioinspired organic-inorganic hybrid composite by cellulose-induced interfacial gelation assisted with Pickering emulsion template. *Chem. Eng. J.* **2019**, *359*, 275-284.
6. Qi, G.; Li, N.; Wang, D.; Sun, X. S., Physicochemical properties of soy protein adhesives modified by 2-octen-1-ylsuccinic anhydride. *Ind. Crops Prod.* **2013**, *46*, 165-172.
7. Zhang, Y.; Zhu, W.; Lu, Y.; Gao, Z.; Gu, J., Nano-scale blocking mechanism of MMT and its effects on the properties of polyisocyanate-modified soybean protein adhesive. *Ind. Crops Prod.* **2014**, *57*, 35-42.
8. Xiao, Z.; Li, Y.; Wu, X.; Qi, G.; Li, N.; Zhang, K.; Wang, D.; Sun, X. S., Utilization of sorghum lignin to improve adhesion strength of soy protein adhesives on wood veneer. *Ind. crops prod.* **2013**, *50*, 501-509.
9. Zheng, P.; Chen, N.; Mahfuzul Islam, S.; Ju, L.-K.; Liu, J.; Zhou, J.; Chen, L.; Zeng, H.; Lin, Q., Development of Self-Cross-Linked Soy Adhesive by Enzyme Complex from *Aspergillus niger* for Production of All-Biomass Composite Materials. *ACS Sustainable Chem. Eng.* **2018**, *7* (4), 3909-3916.
10. 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 Chem. Eng.* **2019**, *7* (8), 7784-7794.
11. Liu, C.; Zhang, Y.; Li, X.; Luo, J.; Gao, Q.; Li, J., A high-performance bio-adhesive derived from soy protein isolate and condensed tannins. *Rsc Advances* **2017**, *7* (34), 21226-21233.

12. Wang, Z.; Zhao, S.; Song, R.; Zhang, W.; Zhang, S.; Li, J., The synergy between natural polyphenol-inspired catechol moieties and plant protein-derived bio-adhesive enhances the wet bonding strength. *Sci. Rep.* **2017**, *7* (1), 9664.
13. Li, R. J.; Gutierrez, J.; Chung, Y.-L.; Frank, C. W.; Billington, S. L.; Sattely, E. S., A lignin-epoxy resin derived from biomass as an alternative to formaldehyde-based wood adhesives. *Green chem.* **2018**, *20* (7), 1459-1466.
14. Pang, B.; Cao, X.-F.; Sun, S.-N.; Wang, X.-L.; Wen, J.-L.; Lam, S. S.; Yuan, T.-Q.; Sun, R.-C., The direct transformation of bioethanol fermentation residues for production of high-quality resins. *Green Chem.* **2020**.
15. Shuttleworth, P. S.; Clark, J. H.; Mantle, R.; Stansfield, N., Switchable adhesives for carpet tiles: a major breakthrough in sustainable flooring. *Green Chem.* **2010**, *12* (5), 798-803.