Supplementary Information

Unravelling cationic cellulose nanofibril hydrogel structure: NMR spectroscopy and small angle neutron scattering analyses

James C. Courtenay, Susana M. Ramalhete, William J. Skuze, Rhea Soni, Yaroslav Z. Khimyak, Karen J. Edler, and Janet L. Scott

Characterisation of modified cellulose:

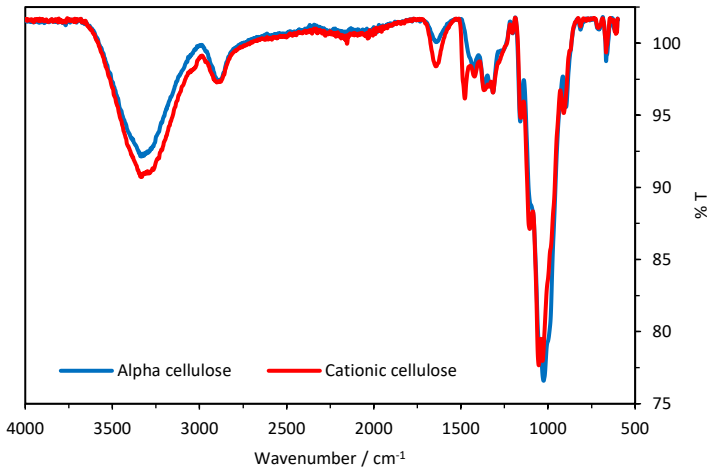

Fig. S1 FTIR spectra for unmodified α-celluloseand CCNF (DS = 23.0 ±0.9 %) powders were obtained on a Perkin Elmer Spectrum 100 with a universal ATR sampling accessory; 10 scans were acquired in the range 4000 – 600 cm^{-1}. FTIR: prominent bands at 1440 cm^{-1} and 1483 cm^{-1} were attributed to the CH_2 bending mode and methyl groups of the cationic cellulose substituents in accordance with data published by Zaman *et al*.[1].

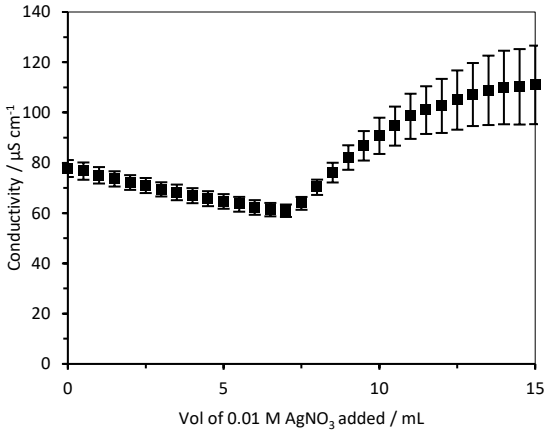

Fig. S2 Conductivity curve for CCNF in DI H_2O titrated with ca ~ 1 m*M* $AgNO_3$ at 0.50 mL intervals.

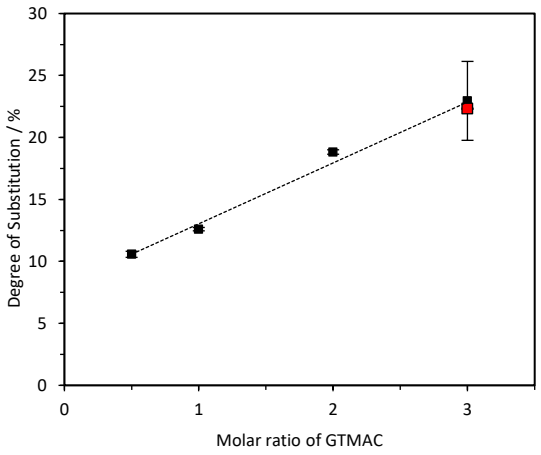

Fig. S3 a) DS of CCNF determined using a Mütek Particle Charge Detector (black points) and by conductometric titration (red point). The average of three values was reported with the standard error shown as error bars.

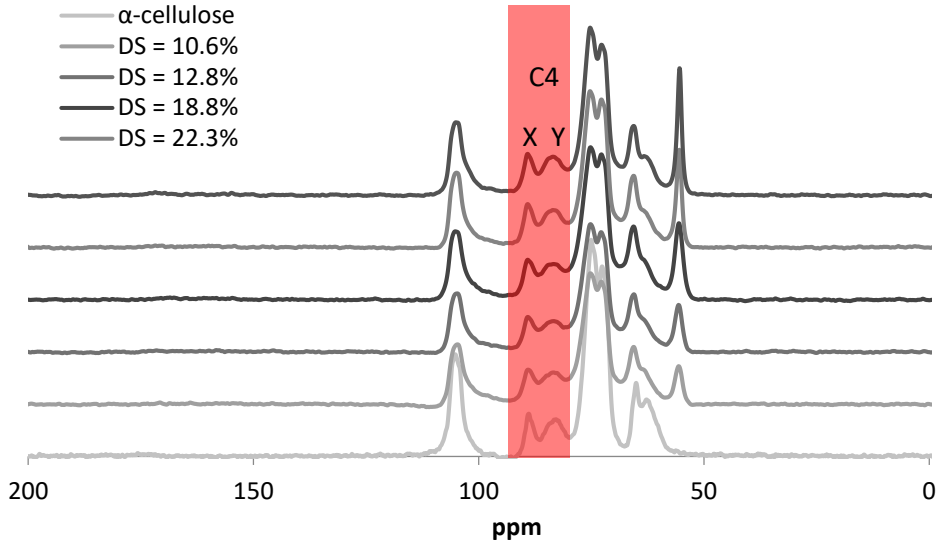

Fig. S4 Summary of ^{1}H-^{13}C CP/MAS NMR spectra for α-cellulose and CCNF (DS 10.6 - 23.0%) powders, acquired using MAS rates of 10 kHz. The signal at 55.5 ppm is assigned to the methyl carbon resonances of the quaternary ammonium group and used to determine DS. The crystallinity index was determined by separating the C4 region of the spectrum into crystalline and amorphous peaks, and calculated by dividing the area of the crystalline peak (87 – 93 ppm) by the total integrated area of the C4 peaks (80 to 93 ppm)

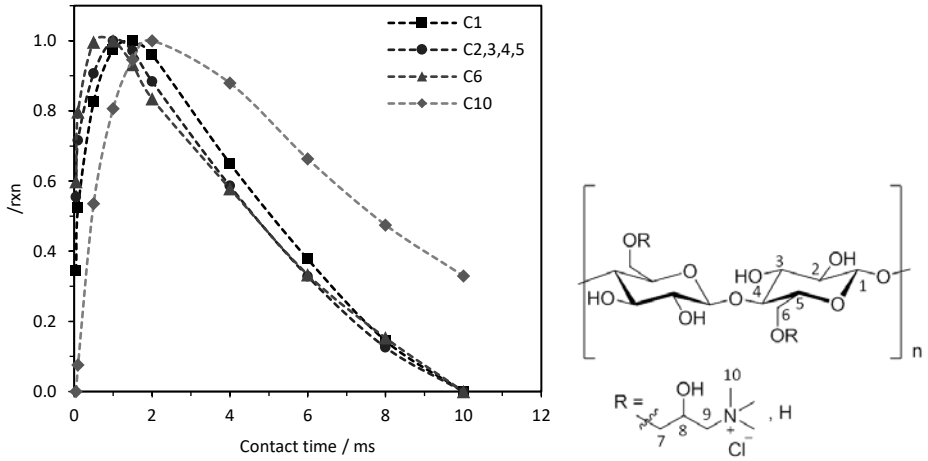

Fig. S5 ^{1}H-^{13}C Cross-polarisation kinetics curves for carbon peaks in CCNF powder (DS = 23.0 %). The experimental error associated with the measurement of peak intensities is below 10 %.

Small angle Neutron scattering:

Table S1: SANS fitting parameters for a flexible cylinder with elliptical cross-section model. The length was held at 1000 Å, sldCyl 1.75 x 10^{-6} and sldSolv: D_2O = 6.34 x 10^{-6}, H_2O = −5.61 x 10^{-7}.

Parameter	Description	Units
Scale	Volume Fraction	None
Background	Source background	cm^{-1}
Lengh	Length of the flexible cylinder	Å
Kuhn_length	Kuhn length of the flexible cylinder	Å
radius	Radius of the flexible cylinder	Å
Axis_ratio	Axis_ratio (major_radius/minor_radius	None
Sld	Cylinder scattering length density	10^{-6}Å
Sld_Solvent	Solvent scattering length density	10^{-6}Å

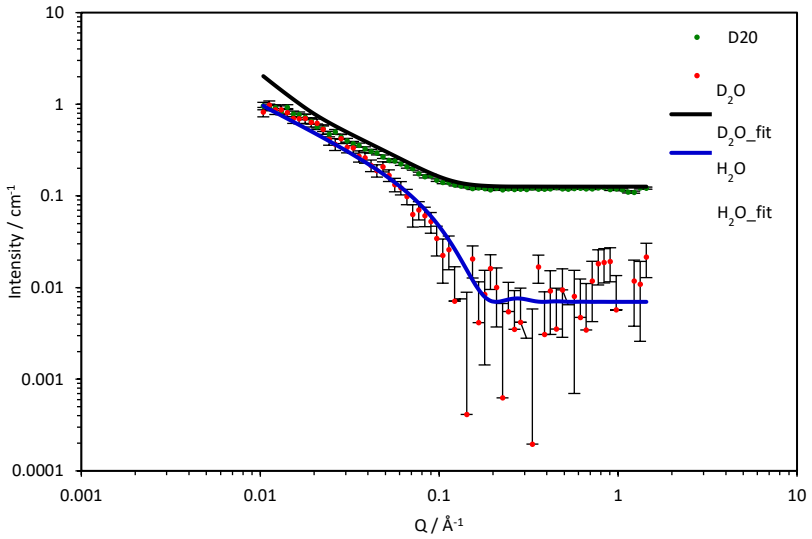

Fig. S6 Experimental SANS spectra of CCNF hydrogels (10.6 % DS) simultainiously fitted to a flexible ellipsoidal cylinder model (scattered points are data and solid lines are the fitted curves) in D_2O or H_2O.

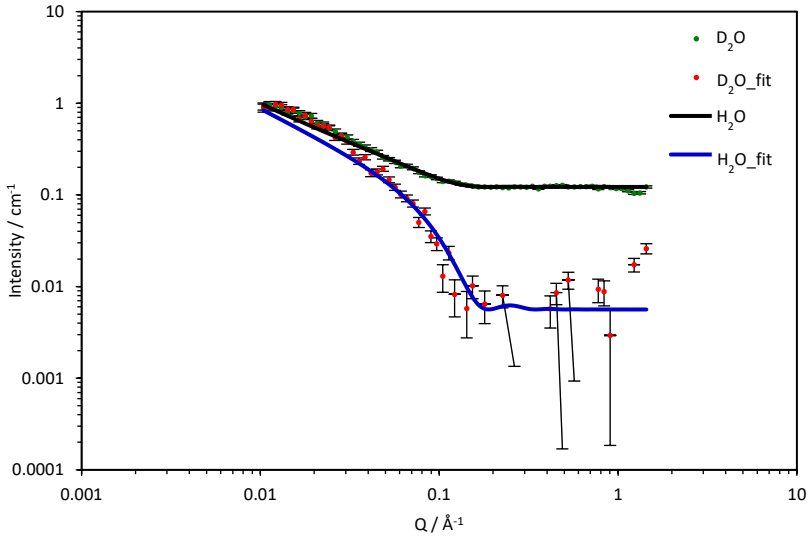

Fig. S7 Experimental SANS spectra of CCNF hydrogels (12.6 % DS) simultaneously fitted to a flexible ellipsoidal cylinder model (scattered points are data and solid lines are the fitted curves) in D_2O or H_2O.

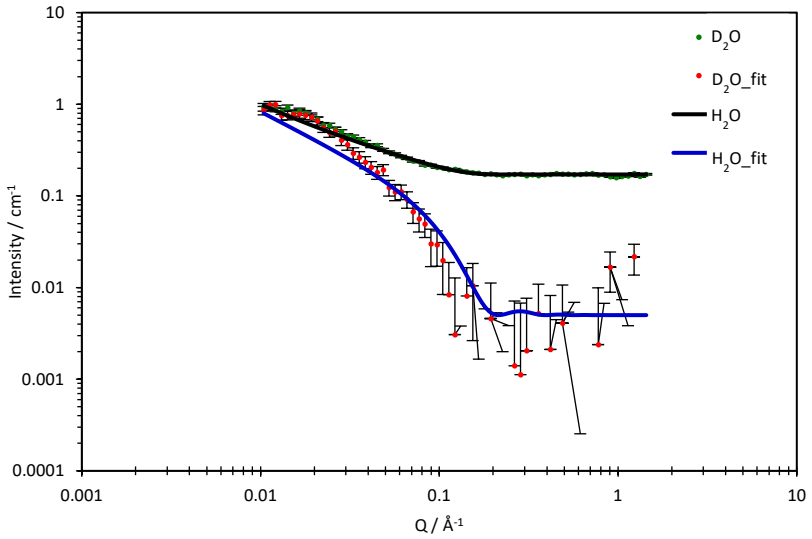

Fig. S8 Experimental SANS spectra of CCNF hydrogels (18.8 % DS) simultaneously fitted to a flexible ellipsoidal cylinder model (scattered points are data and solid lines are the fitted curves) in D_2O or H_2O.

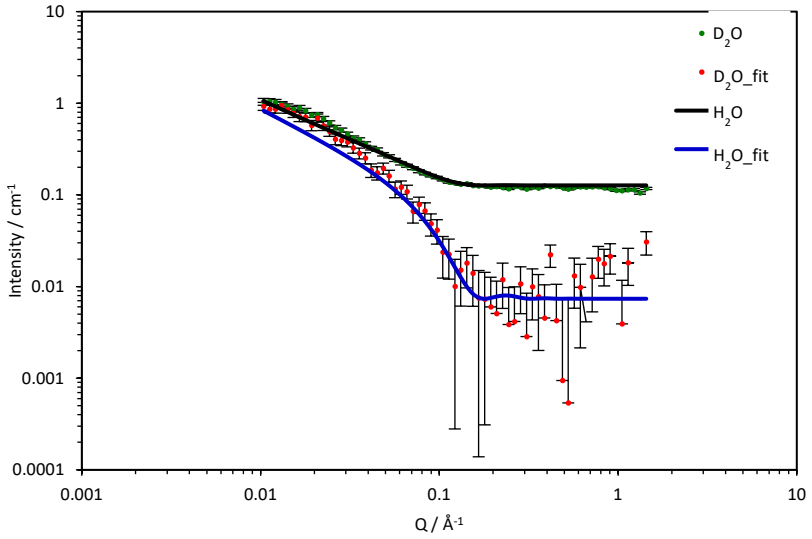

Fig. S9 Experimental SANS spectra of CCNF hydrogels (23.0 % DS) simultaneously fitted to a flexible ellipsoidal cylinder model (scattered points are data and solid lines are the fitted curves) in D_2O or H_2O.

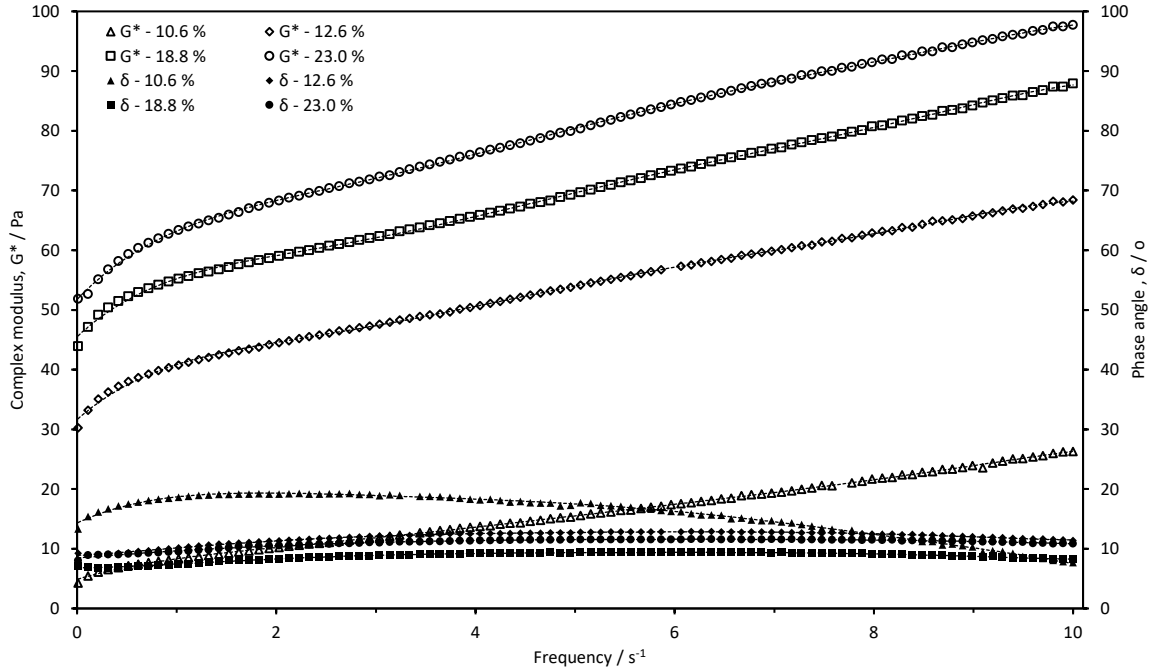

Fig. S10 Complex modulus (*G**) and phase angle (δ) *versus* frequency for 2 wt.% CCNF hydrogels with DS of 10.6, 12.6, 18.0 and 23.0 %. Values obtained at a frequency of 1.02 Hz. As the DS increased the complex modulus increased and the phase angle decreased, this is associated with increased elasticities.

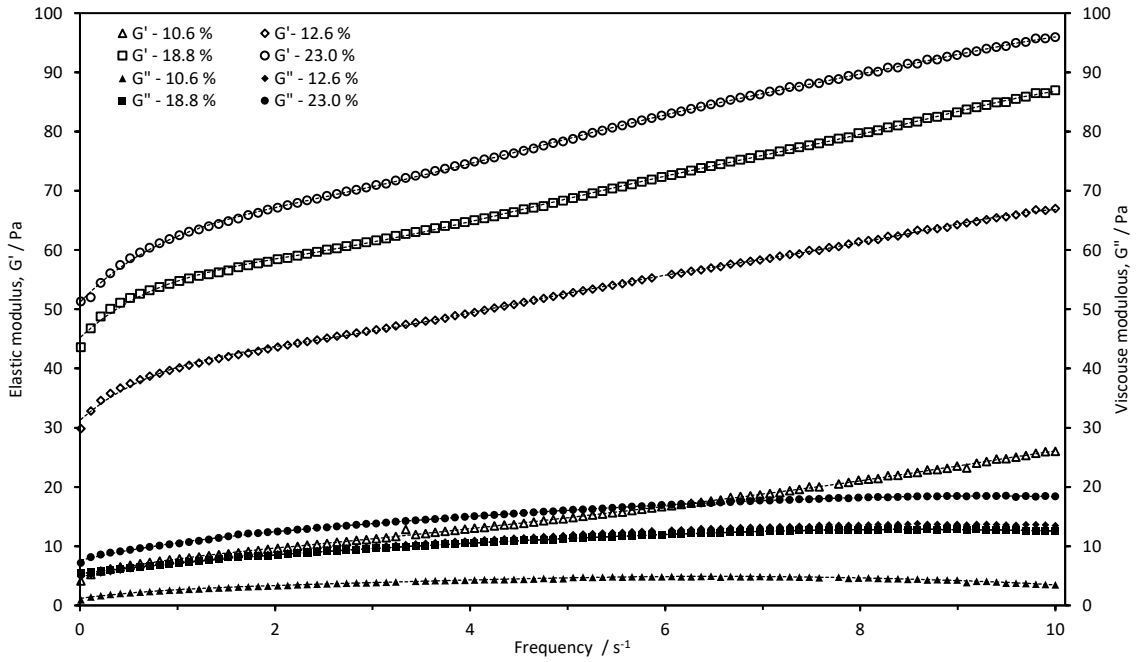

Fig. S11 Elastic (G') and viscous (G") modulus versus frequency for 2 wt.% CCNF hydrogels with DS of 10.6, 12.6, 18.0 and 23.0 %. Values obtained at a frequency of 1.02 Hz. As the DS increased both the elastic and viscous modulus values increased, but the elastic modulus is greater and increased more, which is a good indication of strong structuring within the gel.

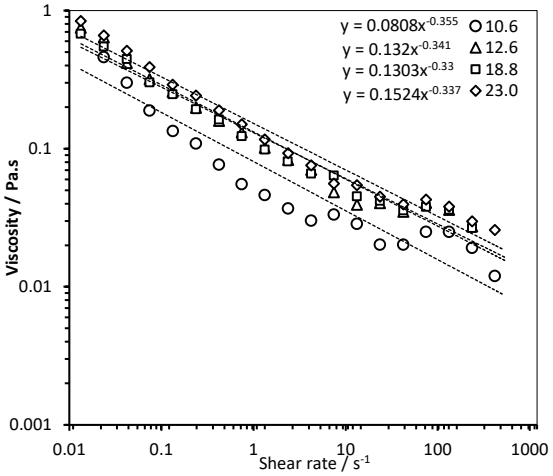

Fig. S12 Viscosity versus shear rate for 2 wt. % CCNF hydrogels with DS of 10.6, 12.6, 18.0 and 23.0 %. Values obtained at a shear sweap of 113.17 s^{-1}. Trend line fitted to a the expression $y = ax^{-b}$ to determine the degree of shear thinning of the hydrogels.

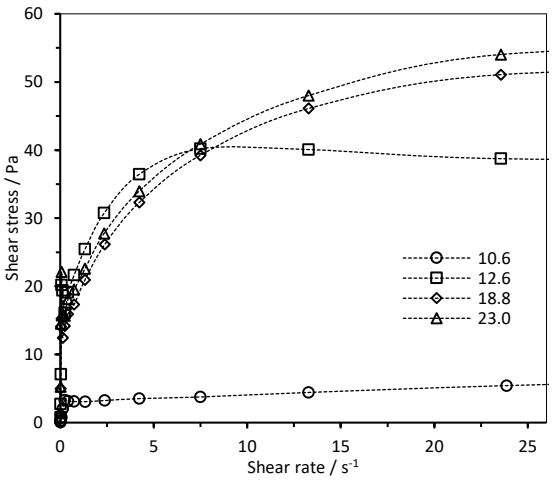

Fig. S13 Elastic (*G*′) and viscous (*G*′′) modulus versus frequency for 2 wt.% CCNF hydrogels with DS of 10.6, 12.6, 18.0 and 23.0 %. Values obtained at a frequency of 1.02 Hz. As the DS increased both the elastic and viscous modulus values increased, but the elastic modulus is greater and increased more, which is a good indication of strong structuring within the gel.

NMR Spectroscopy

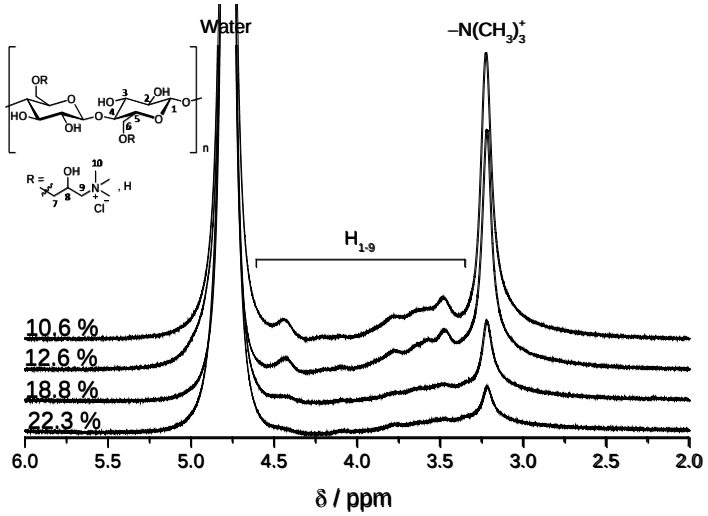

Fig. S14 ^{1}H solution-state NMR spectra of 4 wt. % CCNF hydrogels with DS between 10.6 – 23.0 %, acquired at 25 °C.

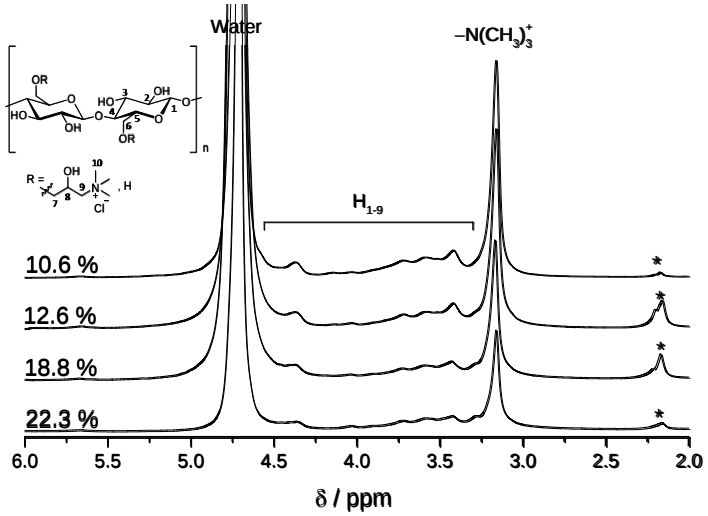

Fig. S15 ^{1}H HR-MAS NMR spectra of 4 wt. % CCNF hydrogels with DS between 10.6 – 23.0 %, acquired at 25 °C with a MAS rate of 2 kHz. Asterisks represent spinning sidebands.

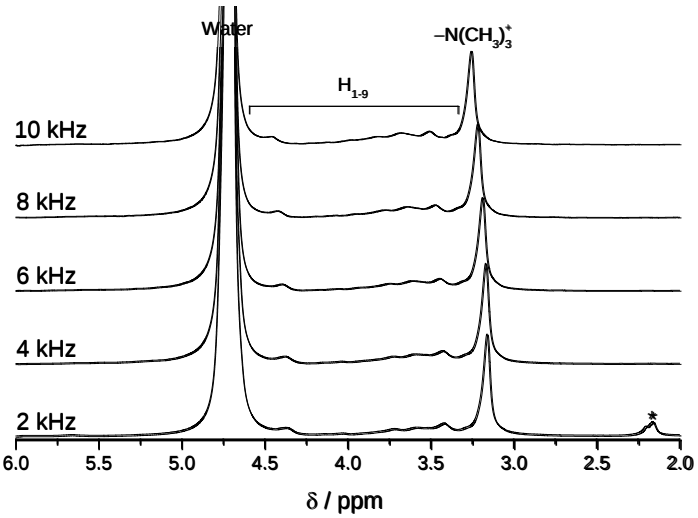

Fig. S16 ^{1}H HR-MAS NMR spectra of 4 wt. % CCNF hydrogels with MAS rates between 2 and 10 kHz, acquired at 25 °C. The asterisk represents spinning sidebands.

Table. S2 ^{1}H solution-state T_1 relaxation times for the trimethyl protons in 4 wt. % CCNF hydrogels with DS 23 %, acquired between 5 and 45 °C.

T / °C	T_1 / s	
	Trimethyl	Water
5	0.41 (± 0.009)	2.14 (± 0.036)
25	0.48 (± 0.008)	2.56 (± 0.041)
45	0.54 (± 0.014)	3.75 (± 0.026)
65	0.79 (± 0.009)	4.73 (± 0.043)

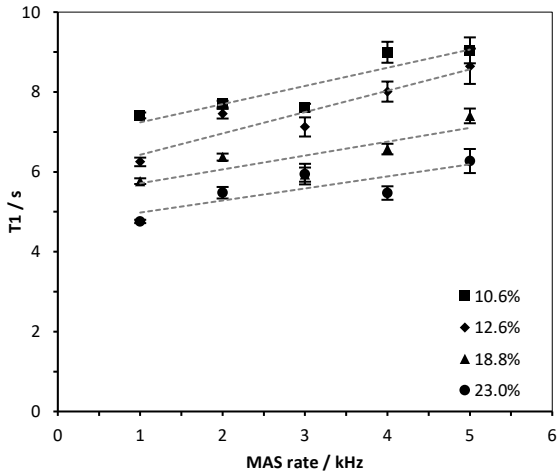

Fig. 17: ^{1}H HRMAS T_1 times for water protons in 4 wt. % CCNF hydrogels with increasing DS, acquired with MAS rates between 2 and 10 kHz.

The following equation was used by Asano *et al.* (2012) to calculate the pressure (*P*) exerted on styrene-butadiene rubber samples from the MAS rate (*k*), using the inner radius of the rotor (*r*) and the sample density (ε),[2]

$$P = \frac{4}{3}\pi^2 k^2 r^2 \varepsilon.$$

Even though the polymeric hydrogels under study are heterogeneous mixtures of liquid and solid components, the same expression can be used to roughly estimate the inner pressure. The pressure inside the rotor due to centrifugal forces was determined to be in the range of 30 to 3000 Pa for CCNF gels (for MAS rates between 2 and 10 kHz), values which are significantly greater than the yield stresses (τ^0 in the range of 3 to 54 Pa).

References:

1. M. Zaman, H. Xiao, F. Chibante, and Y. Ni, *Carbohydr. Polym.*, 2012, **89**, 163–70.
2. A. Asano, S. Hori, M. Kitamura, C. T. Nakazawa, and T. Kurotsu, *Polym. J.*, 2012, **44**, 706–712.