Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information for

Supramolecular Double Networks of Cellulose Nanofibrils and Algal Polysaccharides with Excellent Wet Mechanical Properties

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Measuring the fibril dimensions

The dimensions of the fibrils were determined with atomic force microscopy (AFM) by adsorbing cellulose nanofibrils (CNF) for 1 min from a 0.001 wt% dispersion onto plasma-treated silicon wafers (boron-doped, p-type, 610-640 µm) already covered with a polyvinyl amine anchoring-layer (Lupamin 9095, BASF) adsorbed from a 0.1 g/L solution at pH 7.5 for 2 minutes. Images, 1x1 µm in size, were acquired at random positions on the wafer using a MultiMode 8 AFM (Bruker, Santa Barbara, CA, USA) in the ScanAsyst mode.

Determining the G/M ratio of alginate

The G and M ratio of the alginate was estimated by a method described by Grasdalen et al. in 1979[1] where the ^{1}H-NMR spectra was used to compare three different chemical shifts corresponding to G, M and GG. The alginate was hydrolyzed at pH 3 and 100 °C for 1 h, neutralized, and dried at room temperature. The alginate hydrolysate was dissolved in deuterated water to a dry content of 2 wt% for the ^{1}H-NMR analysis at 500 MHz on a DMX-500 NMR spectrometer (Bruker).

Carrageenan composition

The carrageenan compositions was determined using ^{1}H-NMR at ambient temperature and a concentration of 0.2 wt% where κ-carrageenan has a signature shift at 5.01 ppm and ι-carrageenan has a signature shift at 5.20 ppm (Fig. S2).[2] The ι-carrageenan sample also had a peak at 5.32 which might be λ-carrageenan or contamination from floridean starch.[3] Sharp NMR-shifts indicating oligomer or monomer fractions were also observed but these could be removed by dialysis.

Determining the molecular weight of alginate and carrageenan

The molecular weights of the alginate and carrageenan were characterized by size exclusion chromatography in a Dionex Ultimate-3000 HPLC system (Dionex, Sunnyvale, CA, USA) with a series of three PSS suprema columns in the pore size configuration 30 Å, 1000 Å, and 1000Å, maintained at 40 °C with a mobile phase of 10 mM NaOH (1 ml/min). The relative molecular weight was determined using pullulan standards in the range of 342 to 708,000 Da (PSS, Germany).

SEM Characterization

Characterizing the cross-section of a nanopaper was performed using FE-SEM imaging performed on a Hitachi S-4800 at 1.0 kV. The samples were mounted on a metal stub with carbon tape and coated with a 5 nm layer of Pt/Pd with a Cressington 208HR sputter coater.

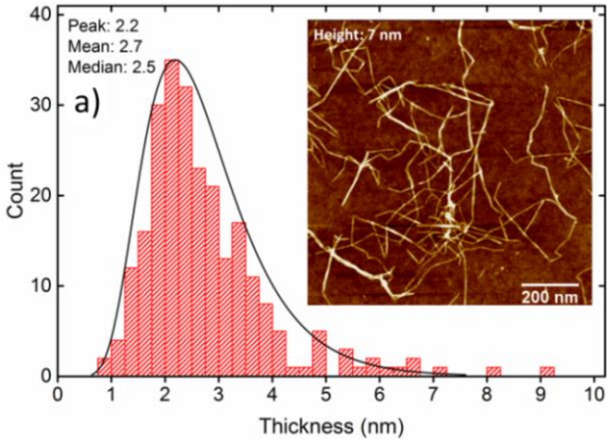

Fig. S1 Distribution histogram and a log-norm fit of the CNF thickness. The inset shows an example of an AFM image used to measure the thickness.

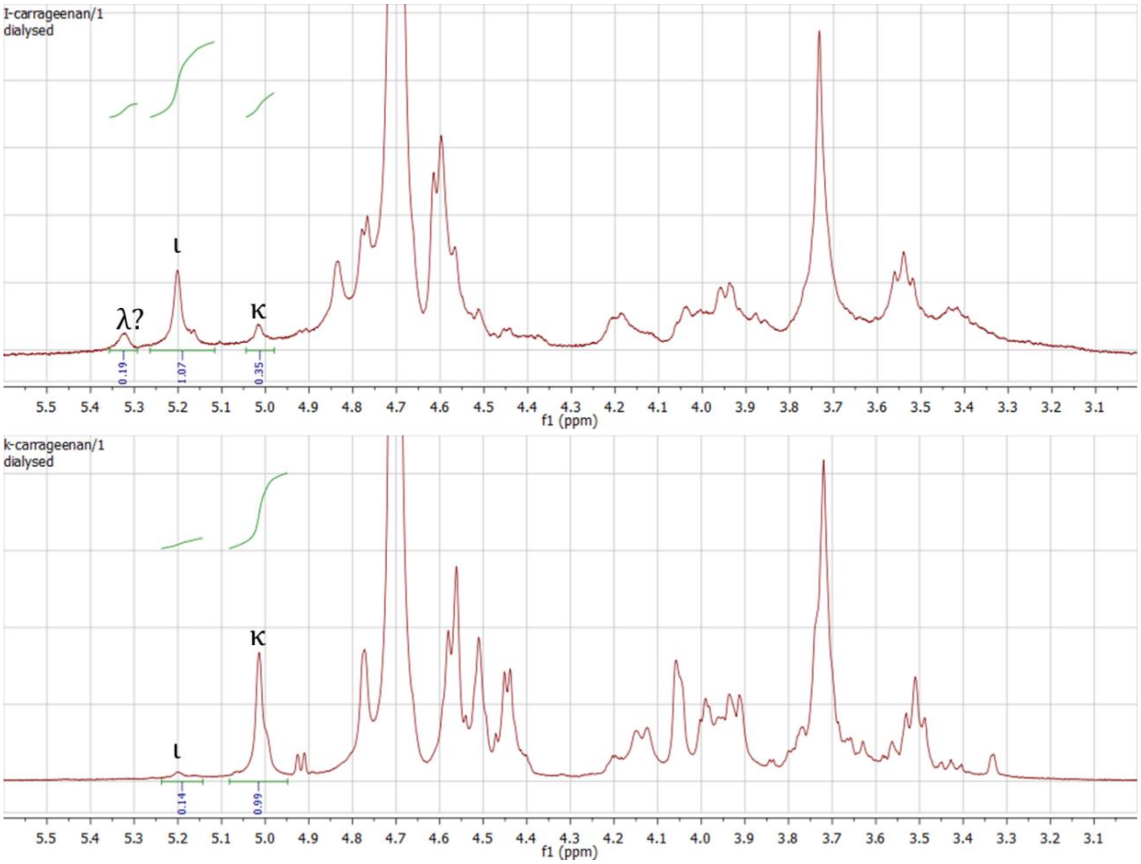

Fig. S2 NMR spectra of dialyzed ι-carrageenan and κ-carrageenan at a concentration of 0.2 wt% and 350 scans. The peaks corresponding to the type of carrageenan are marked with the associated Greek letters.

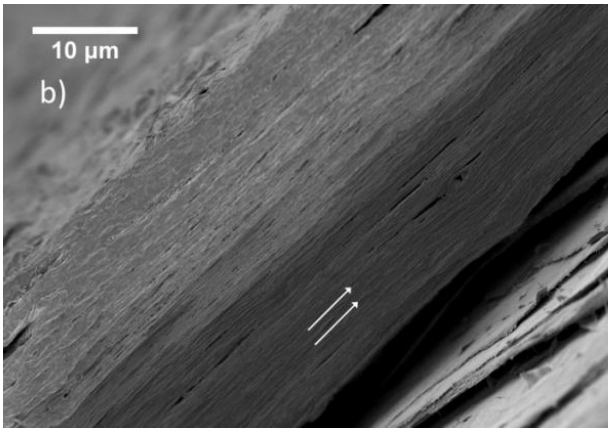

Fig. S3 FE-SEM image of the cross-section after a cryo-fracture, showing the laminar structure of a nanopaper with the arrows indicating the plane direction. The bottom right corner shows delaminated layers produced during the sample preparation.

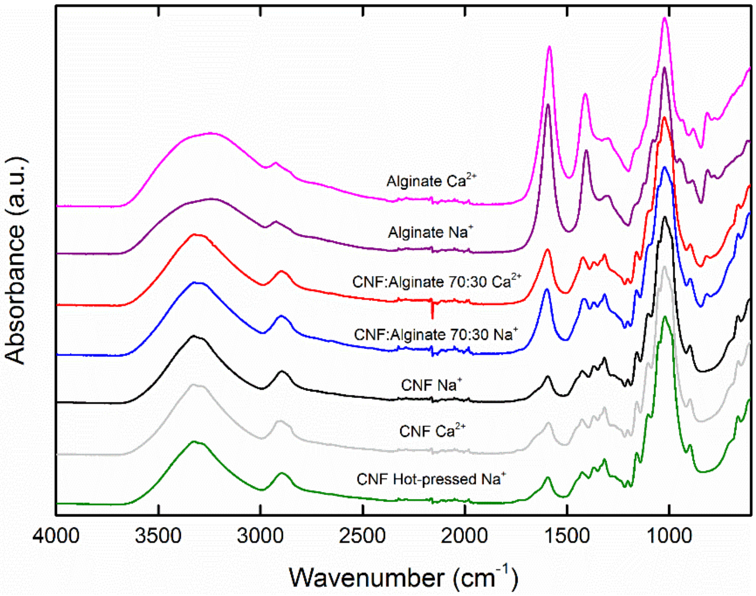

Fig. S4 Normalized FTIR spectra of the CNF, alginate, and composite samples in the sodium or calcium states.

References

1. H. Grasdalen, B. Larsen and O. Smidsrød, *Carbohydr. Res.*, 1979, **68**, 23-31.
2. E. Tojo and J. Prado, *Carbohydr. Polym.*, 2003, **53**, 325-329.
3. F. van de Velde and H. S. Rollema, in *Modern Magnetic Resonance*, ed. G. A. Webb, Springer Netherlands, Dordrecht, 2006, DOI: 10.1007/1-4020-3910-7_178, pp. 1605-1610.