Sustainable Production of Cellulose-Based Hydrogels with Superb Absorbing Potential in Physiological Saline

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ABSTRACT: Nowadays, most of the commonly used superabsorbent polymers (SAPs) are derived from synthetic polymers, particularly acrylic acid and its copolymers made with acrylamide. Here, we describe a novel and environmentally friendly aqueous-based process for fabrication of a new, natural, cellulose-based SAP (hydrogel). In this two-step process, cellulose was first reacted with sodium monochloroacetate (MCA) to obtain carboxymethyl cellulose (CMC) and then cross-linked with epichlorohydrin (ECH). In distilled water (d-water), the water retention value (WRV) of the newly fabricated hydrogels reached 725 g d-water/g gel, which is significantly greater than any other commercially available superabsorbent cellulose-based material (WRV of 10–100 g/g) and comparable to the commercial synthetic (polyacrylate) SAP gels (WRV of up to 1000 g/g). In saline water (s-water; 0.9% NaCl), the maximum WRV attained was 118 g s-water/g gel, which exceeds more than 2-fold the WRV of commercial gels (40–50 g/g). Compositional analysis was carried out to determine the amount of carboxyl groups and average molecular mass, and the parameters for hydrogel preparation were optimized. The natural SAP was characterized using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). The hydrogels showed good re-swelling properties losing only 5–10% of their capabilities to reabsorb d-water when reused in four consecutive cycles. Because of their superior swelling properties in physiological saline, the new hydrogels can compete with their synthetic counterparts in applications such as high-value hygiene and biomedical products.

1. INTRODUCTION

Cross-linked networks of polymer chains with a three-dimensional linear or branched structure, which can absorb and retain significant amounts of water, are termed superabsorbent polymers (SAPs) or hydrogels.1,2 The high water absorption potential of hydrogels is due to the presence of hydrophilic functional groups, such as hydroxyl and carboxyl groups. Because of their hydrophilic nature and ability to swell, hydrogels are broadly used in personal hygiene products,3,4 agriculture,5 biomedical applications,6,7 heavy metal removal,8,9 and drug delivery.10,11 Currently, most of the commercially available hydrogels are cross-linked synthetic polymers, such as polyacrylic acid and acrylic acid-acrylamide-derived copolymers.12–16 The water intake potential of these SAPs is up to 1000 times of their weight (1000 g water/g SAP).17

Hydrogels are normally insoluble in water due to their cross-linked structure and large molecular weight. However, water absorption takes place within the hydrogel matrix, which causes water retention and swelling that are controlled to a great extent by the cross-linking density and the charge groups resided in the hydrogel molecules.18 The greater the charge of the SAPs, the greater their water absorption capacity in both s-water and pure d-water.

Biodegradability and biocompatibility along with insignificant toxicity are the prime characteristics of renewable bio-based hydrogels such as cellulose-derived superabsorbents.19–25 However, most of the hydrogels currently available on the market are mainly based on petroleum-derived acrylic acid and acrylamide, which are of oil-based nonrenewable nature. In addition, some natural polymers, such as carboxyalkyl cellulose, gum, carboxyalkyl starch, and cellulose sulfate may contain a portion of grafted polymeric particles from polyacrylates, sulfonated polystyrene, and poly(vinyl alcohol).26–28 These types of “mixed” superabsorbent materials of the renewable/nonrenewable origin are capable of absorbing 10–100 g d-water/g hydrogel, which is significantly lower than the water intake potential of synthetic SAPs (1000 g d-water/g SAP).17,23,24

In search for new and fully bio-based hydrogels, renewable and biodegradable polymers such as cellulose have been extensively studied as a raw material for SAPs.25–28 Cellulose-based hydrogels prepared by cross-linking with succinic anhydride via etherification were shown to absorb 400 times of the gel’s dry weight.29 A SAP prepared by cross-linking co-dissolved carboxymethyl hydroxyethyl cellulose with divinyl sulfone denoted a maximum water absorbency of 425 g d-water/g material.30 Alam and Christopher11 reported a natural cellulose-chitosan cross-linked hydrogel that was able to absorb up to 610 g d-water/g gel. However, all cellulose-based superabsorbent materials reported to date suffer from inferior water absorbency and production costs compared to their synthetic counterparts.
The objective of this work was to develop a new and completely renewable cellulose-based hydrogel with improved swelling and re-swelling capabilities that could compete with synthetic SAPs of environmental concern. The new hydrogel was prepared using two inexpensive and biodegradable materials: CMC and ECH. The two-step fabrication process is aqueous-based, eco-friendly, and catalyst-free and does not require any energy-intensive post-puriﬁcation step rather than a simple water washing of the hydrogel. Here, we described the process and its advantages and the properties of the newly prepared hydrogel and its potential applications.

2. RESULTS AND DISCUSSION

2.1. Chemical Cross-linking of Hydrogels. The CMC coupling reaction with ECH is presented in Figure 1. Cross-linking occurred between the epoxy group of ECH and the hydroxyl group in CMC (at any position) via an ether bond. This reaction takes place in an alkaline condition (in the presence of NaOH) without a catalyst, with NaCl and water that are the only co-products. As NaCl is highly soluble in water, it can be easily washed out from the hydrogel once the reaction is complete.

The composition and properties of the new hydrogels are shown in Table 1. The first two columns of Table 1 provide information about the initial concentrations of CMC and ECH in weight percent used for the hydrogel preparation. Although the weight ratio of CMC to ECH in the resulting hydrogels was kept at 0.75, the initial concentrations of CMC and ECH had a profound impact on the gel’s composition (carboxyl content) and properties, such as average molar mass ($M_c$) and WRV (Table 1). Best results in terms of water absorbency were obtained with 3 wt % CMC and 4 wt % ECH: the WRV of the hydrogel reached 725 g d-water/g gel water and 118 g s-water/g (Table 1). The gels having higher water absorbency are better suited for water absorption applications. Increasing the CMC concentration above 3 wt % resulted in reduction of gel’s WRV, $M_c$, and carboxyl content. This can be explained with the state of the macromolecular network formed at different initial cellulose concentrations. The gel’s cross-linked network is characterized by the availability of capillary spaces and the cross-linking density (CD). The use of higher CMC concentrations increased the CD (decreased $M_c$) of the forming gel, which resulted in a decrease of the absorption potential and WRV values. The denser cross-linked structure effectively screened the gel’s internal matrix from the flux of incoming water, which limited cellulose hydration. On the other hand, cross-linking of CMC at concentrations lower than 3 wt % produced very weak gels with a changeable physical condition that could not keep water, hence lowering the WRV (Table 1). Therefore, cross-linking plays an important role in the formation and manipulation of the properties of superabsorbent gels. The cross-linking density and swelling capacity of gels can be modified by varying the amount of cross-linker. Moreover, the degree of cross-linking impacts the integrity, strength, swelling, and hygroscopicity of gels.32 Different weight ratios of CMC to ECH in the resulting hydrogels have also been studied, and the corresponding obtained results are provided in Table 1.

The occurrence of the carboxymethylation reaction was conﬁrmed by $^{13}$C solid-state NMR and FTIR investigations. Figure 2a displays the $^{13}$C NMR spectra of unmodiﬁed and Figure 2b shows the FTIR spectra of cellulose cross-linked hydrogels.

Table 1. Composition and Properties of Cellulose-Based Superabsorbent Hydrogels

| CMC conc (wt %)$^a$ | ECH conc (wt %) | CMC/ECH (wt ratio) | COOH groups (mmol/g) | $M_c$ (g/mol) | WRV (g d-H$_2$O/g) | WRV (g s-H$_2$O/g) |
|---------------------|----------------|--------------------|---------------------|--------------|------------------|-------------------|
| 2.0                 | 4.0            | 0.5                | 1.58               | $1.23 \times 10^6$ | 413              | 71                |
| 2.0                 | 2.67           | 0.75               | 1.69               | $1.08 \times 10^6$ | 381              | 65                |
| 3.0                 | 4.00           |                    | 1.68               | $3.16 \times 10^6$ | 725              | 118               |
| 4.0                 | 5.33           |                    | 1.52               | $2.54 \times 10^6$ | 636              | 93                |
| 5.0                 | 6.67           |                    | 1.52               | $7.7 \times 10^5$  | 311              | 47                |
| 5.0                 | 3.33           | 1.5                | 1.60               | $1.45 \times 10^6$ | 455              | 69                |

$^a$CMC containing 3.5 mmol of COOH groups/g cellulose.

Figure 1. Cross-linking reaction of CMC with ECH used for hydrogel preparation.

Figure 2. (a) $^{13}$C NMR spectra of CMC and (b) FTIR spectra of modified cellulose cross-linked hydrogels.
modified cellulose. The unmodified cellulose exhibited carbon peaks at C1 (105 ppm), C4 (85 ppm), C2, C3, and C5 (74 ppm), and C6 (65 ppm), which are all typical of cellulose I.33 On the other hand, a new peak at 173 ppm appeared in the 13C NMR spectra of the CMC samples confirmed the presence of the newly introduced COOH groups.33 The FTIR spectra of unmodified cellulose, CMC, and the new cross-linked hydrogel are exhibited in Figure 2. In the case of unmodified cellulose, the characteristic absorption peaks at 3300 and 2900 cm\(^{-1}\) correspond to O–H and C–H stretching vibrations, respectively.33 The same peaks can be seen for CMC and the CMC–ECH cross-linked gel. In addition, the presence of the carbonyl (C=O) group is evident from the peak at 1740 cm\(^{-1}\), which confirms the successful introduction of carbonyl groups (Figure 2). This result also confirms the presence of COOH groups in the CMC and hydrogel. A new peak at 1328 cm\(^{-1}\) in the cross-linked gel demonstrates the successful ether-based cross-linking of CMC with ECH.33

2.2. Swelling Properties of Hydrogels. The time course of the WRV of the cellulose hydrogel obtained from 3 g/L CMC cross-linked with 4 g/L ECH (Table 1) in d- and s-water is shown in Figure 3. The WRV in d-water increased rapidly and reached to 400 g d-water/g gel in 2 h. Afterward, the water absorption rate became slower, and the equilibrium WRV of 725 g d-water/g gel was attained at 40 h (2400 min). The WRV of the modified cellulose hydrogel in s-water also increased sharply to reach 74 g s-water/g gel in the first 40 min. Thereafter, the absorption rate levelled off, with an equilibrium WRV of 118 g s-water/g gel obtained after 2400 min. The obtained WRV values for this modified cellulose hydrogel (cross-linked by ECH) in d- and s-water are larger than any other cellulose-derived hydrogels reported in the literature (400 g d-water/g cellulose-based hydrogels cross-linked with succinic anhydride;29 425 g d-water/g cross-linking co-dissolved carboxymethyl hydroxyethyl cellulose with divinyl sulfone;30 610 g d-water/g cellulose-chitosan cross-linked hydrogel).31 One disadvantage of the cellulose-based absorbent materials is their lower water absorbency (in d-water) compared to that of the commercial synthetic SAP (~1000 g d-water/g gel).12,26 This work reports the WRVs of cellulose-based hydrogels in d-water that are comparable to the water absorbencies of commercial SAPs. Furthermore, our fabricated cellulose-based hydrogel demonstrated a significantly better WRV in s-water (118 g/g gel) compared to the commercial SAP (40–50 g/g).12,29,31

The water absorption capacity of the fabricated hydrogel following four consecutive re-swelling cycles is exhibited in Figure 4. The WRV of the hydrogel in the second cycle decreased only 5–10% as compared to the first cycle, which is probably due to the formation of hydrogen bonds between –COOH and –OH groups during the first cycle. However, the water absorbencies of the hydrogel in cycles 3 and 4 did not change further and remained similar to the WRV for the cycle 2.

The water absorbency of the gel strongly depends on the type of salt present in the water. The effect of the ion types on the swelling ability of the modified cellulose hydrogel cross-linked by ECH is shown in Table 2. As shown here, the equilibrium swelling capacity \(W_s\) of the gel in the presence of monovalent cations decreased in the following descending order: NH\(_4^+\) > K\(^+\) > Na\(^+\) (Table 2). This can be explained by the fact that the charge screening effect of these cations on the \(W_s\) values decreased in the same order. In the presence of salts with different cationic charges, the absorption capacity of the hydrogel declined in the order monovalent > divalent > trivalent cations.

Table 2. Effect of Salt Type on Salt Sensitivity Factor (\(f\)) and Equilibrium Swelling Capacity (\(W_s\)) of Best Absorbing Hydrogel (WRV of 725 g d-Water/g Gel)

| salt   | salt concentration (mol/L) | swelling period (h) | \(W_s\) (g s-water/g gel) | \(f\)   |
|--------|---------------------------|---------------------|---------------------------|--------|
| NaCl   | 0.08                      | 40                  | 257 ± 2                   | 0.646  |
| KCl    | 0.08                      | 40                  | 168 ± 2                   | 0.768  |
|        | 0.15                      | 40                  | 118 ± 1                   | 0.838  |
| NH\(_4\)Cl | 0.08                    | 40                  | 284 ± 2                   | 0.608  |
|        | 0.11                      | 40                  | 183 ± 1 ± 1.5             | 0.748  |
|        | 0.15                      | 40                  | 128 ± 1                   | 0.824  |
| CaCl\(_2\) | 0.08                    | 40                  | 312 ± 2                   | 0.570  |
|        | 0.11                      | 40                  | 200 ± 1                   | 0.724  |
|        | 0.15                      | 40                  | 138 ± 1 ± 1.5             | 0.810  |
| AlCl\(_3\) | 0.08                    | 40                  | 141 ± 1 ± 1.5             | 0.806  |
|        | 0.11                      | 40                  | 93 ± 0.8 ± 1.5            | 0.872  |
|        | 0.15                      | 40                  | 66 ± 0.7 ± 1.5            | 0.909  |
|        | 0.15                      | 40                  | 31 ± 0.4 ± 1.5            | 0.957  |
|        | 0.11                      | 40                  | 20 ± 0.6 ± 1.5            | 0.972  |
|        | 0.15                      | 40                  | 14 ± 0.5 ± 1.5            | 0.980  |
trivalent (Al³⁺) cations with the carboxylate groups present in the hydrogel matrix.³⁷ This caused a decrease in the gel swelling capacity. Table 2 also demonstrates that the salt sensitivity factor \( f \) was in reverse proportion to \( W' \), as lower \( f \) values corresponded to higher \( W' \) values.

### 2.3. Crystalline Properties of Hydrogels

The crystallinity of the best absorbing hydrogel (WRV of 725 g d-water/g gel and 118 g s-water/g gel, Table 1) was investigated by XRD, and the results are displayed in Figure 5. The typical peaks of cellulose were assigned according to Nishiyama et al.³⁸ and Isogai et al.³⁹ The 2\( \theta \) angles of 15.3\(^°\), 16.5\(^°\), and 22.6\(^°\) correspond to the (110), (110), and (200) peaks, which are typical of cellulose I\( \beta \). Using eq 5, the C.I. of the unmodified cellulose was determined to be 73%. Following cellulose modification to CMC and hydrogels, the C.I. decreased to 52 and 56%. This suggests that some crystalline regions in cellulose were also modified in addition to the amorphous region. The peaks for modified (CMC) and cross-linked cellulose (hydrogel) look very similar (Figure 5). The slight shift of both peaks toward left from the peak for unmodified cellulose may be due to a partial conversion of cellulose I to cellulose II during the carboxymethylation reaction.

### 2.4. Morphological Properties of Hydrogels

The optical microscopic images of the unmodified and modified CMC cellulose fibers are exhibited in Figure 6a,b, respectively. The fiber diameter is enlarged due to the electrostatic repulsions caused by the carboxylate anions (COO⁻) obtained from the ionization of the carboxyl groups (−COOH) following carboxymethylation (Figure 6a,b). The plain (control) fibers presented in Figure 6c are the unmodified cellulose fibers. The carboxymethylation reaction did not convert all hydroxyl groups (−OH) to carboxymethyl groups (−OCH₂−COOH), and some −OH groups remained intact in the modified cellulose. This can explain the two types of fibers that can be seen from Figure 6d: (1) fibers that have a lower degree of carboxymethylation (similar to the unmodified control fibers—images on Figure 6a,c) and (2) modified fibers that are highly carboxymethylated (see images for unmodified cellulose fibers from Figure 6b).

The magnified cross-sectional SEM images of the best absorbing hydrogel can be observed in Figure 6ef. The hydrogel is highly porous with a macroporous architecture. This suggests that the electrostatic repulsions caused by the ionic charge of the carboxylate anions (COO⁻) in the hydrogel have increased the space of the cross-linked hydrogel network. The SEM image shows that the gel has an open porous geometry with a pore size in the range of 300–600 \( \mu \)m, which is separated by sheet-like walls and ultrathin structures, as revealed in Figure 6f. The high porosity of the hydrogels would facilitate rapid mass penetration, which is useful in superabsorbent applications.

### 2.5. Potential Applications of Hydrogels

The new hydrogels hold promise for use as “green superabsorbents” owing to their biodegradable constituents and the eco-friendly cross-linking process employed for their fabrication. The hydrogel was fabricated by a straightforward reaction between CMC and ECH that are both biodegradable, relatively inexpensive, and largely available. This will have a positive impact on the hydrogel production cost. Because of the high absorption capacity of the new hydrogels and in particular, their superb absorbing potential in s-water, they could be suitable for applications such as diapers, feminine hygiene products, wound dressings, meat soaking pads, wiping papers, etc. This material could also serve as a feedstock for development of advanced bioabsorbents with new properties and applications.

### 3. CONCLUSIONS

A novel hydrogel has been prepared from cellulose as a renewable material with the objective of improving the inferior liquid absorption performance of bio-based superabsorbents currently available on the market. The process for fabrication of the new hydrogels is eco-friendly as it utilizes two inexpensive and biodegradable organic compounds, CMC and ECH. The raw material for CMC, bleached kraft pulp, was used without prior removal of the hemicellulose, which translates into a significant yield and cost advantages. In addition, no catalyst, pre- or post-purification, was required to produce the hydrogel. Although a maximum d-water absorbency of 725 g d-water/g gel attained was still lower than that of the commercial synthetic SAPs (1000 g d-water/g SAP), it was significantly larger than any other superabsorbent cellulose material reported in the literature. However, the maximum absorbency of 118 g s-water/g gel of the gel in s-water exceeded approximately 2.5 times the WRV of commercially available synthetic SAPs (40–50 g s-water/g SAP). Furthermore, the new hydrogels demonstrated excellent re-swelling potential as only 5–10% of the maximum water absorption capacity was lost after four consecutive times of gel recycling and reuse. The swelling properties of the gel can be controlled by CD, \( M_r \), carboxyl groups, and cationic charge. Because of their green nature and superior absorption capacity, especially in physiological saline solution, the newly developed hydrogels may be able to compete with synthetic SAPs in personal hygiene, pharmaceuticals, food applications, and other novel applications.

### 4. MATERIALS AND METHODS

#### 4.1. Materials

A kraft pulp mill in Canada supplied bleached softwood kraft pulp. Sodium monochloroacetate (MCA), epichlorohydrin (ECH), and hydrochloric acid (HCl) were purchased from Sigma-Aldrich (Mississauga, Ontario, Canada). Sodium hydroxide (NaOH) and ethanol (\( \text{C}_2\text{H}_5\text{OH} \))

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Figure 5. XRD of cross-linked cellulose hydrogels.
were supplied by Thermo Fisher Scientific (Whitby, Ontario, Canada). All chemicals were used as received.

4.2. Preparation of CMC. The carboxymethylation reaction was carried out in aqueous (water) media according to a previously reported method.40 Air-dried BSWK pulp (50 g) was mixed with 230 g of MCA solution (100 g of MCA in 130 g of water) in a Hobart mixer at room temperature for 10–15 min and then transferred into a Nalgene bottle. The Nalgene bottle was placed in a 50 °C preheated water bath for 4 h to allow impregnation of MCA into the fiber interior. Thereafter, a solution of NaOH (62.5 g of NaOH in 100 g of water) was added to the reaction mixture and agitated for 10–15 min in the Hobart mixer. The reaction was allowed to proceed overnight (12 h) at room temperature. After completing the reaction, the pulp was washed by 60 vol % ethanol, which assisted in coagulation and filtration of the cellulose fibers out of the pulp mixture. Finally, the CMC fibers were washed with 70% ethanol twice and dried at 50 °C in an oven.

4.3. Preparation of Hydrogels. Three weight-based CMC/ECH ratios of 0.5, 0.75, and 1.5 were maintained during hydrogel preparation. Different weight percent concentrations of CMC and ECH (Table 1) were added to a 6 wt % NaOH solution to form a cellulose suspension. For example, to prepare a hydrogel that had WRVs of 118 g s-water/g gel and 725 g d-water/g gel, 3 wt % CMC (containing 3.5 mmol of COOH groups/g cellulose) was mixed with 4 wt % ECH and 93 wt % of NaOH (at 6 wt % concentration). The suspension was stirred until the CMC fibers were fully mixed with the NaOH solution. ECH (Table 1) was then added slowly into the mixture and stirred at 100 rpm and room temperature for 20–30 min until the liquid turned into a

Figure 6. Optical microscopic images of (a) unmodified and (b) modified CMC fibers; SEM images of (c) unmodified and (d) modified CMC fibers; SEM image of (e) 50-fold and (f) 500-fold magnified best absorbing cross-linked hydrogel (WRVs of 725 g d-water/g gel and 118 g s-water/g gel).
highly viscous gel. The viscous gel was transferred into a heated bath at a temperature of 50 °C and allowed to perform the cross-linking reaction for 4–5 h. Thereafter, the cross-linked gel was diced into cubes (1 × 1 cm), immersed into excess d-water, and thoroughly washed to remove excess ECH. The d-water was changed several times until the water conductivity reached 700 S/cm. Finally, the gel was dried in an oven at 50–60 °C and then ground in a lab-scale, high-speed grinder to a particle size of 400–600 μm.

4.4. Characterization of Hydrogels. The carboxyl content of the CMC fibers and the cross-linked gels was determined using a conductometric titration method with a METER pH/conductivity S470-KIT (Mettler Toledo, Switzerland) titrator. A certain amount of CMC fibers and cross-linked gels (with a solid content of ~20 mg dry basis) and 2.5 mL of 0.02 M sodium chloride solution were added, and the mixture was sufficiently stirred to prepare a well-dispersed solution. Then, 0.1 M HCl was slowly added to the mixture to set the pH to 3. Then, the suspension was titrated with a 0.01 M NaOH solution at a rate of 0.1 mL/min until the mixture reached pH 11. The carboxyl group content of CMC fibers and the cross-linked gels was determined from the conductivity curves using the following equation (eq 1) \(^{31}\)

\[
[\text{COOH}]_g = \left(\frac{V_{\text{NaOH}} \times M_{\text{NaOH}}}{DW_g}\right) \quad (1)
\]

where \([\text{COOH}]_g\) is the carboxyl content of the CMC fibers or the cross-linked gels in mmol/g, \(V_{\text{NaOH}}\) is the volume of NaOH (mL) required for deprotonation of the carboxylic groups, \(M_{\text{NaOH}}\) is the molarity of NaOH (mol/L), and \(DW_g\) is the weight (g) of the dry CMC fibers/ gels initially dissolved in d-water.

The water retention value (WRV) of the cross-linked gels was measured by immersing the gels in d-water or 0.9 wt % NaCl aqueous solution (s-water). The swelling gels were withdrawn from the solution at each time interval and weighed out after removing the excess liquid from the surface of the gel. Excess d-water (or s-water) was removed by filtration using a 20 μm mesh nylon cloth. The free swell WRV, a measure of the dynamic water absorption properties of the gel, was calculated using eq 2: \(^{31,34}\)

\[
\text{WRV} = \left(\frac{W_t - W_d}{W_d}\right) \times 100 \quad (2)
\]

where \(W_t\) is the weight of the wet gel at time \(t\) and \(W_d\) is the weight of the dried gel.

To measure the water re-swelling kinetics, the hydrogel was first bone-dried in an oven at 50 °C for 12 h. Thereafter, 0.2 g of the dried gel was soaked in 200 mL of d-water at room temperature for up to 120 min. The WRV of the swollen gel was then measured according to eq. 2. The drying-soaking operation, described above, represented one re-swelling cycle. This re-swelling cycle was repeated four times using the same hydrogel.

The cross-linking density (CD) of the hydrogel is provided by the average molar mass (\(M_c\)) that is entrapped between any two cross-linking points contained in the gel. The CD value is inversely proportional to \(M_c\), therefore, the higher the \(M_c\), the lower the CD. The \(M_c\) value of any hydrogel can be calculated using a previously developed method \(^{35}\) based on the Flory–Huggins theory

\[
M_c = \frac{Q}{5/3(D_vV_f/(0.5 - X_f))} \quad (3)
\]

where \(Q\) is the equilibrium water absorption of the hydrogels, \(D_v\) is the density of the hydrogels, \(V_f\) is the molar volume of the solvent used for swelling, and \(X_f\) is the Flory–Huggins interaction parameter between solvents and hydrogels. Here, we assumed (as per the literature) \(^{31}\) a density of 1.5 g/cm\(^3\) of the hydrogel (density of cellulose) and \(X_f = 0\) because the volume fraction of methanol in water was 0 (the Flory–Huggins interaction parameter comes from the volume fractions of methanol in the methanol/water mixture).

The influence of ions (cations and anions obtained from NaCl, KCl, NH\(_4\)Cl, CaCl\(_2\), and AlCl\(_3\) salts) on the swelling capability of hydrogels (for 40 h) was studied as described by Rodrigues et al. \(^{44}\) The dimensionless salt sensitivity factor \((f)\) was calculated \(^{31,34}\) as follows (eq 4)

\[
f = 1 - \left(\frac{W_t}{W_s}\right) \quad (4)
\]

where \(W_t\) and \(W_s\) is the equilibrium swelling capacity in s- and d-water, respectively. All salts were used at concentrations of 0.08, 0.11, and 0.15 mol/L.

The particle size was measured with an optical microscope (Olympus CKX41, Olympus Corp., Tokyo, Japan). Solid-state \(^{13}\)C NMR spectra of the samples were obtained on a Varian/Agilent VNMR-S400 instrument operating at 100.5 MHz. Samples were packed uniformly inside a 7.5 mm zirconium rotor and spun at 5500 Hz. Spinning sidebands were suppressed using the TOSS sequence.

Fourier transform infrared spectroscopy (FTIR) measurements of the samples were performed on an FTIR spectrometer using a Bruker Tensor 37 (Bruker, Ettlingen, Germany) with a PIKE MIRacle Diamond attenuated total reflectance (ATR) accessory. Solid samples were placed directly on the ATR crystal. The maximum pressure was applied by lowering the tip of the pressure clamp using a rachet-type clutch mechanism. The sample spectra of all 32 scans were averaged (from 550 to 4000 cm\(^{-1}\)) with a resolution of 4 cm\(^{-1}\).

The crystalline properties of the cross-linked gels were examined by X-ray diffraction (XRD). The measurements were performed on a X’Pert Pro diffractometer (PANalytical B.V., Netherlands) with a PIXcel detector and K\(_\alpha\) radiation (\(\lambda = 1.54 \, \text{Å}\)). The X-ray diffractograms were acquired with a 2\(\theta\) (Bragg angle) range of 10°–30° at a scan rate of 0.005° s\(^{-1}\).

The crystallinity index (C.I.) of cellulose was calculated from the XRD spectra as follows \(^{31}\)

\[
\text{C. I.} = 100\left(\frac{I_{200} - I_{\text{Am}}}{I_{200}}\right) \quad (5)
\]

where \(I_{200}\) is the intensity of the (200) plane reflection, typically located around 2\(\theta = 22.6°\), and \(I_{\text{Am}}\) is the intensity at 2\(\theta = 18°\), corresponding to the minimum in a diffractogram. \(^{44}\)

Morphological changes in cellulose fibers were studied using Hoffman modulation contrast optical microscopy (HMC, Nikon Eclipse TE2000-U, Tokyo, Japan) and Hitachi Su-70 field emission scanning electron microscopy (SEM, Hitachi, Chiyoda, Tokyo, Japan). A few drops of 0.01% (w/v) toluidine blue solution were added to the fiber sample suspension at least 30 min prior to imaging for an optical microscopy measurement. For the SEM measurement, the gels were swollen to equilibrium in d- or s-water at 23 °C and neutral pH for 24 h and then freeze-dried using a LABCONCO FreezeZone 2.5 instrument (LABCONCO, Kansas City, USA). The freeze-dried samples were placed on double-sided carbon adhesive discs attached to aluminum specimen stubs and then sputter-
coated with gold to improve specimen conductivity. The images were taken at an accelerating voltage of 5 kV.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the Biorefining Research Institute (BRI) at Lakehead University. Special thanks to Mr. Michael Sorokopud at the Lakehead University Instrumentation Laboratory for the FTIR and SEM facility.

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