

## Article

# Carboxymethyl Cellulose Enhanced Production of Cellulose Nanofibrils

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**Abstract:** Cellulose nanofibrils (CNF) were produced by high-pressure homogenization from kraft pulp in the presence of carboxymethyl cellulose (CMC) of varying molecular weights. CNF pretreated with 250 kD CMC exhibited the maximum specific surface area (SSA) of 641 m<sup>2</sup>/g, which is comparable to that of CNF pretreated by 2,2,6,6-tetramethyl-piperidiny-1-oxyl (TEMPO)-mediated oxidation with a high degree of fibrillation. Rheological and microscopic analyses also indicated a high level of fibrillation for the CMC-pretreated CNF. In contrast, the reference CNF without the CMC pretreatment showed a lower level of fibrillation, which was reflected in decreased viscosity and the reduction of SSA by a factor of 19. With the high-degree fibrillation and low toxicity, the CMC pretreatment is a promising method for the production of high-quality CNF in an environmentally friendly way.

**Keywords:** cellulose nanofibrils; carboxymethyl cellulose; homogenization; specific surface area



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## 1. Introduction

Originating primarily from wood and plant biomass, cellulose is one of the most abundant natural polymers that exhibits sustainability; biocompatibility; and low environmental, health, and safety concerns. Nanocellulose (NC) is engineered nano-structured cellulose, which is categorized into cellulose nanofibrils (CNF), cellulose nanocrystals (CNC), and bacterial nanocellulose (BNC) depending on the size of NC particles and individualization methods [1]. Unique properties of NC involve a high mechanical modulus (Young's modulus ~100 GPa for CNC), a large surface area, and a highly reactive surface arising from abundant surface hydroxyls [2,3]. Among the NCs, CNF has particularly garnered much research interest for various applications, which include food packaging [4], textile dyeing [5–7], water treatment and remediation [8–11], biocomposites [12,13], reinforcement for papers and paperboards [14], interfacial stabilizers for Pickering emulsions [15], and substrates and other components for electronics/energy storage [16,17].

As the name implies, CNF consists of nano-sized cellulosic fibrils, which are generally produced by the delamination of native cellulose fibers (>1 mm in length and >10 µm in width) from wood and plant biomass. Mechanical refining processes—such as high-pressure homogenization, microfluidization, ultrasonication, and cryocrushing—are often combined with various pretreatments of cellulose fibers to increase the degree of fibrillation and reduce the energy consumption [18–20]. Among the pretreatments, carboxymethylation [21,22], enzymatic hydrolysis [23,24], and 2,2,6,6-tetramethyl-piperidiny-1-oxyl (TEMPO)-mediated oxidation [25,26] are the most commonly utilized methods. Carboxylate moieties on the surface of cellulose fibers can weaken inter- and intra-fiber hydrogen

bonds by repulsive electrostatic force, which consequently facilitates the individualization of nano-sized cellulose fibrils (CNF) during the mechanical refining process [27]. Unlike acid hydrolysis used for the production of CNC, these pretreatments selectively modify the surface of cellulose fibers, thus retaining the crystallinity and the length of cellulose fibrils after the individualization [27,28]. However, the use of harmful solvents and chemicals likely incurs substantial environmental costs for the large-scale production of CNF [29,30].

Adsorption of carboxymethyl cellulose (CMC) onto the cellulose surface is a well-known phenomenon [31–33]. A molecular affinity between CMC and cellulose arises from their structural similarity [34]. The adsorption of CMC increased the charge density of cellulose fibers by one order of magnitude [31], and the attached CMC was shown to be highly hydrated (>90%) [32]. These findings led to the utilization of CMC adsorption as a pretreatment method for native cellulose fibers to produce CNF in combination with a high-pressure homogenization process [35]. Specifically, Naderi et al. reported the production of CNF from wood pulp attached with high molecular weight ( $M_w$ ) CMC (1000 kg/mol) [36]. It was hypothesized that the increased charge density and the additional hydrated layer by the adsorbed CMC would facilitate the swelling of native cellulose fibers and subsequently increase the degree of fibrillation during the subsequent homogenization process. Rheological properties of the CNF hydrogels from CMC-adsorbed wood pulp—as well as tensile strength and oxygen permeability of the CNF films—were investigated. The authors concluded that the CMC pretreatment of cellulose fibers could be an alternative for the production of CNF for applications (e.g., strengthening of paper and cardboard) where highly fibrillated CNF is not required [36].

Since CMC is inexpensive and widely used in food and non-food products as a viscosity modifier and a stabilizer, it would have economic and environmental benefits over other pretreatment methods such as carboxymethylation and TEMPO-mediated oxidation. The addition of CMC would reduce the ability of cellulose to form strongly cooperative inter- and intra-hydrogen bonds with carboxymethyl moieties in CMC, decreasing the number of hydrogen bonds between the hydroxyl groups in cellulose [1]. Moreover, CMC-adsorbed CNF would be water-redispersible after drying since CMC has been reported to prevent irreversible agglomeration of CNF during drying, which is also known as hornification [37,38]. However, there has been limited study on the influence of the  $M_w$  of CMC adsorbed onto cellulose fibers on the quality of CNF produced by homogenization.

In this work, we investigate the quality of CNF produced by high-pressure homogenization with a CMC additive onto kraft pulp as a pretreatment. Specific surface area (SSA) and water retention value (WRV) of the produced CNF with varying  $M_w$  of CMC was determined and compared as a quantitative measure of the degree of fibrillation for cellulose fibers. Rheological and microscopic analyses were also performed to examine the produced CNF. Combined results indicate the highest degree of fibrillation of CNF was achieved for a 250 kD CMC additive. Moreover, the degree of fibrillation of the CNF appeared comparable to the CNF pretreated with TEMPO-mediated oxidation. These results suggest that adding CMC to kraft pulp is an economical and eco-friendly pretreatment method for the production of CNF.

## 2. Materials and Methods

### 2.1. Production of CNF Hydrogels

Kraft pulp sheets (provided by Weyerhaeuser, Dacula, GA, USA) were knife-milled three times using a mesh sieve with a pore size of 500  $\mu\text{m}$  to the order of 10 s of micrometers in width and 100 s of micrometers in length. In a typical batch, 10 g of cellulose powders (native cellulose fibers) were mixed with 500 mL of hot water (2% in dry cellulose) and 1.25 g of CMC (average  $M_w$  of 90, 250, and 700 kD, 0.7 carboxymethyl groups per anhydroglucose unit for 90 kD and 0.9 for 250 kD and 700 kD CMC, respectively, Sigma-Aldrich, St. Louis, MO, USA). The slurry-like mixture was blended together by a mechanical blender (Waring Commercial, Stamford, CT, USA) at a speed of at least 22,000 rpm for two minutes before being transferred to a beaker to be heated (80–100  $^{\circ}\text{C}$ ) and cooled to room. The slurry

was again blended for 2 min to ensure a homogenous mixing and eliminate any particle settling. The mixture was then processed into a CNF hydrogel during 2–3 passes in a high-pressure homogenizer (APV-1000, SPX Flow Technology, Charlotte, NC, USA). The reference CNF hydrogel was also prepared without the addition of CMC. The prepared CNF hydrogels remained stable and showed no signs of phase separation or precipitation for many months.

## 2.2. Characterizations

Viscosity of the CNF hydrogel was measured by a parallel plate geometry rheometer (Anton Paar MCR 302, Graz, Austria) equipped with a roughened surface. The rheometer was operated in a strain-controlled mode and frequency sweep measurements were conducted over an angular frequency range of 0.1–100 rad/s with a strain amplitude of 1% under room temperature. For scanning electron microscopy (SEM) imaging, CNF hydrogel was pre-frozen at  $-40\text{ }^{\circ}\text{C}$  for one day and then lyophilized for two days (Labconco Freezone 4.5, Kansas City, MO, USA). SEM imaging (FEI Tecnai20, FEI Co., Eindhoven, The Netherlands) was performed for thin slices of the freeze-dried CNF sample after gold sputtered coating. For atomic force microscopy (AFM) measurements, one droplet of the diluted CNF hydrogel (c.a. 0.02%) was spin-coated onto a silicon wafer that had been freshly pretreated with a piranha solution and then dipped in an aqueous polyethylenimine solution (1%). The spun film was baked at  $120\text{ }^{\circ}\text{C}$  for 20 min. AFM measurements were performed using a Bruker Dimension Icon (Hamburg, Germany) in a tapping mode. Zeta potential of the CNF particles was measured by Zetasizer Nano ZS (Malvern Panalytical, Malvern, UK) at a temperature of  $25\text{ }^{\circ}\text{C}$ .

## 2.3. SSA and WRV Measurements

Specific surface area (SSA) was measured using methylene blue (MB, lab grade powder (100%) from Ward's Science, Rochester, NY, USA), which was dried at  $110\text{ }^{\circ}\text{C}$  for several hours before use without further purification. The absorbance of a MB solution in deionized water at 660 nm was obtained by a UV–vis spectrophotometer (Shimadzu 2401, Kyoto, Japan). This wavelength corresponds to the absorption peak of the molecule [39]. In a typical example, 8 mL of the CNF hydrogel (0.8% concentration in water) was mixed by a shaker with a predetermined concentration of the MB solution (from 0.1 to 50 mM) for two days, in which all surfaces of the cellulosic fibers would be occupied by MB molecules. After two days of shaking, the mixture was centrifuged at 13,000 rpm for an hour to separate cellulose fibers attached with MB molecules from the supernatant solution containing unbound MB molecules. From the absorption intensity of the supernatant solution at 660 nm, the amount of adsorbed MB on the surface of CNF was determined. From the calibration curve of the neat MB solutions at various concentrations, the MB adsorption per gram of CNF (mg/g) was determined and then converted to SSA of CNF,  $S_{cf}$ , by using Equation (1),

$$S_{cf} = \frac{(N_{MB} * a_{MB} * N_A)}{M_{MB}} \quad (1)$$

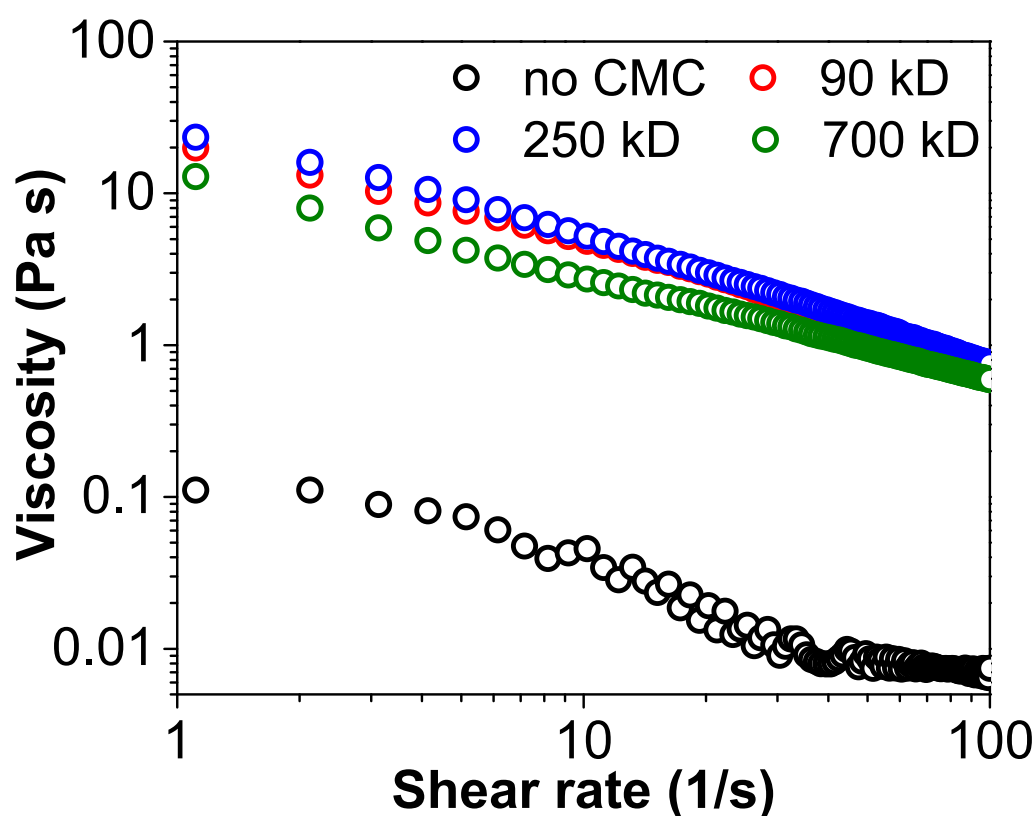
where  $N_{MB}$  equals to the molecular weight of MB ( $M_{MB}$ ) multiplied by the number of moles of MB per gram of fiber needed to form a monolayer;  $a_{MB}$  is the molecular footprint of MB ( $130\text{ }\text{\AA}^2$ ) [40]; and  $N_A$  is Avogadro's number. The maximum adsorption of MB was used as  $N_{MB}$ . Water retention value (WRV) of CNF was determined by centrifuging the CNF hydrogel (2% dry cellulose in water) at 13,000 rpm for an hour. Then, the centrifuged CNF sample was weighed before and after lyophilization at around 0.1 mbar for two days to determine WRV by using Equation (2),

$$\text{WRV (\%)} = \frac{(m_{cen} - m_{lyo})}{m_{lyo}} * 100 \quad (2)$$

where  $m_{cen}$  and  $m_{lyo}$  are the mass of the centrifuged CNF sample before and after lyophilization, respectively. WRV of neat CMC (0.25% in water) with three different  $M_w$  was determined by the same method.

### 3. Results and Discussion

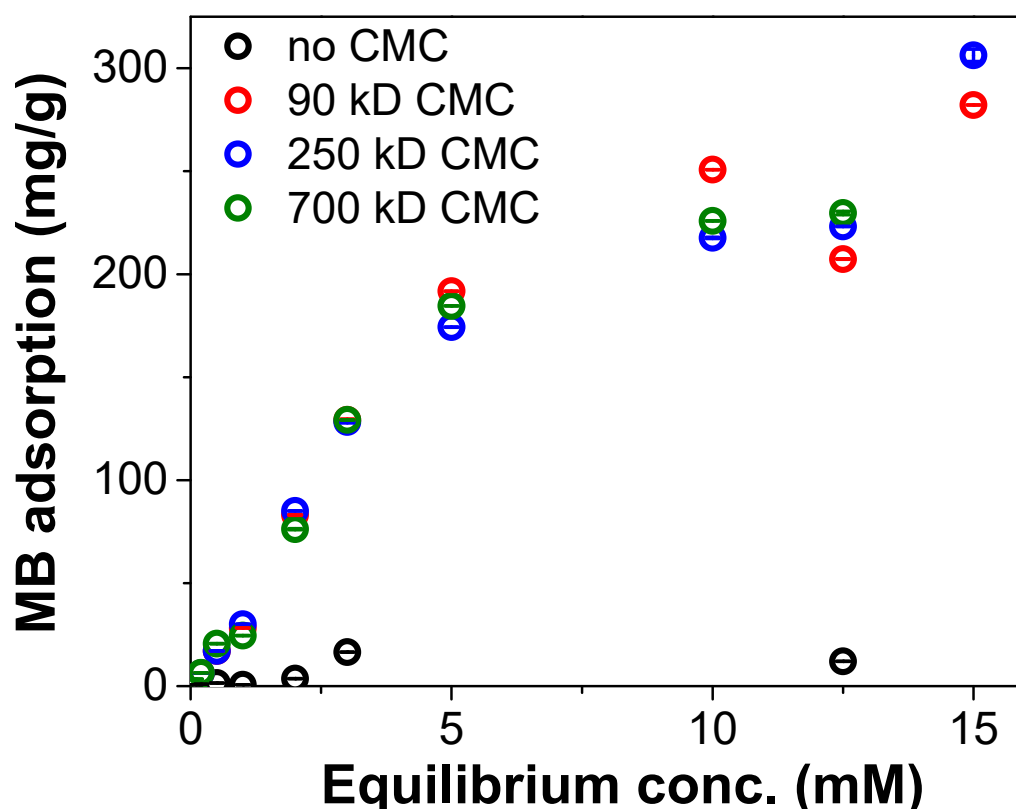
CNF was produced by high-pressure homogenization starting from kraft pulp sheets to fine powders, and to a CNF hydrogel. The CNF hydrogels (with a concentration of 2%) prepared with CMC of different  $M_w$  exhibited shear-thinning rheological properties (Figure 1). This is believed to be due to the strong entanglements of high aspect ratio nano-sized fibrils. A shear flow measurement can be used to estimate the degree of fibrillation for CNF hydrogels produced by mechanical refining methods. An increase in viscosity with an increasing level of fibrillation was reported for the CNF hydrogels pretreated with TEMPO-mediated oxidation and carboxymethylation [41]. As shown in Figure 1, the viscosity of the CNF hydrogel without CMC pretreatment was substantially lower than the CNF with the CMC pretreatment. The lower viscosity indicates a lower degree of fibrillation. In addition, the fluctuating viscosity of the CNF without CMC also suggests the presence of aggregates. The CNF hydrogels pretreated with 90 and 250 kD CMC showed marginally higher viscosity than the one with 700 kD CMC throughout the range of the shear rate, which indicates a higher level of fibrillation. We note that the viscosity of pristine CMC would not affect the viscosity of CNF hydrogels, given the viscosity of 90, 250, and 700 kD CMC (0.25% in water) solutions  $\ll 1$  Pa·s [42–44].



**Figure 1.** Viscosity of the CNF hydrogels pretreated with varying  $M_w$  of CMC as a function of shear rate. The concentration of the CNF gels was 2%.

The zeta potential of the CNF pre-treated without CMC and with 90 kD, 250 kD, and 700 kD  $M_w$  CMC are  $-46.9$  mV,  $-46.2$  mV,  $-56.2$  mV, and  $-60.7$  mV, respectively. Although it is not necessarily a quantitative measure of surface charge density on CNF, the zeta potential values between  $-46$  and  $-60$  mV are well aligned with the values in the literature, indicating the colloidal stability of negatively charged CNF particles [3].

To quantify the degree of fibrillation, SSA of the CNF pretreated with various  $M_w$  of CMC was measured and compared. As fibrillation progresses, both the number of isolated nano-sized cellulose fibrils and SSA of the CNF increase. Since MB molecules are known to adsorb onto the surface of cellulose without chemical reaction nor molecular stacking, using the adsorption of MB has been one of the established methods for the determination of SSA of cellulose [39]. It should be noted that our SSA measurements with MB molecules were performed on the CMC-pretreated CNF, in which the mass ratio of dry CNF to CMC was 8 to 1. We assume the MB molecules would primarily adsorb onto the surface of cellulose fibers unoccupied by CMC since the adsorbed CMC polymers consist of trains (segments in direct contact with the surface) and loops and tails (segments exposed to the solution), leaving most of the adsorbent surface of the cellulose fibers available for small molecules [45]. Figure 2 shows Langmuir-type adsorption isotherms for adsorption of MB on CNF (MB in mg per CNF in gram) as a function of MB concentration. The Langmuir-type MB adsorption isotherms increased linearly at a low concentration (<5 mM for the CNF with CMC) and exhibited saturation with increasing MB concentration. The reference experiment for CNF prepared with no CMC additive demonstrated the dramatic difference in SSA of the CNF samples prepared with and without the additive.



**Figure 2.** Adsorption of methylene blue (MB) on CNF (per one gram of CNF) with varying  $M_w$  of CMC as a function of MB concentration.

Table 1 summarizes the maximum MB adsorption and SSA of the CNF determined by using Equation (1). SSA of the CNF pretreated with 250 kD CMC was determined to be  $641 \text{ m}^2/\text{g}$ . This surface area is comparable to a nanopaper made by the CNF with TEMPO-mediated oxidation followed by supercritical  $\text{CO}_2$  drying ( $482 \text{ m}^2/\text{g}$ ) and liquid  $\text{CO}_2$  evaporation ( $415 \text{ m}^2/\text{g}$ ), which was determined by a BET surface area method [46]. It is commonly recognized that the TEMPO-oxidation pretreatment yields the finest CNF [18,19,27]. We note that our surface area result may not be directly compared to that of the TEMPO-oxidized CNF due to the difference in the SSA measurement method. Nonetheless, the high SSA of the CMC-treated CNF indicates high efficiency of the CMC pretreatment on



native cellulose fibers for the fibrillation process. As compared with the reference CNF (no CMC additive), the CMC pretreatment increased SSA of the CNF by a factor of 19. SSA of the CNF with 90 and 250 kD CMC were very similar, but it decreased with 700 kD CMC, indicating a lower degree of fibrillation. The same tendency can be seen in Figure 1 where the viscosity of the CNF with 700 kD CMC is lower than that for other samples with CMC. The reduced degree of fibrillation of CNF with 700 kD CMC may possibly be attributed to the less efficient adsorption of the high- $M_w$  CMC polymer on cellulose fibers, which would arise from entropic penalty of the CMC polymer to move into interfibrillar space of the cellulose fibers. In addition to the entropic penalty, the adsorption of the high- $M_w$  CMC polymer would likely be limited by diffusion due to increased viscosity. Thus, we believe the degree of CNF fibrillation is a function of the  $M_w$  of CMC with a maximum at some intermediate range of  $M_w$ . We note that the previous work by Naderi et al. [36] used the even higher- $M_w$  CMC polymer (1000 kg/mol) to pretreat cellulose fibers to produce CNF that resulted in a slightly poor degree of delamination, compared to highly charged fibrous systems (obtained through, e.g., carboxymethylation or TEMPO-oxidation).

**Table 1.** Maximum MB adsorption on the CNF and SSA of the CNF produced with the CMC pretreatment including the reference CNF with no CMC treatment.

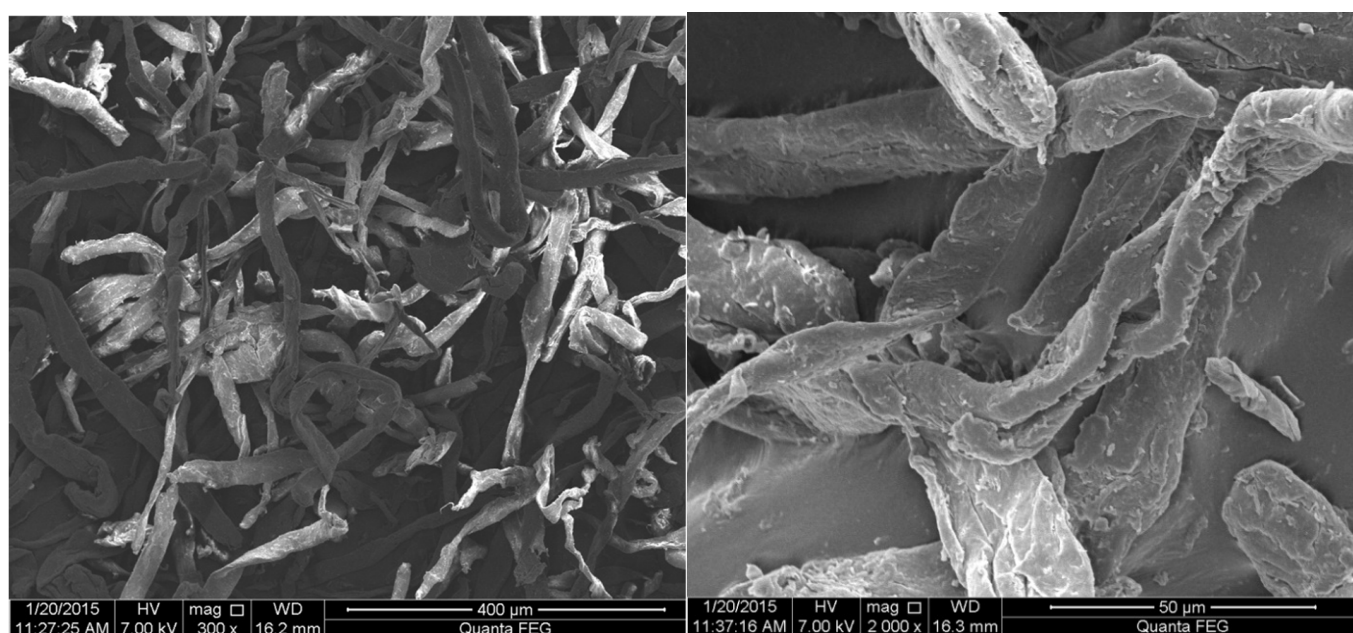
	No CMC	CMC, 90 kD	CMC, 250 kD	CMC, 700 kD
MB adsorption on CNF (mg/g)	16.4	282	306	229
SSA of CNF (m <sup>2</sup> /g)	34.5	591	641	481

WRV has been widely used in the pulp and paper industry to assess the degree of fiber fibrillation. It measures the ability of a fiber sample to retain water, which would increase with refining a fiber due to the increased fiber swelling through internal and external fibrillation. Particularly, WRV has been reported to be useful to characterize the degree of fibrillation of cellulose fibers at micro- and nano-meter scales [47,48]. As shown in Table 2, the CNF pretreated with 90 kD and 250 kD CMC exhibited 15 times greater WRV than the CNF without CMC. In the control WRV experiment for neat CMCs with all three  $M_w$ , no CMC sediment was found after the high-speed centrifugation, indicating CMC was completely hydrated. Thus, the increased WRV of CNF treated with CMC is attributed to the increased surface area by fibrillation of cellulose fibers and possibly additional hydration of the adsorbed CMC layer on them [32]. Even greater water retention of the CNF with 700 kD CMC may be due to a larger amount of water held on the high- $M_w$  CMC layer because SSAs of the CNF pretreated with CMC were similar to each other (Table 1).

**Table 2.** Water retention value of the CNFs.

	No CMC	CMC, 90 kD	CMC, 250 kD	CMC, 700 kD
WRV (%)	60 ± 58	870 ± 19	977 ± 132	1446 ± 6

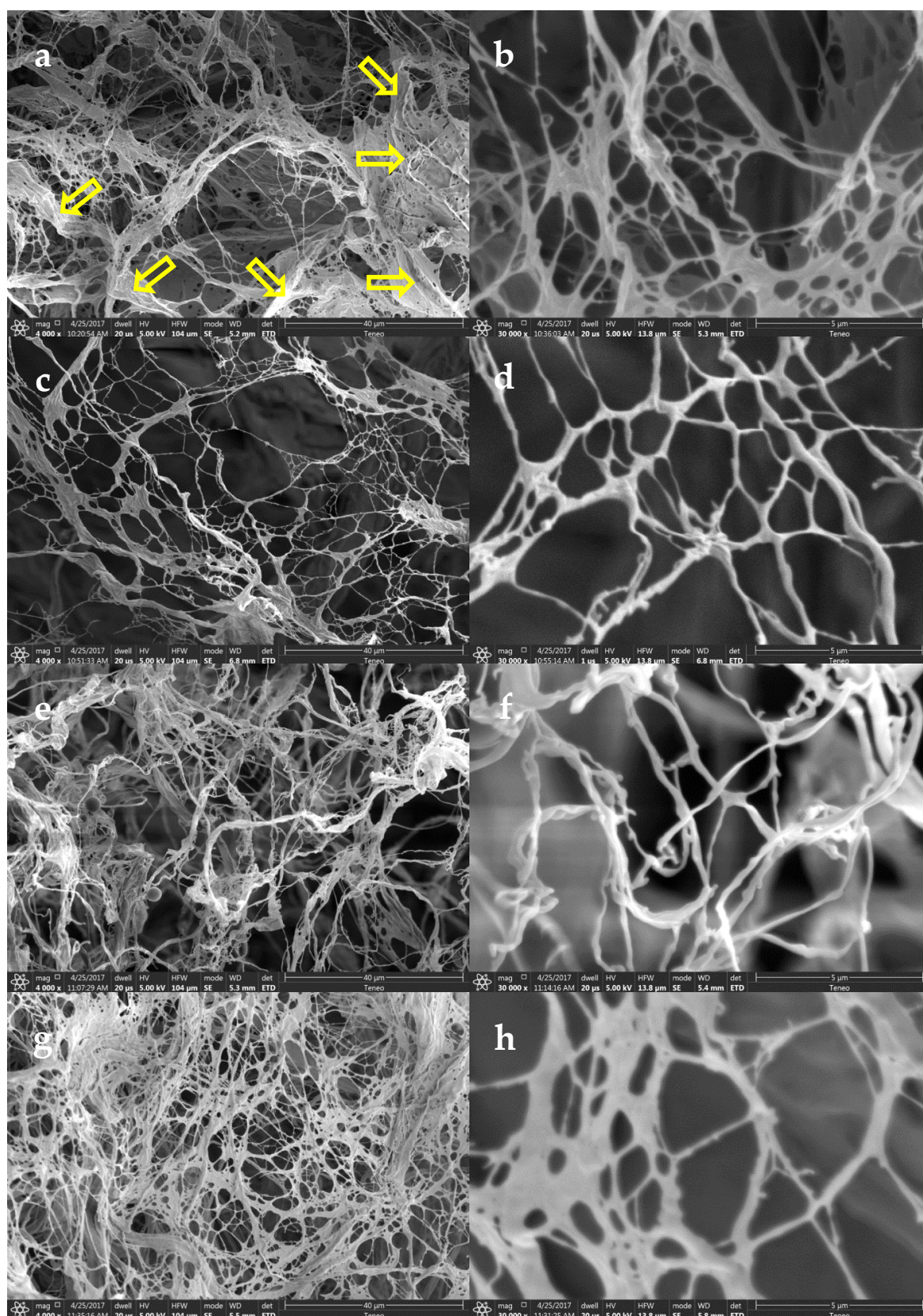
Morphology of knife-milled cellulose particles prior to the homogenization and CNF (after homogenization) was examined by using SEM. Figure 3 shows the milled powders from kraft pulp sheets before the homogenization. The length and width of the particles and/or fibers were >1 mm and 10–30 µm, respectively, which are typical particle sizes for wood-based and plant-based fibers [2].



**Figure 3.** SEM images of cellulose powders after knife milling in various magnifications.

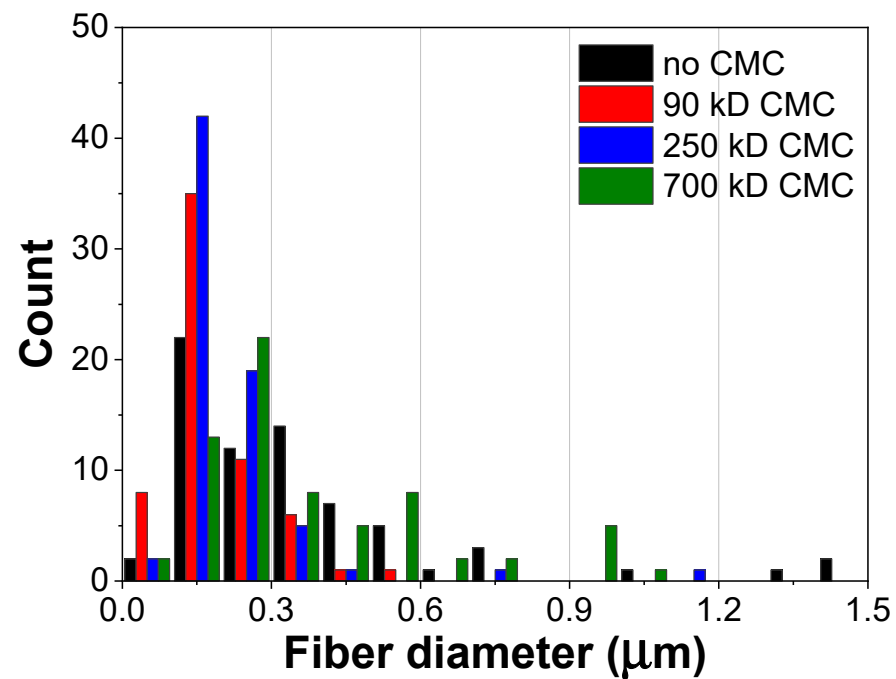
Figure 4 displays SEM micrographs of CNF. The CNF hydrogel samples were lyophilized before SEM imaging to preserve the microstructure of the individualized CNF and prevent agglomeration of nanofibers under the action of capillary forces [49], which could result in the assembly of agglomerated particles due to the inter- and intramolecular hydrogen bonds between cellulose fibers upon drying [50]. The reference CNF (no CMC) in Figure 4a,b contained a large number of non-fibrillated cellulose particles and fragments, which are indicated by yellow arrows in the image. In contrast, the CNF samples pretreated with CMC (Figure 4c–h) show much finer fibrils with a higher degree of fibrillation along with a limited number of aggregated particles, which corroborates the high surface area of CNF pretreated with CMC. A histogram plot in Figure 5 shows the comparative size distribution of a CNF fiber diameter, obtained by ImageJ analysis using the SEM images of CNFs under the same magnification ( $16,000\times$ ). The CNFs pretreated with CMC, particularly with 90 and 250 kD CMC, exhibit a smaller fiber diameter and narrower size distribution than the reference CNF (no CMC), which is also summarized in Table 3. We note that the fiber diameter of the CNF with 700 kD CMC is not significantly different to that of reference CNF, indicating the reduced degree of fibrillation of the CNF with 700 kD CMC, which has also been suggested by the reduced viscosity (Figure 1) and the reduced SSA (Table 1). Additionally, AFM images in Figure 6 display a similar trend, in which the CNF samples pretreated with CMC exhibit a higher degree of fibrillation than the reference CNF with no CMC.



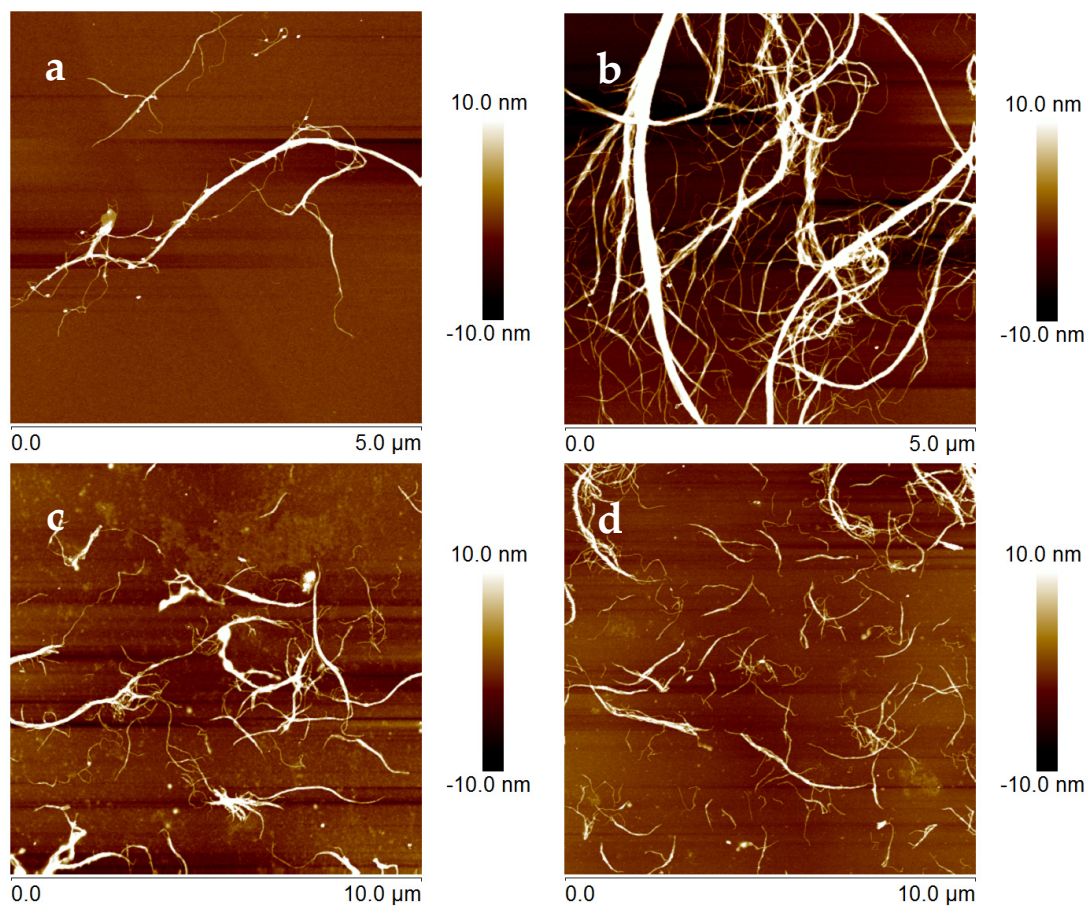


**Figure 4.** SEM micrographs of the freeze-dried CNF fibers: (a,b) with no CMC, (c,d) with 90 kD CMC, (e,f) with 250 kD CMC, and (g,h) with 700 kD CMC. Low- and high-magnification images are shown in the left (a,c,e,g) and right (b,d,f,h) columns, respectively.





**Figure 5.** Histogram plot showing the size distribution of the fiber diameter for CNFs processed with and without CMC. Fiber diameter data were obtained by ImageJ analysis using the SEM images of CNFs under the same magnification (16,000 $\times$ ). The total number of data was more than 60 for each sample.



**Figure 6.** AFM images of the CNF fibers pretreated with: (a) no CMC, (b) 90 kD CMC, (c) 250 kD CMC, and (d) 700 kD CMC.

**Table 3.** Average and standard deviation of the fiber diameter of CNF. The same set of data shown in Figure 5 was used.

	No CMC	CMC, 90 kD	CMC, 250 kD	CMC, 700 kD
Fiber diameter of CNF ( $\mu\text{m}$ )	$0.36 \pm 0.30$	$0.19 \pm 0.093$	$0.21 \pm 0.14$	$0.38 \pm 0.24$

#### 4. Conclusions

We have shown that adding CMC to cellulose particles can be employed as an effective pretreatment strategy for the production of high-degree fibrillated CNF in combination with the high-pressure, mechanical homogenization process. The produced CNF exhibited much greater water retention and SSA ( $641 \text{ m}^2/\text{g}$ ) than the reference CNF without CMC as an additive. The highest degree of fibrillation was achieved when CNF was pretreated with 250 kD CMC. The degree of fibrillation declined with 700 kD CMC, suggesting too bulky CMC polymer would experience entropic penalty for optimal adsorption on the surface of cellulose fibers, limiting fibrillation of them to nano-sized CNF. Given low toxicity and simplicity, the pretreatment with CMC presents a promising and scalable method for the production of high-quality CNF, compared with other highly charged systems such as carboxymethylated and TEMPO-modified CNF.

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**Data Availability Statement:** The data presented in this study are available upon request from the corresponding author. The data are not publicly available due to privacy.

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