ABSTRACT: Cellulose-based model materials in the form of fibrillar networks and macromolecular hydrogels were used to investigate the ion-induced swelling in relation to the elasticity and structure of the network. Both networks were charged by the introduction of carboxyl groups onto the cellulose surface, and the dimensions of the networks in aqueous solution were measured as a function of pH. The use of cellulose-model materials that contained either noncrystalline cellulose or cellulose I fibrils made it possible to model the effect of the ion-induced osmotic pressure of a delignified wood fiber wall. The noncrystalline hydrogels represented the noncrystalline domains of the fiber wall and the fibrillar network represented the supramolecular network of cellulose I fibrils of the fiber wall. The experimental results were compared to swelling potentials computed using the Donnan theory, and it was found that the ion-induced water uptake within the cellulose networks followed the theoretical predictions to a large extent. However, fibrillar networks were found to plastically deform upon swelling and deviated from the ideal Donnan theory for polyelectrolyte gel networks. Upon addition of salt to the aqueous phase surrounding the cellulose materials, both hydrogels and fibrillar networks deviated from the Donnan theory predictions, suggesting that structural differences between the networks impact their swelling.

INTRODUCTION

The interest in forest-based raw materials has grown as the demand for biobased fossil-free products has increased. Substantial commercial and research efforts have been devoted to utilize the properties of wood at all structural levels. While native materials have excellent properties, to more efficiently utilize the wood-based materials, different chemical modifications are often performed, to alter properties or provide different functional groups for further processing. One common way of creating functional handles for further modification and/or processing is to attach carboxyl groups to the cellulose fibers via oxidation. Oxidation is often performed using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or monochloroacetic acid (carboxymethylation). The oxidized fibers can be used at the macroscale or they can be further processed to produce cellulose nano fibrils (CNFs) with a cellulose I crystal structure. CNFs from wood cellulose are high-aspect-ratio particles with widths of approximately 3–5 nm and lengths on the order of several micrometers. CNFs have received great interest due to their high strength, high stiffness, and comparatively low weight. CNFs have been used in, for example, nanocomposites, barrier films, flame-retardant materials, and improved paper products. CNFs are often prepared by disintegrating oxidized fibers using a high-pressure homogenizer, and it has been shown that oxidation of fibers facilitates the liberation of nano fibrils via an increased fiber wall swelling.

Regardless of whether oxidized fibers or oxidized nano fibrils are used as the raw material, the increase in swelling or water affinity, caused by the presence of surface charge groups, can be a major drawback, as many fabrication processes require a dewatering step in which water removal can be energy-demanding and costly. The removal of water in conventional papermaking is also a high energy-demanding process and therefore there is great interest in being able to predict water uptake and removal of different types of cellulose-rich networks. Studies performed with pulp fibers have made it possible to estimate the water uptake in the fiber wall using centrifugation (water retention value) and/or solute exclusion techniques under different conditions, such as alkaline or acidic aqueous solutions. While these methods provide good insight, they are largely indirect and are based on assumptions and cannot provide detailed information about...
the molecular mechanisms behind the swelling and deswelling. As a result, more advanced studies are needed to quantify water uptake in these structures to identify the molecular mechanisms responsible for the water uptake and, more specifically, how to control it. In addition, fibers originating from different sources (wood/plant species, pulping processes, etc.) do not have exactly the same chemical composition, surface chemistry, or fiber wall structure/dimensions. This heterogeneous nature of the fibers makes it difficult to obtain generality and statistics when studying the swelling of delignified fibers from a typical pulp source. It is thus beneficial to use well-defined model materials to establish a qualitative understanding of the phenomena. The use of such materials also makes it possible to mimic the properties of the fiber wall at different structural levels, for example, the noncrystalline regions and the cellulose I fibril network. The authors have previously developed and characterized a cellulose-model material consisting of cellulose hydrogel beads. The gel beads were shown to be noncrystalline and have polyelectrolyte swelling behavior similar to that of fibers in response to different pH values, salt concentrations, osmotic deswelling by nonionic polymers, and hornification upon drying and rewetting. However, due to differences in the supramolecular cellulose network structure/strength, the absolute values for the water uptake of the gel bead system and fiber wall differed considerably and the never-dried gel system reached a water uptake of about 44 g of water per gram solid (g/g), whereas the water uptake in a typical fiber wall has been reported to be in the range of 1 g/g. As a continuation of the work on the gel beads, the aim of the present work is to study the swelling of model cellulose filaments, in which the hierarchal structure (cellulose supramolecular structure) of a fiber wall was mimicked more accurately. Specifically, filaments were prepared from aligned CNFs by flow focusing, and the water uptake was estimated to range between 0.9 and 1.9 g/g, a range close to that of a typical fiber wall. Comparing gel beads and filaments prepared from the same initial fibers made it possible to capture the effect of the molecular arrangement in different structural levels on the swelling ability of the fibers without the influence of variations caused by different fiber origins and other variations usually found in natural fibers. The fibers used to prepare the filaments and the gel beads were oxidized to different charges. The swelling was measured by optical microscopy as a dimensional change, in response to different experimental conditions. The swelling caused by the dissociation of counterions from charged groups in the gel beads or filament network was determined and compared to calculated values using the classical Donnan theory, commonly used to describe the swelling potential of cellulose-rich fiber systems. The experimental swelling data was compared with the computed Donnan potential to determine how well the theory describes the observed ion-induced swelling of different types of cellulose networks. It was shown that the swelling of the gel beads followed the theoretical predictions to a greater extent than the fibrillar network and that the effect on the swelling due to the ionic swelling pressure was dependent on the elasticity and structure of the network.

**EXPERIMENTAL SECTION**

**Materials.** Dissolving grade pulp fibers (96% glucose according to sugar analysis by acid hydrolysis) received from Domsjö Fabriker AB, Ornsköldsvik, Sweden, were used as the starting material to prepare both the gel beads and filaments.

The carboxymethylation of the pulp prior to gel bead preparation required the following chemicals: methanol (ACS reagent), ethanol (96 vol %), and 2-propanol (ACS reagent) purchased from VWR International AB, Sweden; monochloroacetic acid (CICH2-COOH) (ACS reagent ≥99.0%) and sodium hydroxide (NaOH) (puriss p.a., ACS reagent ≥98%) purchased from Sigma-Aldrich AB, Sweden; and acetic acid (CH3CO2H) (glacial ACS grade ≥99.7%) purchased from Thermo Fisher Scientific.

To dissolve the pulp for the gel bead preparation, the following chemicals were used: ethanol (96 vol %) purchased from VWR International AB, Sweden, and N,N-dimethylacetamide (DMAc) (puriss p.a., ≥99.5%) and lithium chloride (LiCl) (puriss p.a., anhydrous ≥99%) purchased from Sigma-Aldrich Sweden AB.

The nonsolvent used in the precipitation bath was ethanol (96 vol %) purchased from VWR International AB, Sweden, and hydrochloric acid (HCl) (37% analytic reagent) purchased from Thermo Fisher Scientific, Sweden.

The chemicals used to TEMPO-oxidize the fibers used to prepare CNF filaments were as follows: 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (98%) purchased from Sigma-Aldrich Sweden AB, potassium dihydrogen phosphate (KH2PO4) and sodium hypochlorite (NaClO) (14%) both purchased from VWR International AB, Sweden, and sodium chlorite (NaClO2) purchased from Alfa Aesar Thermo Fisher Scientific, Sweden.

All aqueous solutions and dispersions were made using water purified by a Milli-Q purification system: Advantage A10 model with a 0.22 μm Millipak Express 40 filter from Merck Millipore Merck AB, Sweden.

The pH of the aqueous solutions was set using hydrochloric acid (HCl) (37% analytic reagent from Thermo Fisher Scientific, Sweden, or sodium hydroxide (NaOH) (puriss p.a. ACS reagent ≥98%) purchased from Sigma-Aldrich Sweden AB). The ionic strength of the aqueous solutions was increased using sodium chloride (NaCl) (ACS reagent ≥99.0%) purchased from Sigma-Aldrich Sweden AB.

**Preparation of Model Materials. Oxidation of Fibers.**

The carboxymethylation to a charge density of 600 μequiv/g was carried out following the procedure described by Wächter et al. 20 g of never-dried dissolving fibers were dispersed in 2 L of deionized water and mixed using a PTI Austria-disintegrator model 95568 for 30 000 revolutions. The fibers were drained from the water and washed with 0.8 L of ethanol using filtration. The fibers were impregnated for 30 min in a closed beaker containing 2 g of CICH2-COOH predissolved in 0.1 L of 2-Methanol to dissolve 2.2 g of NaOH before 0.4 L of isopropanol was added, and the mixture was heated to 85 °C. The impregnated fibers were added to the heated solution and the reaction time was set to 1 h. After the reaction, the fibers were washed with 4 L of deionized water before being washed with 0.4 L of 0.1 M acetic acid and finally with 1 L of deionized water. Using conductometric titration, the charge densities of three different batches were determined to be 300, 600, and 1150 μequiv/g. The amounts of CICH2-COOH used to obtain 300 and 1150 μequiv/g were 45 mg/g fibers and 0.41 g/g fibers, respectively.

**TEMPO-Oxidation.** Carboxyl groups were introduced onto the fibril surface using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)-oxidation of never-dried dissolving fibers. The oxidation was performed under neutral conditions (pH 6.8) in accordance with the method previously presented by Saito et al.

Briefly, 10 g of never-dried dissolving fibers were dispersed in 900 mL of 0.05 M sodium phosphate buffer (pH 6.8) heated to 60 °C. Further, 0.16 g of TEMPO and 11.3 g of sodium chlorite (NaClO2) were added to the dispersion. Further, 5 mL of MS sodium hypochlorite was diluted to 0.1 M with 100 mL of phosphate buffer before being poured into the fiber dispersion starting the reaction. An overhead stirrer was placed in the dispersion and the container was sealed. The reaction time was 2 h and 20 min. After the reaction, the fibers were washed with deionized water.

https://dx.doi.org/10.1021/acs.langmuir.0c02051

Langmuir 2020, 36, 12261−12271
Preparation of Gel Beads. Unmodified or carboxymethylated fibers were dissolved in a DMAC/LiCl solution following the procedure described earlier. Wet fibers containing 1 g of dry mass were drained from water by filtration and placed in ethanol to displace the remaining fibers to ethanol. The displacement from water to ethanol was performed for 2 days by filtration and addition of new ethanol twice per day. The sorption displacement process was then repeated displacing the ethanol with DMAC. The DMAC-soaked fibers were placed in a dehydrated DMAC solution containing 7 wt % LiCl. The fibers were dissolved under stirring at a temperature of 5 °C during a period of about 24 h. The solution was filtered through a 45 μm acrodisc PTFE-filter (VWR, Sweden), and the filtered solution was solidified by dropwise precipitation in a 100 mL beaker containing a mixture of ethanol/ water (20:80).

The solidified gel beads were left at the bottom of the beaker for 24 h before being washed with Milli-Q water several times per day for about 1 week.

Preparation of Cellulose Nanofibril (CNF) Dispersions. TEMPO-oxidized fibers were disintegrated into cellulose nanofibrils (CNFs) using a high-pressure homogenizer, Microfluidizer M-110 EH (Microfluidics Corp. Westwood, MA), with a setup of two combinations of chambers in series. The first combination contained one chamber with a diameter of 400 μm followed by another with a diameter of 200 μm and was run under a pressure of about 900 bar. In the second combination, one chamber with a diameter of 200 μm was followed by a chamber with a diameter of 100 μm and run under a pressure of about 1600 bar. The fibers were passed through the 400/200 μm chamber section once, followed by four passages through the 200/100 μm chamber combination.

The CNF gels resulting from the homogenization had a solid content between 5.1 and 9.6 g/L. The CNF gels were diluted to a volume fraction of cellulose obtained from TGA.

Swelling Studies Using Optical Microscopy. The dimensions of the gel beads and filaments in different aqueous environments were determined using two different optical microscopes. A Dino-Lite USB microscope was used to measure the radius of the millimeter-sized beads and an Olympus U-TVO microscope with a 50X UMPPlanFI objective was used to measure the width of the micrometer-sized filaments.

Characterization. Charge Content of TEMPO CNF. After the TEMPO-oxidized pulp fibers had been homogenized into fibrils, the surface charge of the fibrils was determined using a Stabino particle charge mapping equipment (Particle Metrix Gmbh, Germany) in which the fibrils were titrated with a 1 g/L solution of poly-diallyldimethylammonium chloride (poly-DADMAC). The charge densities of the fibrils were measured to be 340 μequiv/g (CNF340), 640 μequiv/g (CNF640), and 1160 μequiv/g (CNF1160).

Morphology of Filaments. A field-emission scanning electron microscope (FE-SEM, Hitachi S-4800) was used to study the morphology of the filaments. The filaments were sputter-coated (Cressington 208 HR) with a thin layer of platinum/palladium prior to the investigation.

The swelling was expressed as water uptake (Wupt) and calculated as grams of water, mwater, per gram of cellulose, mcellulose, and was assumed to be constant and their expansion/contraction in different aqueous solutions was therefore due to the flow of water.

To determine the increase in water uptake caused by the dissociation of carboxyl groups, ΔWupt, was calculated by subtracting the Wupt at pH 2 (gel beads) or pH 3 (filaments) (Wupt(ϕ=2)/pH3) from the Wupt at a given pH (Wupt(ϕ=3))

\[ ΔW_{upt} = W_{upt, pH3} - W_{upt, pH2}/3 \]  

The maximum water uptake was denoted as Wupt,max or ΔWupt,max.

To calculate the fraction of the water uptake, F, that emanates from the dissociated carboxyl groups within the network, the following equation was used

\[ F = \frac{W_{upt,max} - W_{upt, pH3}/3}{W_{upt,max}} \times 100 \]  

Atomic Force Microscopy. The wet elastic modulus of the filament was determined using an atomic force microscope (AFM) (MultiMode IIIa, Veeco Instrument, CA) with a picoforce extension.

The filaments were placed on a silicon wafer and clamped with a thin slice of magnetic metal (50 μm) to restrict movement during the measurement. The filaments were submerged in Milli-Q water, and the setup was placed in a liquid cell to prevent evaporation. The
performed in the order of pH 2/3 (light gray), pH 10 (GB600), and (B) water uptake of filaments outlined by Grignon and Scallan\textsuperscript{20} and is described in detail in the Supporting Information.

indentation was performed in force mode using an OLTESPA (Bruker) cantilever with a spring constant of 1.9 N m\textsuperscript{-1} carrying a tetrahedral tip with a length of 9–19 \textmu m and a tip radius of 7 nm. The ramping rate was set to 1 \textmu m/s with a maximum force of 200 nN. The indentation part of the force vs indentation profile (50–150 nN) was fit to the linearized cone Hertz model.\textsuperscript{27} The filaments were presoaked in Milli-Q for at least 48 h before measurement. The average modulus of the filaments was based on three filaments on which 10 measurements were made at three different positions.

\section*{COMPUTATION OF THE SWELLING POTENTIAL USING DONNAN THEORY}

The swelling potential, $E$ (mol/L), describes the excess concentration of ions in the network compared to the bulk water and was computed in this work based on the Donnan theory. It was computed for aqueous solutions with and without added NaCl. The number of excess ions depends on the degree of dissociation of the carboxyl groups (determined by the pH) within the network and the salt concentration. This excess creates an osmotic pressure gradient causing water to flow into the network to dilute the ionic species and thus expands the network until the networks’ mechanical energy balances any further expansion.

The methodology of the present work closely follows the procedure outlined by Grignon and Scallan\textsuperscript{20} and is described in detail in the Supporting Information.

The computations were performed using a MATLAB script adjusting the model to the experimental conditions for the gels and the filaments. The concentration of immobile ions was based on estimates from the experimental data using the concentration of carboxyl groups on the cellulose together with the water volume of the filament or gel bead in a nondissociated state, assuming a cylindrical shape of the filaments and a density of the dry filament of 1.5 g/cm\textsuperscript{3}.

\section*{RESULTS}

Determination of Elasticity of Gel Beads and Filaments Using AFM Indentation and Swelling Measurements. The wet modulus of charged gel beads was previously measured using (i) indentation via colloidal probe AFM and (ii) volumetric expansion and osmotic stress induced by carboxyl group countermers.\textsuperscript{16} The osmotic stress method has previously been used to calculate the transverse modulus of a fiber wall by Scallan and Tigerström.\textsuperscript{14} The modulus of the gel beads was found to decrease with increasing charge density and ranged from 13 to 120 kPa depending on the method of measurement.

The transverse wet modulus of the filaments was similarly measured via volumetric expansion and AFM. Using a linearized Hertz model, the Young’s modulus was calculated to range between 6.7 and 35.4 MPa without any apparent correlation with the charge density (Table 1). The bulk modulus, calculated using the osmotic stress, was found to drop from approximately 3 to 0.14 MPa as the charge density increased from 340 \textmu equiv/g (CNF340) to 1160 \textmu equiv/g (CNF1160) (Table 1). An apparent density was calculated for the filaments using a density of 1.5 g/cm\textsuperscript{3} for the cellulose fibrils and 1.0 g/cm\textsuperscript{3} for the water within the network. A specific bulk modulus was then calculated by dividing the bulk modulus by the density of the filament (Table 1).

The ion concentration in the fully swollen filaments (no salt addition) was calculated and used to calculate the osmotic pressure exerted by these ions (Table 1). The bulk modulus of the gel beads and filaments was determined from swelling measurements by increasing the pH from 2 to 10–12. To determine the reversibility/irreversibility of the swelling, the beads and filaments were returned to pH 2, and the water uptake values are summarized in Figure 2. From Figure 2, it can be seen that the gel beads show reversible swelling/deswelling whereas the filaments show considerable swelling irreversibility, suggesting that the filament network plastically deforms upon expansion whereas the gel beads’ network shows an elastic response.

\begin{table}
\centering
\small
\begin{tabular}{|l|c|c|c|c|c|c|}
\hline
Sample & Young’s modulus (MPa) & Bulk modulus (MPa) & Apparent density of fully swollen filament (g/cm\textsuperscript{3}) & Specific bulk modulus $10^3$ (N m/kg) & Ion concentration in fully swollen filament (mol/L) & Osmotic pressure from ions in fully swollen filament (MPa) \\
\hline
CNF340 & 35.4 (16.6) & 2.96 (0.72) & 1.15 & 2.58 & 0.29 (0.06) & 0.71 \\
CNF640 & 6.7 (4.5) & 0.63 (0.16) & 1.09 & 0.58 & 0.24 (0.02) & 0.59 \\
CNF1160 & 19.1 (15.1) & 0.14 (0.03) & 1.04 & 0.13 & 0.16 (0.02) & 0.39 \\
\hline
\end{tabular}
\caption{Young’s Modulus for Filaments Measured with AFM, the Bulk Modulus and the Specific Bulk Modulus Calculated Using the Osmotic Stress Caused by the Dissociation of Carboxyl Groups, and the Ion Concentration in the Fully Swollen Filament at High pH and the Corresponding Osmotic Stress\textsuperscript{a}}
\label{tab:1}
\end{table}

\textsuperscript{a}Values within parentheses are standard errors.
Filaments. The gel beads were prepared using dissolved unmodified fibers or fibers carboxymethylated to different degrees. The charge density of the unmodified fibers was 30 μequiv/g and the charge densities of the carboxymethylated fibers were 300, 600, and 1150 μequiv/g as measured by conductometric titration. The solid content of the gel beads (in water at a pH of 2) were 2.5 wt % (GB30), 2.0 wt % (GB300), 1.9 wt % (GB600), and 1.5 wt % (GB1150). In previous investigations, the gel bead structure was characterized using solid-state NMR and SAXS. The results showed that the beads are noncrystalline with a network structure containing denser entities tethered with stretched cellulose chains. The portion of stretched cellulose chains (tethers) increased with an increasing charge density of the gel beads.

The CNF-suspension used to prepare filaments contained fibrils that were charged to different degrees by TEMPO-oxidation of the never-dried fibers. The fibrils of the three different CNF-suspensions had charge concentrations of 340 μequiv/g (CNF340), 640 μequiv/g (CNF640), and 1160 μequiv/g (CNF1160), as measured by polyelectrolyte titration. The width of the dried filaments ranged between 10 and 25 μm and the solid contents of the filaments in aqueous solution (pH 2) were 53.2 wt % (CNF340), 54.1 wt % (CNF640), and 43.2 wt % (CNF1160). The morphology of the filaments prepared from CNFs with a charge content of 640 μequiv/g was monitored using field-emission scanning electron microscopy at two different magnifications, as shown in Figure 3.

Swelling of Gel Beads and Filaments in Water at Different pH Values. The dimensional change of gel beads with charge densities of 30 μequiv/g (GB30), 300 μequiv/g (GB300), 600 μequiv/g (GB600), and 1150 μequiv/g (GB1150) was measured with a microscope as the pH was stepwise increased from 2 to 13. The ΔW_{upt} of gel beads with different charge densities is shown in Figure 4A. The largest increase in water uptake of the gel beads (ΔW_{upt,max}) at pH 10 (i.e., W_{upt,pH10}−W_{upt,pH2}) was plotted against the charge density of the gel beads in Figure 4B. The W_{opt} values of the gel beads at pH values of 2 and 10 are summarized in Table S1 in the SI.

The swelling potential, E (mol/L), with increasing pH, was computed using the same carboxyl concentration as in the gel beads at a pH of 2 (Figure 4C). The curves in Figure 4C show the theoretical prediction of the swelling potential from the ionizable groups due to an excess of ionic species in the network (mol/L) compared to the surrounding solution. The...
model considers the pH within the gel (i.e., degree of dissociation), the number of ionizable groups, and the salt concentration (see the SI for detailed information).

CNF filaments were also studied in aqueous solutions with pH ranging from 3 to 13.5. The width of the filaments was determined optically and the $W_{\text{upt}}$ was calculated in the same way as for the gel beads (dimensional change, eq 1). The $W_{\text{upt}}$ under acidic conditions (pH 3) was 0.99 g/g (CNF340), 0.91 g/g (CNF640), and 1.90 g/g (CNF1160) and the $W_{\text{upt}}$ under alkaline conditions (pH 11) was 1.6 g/g (CNF340), 2.9 g/g (CNF640), and 12.9 g/g (CNF1160). The difference in water uptake between pH 3 and pH (Δ$W_{\text{upt}}$) and the difference in maximum water uptake between pH 3 and 11 (Δ$W_{\text{upt,max}}$) were also calculated (according to eq 2) and are displayed in Figure 5A,B, respectively.

Theoretical computations were performed to simulate the swelling potential, $E$, of a charged network based on Donnan theory for a concentration of ionizable groups equal to the concentrations in the filaments at pH 3, 0.4 equiv/L (CNF340), 0.8 equiv/L (CNF640), and 1.1 equiv/L (CNF1160), and the results are shown in Figure 5C. The swelling potential is the theoretical concentration of ions (at a specific degree of dissociation) giving rise to a swelling pressure at a fixed volume.

Swelling of Gel Beads and Filaments in Water at Different Salt Concentrations. The ion-induced swelling of the gel beads was further studied by measuring the dimensional change of GB600 from pH 2 to 13 with the addition of 0.001 or 0.01 M sodium chloride (NaCl). The Δ$W_{\text{upt}}$ values in 0.001 and 0.01 M NaCl (aq) are shown in Figure 6A together with the measurements for GB600 without added NaCl. The computed Donnan swelling potentials, $E$ (mol/L), of GB600 with increasing pH of the solution and a background of 0.001 or 0.01 M NaCl (aq) are shown in Figure 6B. The $W_{\text{upt}}$ values of GB600 at pH 2 and 10 with salt concentrations of 0.001 and 0.01 M NaCl (aq) are summarized in Table S2 in the SI.

CNF1160 filaments were also placed in solutions with different pH values at three different salt concentrations, 0.001 M (aq), 0.01 M (aq), and 0.1 M (aq), and the Δ$W_{\text{upt}}$ was
calculated. The pH was increased stepwise from a pH of 3 to a pH of 13.5. The results, together with the measurements on CNF1160 in pH solutions without added NaCl, are shown in Figure 7A.

The effect on the swelling potential, $E$, at different salt concentrations was computed (Donnan theory) using a concentration of ionizable carboxyl groups of 1.1 equiv/L (CNF1160) within the filaments and 0.001, 0.01, and 0.1 M NaCl (aq) (Figure 7B).

The fraction of the water uptake, $F$, that emanates from the dissociated carboxyl groups within the network (the ion-induced water uptake) was calculated according to eq 3. In Figure 8, $F$ is plotted versus the swelling potential of ionizable groups at pH 2 (gel beads) or pH 3 (filaments) to compare the two model systems.

## DISCUSSION

### Water Uptake in Different Cellulose Network Structures.

The $W_{upt,max}$ in the gel beads ranged from 38.8 to 105 g/g and in the filaments from 1.6 to 12.9 g/g depending on the charge density. To understand and explain the differences between the materials, it is necessary to separate the different components that contribute to the swelling. Traditionally, the swelling of a hydrogel is described by three different osmotic pressure terms: the ionic contribution, $\pi_{ion}$, the macromolecule−solvent mixing contribution, $\pi_{mix}$, and the network pressure contribution, $\pi_{net}$, which together make up the total swelling pressure in the network, $\pi_{tot}$, as given by eq 4:

$$\pi_{tot} = \pi_{ion} + \pi_{mix} + \pi_{net}$$

The balance between the three terms is thus dependent on the concentration of ionic groups, the “willingness” of the macromolecule to mix/interact with the surrounding liquid, and the structural integrity of the network, i.e., the restraining network pressure within the gel. The $\pi_{ion}$ is essentially independent of the mixing and network contributions and is only dependent on the concentration of ionic species. $\pi_{mix}$ is described by the Flory−Huggins model and, in the case of cellulose hydrogels, is based on the interaction between the individual macromolecules and water. The Flory−Huggins model can be directly applied to the gel beads as they contain a macromolecular system with nearly all its segments in contact with water. Within a fibrillar network, however, it is important to account for the fact that the network is no longer a macromolecular network. The macromolecules in contact with water within the fibrillar network are mainly those situated on the fibrillar surface (about 50% of the total polymer given a lateral fibrillar dimension of 4 nm × 4 nm). It is thus expected...
that the impact on the water uptake of $\pi_{\text{osm}}$ at the same volume fraction of solids, is less in the filaments than in the gel beads. $\pi_{\text{osm}}$, the pressure induced by the network itself, is an important factor as it is based on the direction (expansion or contraction) in which the network prefers to move and is dependent on the stiffness/ flexibility of the network components, cross-links, and the supramolecular structure. The structures within the gel beads and filaments differ to a great extent as the gel beads contain a more flexible molecular structure than the stiffer bundles of partly crystalline cellulose (fibrils) within the filaments (illustrated in Figure 9). The interaction between the fibrils in the filaments is dominated by larger domains of effective short-range interactions between fibrils and not by sparsely distributed contact points between macromolecules as in the gel beads. Because of the differences in structure, $\pi_{\text{osm}}$ is expected to have a larger impact on the degree of expansion of the CNF filament networks.

The wet modulus of the gel beads was previously measured and found to range from 13 to 120 kPa depending on the charge of the material in the beads and on the method used. The results in Figure 2A show that the swelling of the gel beads seems to be in the elastic regime since the gel contracts to the same volume when the pH is changed back to 2 after being increased to 10. The situation in the case of the filaments was significantly different. It was shown that the wet Young’s modulus of the filaments in Milli-Q water was 35.4 (±16.6), 6.7 (±4.5), and 19.1 (±15.1) MPa for CNF340, CNF640, and CNF1160, respectively. There was thus no apparent correlation between the modulus and the charge density. A comparison between the Young’s modulus of the filaments and that of wood fibers with the same method showed that the transverse Young’s modulus was higher for the filaments.

The somewhat inhomogeneous nature of the filaments was reflected in the relatively high standard deviations. Taking this uncertainty into account, the moduli of the wood fibers and of the filaments could be considered to be of the same order of magnitude. The bulk modulus was also calculated from the swelling and was found to be 2.96, 0.63, and 0.14 MPa for CNF340, CNF640, and CNF1160, respectively. Thus, the bulk modulus decreased with an increasing charge density of the filaments. The specific bulk modulus, calculated by dividing the bulk modulus by the density of the filaments, was 2.6, 0.58, and 0.13 (N m)/kg for CNF340, CNF640, and CNF1160, respectively. The trend toward a less stiff filament as the charge density increased thus remained for the specific bulk modulus. The decrease in bulk modulus indicated that the charged groups affect the ease with which the fibrils in the network separate from each other with increasing charge on the fibrils, which in turn leads to an expansion of the network.

It is possible to argue that the easier separation is a result of fewer contact points/domains between the fibrils (physical cross-links) caused by the carboxyl groups situated on the surface. The ability for the highly charged filaments to expand by the exerted osmotic pressure is thus easier and the network structure changes as it swells. This hypothesis is supported by the inability of the network to contract back to the initial dimensions after the osmotic pressure from the counterions is released (Figure 2B), indicating that irreversible changes occur within the network as it swells dependent on the charge density. It is worth mentioning that despite this irreversibility in swelling, the filaments are still intact and the irreversibility should hence be viewed as a plastically deformed network and not a disintegrated network.

The $\pi_{\text{ion}}$ was calculated for the filaments in a fully swollen state (pH 10-12) and it was found that $\pi_{\text{ion}}$ decreased with increasing charge density (Table 1, column 7). For eq 4 to be valid, an increase in $\pi_{\text{ion}}$ must be accompanied by a change in $\pi_{\text{osm}}$ and/or $\pi_{\text{net}}$. This means that, if we assume that $\pi_{\text{osm}}$ is constant for all three filaments independent of their degree of oxidation, a change in $\pi_{\text{ion}}$ needs to be balanced with a change in $\pi_{\text{net}}$. If the swelling response of the network was the same for the three different filaments, the equilibrium swelling would occur at the same $\pi_{\text{net}}$. This is not the case for the filaments where the network expands to different degrees depending on its degree of oxidation. In other words, it can be concluded that the charge of the filaments most probably also affects the $\pi_{\text{net}}$ term in the equation. As such, this is not so surprising since the decoration of the external surface of the fibrils with carboxyl groups indeed affects their interaction even when the charged groups are protonated during filament preparation.

However, based on the data presented in this work, it is not possible to determine the exact balance of the three terms.

The importance of the network structure to the degree of swelling was also noted when the bulk modulus of CNF1160 of 0.14 MPa was compared to the bulk modulus of 2.7 MPa calculated for TEMPO-oxidized dissolving pulp fibers (1280 μequiv/g) using the water retention values published by Sjöstedt et al. The deviation between the values shows that differences in the network structure play an important role in the swelling of cellulose-based materials with similar charge densities.

The effect of the network structure on the ion-induced swelling is further shown in Figure 8, where the fraction of the $W_{\text{upt,max}}$ which emanates from the dissociated carboxyl groups within the networks of the gel beads and the filaments, is plotted against the ionic swelling potential (mol/L). The steeper increase in the fraction of the $W_{\text{upt,max}}$ for the gel beads than for the filaments shows that the response in swelling is higher in the gel beads compared to that in the filaments and thus that the network structure plays a major role in the degree of swelling of any kind of cellulose network.

Swelling of Cellulose Networks at Different pH Values without Addition of Salt. The swelling of the gel beads in aqueous solutions with different pH values was studied as a dimensional change, which was recalculated to give the water uptake, $W_{\text{upt}}$ (g water/g solid content). The maximum $W_{\text{upt}}$ ($W_{\text{upt,max}}$) value ranged from 39 g/g for GB30 to 105 g/g for GB1150 (Table S1). To study the effect of the ionic contribution to swelling, $\Delta W_{\text{upt}}$ was calculated as the difference in $W_{\text{upt}}$ at a specific pH compared to at pH 2 ($W_{\text{upt},pH2}$) (eq 2) where all carboxyl groups are protonated. The $\Delta W_{\text{upt}}$ values for the gel beads are shown in Figure 4A, and the $W_{\text{upt}}$ are summarized in Table S1. The $\Delta W_{\text{upt}}$ value of uncharged gel beads (GB30) was largely unaffected by pH. When the charge density of the gel beads increased (GB300, GB600, and GB1150), the $\Delta W_{\text{upt}}$ increased starting from a pH of 5 to a pH of 10 ($\Delta W_{\text{upt},pH5}$). The $\Delta W_{\text{upt}}$ increased almost linearly with increasing charge density (Figure 4B). This implies that the network of the gel beads responded to the ion-induced osmotic pressure in the same way regardless of the charge density, indicating that the beads have a similar structure, throughout the investigated charge range. At a pH above 10, the $\Delta W_{\text{upt}}$ started to decrease, which is caused by a decrease in the ionic imbalance between the gel interior and the surrounding solution as the amount of NaOH is increased.

12268
The swelling of CNF filaments in water with different pH values was studied. For the filaments, the $\Delta W_{\text{opt}}$ increased significantly starting at a pH of about 8 and reached a $\Delta W_{\text{opt, max}}$ at a pH value in the range of 10–12 (Figure 5A). A clear increase in $\Delta W_{\text{opt, max}}$ with increasing charge density was observed.

The $W_{\text{opt}}$ values at pH 3 (protonated carboxyl groups) for CNF340 and CNF640 were similar, about 0.99 and 0.91 g/g, respectively, and CNF1160 had a significantly higher water uptake of 1.90 g/g, likely due to differences in the supramolecular structure between the filaments. CNF1160 may have had a more porous or less physically cross-linked fibrillar network than its less charged counterparts. It is likely that the structure was induced during the drying step as a result of the higher density of carboxyl groups on the fibril surfaces (i.e., the dried fibers were less hornified due to the disturbing action of the carboxyl groups as discussed earlier).

Under alkaline conditions, CNF1160 reached a $W_{\text{opt, max}}$ of about 12.9 g/g while the values for CNF640 and CNF340 were 2.92 and 1.55 g/g, respectively. This corresponds to a $\Delta W_{\text{opt, max}}$ between alkaline and acidic conditions of 0.6, 2.0, and 11 g/g for CNF340, CNF640, and CNF1160, respectively. Figure 5B shows a nonlinear relationship between the charge content and $W_{\text{opt, max}}$. Under alkaline conditions, the osmotic pressure increases with increasing charge and is possibly enough to rupture physical cross-links and CNF–CNF joints, in highly charged filaments, causing a plastic deformation of the fibrillar network.

Using Donnan theory to estimate the counterion concentration inside the gel beads and filaments along with the pH of the surrounding solution, it was possible to determine the theoretical swelling potential (Figures 4C and 5C). The predicted results agree reasonably well with the experimental findings regarding the increasing maximum swelling with increasing charge content in the gel beads and filaments. The simulations also predicted that swelling would start at a pH value of approximately 7 for the gel beads and at pH 8–9 for the filaments. The theoretical prediction and the experimental results diverged somewhat regarding the deswelling at high pH for the filaments as the deswelling was more pronounced in the computations than in the experiments. The inability to deswell from a high pH is most probably due to the plastic behavior of the filaments after being swollen to their maximum size as discussed earlier.

The ion-induced swelling depends on the pH and the counterion concentration within the cellulose network. At pH 2–3, the carboxyl groups are protonated and the Donnan effect has a negligible contribution to the $W_{\text{opt}}$. At high pH values, the immobile carboxyl groups become successively more dissociated with the counterions entrapped in the network to maintain electroneutrality. This imbalance in ionic concentration across the phase boundary between the network and the surrounding solution leads to an osmotic pressure difference, which induces a flow of water into the network, causing it to swell.

For both gel beads and filaments, the initial increase in $W_{\text{opt}}$ occurred at a pH higher than 4. The $pK_a$ of carboxyl groups is just below 4, which means that half the carboxyl groups should be in a dissociated state at pH 4. If the pH in the surrounding solution were equal to the pH inside the network, the dissociated counterions would make a significant ionic contribution to the $W_{\text{opt}}$ at pH 4, contrary to observations. The increased concentration of hydrogen ions inside the network keeps the pH at a lower level inside the cellulose network, effectively limiting dissociation and the buildup of anionic concentration gradient across the network phase boundary. These findings are in agreement with the predictions of the Donnan theory, and previous work has shown that the pH difference across polyelectrolyte gel phase boundaries can approach 4 pH units.20

The uptake of water by pulp fibers at a low pH has been studied previously using both water retention values and the solute exclusion technique31 and it was found that the water uptake under acidic conditions ranged from about 1.35–3.5 g of water per g solid material, depending on the type of pulp and the yield.11,20 Sjöstedt et al. showed that water uptake of never-dried dissolving grade, TEMPO-oxidized pulp fibers ranged from 1.1 to 1.35 g/g for charge densities from 20 to 1280 $\mu$equiv/g under acidic conditions. These results are in the same range as that for the water uptake of filaments found in our work. In the study by Sjöstedt et al.,30 the authors also measured the water retention value of pulp fibers under alkaline conditions (pH 9) and found water retention values between 1.25 g/g (unmodified) and 2.35 g/g (1280 $\mu$equiv/g). These values are significantly lower than the corresponding $W_{\text{opt, max}}$ values found for our filaments. One potential reason for this discrepancy is the more sophisticated structure of the pulp fiber wall that can withstand the increasing osmotic pressure.

**Swelling of Cellulose Networks with Increasing Ionic Strength.** The swelling of gel bead GB600 was studied at different pH values in a solution of 0, 0.001, and 0.010 M sodium chloride (NaCl) to clarify how the increase in ionic strength of the surrounding solution decreased the osmotic pressure and overall swelling. The $\Delta W_{\text{opt}}$ value decreased with increasing concentration of NaCl compared to the salt-free case (Figure 6A). The increase in $\Delta W_{\text{opt}}$ began at pH 4–5 instead of at pH 6–7 as it did without added NaCl.

Filaments with the highest charge density (CNF1160) were also studied at different pH levels at concentrations of 0, 0.001, 0.010, and 0.1 M NaCl (aq) to clarify how the increase in ionic strength of the surrounding solution decreased the osmotic pressure and overall swelling. The $\Delta W_{\text{opt}}$ decreased with increasing concentration of NaCl and the initial increase in the $\Delta W_{\text{opt}}$ started at pH 4–5 instead of at pH 9–10, as seen in pH solutions without added NaCl. In 0.1 M NaCl (aq), the plateau of $\Delta W_{\text{opt, max}}$ was reached at a pH of about 6, and in 0.001 M, the plateau was reached at pH 10, in comparison to the NaCl-free case in which $\Delta W_{\text{opt, max}}$ was reached at pH 11.

Computations generally showed similar trends to the experimental results (Figures 6B and 7B), but notably, the pH at which the swelling plateau occurred for the filaments was lower than the measured level. When NaCl is added, sodium ions in the solution displace some hydrogen ions and effectively increase the diffusion of hydrogen ions into the surrounding solution at higher ionic strengths. An effect of this is that the swelling starts closer to the average $pK_a$ of the carboxylic acid groups.20 Addition of NaCl also decreases the ionic concentration gradient across the phase boundary, decreasing the osmotic pressure difference and resulting in a lower $W_{\text{opt}}$.

The swelling behavior of the filaments was similar to that of fibers, but the swelling of the filaments introduces a plastic effect on the CNF network, which is not found in cellulose gel beads or fibers. The elastic behavior of the fibrillar network in the fiber wall may be due to the closed fiber ends that prevent the fibrils from separating as much as in the filaments.

https://dx.doi.org/10.1021/acs.langmuir.0c02051
Langmuir 2020, 36, 12261–12271
Nevertheless, the similarity in the swelling behavior of the filaments and of the gel beads to that of fibers makes them valuable model materials that can be combined to study not only the fiber–water interaction but also other types of interactions involving cellulose.

**CONCLUSIONS**

In this study, cellulose gel beads and CNF filaments were used to mimic the ion-induced water uptake at different structural levels of a cellulose-rich fiber wall found in most living plants. The swelling was measured as a dimensional change when the materials were equilibrated in water with different pH values and salt concentrations. In both gel beads and filaments, the water uptake caused by the dissociation of carboxyl groups within the network was initiated at a pH higher than the average pK\_a values for the carboxyl groups, however, and the initial increase in water uptake began at a lower pH when NaCl (aq) was added. This was expected from the pH suppression in the network caused by the protonation of the carboxyl groups as predicted by the Donnan theory. The maximum water uptake in the gel beads increased linearly with charge density indicating that the increase in water uptake was proportional to the induced ionic osmotic pressure. The gel beads showed an elastic behavior to the strain caused by the osmotic pressure and had no obvious linearity between the maximum water uptake and charge density. This indicates that the water uptake was not continuous but rather discrete, suggesting that the pressure needed to break the physical interactions between the fibrils in the filaments was dependent on the charge concentration. This difference was potentially introduced during the drying (i.e., hornification) of the filaments, a process that has been shown to be dependent on the charge density (and ionic form) of the dried material.

This study has also shown that the swelling behavior of the filaments followed the same trend as previously shown for a fiber wall, indicating that it is a suitable model material. The absolute value of the water uptake in the filaments somewhat exceeded the values for fibers, suggesting structural differences between the two. The large difference in bulk modulus between the filaments with different charge densities implied that the network structure and response to osmotic pressure changed when carboxyl groups were attached to the surface of the fibrils. Overall this work has shown that to be able to control the swelling of cellulotic materials, it is important not only to tune the surface chemistry of the cellulose but also that the mesostructure plays a key role. Therefore, to reduce the cost of dewatering advanced cellulotic materials, production and processes, along with advanced characterization methods, that control the mesostructure of cellulose networks will be of high importance.

**ASSOCIATED CONTENT**

1. Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.0c02051.

Computation of the swelling potential; calculations of carboxyl concentration; two tables containing the water uptake in gel beads (PDF)

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The Knut and Alice Wallenberg Foundation is acknowledged for financing this project as a part of the Wallenberg Wood Science Center. Aditya Birla Domsjö Fabriker AB is thanked for supplying the dissolving fibers. Prof. Fredrik Lundell and Krishnegowda Vijayakumar in the Department of Mechanics at KTH are acknowledged for help and instructions with the flow-focusing device. Malin Nordenström (Fiber technology group) and Céline Montanari (Biocomposite group) at KTH are thanked for their help with the initial sample preparation.

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