Supporting Information for

# Vitrimer Chemistry Meets Cellulose Nanofibrils: Bioinspired Nanopapers with High Water Resistance and Strong Adhesion

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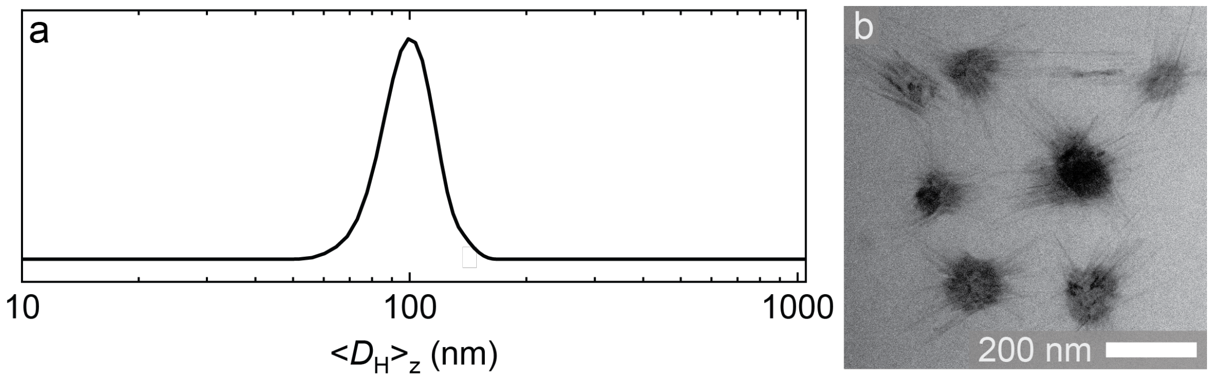


**Figure S1.** Average size of VP measured by (a) dynamic light scattering (DLS) and (b) transmission electron microscopy (TEM).

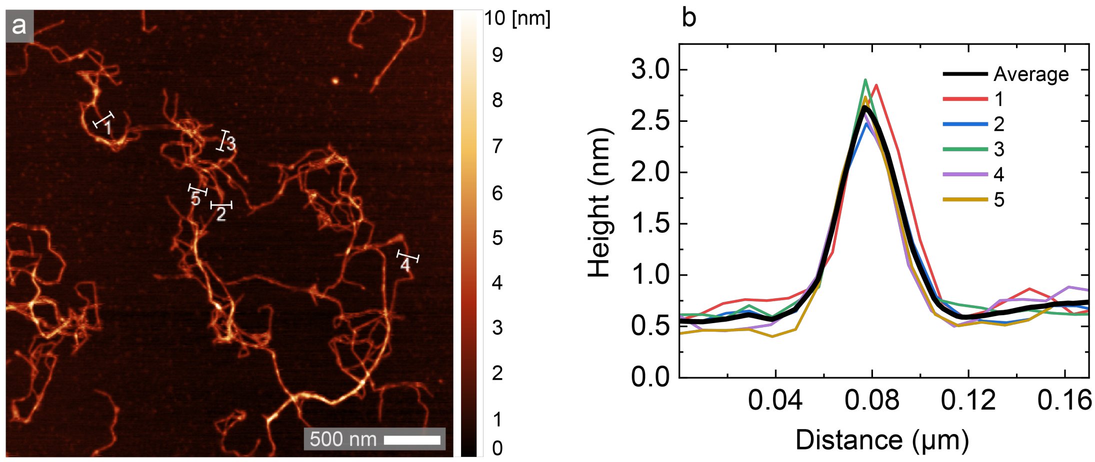


**Figure S2.** Atomic force microscopy (AFM) characterization of the diameters of CNFs. (a) AFM height image of CNFs. (b) 5 selected CNFs height profiles with their average.

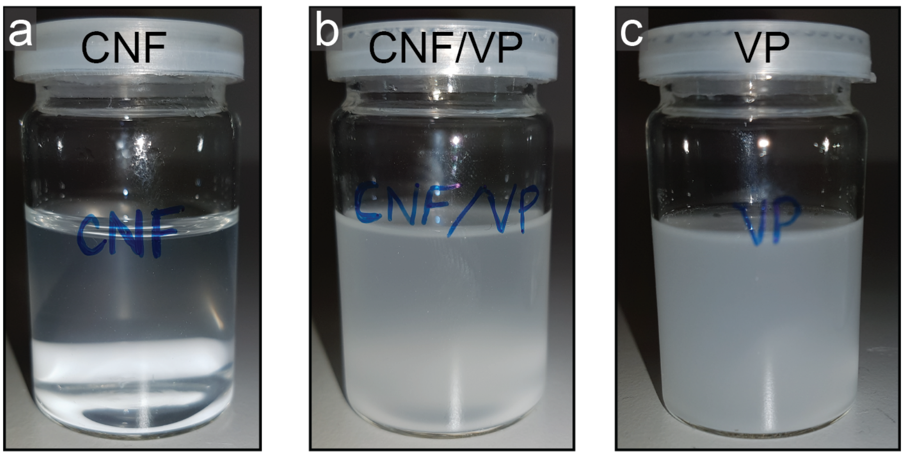


**Figure S3.** Photographs of dispersions (0.25 wt%) without aggregation and phase separation for (a) CNF, (b) $CNF_{50}/VP_{50}$ and (c) VP.

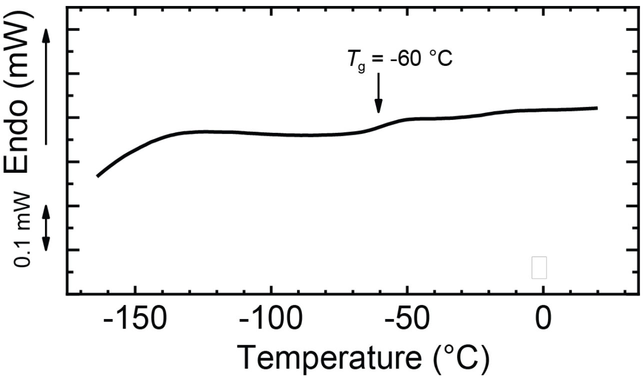


**Figure S4.** DSC thermogram of cured VP with its denoted $T_g$.

**Table S1. Tensile properties as function of Relative Humidity for CNF/VP nanocomposites**

| Sample | RH (%) | PDMS (wt%) | $E$ (GPa) | $\sigma_y$ (MPa) | $\sigma_b$ (MPa) | $\varepsilon_b$ (%) | $U_t$ (MJ/m$^3$) |
|---|---|---|---|---|---|---|---|
| CNF | | 0 | 11.5 ± 0.6 | 111 ± 2 | 260 ± 19 | 5.4 ± 0.7 | 9 ± 2 |
| $CNF_{65}/VP_{35}$ (NC) | | 35 | 8 ± 2 | 83 ± 4 | 169 ± 14 | 10 ± 2 | 13 ± 3 |
| $CNF_{65}/VP_{35}$ (C) | 20 | | 10.4 ± 0.6 | 113 ± 7 | 222 ± 11 | 6.4 ± 0.5 | 10 ± 1 |
| $CNF_{50}/VP_{50}$ (NC) | | 50 | 2.5 ± 0.4 | 18 ± 2 | 39 ± 1 | 11 ± 2 | 3.5 ± 0.9 |
| $CNF_{50}/VP_{50}$ (C) | | | 2.6 ± 0.4 | 30 ± 3 | 55.5 ± 0.1 | 7 ± 2 | 2.5 ± 0.9 |
| CNF | | 0 | 8.9 ± 0.8 | 79 ± 11 | 210 ± 17 | 7.6 ± 0.9 | 10 ± 2 |
| $CNF_{65}/VP_{35}$ (NC) | | 35 | 6.6 ± 0.6 | 24 ± 1 | 68 ± 4 | 16 ± 2 | 9 ± 1 |
| $CNF_{65}/VP_{35}$ (C) | 55 | | 8 ± 2 | 43 ± 1 | 115 ± 2 | 11 ± 2 | 10 ± 2 |
| $CNF_{50}/VP_{50}$ (NC) | | 50 | 1.2 ± 0.2 | 11.1 ± 0.6 | 28 ± 1 | 19 ± 1 | 4.2 ± 0.3 |
| $CNF_{50}/VP_{50}$ (C) | | | 1.9 ± 0.1 | 15 ± 1 | 44 ± 4 | 11 ± 2 | 3.7 ± 0.5 |
| CNF | | 0 | 5.9 ± 0.6 | 32 ± 2 | 141 ± 10 | 13 ± 1 | 13 ± 1 |
| $CNF_{65}/VP_{35}$ (NC) | | 35 | 2.4 ± 0.4 | 14.4 ± 0.5 | 59 ± 2 | 24 ± 3 | 10 ± 1 |
| $CNF_{65}/VP_{35}$ (C) | 80 | | 3.2 ± 0.7 | 19 ± 2 | 68 ± 4 | 13 ± 3 | 6 ± 1 |
| $CNF_{50}/VP_{50}$ (NC) | | 50 | 0.9 ± 0.2 | 4.5 ± 0.3 | 18.2 ± 0.6 | 37 ± 2 | 4.6 ± 0.3 |
| $CNF_{50}/VP_{50}$ (C) | | | 1.0 ± 0.1 | 13 ± 3 | 36 ± 1 | 25 ± 4 | 7 ± 1 |
| CNF | | 0 | 0.6 ± 0.1 | 5 ± 1 | 36 ± 6 | 20 ± 9 | 5 ± 2 |
| $CNF_{65}/VP_{35}$ (NC) | | 35 | 1.1 ± 0.3 | 5 ± 1 | 37 ± 2 | 40 ± 2 | 8.8 ± 0.9 |
| $CNF_{65}/VP_{35}$ (C) | 99 | | 1.5 ± 0.2 | 6.5 ± 0.7 | 45 ± 4 | 27 ± 3 | 8 ± 1 |
| $CNF_{50}/VP_{50}$ (NC) | | 50 | 0.16 ± 0.03 | 3.13 ± 0.02 | 13 ± 1 | 38 ± 4 | 3.2 ± 0.4 |
| $CNF_{50}/VP_{50}$ (C) | | | 0.35 ± 0.03 | 5 ± 1 | 23 ± 2 | 25 ± 7 | 4 ± 1 |
| CNF | | 0 | 0.023 ± 0.008 | 1.27 ± 0.08 | 2.8 ± 0.3 | 35 ± 3 | 0.67 ± 0.09 |
| $CNF_{65}/VP_{35}$ (NC) | | 35 | 0.011 ± 0.001 | 0.13 ± 0.03 | 2.1 ± 0.4 | 31 ± 1 | 0.29 ± 0.02 |
| $CNF_{65}/VP_{35}$ (C) | In water | | 0.28 ± 0.06 | 6 ± 2 | 31 ± 5 | 26 ± 7 | 5 ± 2 |
| $CNF_{50}/VP_{50}$ (NC) | | 50 | 0.010 ± 0.001 | 1.1 ± 0.1 | 4.6 ± 0.3 | 44 ± 1 | 1.1 ± 0.1 |
| $CNF_{50}/VP_{50}$ (C) | | | 0.20 ±0.02 | 5 ± 1 | 22 ± 1 | 24 ± 3 | 3.5 ± 0.7 |

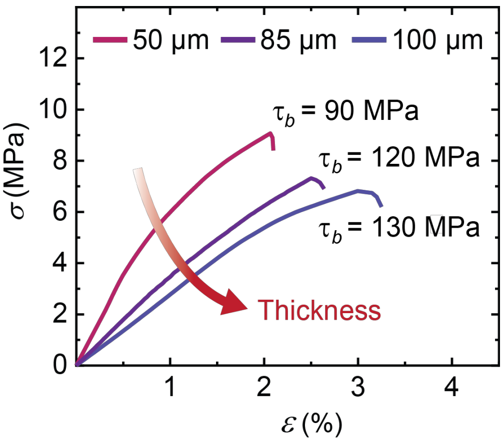


**Figure S5.** Tensile curves for shear-lap tests as function of the VP (*C*) thickness between the hot-pressed CNF films. Depending on the thickness of the VP joint, the tensile strength ranged from 6 MPa to 9 MPa, presenting lower values for thicker VP. The shear strength, as calculated by eq 1 (main MS), ranges from 90 – 130 MPa, demonstrating good interfacial adhesion and strong bond formation with the interface of cellulose material, allowing to sustain high stresses evenly during the tensile loading. Fracture happens in the interstitial vitrimer layers. Note that similar investigations cannot be done for the non-cured VP, as it is liquid like and is squeezed out from the joined area, leaving behind a very thin film.