Supplementary Information

Wood-water interactions of primers to enhance wood-polyurethane bonding performance

Authors:	Thomas BÖGER[1,*]	(boeger@hfm.tum.de)	(0000-0001-8747-8506)
	Max ENGELHARDT[1]	(engelhardt@hfm.tum.de)	(0000-0002-9781-7476)
	Francis Tangwa SUH[2]	(tangwasuh86@gmail.com)	(no ORCiD)
	Klaus RICHTER[1]	(richter@hfm.tum.de)	(0000-0002-6583-0254)
	Antoni SANCHEZ-FERRER[1,*]	(sanchez@hfm.tum.de)	(0000-0002-1041-0324)

[1] Chair of Wood Science, Technical University of Munich

[2] Rosenheim University of Applied Sciences

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Table SI-1: (a) Comparison of the calculated (Calc.) and measured (Meas.) mass of active material [g/m²] applied to the specimens for sorption measurements at 20 °C and 65% RH. **(b)** The mass ratio of wood to primer [g/g] at 20 °C and 65% RH.

(a)	Beech		Birch		Larch		Douglas fir	
	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.
HMR	7.5	4.5	7.5	5.0	7.5	3.8	7.5	4.5
PS20-based	4.0	3.5	4.0	3.2	2.0	1.3	2.0	2.6
PEG-based	6.0	3.6	/	/	3.0	1.7	/	/

(b)	Beech	Birch	Larch	Douglas fir
HMR	10.1	9.7	10.3	14.7
PS20-based	6.6	6.4	4.3	8.8
PEG-based	6.8	/	4.5	/

Fig. SI-1: (Left) Schematic drawing of three-piece cups with the wood specimen placed between the upper and middle part, as well as the bottom part filled with water. **(Right)** Measurement cups with the wood specimen (above, left) and the aluminum reference (above, right) fixed between the upper and middle piece and the bottom part with the water bin in front (below).

Both moisture transmission cups are identical and each of the three components is 3D-printed out of polylactic acid (PLA, BASF Ultrafuse). The upper component consists of an open cup of 7.8 mm diameter with an O-ring seal (Ø 10.5 mm), which faces towards the specimen. The middle part consists of two male screws; one with an O-ring seal (Ø 10.5 mm) that connects and seals the specimen to the upper component, and one connecting to the bottom component. The bottom component consists of a cylindrical reservoir where water or a drying agent can be placed to generate a condition close to 100% or 0% RH, respectively, and an O-ring seal (Ø 10.5 mm) which is pressed and sealed against the middle component.

Prior to experiments, the setup was tested for feasibility, especially, to avoid uncontrolled moisture flow. Initial concerns that the semi-crystalline PLA would distort the results were confuted, because, with the identically exposed two cups (one on each side of the beam balance), just very minor deviations were observable. For more details, we refer to the publication by Sanchez-Ferrer *et al.* (2023) (https://doi.org/10.1007/s10570-023-05093-z).

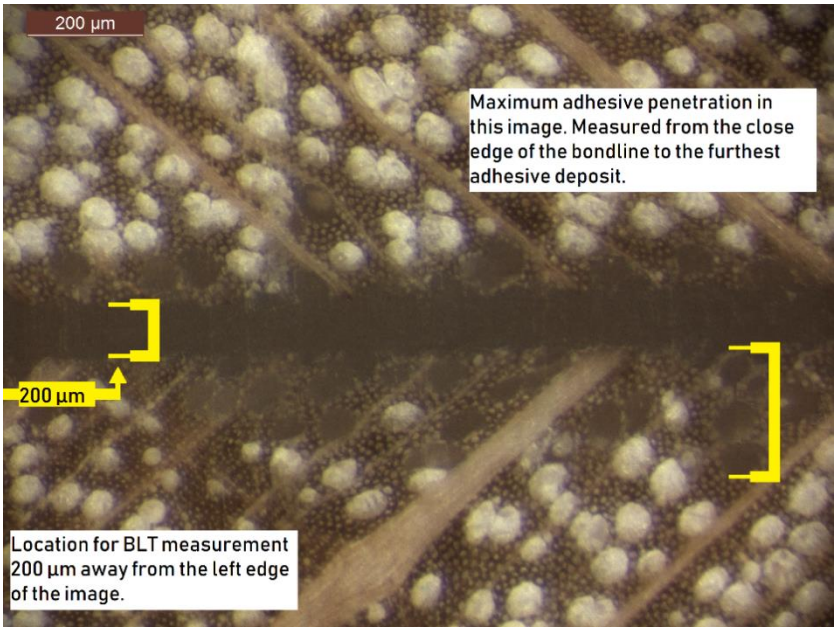

Fig. SI-2: Visualisation of the location for measuring the bond line thickness (BLT) and the maximum adhesive void penetration (MAP) on the example of unprimed beech wood bonded with 1c-PUR.

Follow-up experiment: Swelling with thicker specimens

To back the assumption of a parallel occurring swelling and plasticization of the specimens experimentally, it was considered that, with thicker specimens, the ratio between wood compressed by the tactile measurement and the assumed swelling would be smaller compared to the thin specimens.

Therefore, cubes of beech wood with 15 mm edge length (n=30) were submerged for 14 days in deionized water, in a 50% solution of PS20 and a 50% solution of PEG, followed by a reconditioning at 20 °C and 65% RH.

The volume (α_V) increased by the water treatment by 2.1% (α_l: 1.002, α_r: 1.005, α_t: 1.014) while with the PS20 treatment by 9.9% (α_l: 1.009, α_r: 1.023, α_t: 1.065), and the mass increased by 0.3% and 23.6%, respectively. By the PEG treatment, the volume (α_V) increased by 16.8% (α_l: 1.013, α_r: 1.037, α_t: 1.112) and the mass by 25.3%.

With this modified experiment, it becomes visible that the PS20 and PEG cause swelling of the cell wall, which exceeds that of water. When comparing the results of the thin specimen and the cubes, both geometries show a higher uptake of the hydrophilic PEG, compared to the amphiphilic PS20, which can be explained by better compatibility with the wood.

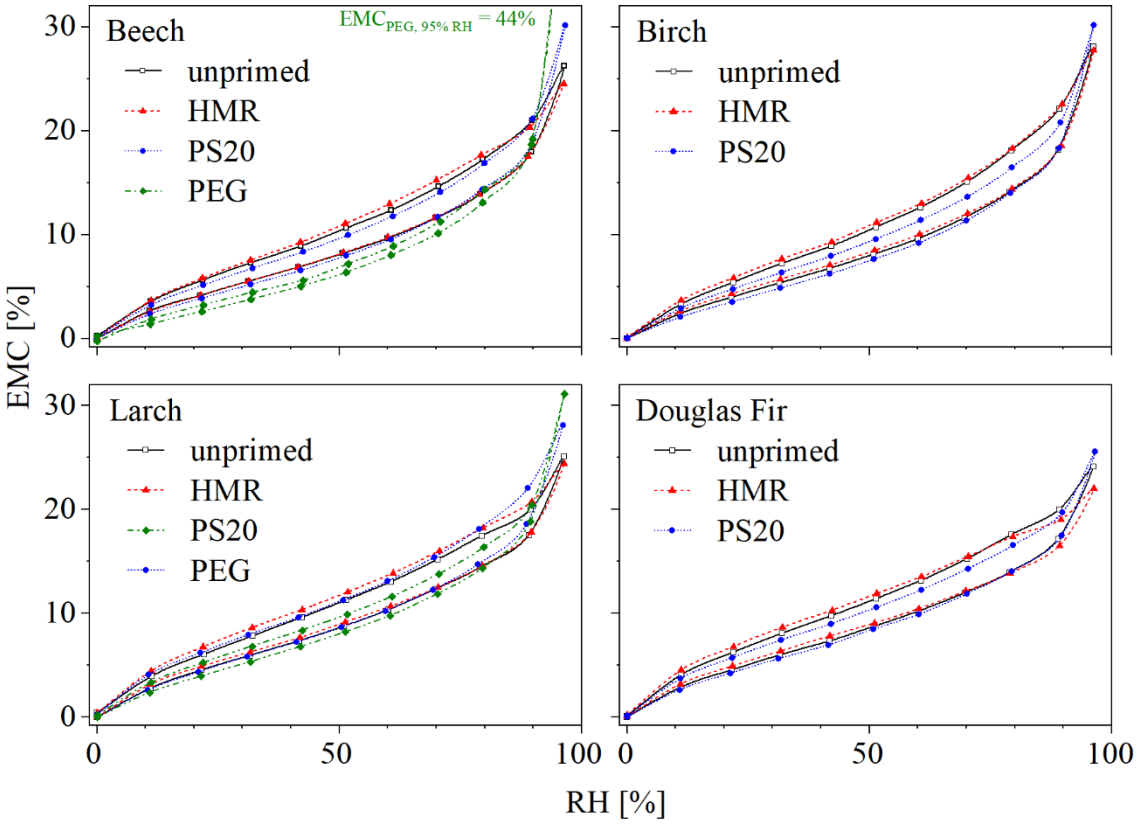

Fig. SI-3: Moisture sorption isotherms of primed wood species compared to the corresponding unprimed wood (n=5).

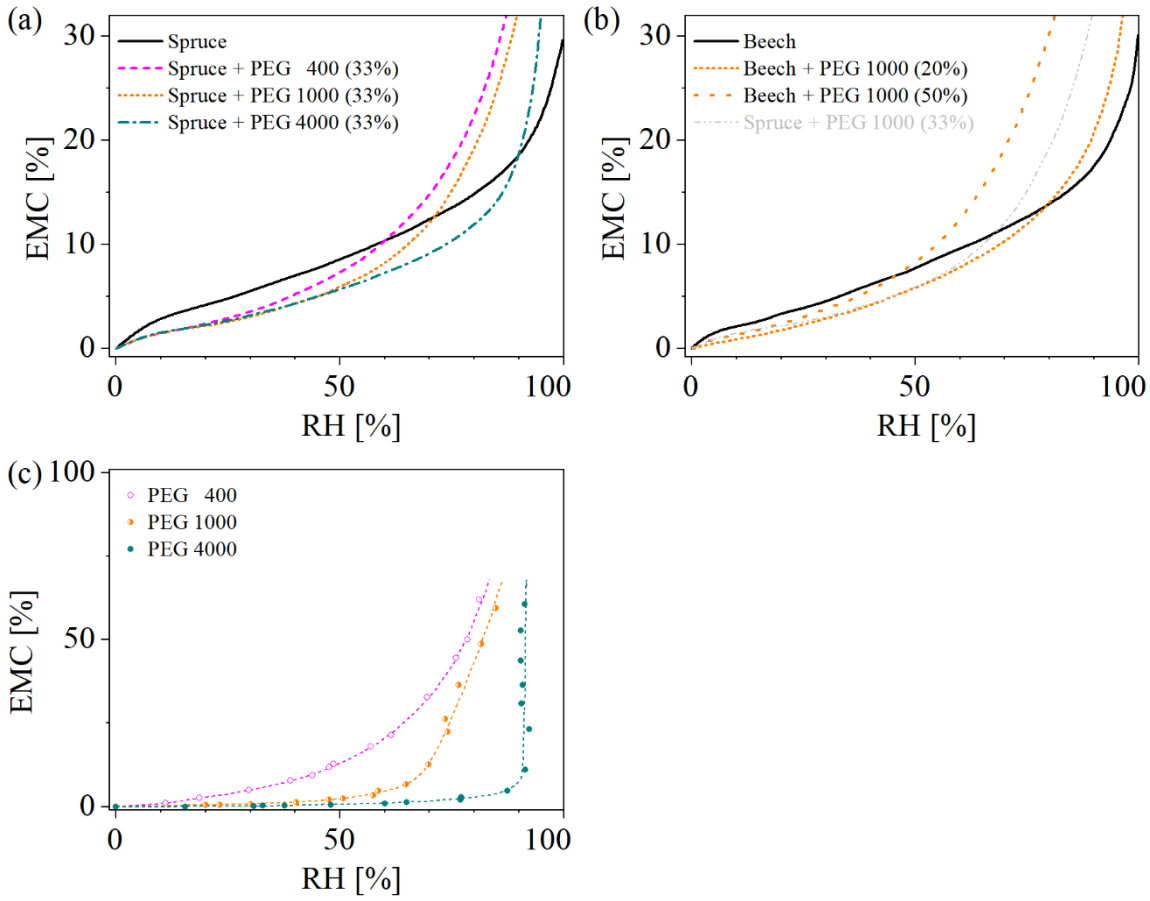

Fig. SI-4: The graphs extracted from *Schneider* (1969) – doi.org/10.1007/BF02612917: **(a)** "*Figure 6. Adsorption isotherms for 20° C from spruce wood samples after soaking in a 33% aqueous solution of PEG 400, PEG 1000 and PEG 4000 as well as in the untreated state. […]*" PEG-content: PEG 400 - 43.3%, PEG 1000 - 43.2%, PEG 4000 - 39.2%; **(b)** "*Figure 8. Adsorption isotherms for 20° C from beech wood samples after soaking in 20-and 50% aqueous solution of PEG 1000 as well as in the untreated state. […]*" PEG-content: 20%-solution - 18.5%, 50%-solution - 53.8%. Note: The result of Spruce + PEG 1000 (33%) was added to the original graph from Schneider. (1969), to have an additional suggestion of the effect of different concentrations of PEG, even though it is with another wood species; and **(c)** "*Figure 5. Adsorption isotherms for 20° C of polyethyleneglycols with molecular weights (MW) of 400, 1000 and 4000. […]*"

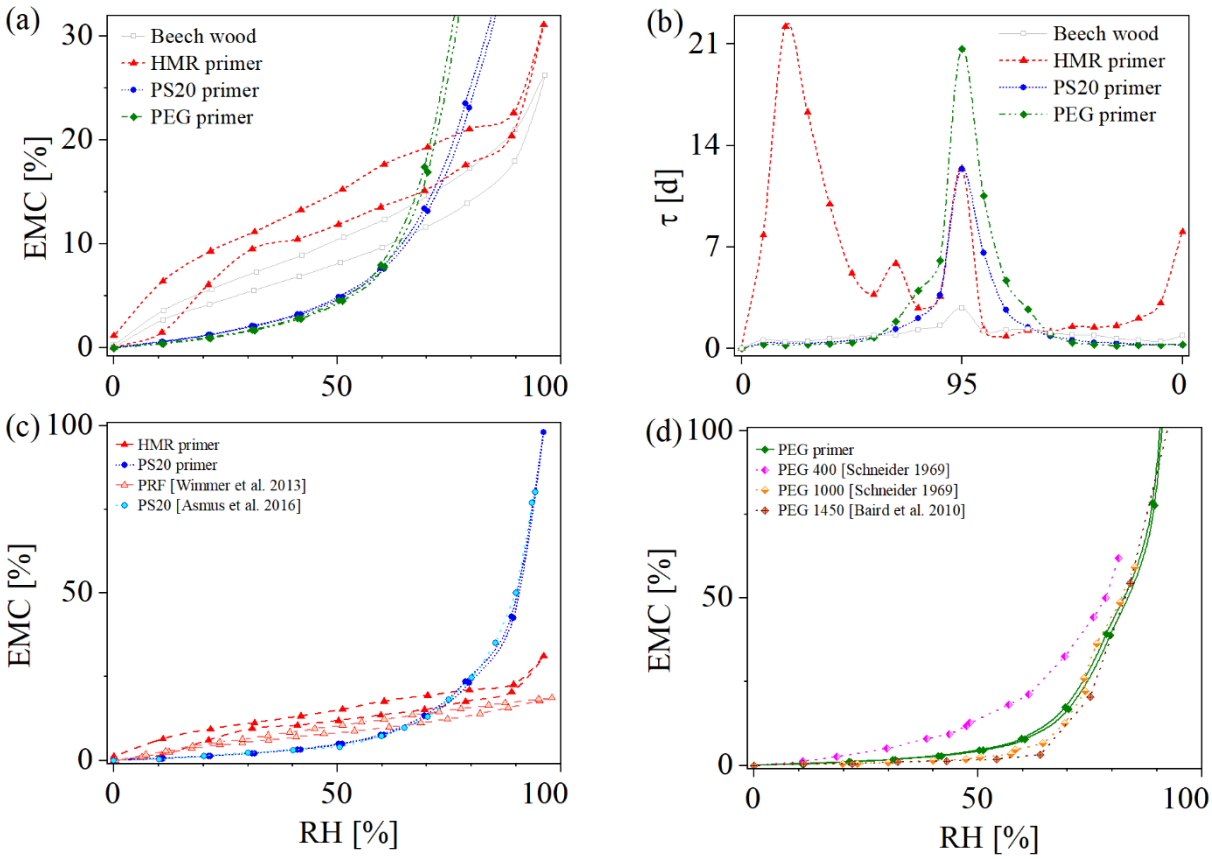

Fig. SI-5: (a) Moisture sorption isotherms of pure primers and untreated beech wood as a reference, and **(b)** time constant values (τ) evaluated from the sorption measurements (n=5). *(Note: For the τ value of the pure HMR primer, the high values in the adsorption appear out of place. However, this slow process was observed in all 5 specimens and is also not the result of a fitting error.)* **(c)** and **(d)** show a comparison of the sorption isotherms from these measurements in (a) with literature values for the HMR and PS20- as well as for the PEG-based primer.

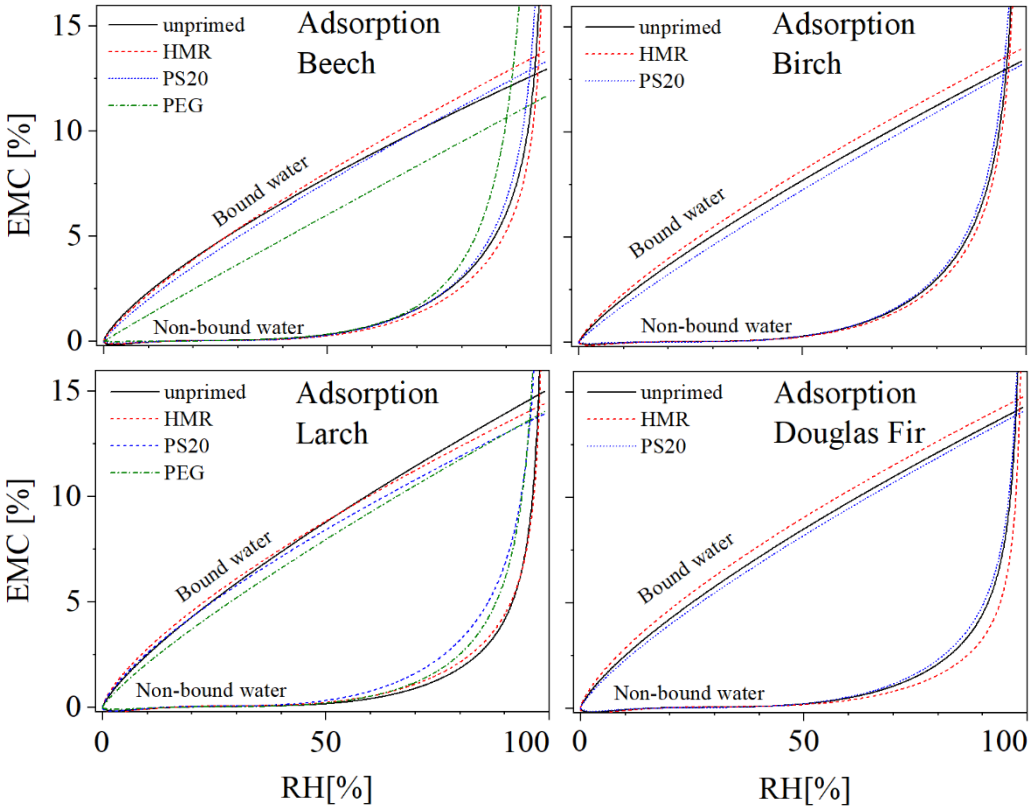

Fig. SI-6: Bound and non-bound water profiles as a function of the relative humidity from the SSO model for primed and unprimed beech, birch, larch, and Douglas fir samples based on the dry mass of the wood.

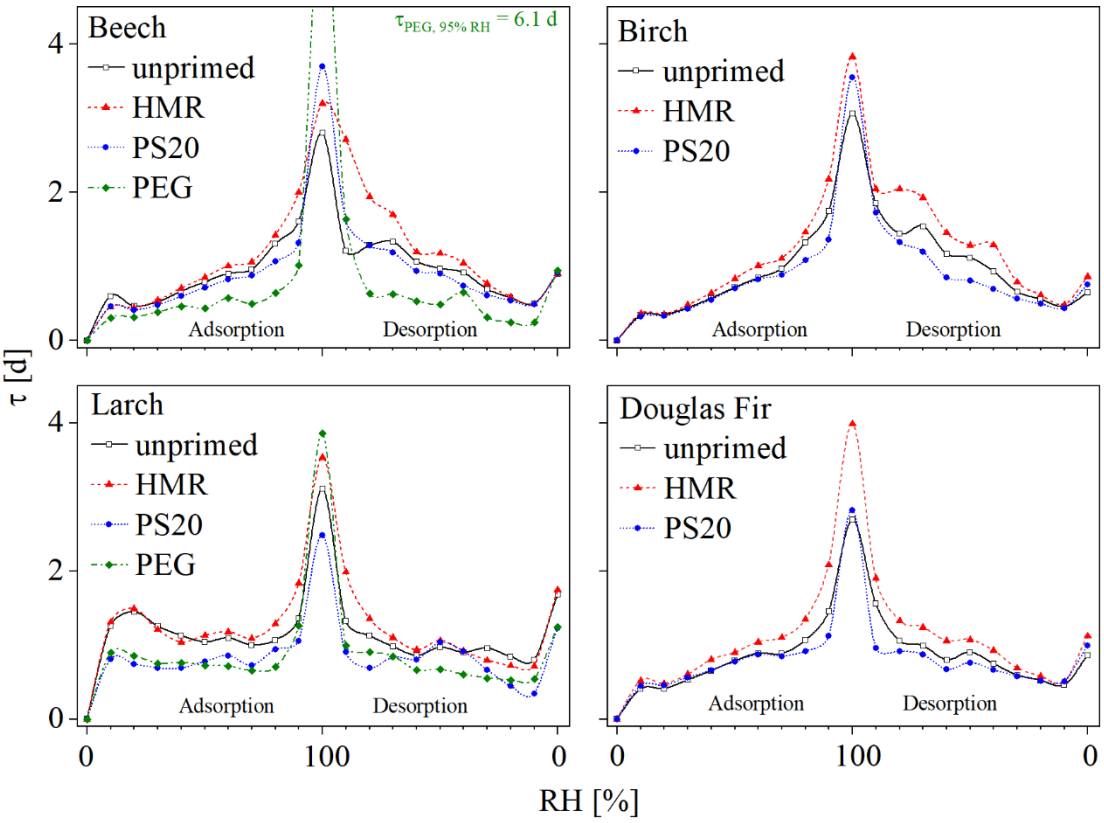

Fig. SI-7: Time constant (τ) values as a function of the relative humidity for the unprimed wood samples compared to the primed wood samples with HMR-, PS20- and PEG-primer (n=5) for each sorption step along the DVS experiment.

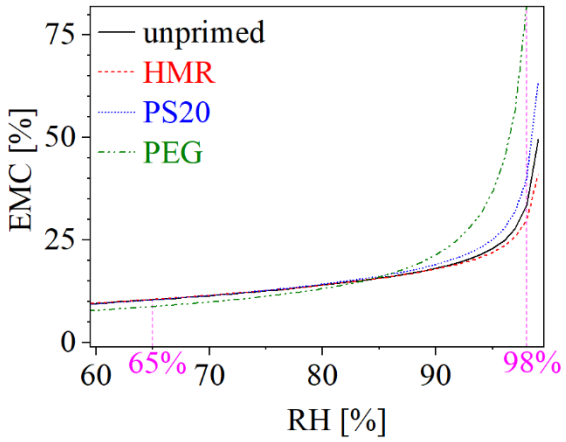

Fig. SI-8 Moisture sorption isotherm generated with the modified GAB-model of unprimed beech wood and treated with HMR, PS20 and PEG primer. From the isotherm, the average EMC ($\overline{EMC}$) over the cross-section of the specimen in the diffusivity and permeability measurement can be calculated between the RH-values of 65% and 98%. The $\overline{EMC}$ was obtained by calculating the area below each isotherm and dividing this area by the RH-range (33%-points RH).

Table SI-2: Average EMC ($\overline{EMC}$) over the cross-section of unprimed beech wood and treated with HMR, PS20 and PEG primer for the RH region of 65% to 98%. The sorption coefficient, calculated from the diffusivity and permeability measurement (S = P/D) and the $\overline{EMC}$ (Eq. SI-1) are listed for comparison.

	$\overline{EMC}$ [%]	S $_{(\overline{EMC})}$ [mol m^{-3} Pa^{-1}]	S $_{(P/D)}$ [mol m^{-3} Pa^{-1}]
Unprimed	15.8	3.83	10.0
HMR	15.6	3.79	7.3
PS20	16.6	4.10	11.6
PEG	18.9	4.71	14.3

$$S_{(\overline{EMC})} = \frac{m_{dry}\,[g] \qquad (\overline{EMC}\,[\%]/100)}{mw_{(water)}\,[\mathrm{g}/mol] \quad V\,[m^3] \quad \Delta p\,[Pa]} \qquad \text{(Eq. SI-1)}$$

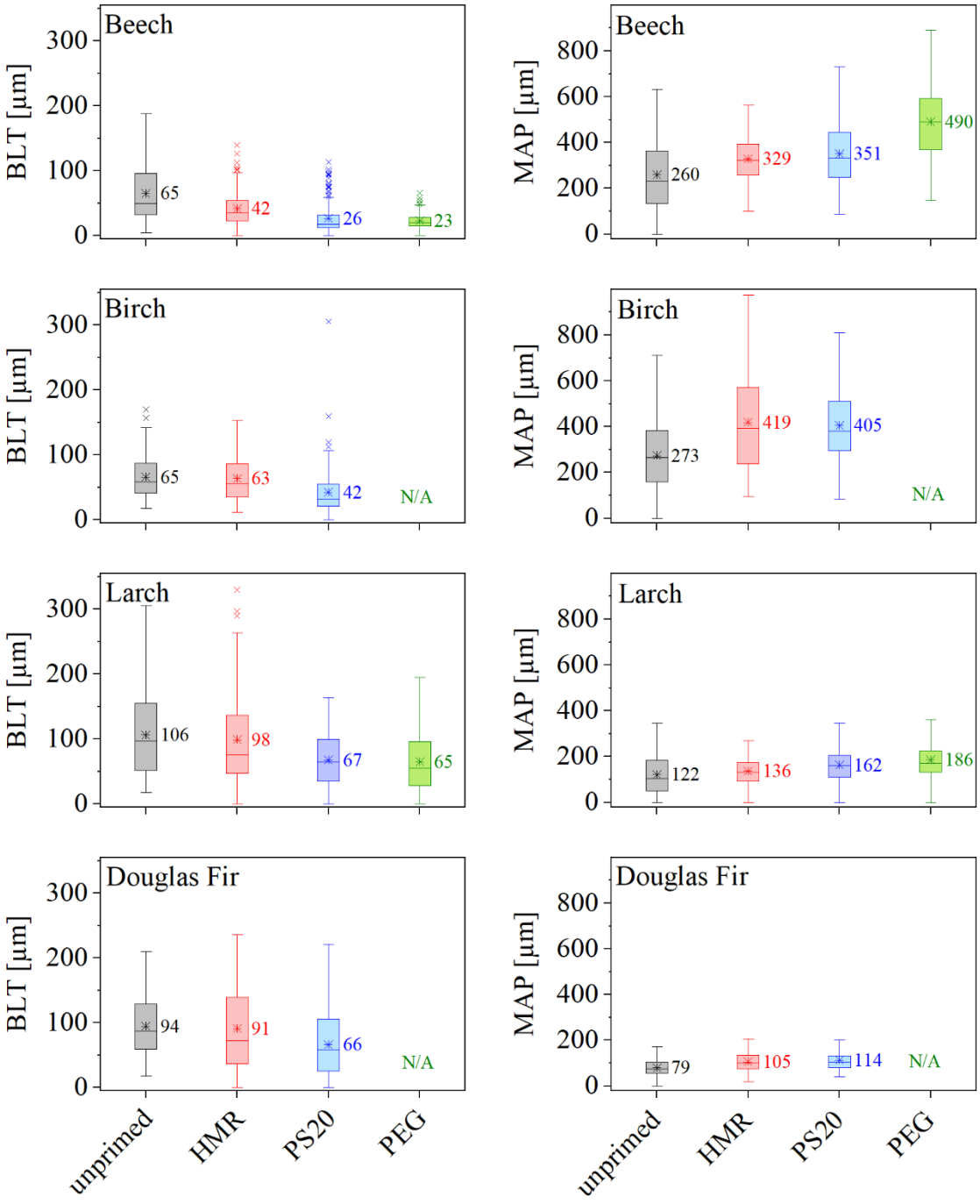

Fig. SI-9: Bond line thickness (BLT) and maximum adhesive penetration (MAP) for the specimens in Fig. **SI**. The number near the boxplot is the group's average (n=150). Note: Box = 25-75 percentile, line = median, star = average, whiskers = 1.5 IQR, cross = outlier.

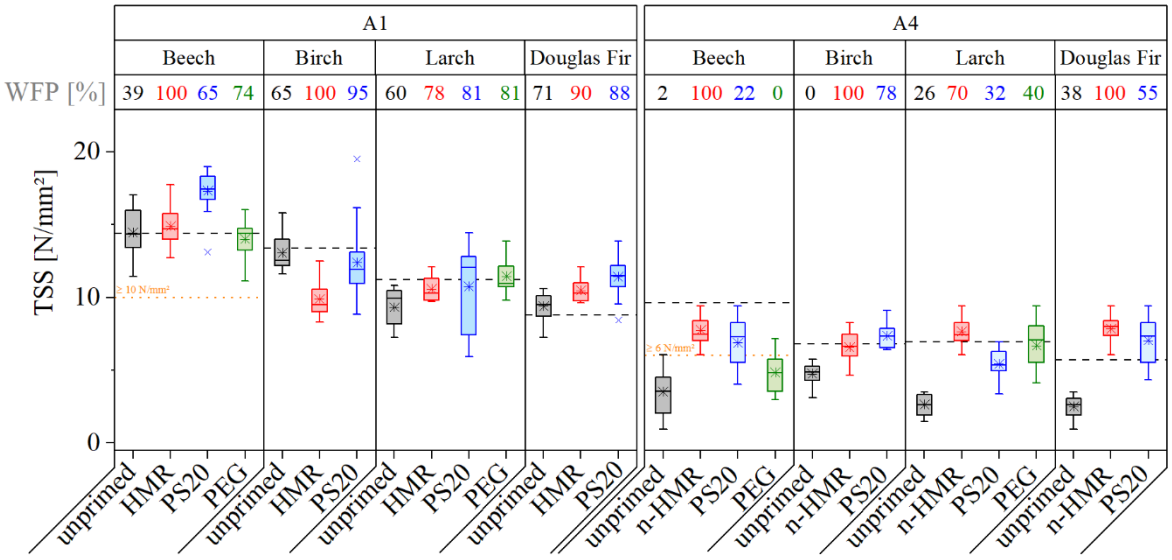

Fig. SI-10: Tensile shear strength (TSS) values and wood failure percentage (WFP) determined on different wood species bonded with 1C-PUR adhesive with and without primer treatment under A1 and A4 conditions (n=15). The orange dot line in beech wood indicates the 10 N/mm² and 6 N/mm² TSS required value in EN 15425 for A1 and A4, respectively. For birch, larch and Douglas Fir no TSS requierement exists. To give another reference about the performance of the bonds with all wood species, the black dashed line represents the average TSS of solid wood specimens (without adhesive and bond line) with the identical geometry of the other specimen. Note: Box = 25-75 percentile, line = median, star = average, whiskers = 1.5 IQR, cross = outlier.