Supplementary Information

Grafting polyanhydride polymers to cellulose microfibrils

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Grafting Aqueous PEMAc onto CMC

CNF sheets were impregnated with PEMAc solution, mimicking the approach we developed for small-scale grafting to wood pulp fibers. 1.93 g CNF gel was diluted to 0.1 wt% suspensions and treated with VWR homogenizer at 13500 rpm for 2 min and probe sonicator at 50% duty cycle and 20% output for 10 mins. The suspension was then filtered through a membrane (0.45 µm, hydrophilic PVDF, diameter 35mm) under vacuum. The wet CNF sheets were dried in a room with constant humidity and temperature for 24 h, giving a final basis weight of 60 g/m^2.

The dried CNF sheets were soaked in PEMA solution (12.5 mM and 100 mM RU) from 1 min to 24 h. The wet pick-up ratios (mass of polymer solution/mass of dried sheet) were plotted as a function of soaking time, as shown in **Figure S1 A**. About 12 h were required to saturate the CNF sheets, and the wet-pickup was low, indicating low porosity.

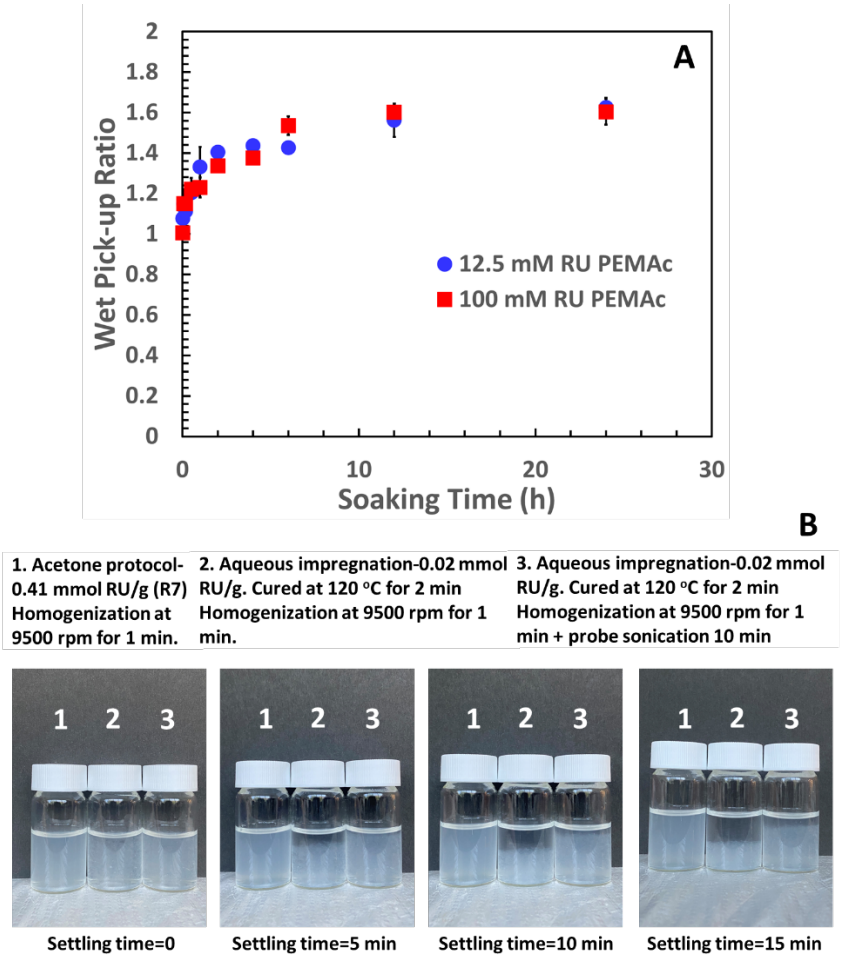


Figure S1 A: Wet pick-up ratio of the CNF sheets after soaking in PEMA solutions (12.5 mM RU and 100 mM RU) for various times. B: Settling images of the redispersed CNF 0.5 g/L in 1 mM $NaHCO_3$ after impregnation and washing.

After soaking for 24 h, the sheets were cured in a speed dryer at 120 ºC for 2 min. The dried sheets were torn into small pieces, added to water (**60** mg CNF/ **100** mL) and homogenized (9500 rpm for 1 min) followed by probe sonication (50% duty cycle and 20% output for 10 mins).

Figure S1 B compares the sedimentation rates of acetone grafting, #1, with aqueous grafting, #2 and #3, PEMA grafted CNF. Sample 1, did not settle over 15 min whereas the aqueous grafted samples did, indicating larger CNF aggregates. .

Polymer Characterization

Conductometric Titration Reproducibility Figure S2

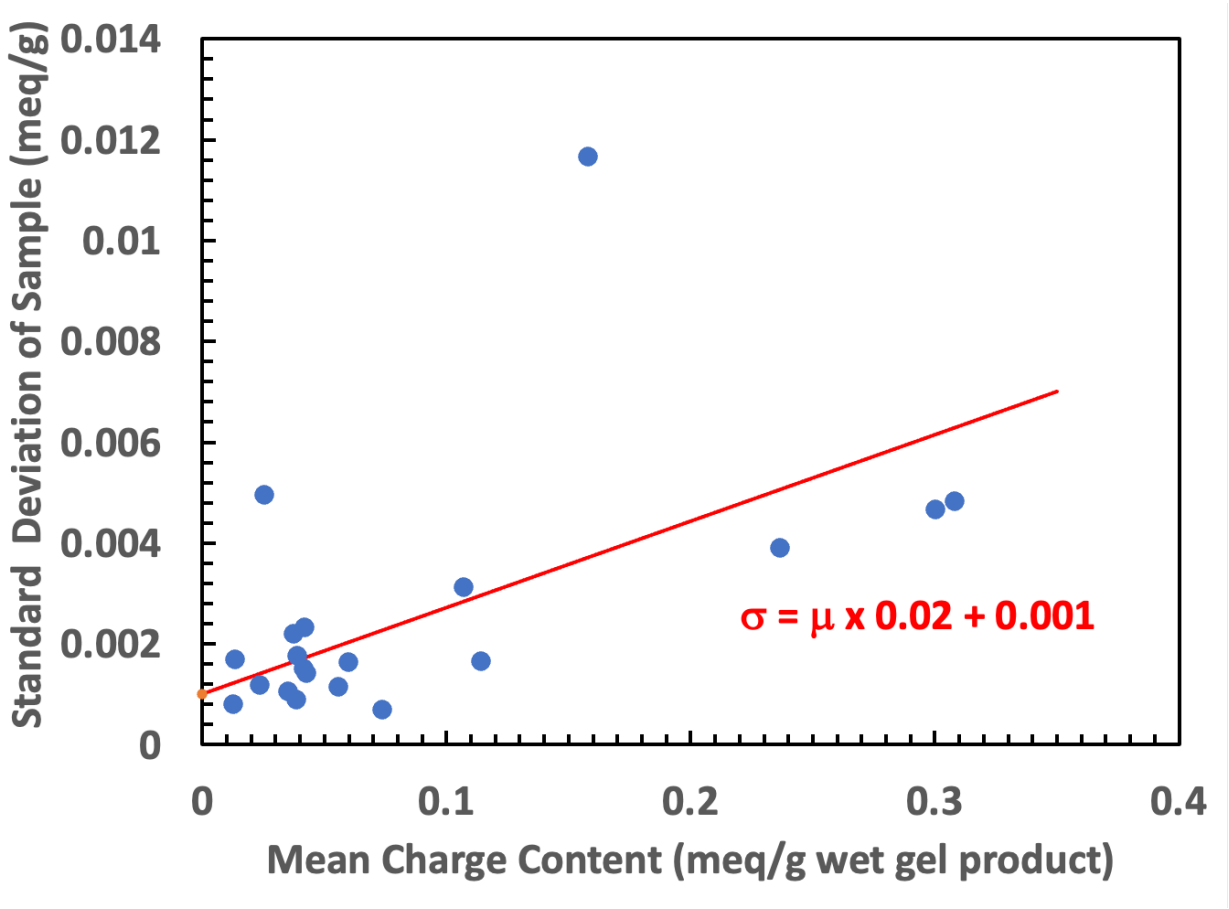


Figure S2 Standard deviations (n =3) for conductometric titrations as functions of the means. The red line corresponds to the standard deviation of 2% of the mean plus a slight offset.

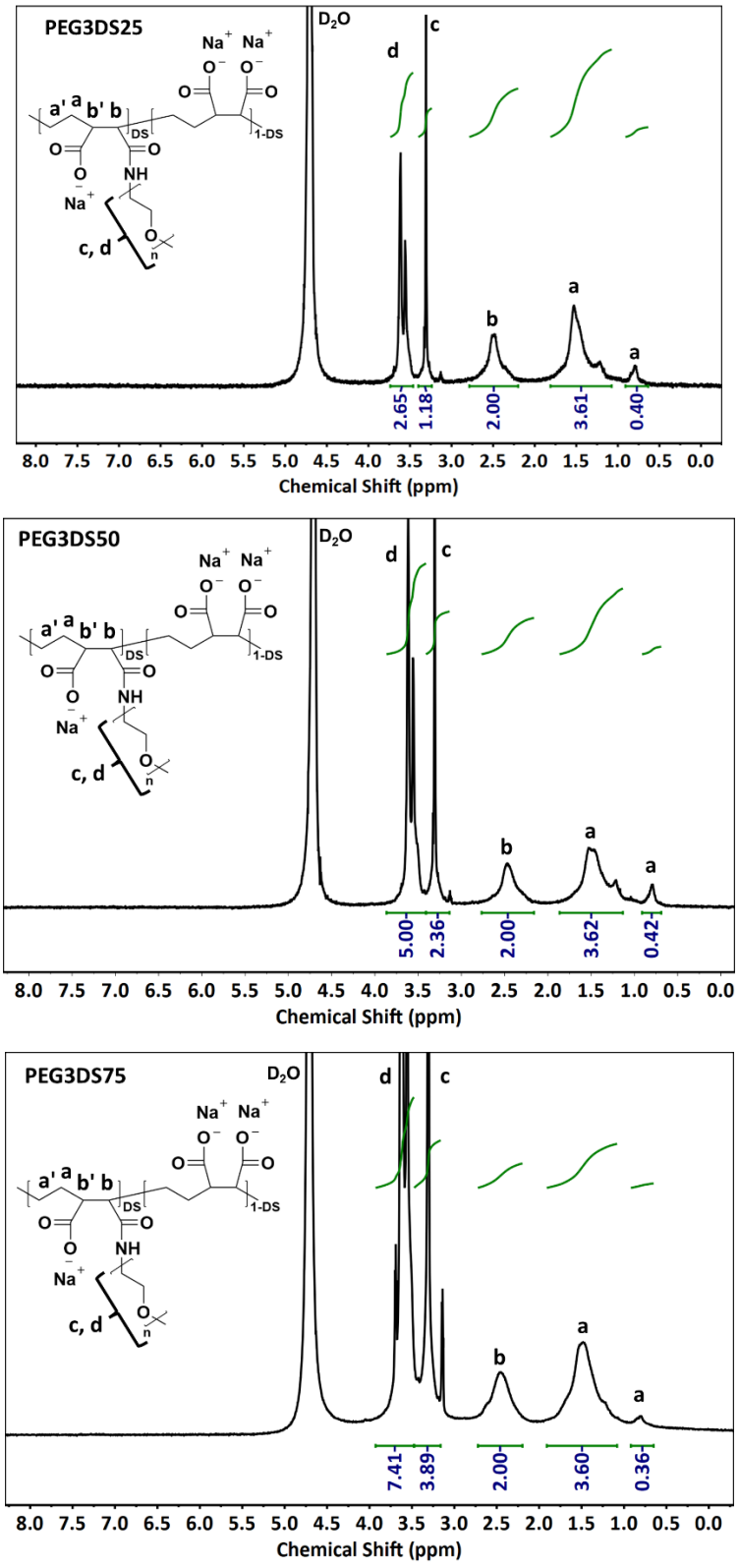
Note that the results in **Figure S2** are titrations divided by wet mass, whereas the CNF charge contents in Table 2 correspond to the charge per mass of dry CNF.

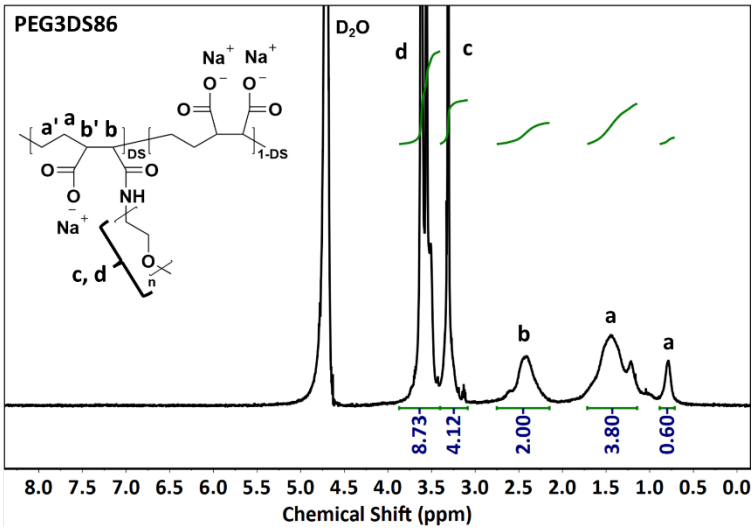
Methoxy PEG Amine Characterization

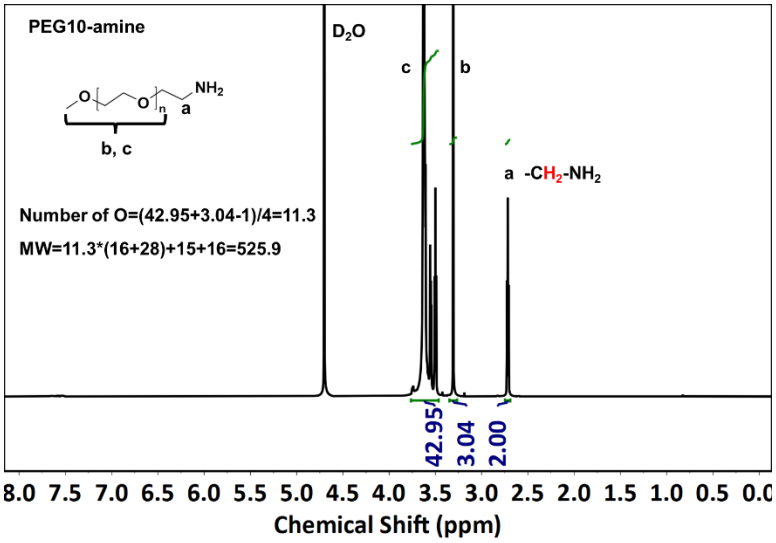
The degrees of polymerization of three commercial PEG amines were determined by NMR.

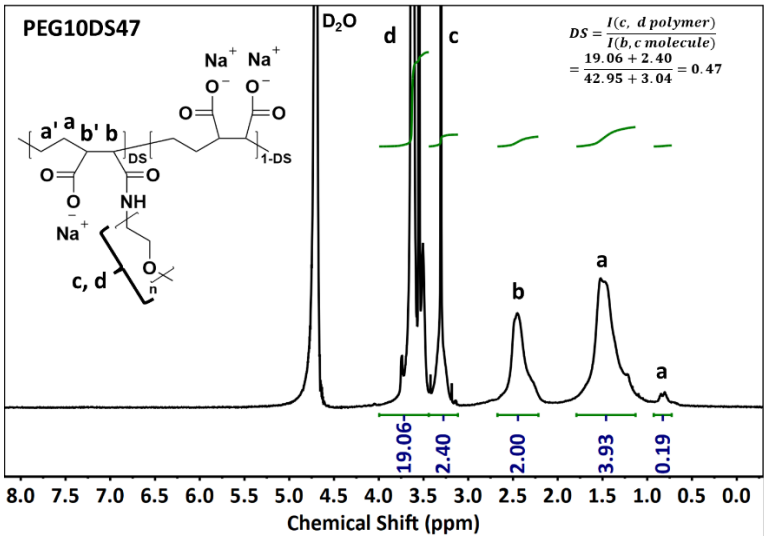
Full Name	Degree of polymerization (DP)	Short Name
2-(2-(2-Methoxyethoxy)ethoxy) ethanamine	3.0	PEG3
Poly(ethylene glycol) methyl ether amine, 500	11.3	PEG10
Methoxypolyethylene glycol propyl amine 1,000	22.1	PEG20

[1]H-NMR of PEMA derivatives




PEG3DS86
D2O
d
c
b
a
a
8.73
4.12
2.00
3.80
0.60
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)


PEG10-amine
D2O
c
b
a -CH2-NH2
b, c
Number of O=(42.95+3.04-1)/4=11.3
MW=11.3*(16+28)+15+16=525.9
42.95
3.04
2.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)


PEG10DS47
D2O
d
c
DS = I(c, d polymer) / I(b,c molecule) = (19.06 + 2.40) / (42.95 + 3.04) = 0.47
b
a
a
19.06
2.40
2.00
3.93
0.19
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

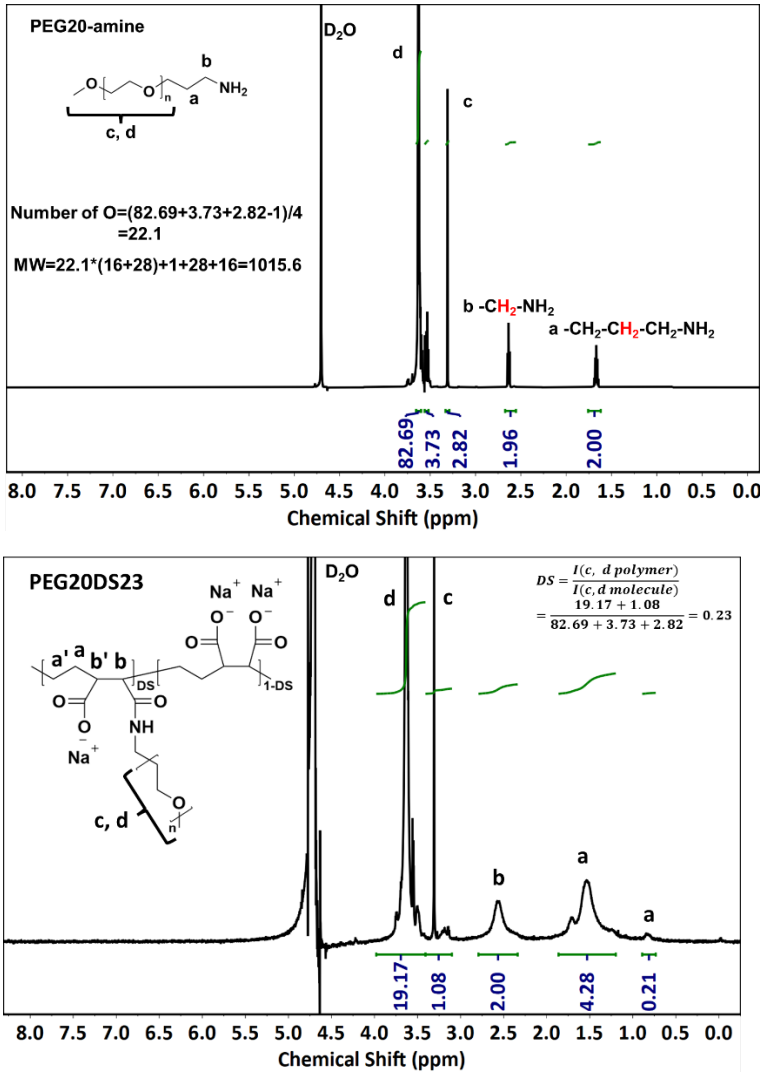


Figure S3 ^{1}H-NMR spectra of PEMAc-PEG derivatives

Dispersing and Characterizing Unmodified CNF

The CNF wet dispersion, obtained from the University of Maine, was a defibrillated Brazilian bleached eucalyptus kraft pulp. The supplier specifications included "nominal fiber width of 50 nm and length of several hundred microns" and a specific surface area of 31-33 m^2/g. **Figure S4** summarizes various measurements starting with 0.02 g/L, never-dried CNF dispersed in 1 mM $NaHCO_3$ and dispersed with a homogenizer followed by probe sonication. **Figure S4A** is an optical micrograph of dried CNF on APTES-treated glass. Individualized microfibrils are invisible at this magnification.

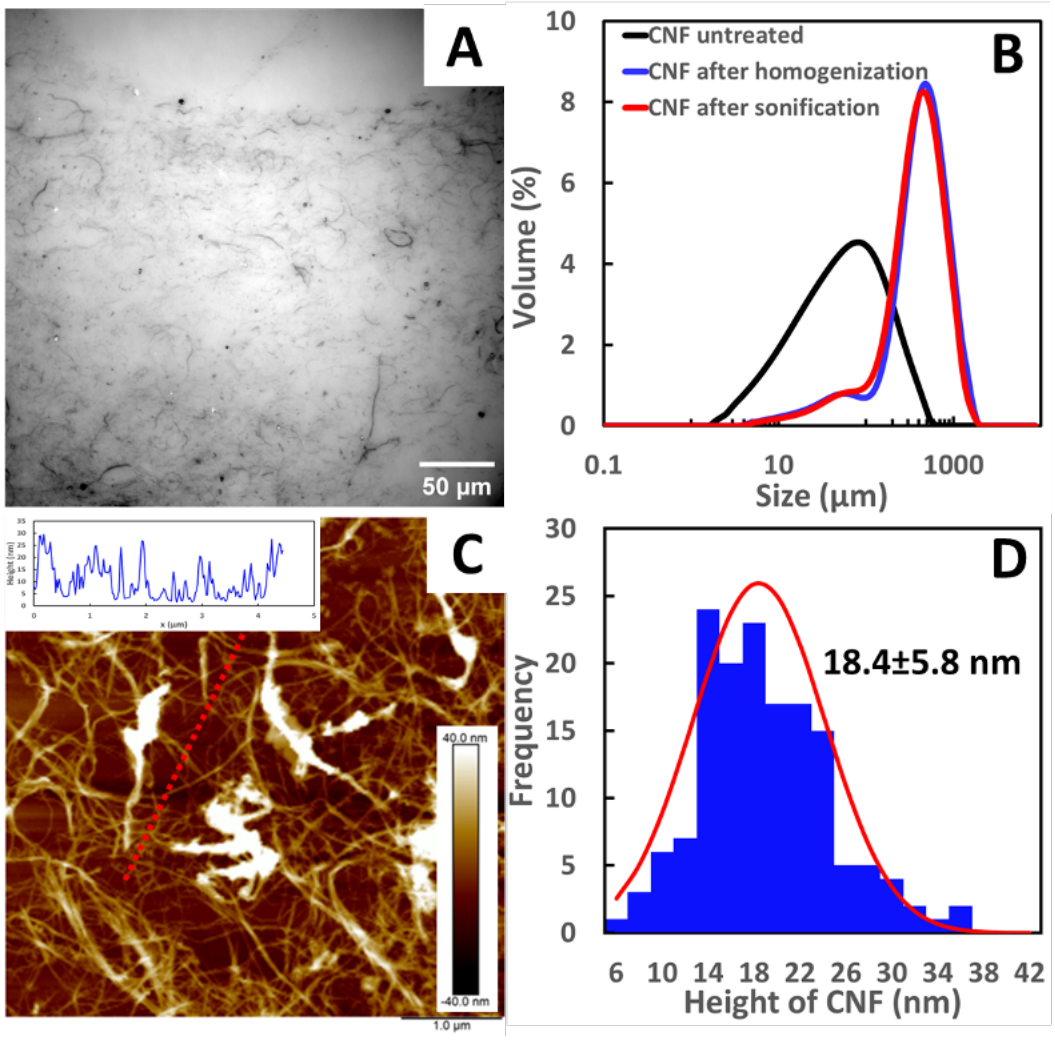


Figure S4 Properties of unmodified CNF before solvent exchange. Optical (A) and AFM (C) images of CNF settled onto glass surfaces treated with APTES. Samples were dried from 0.02 g/L suspension treated with homogenization and probe sonication. B: Diameter of untreated CNF, CNF after homogenization, and ultrasonication. D: Microfibril bundle height distribution from 200 measurements along the dashed line in image C.

A Mastersizer was used to characterize the CNF dispersions (Peng et al. 2016) (Amini et al. 2020; Tayeb et al. 2020). **Figure S4B** shows the influence of dispersion on the particle size distribution. The "CNF Untreated" was gently dispersed with a magnetic stirrer, giving a broad distribution with a maximum of ~ 100 µm. Note that the individualized dispersed microfibrils are too dilute to be measured. **Figure S5** shows Mastersizer results for CNF supernatants after centrifugation. However, the data quality was poor, reflecting the limited light scattering from fully dispersed microfibrils. Sizes increased by nearly an order of magnitude after homogenization or probe sonication techniques compared to the mildly dispersed untreated CNF - **Figure S4**B.

Microfibril Mastersizer Distributions

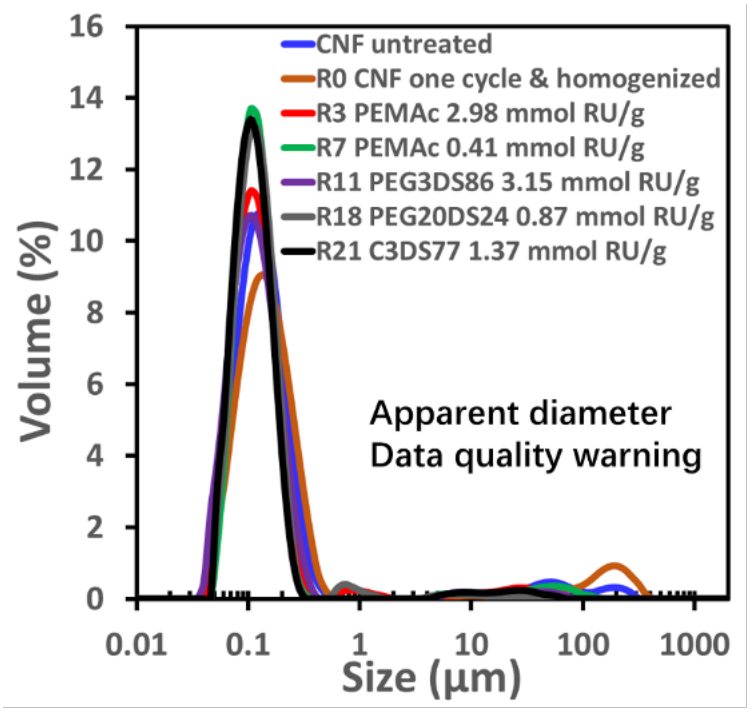


Figure S5 Apparent diameter of microfibrils in the supernatant after nano-fraction measurements. In all cases, the instrument warned of poor data quality.

AFM Images of Unmodified CNF after Solvent Exchange - Figure S6

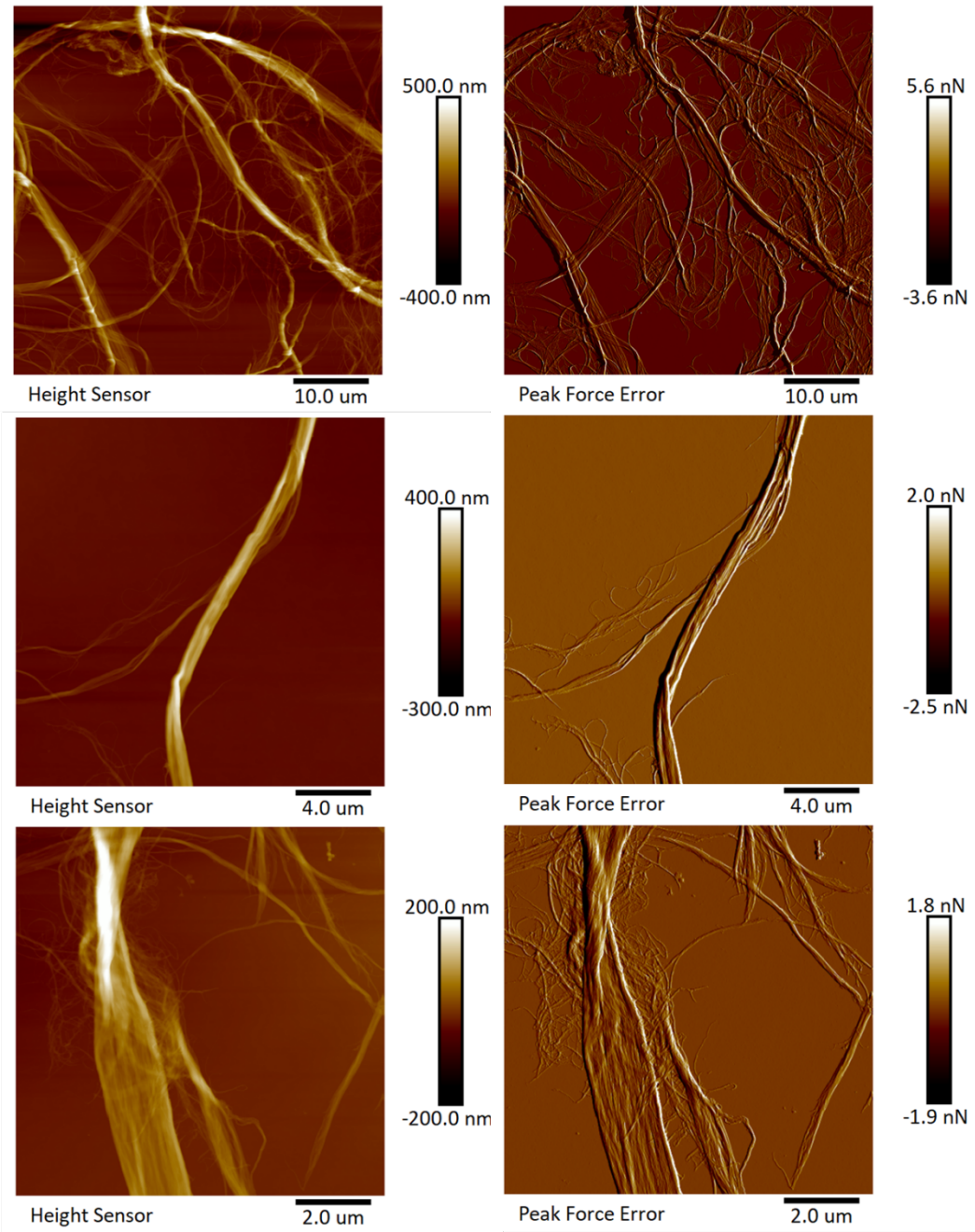


Figure S6 AFM images were taken from CNF aggregates after one solvent exchange cycle (water-acetone-water). The CNF was stirred in acetone for 24 h before rehydration.

Influence of PEG Chain Length – Micrographs -Figure S7

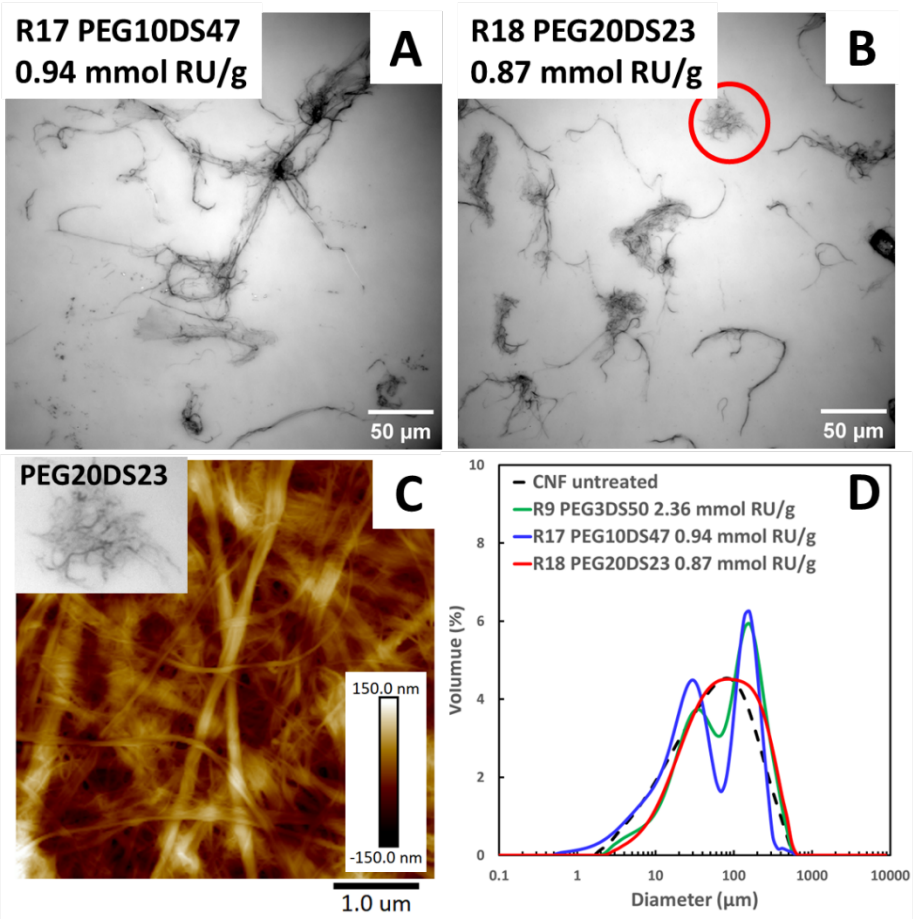


Figure S7 Optical images showing grafted CNF with PEG10DS47 (A) content of 0.94 mmol RU/g and PEG20DS24 (B) content of 0.87 mmol RU/g. (C) AFM height image of area selected from PEG20DS24 sample. (D) Size distribution of CNF samples grafted with PEMAc-PEG derivatives with different PEG chain lengths. The black dashed line represents CNF without homogenization and polymer grafting.

FTIR of Grafted CNF - Figure S8

Modified CNF gel was redispersed in 0.1 N NaOH solution, filtered through a membrane (hydrophilic PVDF, Durapore®, 0.45 µm), and dried at room temperature overnight. The dried CNF sheets were characterized by FTIR spectroscopy (Nicolet 6700, Thermo Fisher Scientific) under attenuated total reflection (ATR) model.

The FTIR spectra did not confirm the presence of ester bonds in **Figure S8**. The carboxyl groups were converted into the sodium salt form using 0.1 N NaOH to differentiate the peak corresponding to the ester bond. In this case, the peaks for the carboxylate groups shifted to 1560 cm^{-1}. Additionally, the amide bonds display a peak between 1600-1700 cm^{-1}. Therefore, we would expect to observe an ester peak at 1717 cm^{-1}.

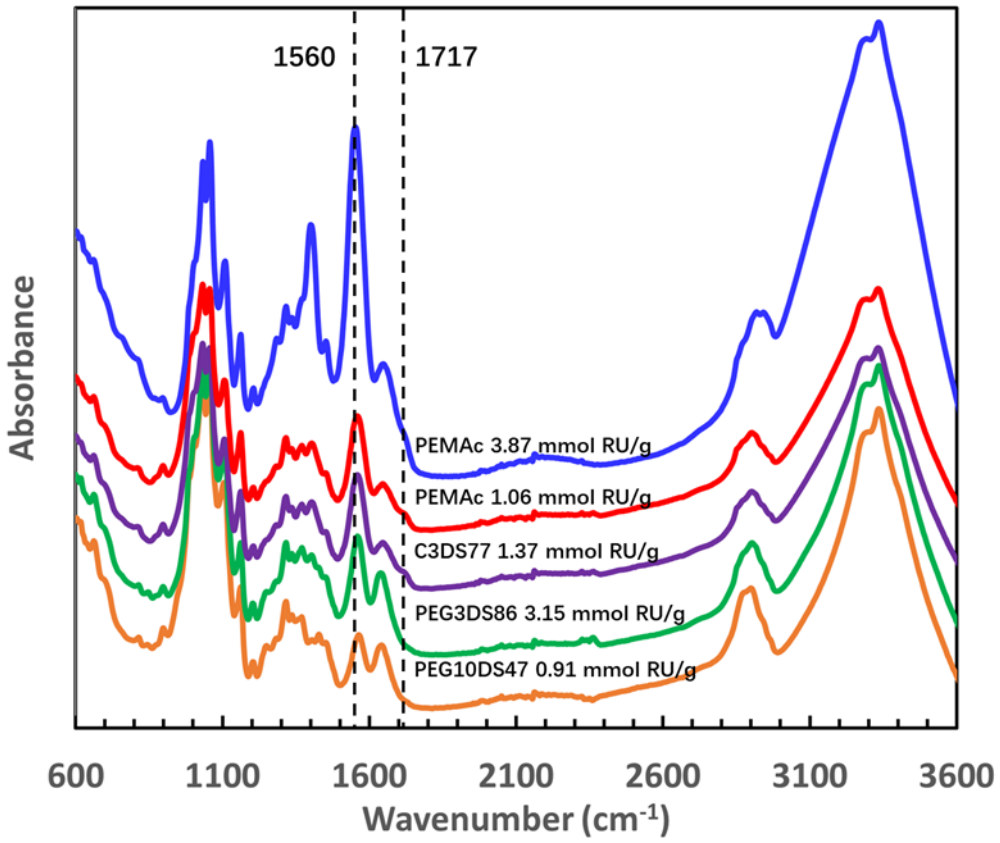


Figure S8 FTIR spectra of grafted CNF

AFM Images of PEG3DS86 - Figure S9

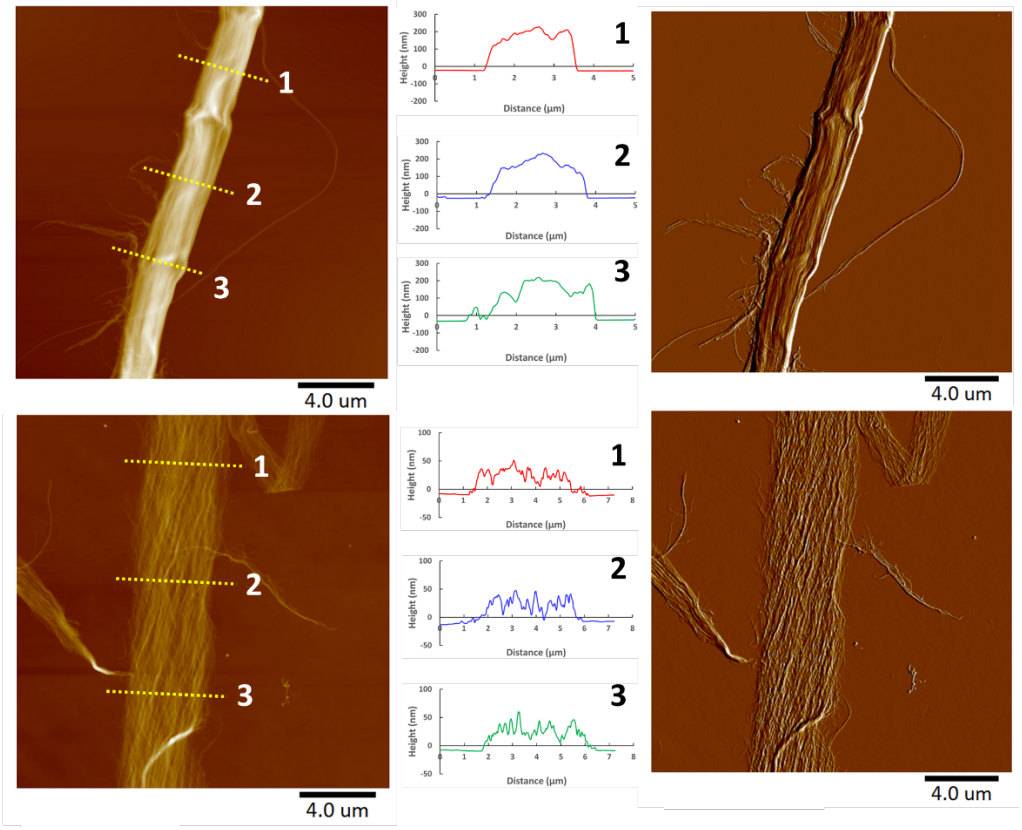


Figure S9 AFM images showing the thickest and thinnest ribbons obtained from 20 randomly selected ribbons with a PEG3DS86 content of 3.15 mmol RU/g.

Native ribbons are shown in Figure S6. They are also a mixture of "packed" and "defibrillated" structures. The different morphology depends on the thickness of the ribbon. If the ribbon is thin they all look like "defibrillated" or "open-up" for both PEMA and PEG3 modified.

References

Amini E, Hafez I, Tajvidi M, Bousfield DW (2020) Cellulose and lignocellulose nanofibril suspensions and films: A comparison. Carbohydr. Polym. 250:117011. https://doi.org/10.1016/j.carbpol.2020.117011

Peng Y, Gallegos SA, Gardner DJ, Han Y, Cai Z (2016) Maleic anhydride polypropylene modified cellulose nanofibril polypropylene nanocomposites with enhanced impact strength. Polymer Composites 37:782-793. https://doi.org/10.1002/pc.23235

Tayeb A, Tajvidi M, Bousfield D (2020) Paper-based oil barrier packaging using lignin-containing cellulose nanofibrils. Molecules 25:Molecules 2020, 2025, 1344; doi:2010.3390/molecules25061344. https://doi.org/10.3390/molecules25061344

Example Calculation for Row 11 in Table 2

Example calculation for Row 11 in Table 2 PEG3DS86

Input Data

$m_{pema} := 0.4\ gm$ The mass of PEMA used to prepare PEG3DS86

$DS := 0.86$ The fraction of anhydrides consumed by amide formation

$m_{cnfl} := 0.2\ gm$ The dry mass of CNF dose used in the derivatization

$ssa := 32\ \frac{m^2}{gm}$ Assumed CNF specific surface area

$RUamw := 294.0281\ Da$ Average RU mw of PEG3DS86, sodium salt, Table 1 and MC131

$PEMAmw := 126.0954\ Da$ PEMA RU mw, MC131

Grafted Product Properties

$gelm := 14.29\ gm$ Mass of recovered wet product

$gelsc := 2.25\ \frac{gm}{100\ gm} = 0.0225$ Corresponding solids content

$MT := gelm \cdot gelsc = 321.525\ mg$ Total mass of dry product

Conductometric Titration

$CNFc := 0.06\ \frac{meq}{gm}$ Charge content of unmodified CNF, meq/g dry CNF

$Tit := 0.042651\ \frac{meq}{gm}$ Mean meq/ wet gel mass obtained from titration

$ET := Tit \cdot gelm = 0.6095\ meq$ Total charge of recovered product

$\sigma := \frac{ET}{MT} = 1.8956\ \frac{mmol}{gm}$ Total charge/mass dry product

Pema grafting

$dose := \frac{m_{pema}}{PEMAmw} = 3.1722\ mmol$ Number of RU added

$m_{dpoly} := dose \cdot RUamw = 0.9327\ gm$ Mass of hydrolyzed grafting polymer dosed in grafting suspension

Polymer Content of the product

$Mp := \frac{(CNFc \cdot MT - ET) \cdot RUamw}{CNFc \cdot RUamw + (DS - 2)} = 0.1546\ gm$ **Equation 7 derived in appendix**

$Mcnf := MT - Mp = 0.1669\ gm$ Mass of Cellulose in final product

Entries for Table 2 Row 11

$m_{cnfI} = 0.2\ gm$ CNF dose

$m_{dpoly} = 0.9327\ gm$ Polymer dose, g

$RUg := \frac{Mp}{RUamw \cdot Mcnf} = 3.1505\ \frac{mol}{kg}$ Product RU polymer /g recovered CNF
This is RU in Table 2

$MF := \frac{Mp}{Mp + Mcnf} = 0.4809$ Mass fraction of polymer in product

$\Gamma m := \frac{Mp}{ssa \cdot Mcnf} = 28.9479\ \frac{mg}{m^2}$ Coverage of polymer

$\sigma = 1.8956\ \frac{mmol}{gm}$ Titratable Charge

$Yg := \frac{Mp}{m_{dpoly}} = 0.1658$ Yield of grafted polymer

$Ycel := \frac{Mcnf}{m_{cnfI}} = 0.8346$ Yield of carbohydrate in product

Appendix - deriving Eq7 that give the mass of polymer in the recovered product

$MT = 0.3215\ gm$ Total mass of dry product

$Mp = 0.1546\ gm$ Total mass of polymer in dry product

$Mcnf = 0.1669\ gm$ Total mass cnf in dry product

$ET = 0.6095\ meq$ Total titratable charge in final product

$CNFc = 0.06\ \frac{meq}{gm}$ The charge content of unmodified cnf

$Ecnf := CNFc \cdot Mcnf = 0.01\ meq$ Total CNF charge in the final product

$Ep := ET - Ecnf = 0.5995\ meq$ Total polymer charge in final product

$DS = 0.86$ Fraction of amide RU groups in polymer

Deriving Equation 7

1 $MT = Mp + Mcnf$ Mass balance final dry product

2 $ET = Ep + Ecnf$ Charge balance final dry product

3 $Ecnf = CNFc \cdot Mcnf$ Contribution of unmodifed cnf to ET

4 $Ep = \frac{Mp}{RUamw}(2 - ds)$ Contribution of added polymer to final total charge

Sub 3 and 4 into 2 gives

5 $ET = \frac{Mp}{RUamw}(2 - ds) + CNFc \cdot Mcnf$

Rearranging 1 and substituting for Mcnf in 5 gives

$\mathbf{clear.sym}(ET, Mp, RUamw, CNFc, MT, DS)$ solving for MP

6 $ET = \frac{Mp}{RUamw}(2 - DS) + CNFc \cdot (MT - Mp) \xrightarrow{solve, Mp} \frac{(CNFc \cdot MT - ET) \cdot RUamw}{CNFc \cdot RUamw + (DS - 2)}$

7 $Mp = \frac{(CNFc \cdot MT - ET) \cdot RUamw}{CNFc \cdot RUamw + (DS - 2)}$ 7 expresses the solution in 6,

$\frac{(CNFc \cdot MT - ET) \cdot RUamw}{DS + (CNFc \cdot RUamw - 2)} = 0.1546\ gm$ Applying the numerical values