Supplementary Information

Interface Tailoring by a Versatile Functionalization Platform for Nanostructured Wood Biocomposites

Céline Montanari, ^a Peter Olsén*^a and Lars A. Berglund ^a

^a Department of Fiber and Polymer Technology, Wallenberg Wood Science Center, KTH Royal Institute of Technology, Teknikringen 56, 100 44 Stockholm, Sweden. *Email: polsen@kth.se*

CONTENT

Supplementary Methods	p. S-1
Supplementary Figures	p. S-2
References	p. S-13

SUPPLEMENTARY METHODS

Materials

Sodium chlorite (NaClO₂, 80%), sodium acetate, acetic acid (AcOH, 99%), dimethylformamide (DMF, 99.8%) were purchased from Sigma Aldrich (Sweden). Acetone was purchased from VWR (Sweden). The reagents were used as received.

Methods

Chlorite delignification. The balsa wood veneers were treated in 1 wt % of $NaClO_2$ with an acetate buffer solution (pH 4.6) at 80 °C for 4 h. The delignified wood samples were then washed three times with deionized water in low-vacuum condition to remove excess of chemicals.

Cyclic anhydride recovery. Ring-opening esterification was performed on the DW templates using MA under neat conditions without solvent, and left to react without stirring for 24 h at 100 °C. After the reaction, the DW samples were removed from the molten MA and thoroughly washed with acetone five times to remove any non-bonded reagent. A new batch of DW samples were added to the previously used MA, and left to react under the same reaction conditions. The MA was recovered five times in total and new DW samples were added for each cycle. The DW-MA templates were washed with acetone several times and dried in oven before FTIR characterization.

PMMA leaching. The TW composites were placed in DMF for 2 weeks while regularly changing the solvent. After leaching, the samples were washed in deionized water and dried in oven.

SUPPLEMENTARY FIGURES



Fig. S1. Wood composition of the balsa wood before (native wood) and after the delignification process using sodium chlorite (NaClO₂) and peracetic acid (PAA).



Fig. S2. FTIR spectra of native wood (NW) and delignified wood (DW) showing the disappearance of the characteristic lignin peaks at 1455 cm⁻¹, 1505 cm⁻¹, 1590 cm⁻¹ (aromatic skeletal vibrations), 1260 cm⁻¹ (guaiacyl ring) and 1330 cm⁻¹ (syringyl ring).^{1,2}



Fig. S3. Isotherms of NW (a), DW (b), DW-MA (c), DW-IA (d), and DW-SA (e).



Fig. S4. DSC curves of neat MA, IA, and SA.



Fig. S5. Absorbance of the v(C=O) band of DW-MA, DW-IA and DW-SA as a function of reaction temperature for 24 h reaction time, where T_m indicates the melting temperature of the compound.



Fig. S6. Effect of the time on the ring-opening esterification of DW with MA, IA, and SA. The lines show the rate of each reaction.



Fig. S7. FTIR spectra of DW-MA before and after five recycling cycles of the MA compound.



Fig. S8. Photographs showing a deprotonated DW-MA template in the wet state.



Fig. S9. FTIR spectra esterified template, DW-MA (a), DW-IA (b) and DW-SA (c) showing the carboxylate peak shift after deprotonation of the carboxyl group.



Fig. S10. TG curves of the DW and esterified DW in the temperature range 30 - 150 °C showing the weight loss attributed to moisture.



Fig. S11. Contact angle as a function of time for the unmodified DW and esterified DW templates, where t = 0.0 s corresponds to the initial contact of the water droplet on the surface of the template.



Scheme S1. Interface tailoring mechanism during the copolymerization of DW-MA and MMA.



Scheme S2. Interface tailoring mechanism during the copolymerization of DW-IA and MMA.



Fig. S12. FTIR spectra of TW reference (a) and esterified TW-MA (b), TW-IA (c) and TW-SA (d) before and after PMMA leaching, and the corresponding leached templates before and after deprotonation of the carboxylic acids to their carboxylate form.



Fig. S13. Photographs of dried DW-MA, DW-IA and DW-SA templates.



Fig. S14. SEM micrographs of TW-MA (a) and TW-IA (b) showing the infiltrated wood cells and the interface between the wood cell wall and PMMA matrix.



Fig. S15. SEM micrograph of the interface between wood cell wall and PMMA matrix in the TW biocomposite reference.

	Vf	Density (kg/m ³)	Strength (MPa)	Effective strength (MPa)
TW	0.064	1205	41.4	12
TW-MA	0.060	1200	46.2	90
TW-IA	0.065	1202	54.9	220
TW-SA	0.062	1206	61.7	339

Table S1. Mechanical properties of the TW biocomposites.

The effective strength of the DW reinforcement in the biocomposites was estimated according to the following equation:

$$\sigma = V_f \sigma_f + (1 - V_f) \sigma_m$$

where σ_f is the strength of the DW reinforcement and σ_m is the strength of the PLIMA matrix phase. Note that the mechanical properties of the neat PMMA matrix used for the estimations were taken from a previous work (Jungstedt, C. Montanari, S. Östlund and L. Berglund, Compos. Part A Appl. Sci. Manuf., 2020, **133**, 105853).



Fig. S16. SEM micrographs of the TW reference (a), TW-MA (b), TW-IA(c) and TW-SA (d) fracture surfaces after loading in the longitudinal direction.



Fig. S17. Strength *versus* Young's modulus of TW-MA, TW-IA and TW-SA compared with various transparent wood composites in the literature.^{3–19}

REFERENCES

- 1 O. Faix, in *Methods in Lignin Chemistry*, eds. S. Y. Lin and C. W. Dence, Springer Berlin Heidelberg, Berlin, Heidelberg, 1992, pp. 83–109.
- 2 O. Gordobil, R. Moriana, L. Zhang, J. Labidi and O. Sevastyanova, *Ind. Crops Prod.*, 2016, 83, 155–165.
- 3 L. Chen, Z. Xu, F. Wang, G. Duan, W. Xu, G. Zhang, H. Yang, J. Liu and S. Jiang, *Compos. Commun.*, 2020, **20**, 100355.
- 4 E. Jungstedt, C. Montanari, S. Östlund and L. Berglund, *Compos. Part A Appl. Sci. Manuf.*, 2020, **133**, 105853.
- 5 R. Mi, T. Li, D. Dalgo, C. Chen, Y. Kuang, S. He, X. Zhao, W. Xie, W. Gan, J. Zhu, J. Srebric, R. Yang and L. Hu, *Adv. Funct. Mater.*, 2020, **30**, 1907511.
- 6 A. N. Subba Rao, G. B. Nagarajappa, S. Nair, A. M. Chathoth and K. K. Pandey, *Compos. Sci. Technol.*, 2019, **182**, 107719.
- 7 K. E. O. Foster, K. M. Hess, G. M. Miyake and W. V. Srubar, *Materials (Basel).*, 2019, **12**, 2256.
- 8 C. Montanari, Y. Li, H. Chen, M. Yan and L. A. Berglund, *ACS Appl. Mater. Interfaces*, 2019, **11**, 20465–20472.
- 9 M. Wang, R. Li, G. Chen, S. Zhou, X. Feng, Y. Chen, M. He, D. Liu, T. Song and H. Qi, *ACS Appl. Mater. Interfaces*, 2019, **11**, 14313–14321.
- 10 Z. Qiu, Z. Xiao, L. Gao, J. Li, H. Wang, Y. Wang and Y. Xie, *Compos. Sci. Technol.*, 2019, **172**, 43–48.
- X. Wang, T. Zhan, Y. Liu, J. Shi, B. Pan, Y. Zhang, L. Cai and S. Q. Shi, *ChemSusChem*, 2018, 11, 4086–4093.
- 12 Q. Fu, M. Yan, E. Jungstedt, X. Yang, Y. Li and L. A. Berglund, *Compos. Sci. Technol.*, 2018, **164**, 296–303.
- 13 Z. Bi, T. Li, H. Su, Y. Ni and L. Yan, ACS Sustain. Chem. Eng., 2018, 6, 9314–9323.
- 14 H. S. Yaddanapudi, N. Hickerson, S. Saini and A. Tiwari, *Vacuum*, 2017, **146**, 649–654.
- 15 W. Gan, L. Gao, S. Xiao, W. Zhang, X. Zhan and J. Li, *J. Mater. Sci.*, 2017, **52**, 3321–3329.
- 16 W. Gan, S. Xiao, L. Gao, R. Gao, J. Li and X. Zhan, *ACS Sustain. Chem. Eng.*, 2017, **5**, 3855–3862.
- 17 Z. Yu, Y. Yao, J. Yao, L. Zhang, Z. Chen, Y. Gao and H. Luo, *J. Mater. Chem. A*, 2017, **5**, 6019–6024.
- 18 M. Zhu, J. Song, T. Li, A. Gong, Y. Wang, J. Dai, Y. Yao, W. Luo, D. Henderson and L. Hu, *Adv. Mater.*, 2016, **28**, 5181–5187.
- 19 Y. Li, Q. Fu, S. Yu, M. Yan and L. Berglund, *Biomacromolecules*, 2016, **17**, 1358–1364.