Supplementary Information

Rheo-SAXS study of shear-induced orientation and relaxation of cellulose nanocrystal and montmorillonite nanoplatelet dispersions

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The x-ray scattering length density (SLD) of the MNT ($(Na)_{0.33}(Al)_{1.67}(Mg)_{0.33}(Si)_4(O)_{10}(OH)_2$. x H_2O) is estimated to be 24.5 ± 0.1 × 10^{-6}/Å^2 using the manufacturer's reported bulk density of 2.86 g.cm^{-3}. We have used previously reported x-ray SLDs of crystalline cellulose and bulk water of 14.46 × 10^{-6}/Å^2 and 9.47 × 10^{-6}/Å^2, respectively.[1] The pH values for MNT-only, CNC 3.6 wt% and MNT 2.5 wt% composite, and CNC-only dispersions are approximately 9, 6, and 5, respectively.

Effective diameter estimation:

After estimation of the ionic strength (Equation S1) of the CNC-only 3.6 wt% dispersion, the Debye length has been calculated using Equation S2:

$$I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2 \quad \text{(S1)}$$

$$\kappa^{-1} = \sqrt{\frac{\varepsilon_r \varepsilon_0 k_B T}{2 N_A e^2 I}} \quad \text{(S2)}$$

Effective diameter of CNC particles can be calculated using Equation S3:

$$D_{eff} = D + \kappa^{-1}(lnA + C + ln2 - \frac{1}{2}) \quad \text{(S3)}$$

where C is the Euler constant, $\kappa^{-1}$is the Debye length, D is diameter of the particle and A can be calculated by using Equation S4:

$$A = 2\pi \upsilon_{eff}^2 \kappa^{-1} Q exp(-\kappa D) \quad \text{(S4)}$$

Where υ_{eff} denotes the effective linear charge density and Q is the Bjerrum length (0.714 nm). Given that, by considering D and L 4.3 nm and 173 nm, respectively, the Debye length κ^{-1}= 5.25 nm and charge density of 0.314 mmol/g (measured by titrimetrically) and a pKa of 2.5 for sulfate half-ester groups which yields degree of disassociation to be around 0.4, and assuming all charges are on the surface of CNC, and density of the CNC to be 1.6 g.cm^{-3}, the surface charge density of the CNC is estimated to be around 0.13 e/nm^2. The effective linear charge density has been calculated using Equation S5:

$$\upsilon_{eff} = \frac{2\pi\sigma_S}{(\kappa K_1(\kappa\frac{D}{2}))} \quad \text{(S5)}$$

Where the σ_S is the surface charge density, and K_1 is the first order modified Bessel function of the second kind, and κ^{-1} is the Debye length.

Using Equation S5 yielded the effective linear charge density to be around 2 e/nm. Given that, by using Equation S3 the effective diameter is estimated to be around 28 nm.[2,3]

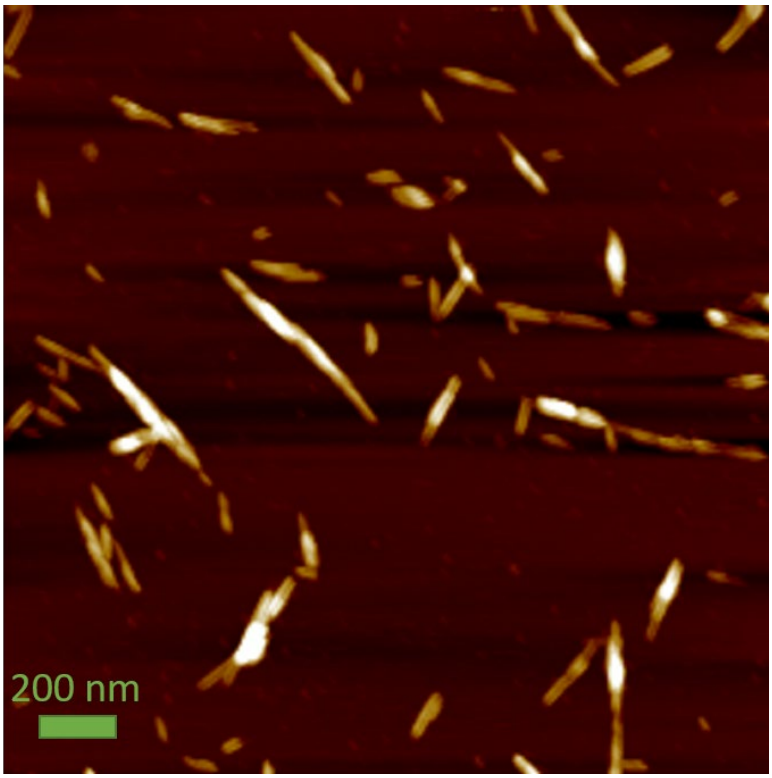

Figure S1. AFM micrograph showing the CNC used in this study, and from which the average particle dimensions were estimated.

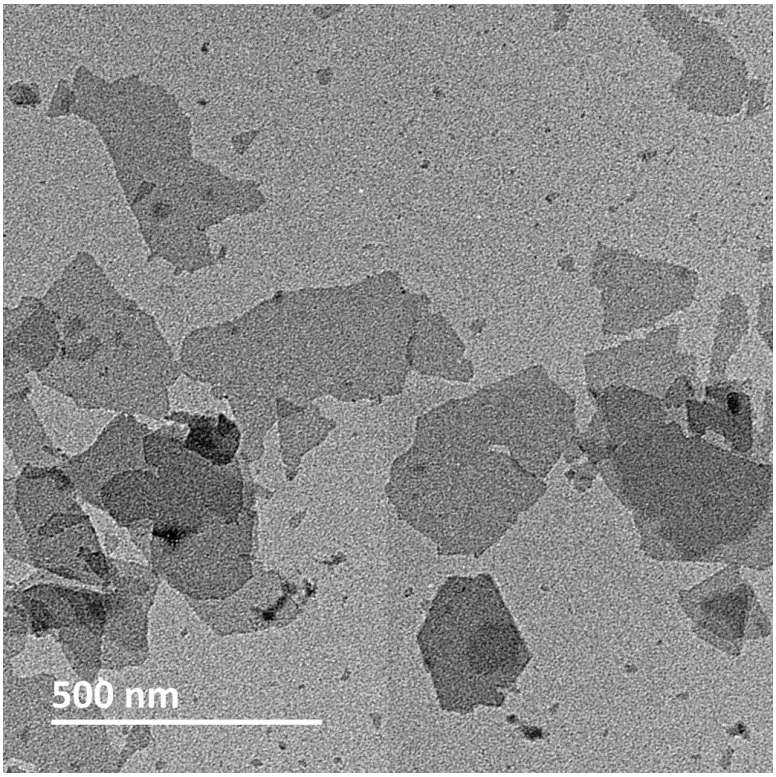

Figure S2. TEM micrograph showing the MNT used in this study, and from which the average platelet diameter was estimated.

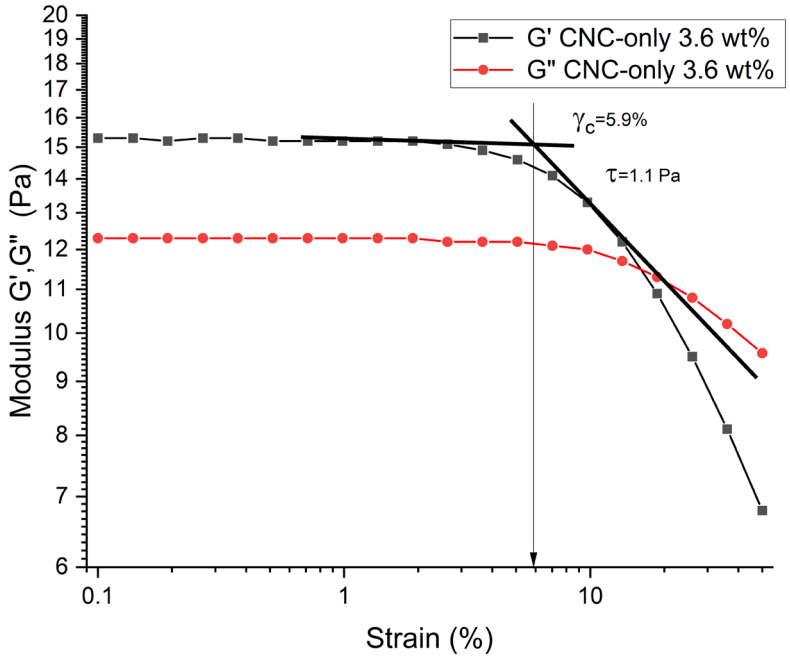

Figure S3. Strain sweep of CNC-only 3.6 wt% dispersion. The measurement has been performed at 25 °C with a constant angular frequency of 1 rad.s^{-1}.

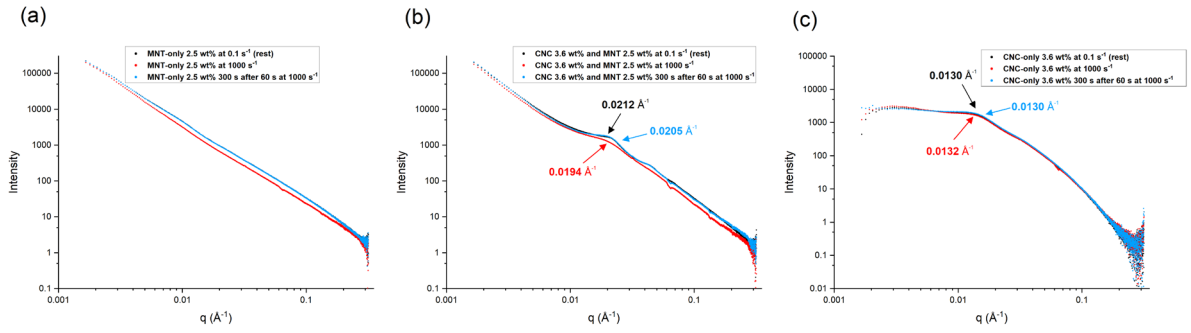

Figure S4. Radial integration of SAXS patterns of (a) MNT-only 2.5 wt%, (b) CNC 3.6 wt% and MNT 2.5 wt% composite, and (c) CNC-only 3.6 wt% dispersions obtained at the shear rate of 0.1 s^{-1} (rest), at second 59 of a 60-second shearing at the shear rate of 1000 s^{-1}, and at 300 seconds after a 60-second shearing at the shear rate of 1000 s^{-1} (relaxation). The positions of the peaks are indicated in the corresponding legend.

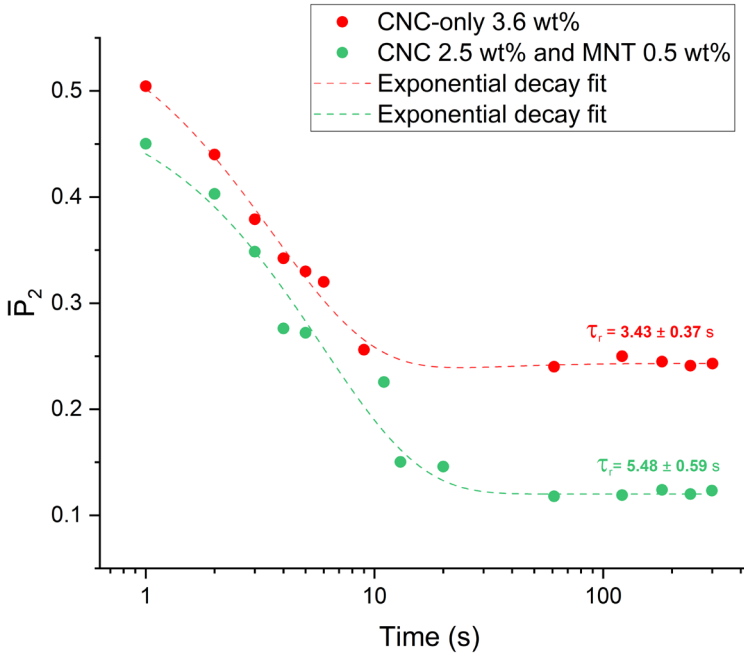

Figure S5. Hermans' orientation parameter as a function of time for a CNC-only 3.6 wt% and a CNC:MNT composite dispersion containing 2.5 wt% CNC and 0.5 wt% MNT. The dashed curves represent least-square fit to exponential decay functions with a single time constant ($y = (A_1 - y_0)exp(^{-x}/_{t_1}) + y_0$), of which the value is indicated in the corresponding legend. The R^2 values for CNC-only 3.6 wt% and CNC 2.5 wt% and MNT 0.5 wt% composite fittings are 0.99 and 0.97, respectively.

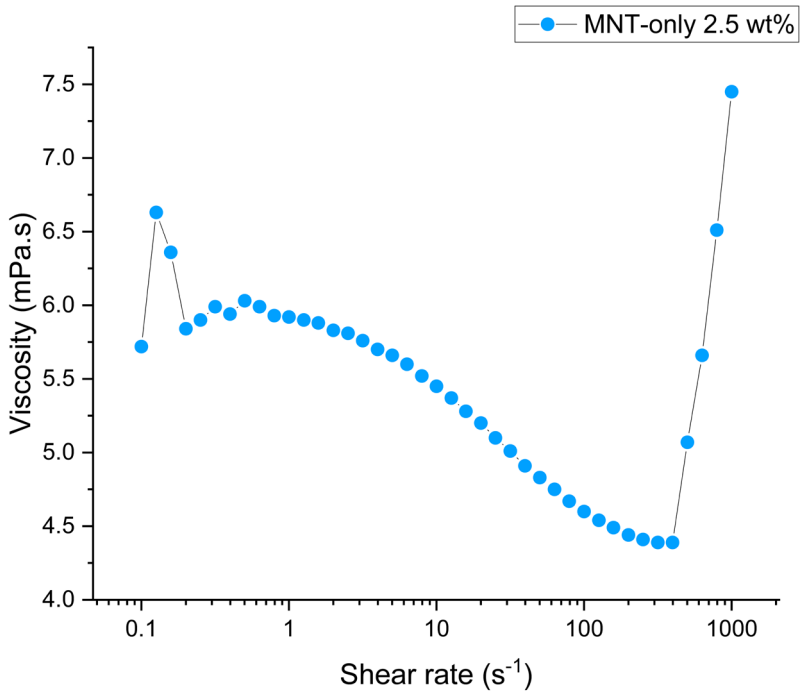

Figure S6. Steady-state shear viscosity against shear rate obtained via rotational measurements on MNT-only 2.5 wt% dispersion at 25 °C.

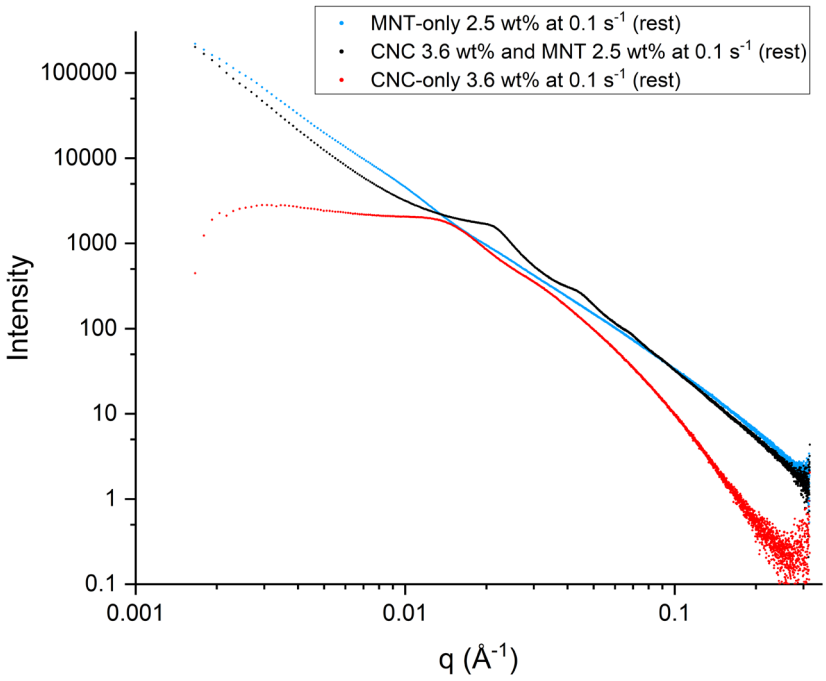

Figure S7. Radial integration of SAXS patterns of CNC-only, CNC:MNT composite, and MNT-only dispersions at the shear rate of 0.1 s^{-1} (rest).

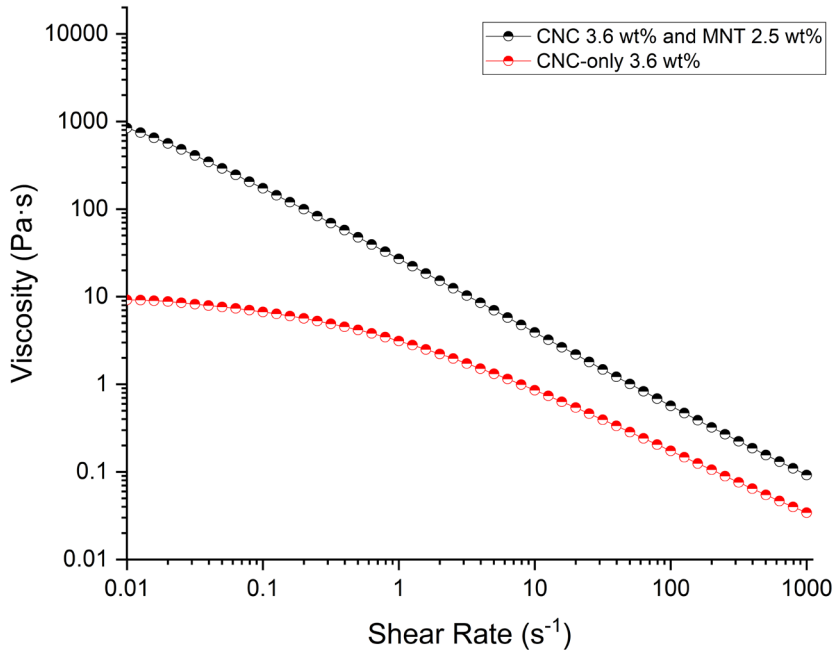

Figure S8. Steady-state shear viscosity against shear rate obtained via rotational measurements on CNC-only and CNC:MNT dispersions at 25 °C. All samples are subjected to vigorous vortexing and are immediately measured.

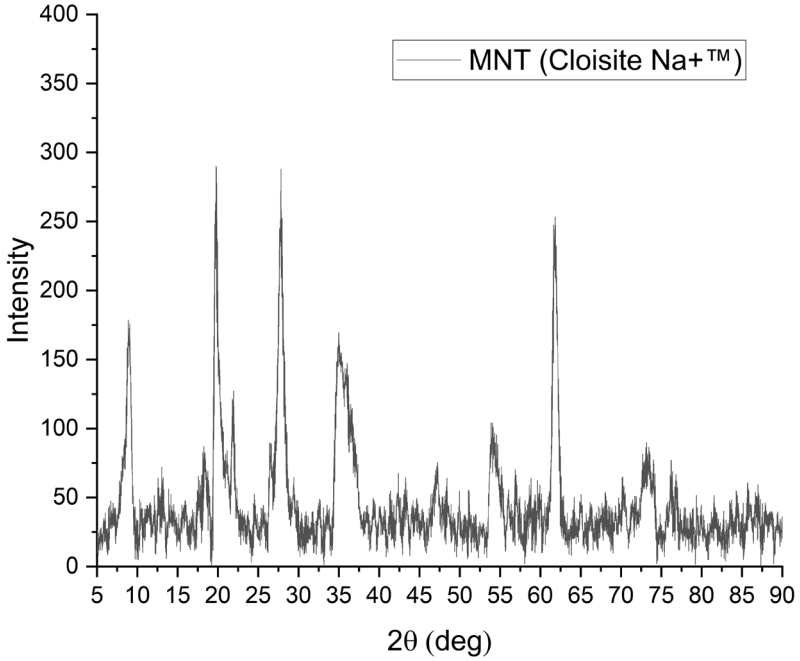

Figure S9. X-ray diffraction pattern of MNT (Cloisite Na+™). The sample was dried at 102 °C for 5 hours prior to the measurement.

References

1. M. Martínez-Sanz, M. J. Gidley and E. P. Gilbert, *Soft Matter*, 2016, **12**, 1534–1549.
2. X. M. Dong, T. Kimura, J.-F. Revol and D. G. Gray, *Langmuir*, 1996, **12**, 2076–2082.
3. T. Abitbol, H. Marway and E. D. Cranston, *Nordic Pulp & Paper Research Journal*, 2014, **29**, 46–57.