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Hydrothermally induced changes in the properties of MFC and characterization of the low molar mass degradation products

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Abstract The aim of this study was to determine hydrothermally induced changes in the physico-chemical properties of a fine microfibrillated cellulose (MFC). The MFC was prepared from a monocomponent endoglucanase-treated never-dried birch kraft pulp which had been run several times through a microfluidizer in order to obtain a sample substantially free from fibers or fiber fragments. The fine MFC was subjected to hydrothermal treatment at 150 °C for 0.5, 2.5, 4.5, 8.5 and 20.5 h, after which the viscosity, water-retention capacity, surface charge, discoloration and formation of hydrolysis products were determined. The viscosity, surface charge and water-retention capacity of MFC decreased as a result of the treatment but in oscillatory measurements the storage and loss moduli increased. Hydrothermal

treatment also caused discoloration of the sample which could not be fully washed away with water. Surface analysis with XPS revealed no significant changes in the surface structure of the dried MFC cakes but the filtrates after the hydrothermal treatment were complex mixtures of sugars, organic acids and furans. The main degradation products detected were xylose and xylobiose, but isomerization products of sugars (xylulose, fructose) were also found in the filtrates. In addition numerous organic acids, including formic, glycolic, lactic and xylonic acid, were identified in the filtrates, showing that both acid and alkaline catalyzed reactions occur due to dissociation of water into H^+ and OH^- .

Keywords Microfibrillated cellulose · Hydrothermal treatment · Hydrolysis · Degradation

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Introduction

Microfibrillated cellulose (MFC) has a vast potential as a rheological modifier, but many of the applications also require thermal stability, as MFC suspensions may be exposed to high temperatures under operating conditions. In the oil industry, for example, MFC could be applied in drilling, hydraulic fracturing and enhanced oil recovery (EOR) to bring the cuttings to the surface, to control fluid loss, to increase viscosity

and to enhance the proppant suspending ability. The operating temperatures in the oil industry may be above 100 °C and the time of exposure to heat are up to several days (Heggset et al. 2017). In the food industry, MFC has a potential as thickener and stabilizer, structure provider and oral feel improver but these properties may also be weakened by cooking or heating. Another application is in the heat sterilization of gels that relate to safety and purity which are important in food, pharmaceutical and cosmetics applications. MFC has a good biocompatibility, which makes it amenable in pharmaceutical and biomedical fields (Lin and Dufresne 2014) as in wound dressings (Hakkarainen et al. 2016) or as a scaffold for cellular culture, but there is a lack of information as to how hydrothermal exposure influences the physicochemical properties of MFC and the formation of hydrolysis products, and it is also important to understand at which temperatures and for how long MFC can provide support until an irreversible breakdown of the gel network takes place and the key properties are lost.

The hydrothermal stability of MFC gels has mostly been studied at temperatures below 100 °C. In the case of carboxymethylated MFC, the viscosity and storage and loss moduli were stable at temperatures of 5–50 °C (Naderi and Lindström 2016), but the viscosity of suspensions of chemically unmodified MFC and of CMC-grafted MFC decrease between temperatures of 5 and 80 °C (Herric et al. 1983; Iotti et al. 2011; Naderi and Lindström 2016). The results of oscillatory measurements are somewhat conflicting. Pääkkö et al. (2007) reported that storage and loss modulus of MFC were not affected by temperatures below 40 °C and that a slight increase in the moduli was observed at higher temperatures (50–80 °C). The concentration of the gel (1, 2 and 5.9 wt%) did not affect the results. On the other hand, Shafiei-Sabet et al. (2016) reported that the storage modulus decreased with increasing temperature (25–85 °C) and that the viscoelastic behavior became liquid-like at 85 °C. The effect of temperature on the storage modulus was more pronounced at a concentration of 2 wt% than at 1 wt%. Shafiei-Sabet et al. (2016) also reported that highly refined MFC showed thermoreversible properties, as the gel was able to recover its strength when the samples were cooled back to the initial conditions after heating.

The effects of high temperature (110–150 °C) and a long, 3-day treatment time on the viscosity of different nanocelluloses was studied by Heggset et al. (2017), who reported that the reduction of viscosity due to thermal treatment could be effectively controlled by the addition of cesium or sodium formate, probably because the formate acts as radical scavenger. Based on the amount of degradation products (furfural and 5-hydroxymethyl furfural) and the sample discoloration, it was estimated that chemically unmodified nanocelluloses were more thermally resistant than TEMPO-oxidized or carboxymethylated nanocelluloses (Heggset et al. 2017).

The aim of the present study was to find out how MFC gel prepared from enzymatically pretreated pulp can withstand hydrothermal treatment and what kinds of heat-initiated changes occur in the properties of MFC. Birch kraf pulp was chosen as raw material because of its high hemicellulose content which has been shown to facilitate fibrillation in previous studies (Iwamoto et al. 2008; Fall et al. 2014) and to compare it with dissolving pulp which was used in our previous study (Hiltunen et al. 2018). A temperature of 150 °C and a pressure of 4.5 bar were applied assuming that this temperature would be sufficiently high to initiate a change in the properties of MFC and to roughly imitate mid-range temperature of possible applications. The isothermal treatment times were 0, 0.5, 2.5, 4.5, 8.5 and 20.5 h. Changes in viscosity, visco-elastic behavior (G' , G''), water-retention capacity, surface charge and color were measured. The formation of low molar mass degradation products during the hydrothermal treatment was evaluated in order to obtain further information about the hydrolysis reactions occurring and about the chemical changes in MFC structure. Some experiments were also carried out with model compounds (xylose and glucose) to determine whether certain degradation products come from xylan or cellulose or both and to support the analysis of the degradation mechanisms under hydrothermal treatment.

Materials and methods

Enzymatic pre-treatment of pulp

A never-dried, elemental-chlorine-free (ECF) bleached birch kraft pulp (Stora Enso, Imatra) was ground to °SR = 22 in a Voith LR 40 laboratory-scale refiner (SEC ≈ 75 kWh/t) at a consistency of 4 wt%. After grinding, the pulp was treated enzymatically (at 4 wt% consistency) using a monocomponent endoglucanase (FiberCare R, Novozymes). The enzyme dosage was 2.2 mg/g_{pulp} and the pH was adjusted to 7.0 with a phosphate buffer (11 mM KH₂PO₄ + 9 mM Na₂HPO₄). The enzymatic treatment lasted for 120 min with the pulp suspension incubated at 45 °C on a water bath and mixed manually every 30 min. The enzyme was then deactivated by boiling (95–100 °C) the pulp suspension for 30 min, followed by a washing step with ion-exchanged water (conductivity of the pulp was adjusted with rinsing > 5 µS/cm) to remove the buffer solution and the deactivated enzyme protein.

Microfluidization of the pulp

The ground and enzyme-treated pulp was diluted to a consistency of 2.0 wt% and fibrillated using a microfluidizer (M-110EH-30, Microfluidics Corp.). The pulp was run twice through the device using two chambers connected in series with diameters of 400/200 µm and a pressure of 1100 bar and then three times using chambers connected in series with diameters of 200/100 µm and a pressure of 1500 bar (= coarse grade 5x). Subsequent passes were all made with 200/100 µm chambers connected in series and pressure of 1500 bar (Fig. 1). The pulp was diluted every fifth time with ion-exchanged water (approx. 0.5 wt% units) in order to facilitate the feed in fluidization.

Hydrothermal treatment of MFC and monosaccharides

The hydrothermal stability of MFC gel was investigated under static conditions in sealed metal containers (alloy C-276) having a volume of 0.2 L. The metal containers contained 150 g of 0.99 wt% MFC gel so that the containers were not totally full and a small air space existed above the surface. The containers were placed in an oven at room temperature (20 °C) and the oven was then heated to the reaction temperature of 150 °C during 11 min. The samples were kept in the oven for total times of 4, 6, 8, 12 and 24 h. The temperature and pressure in the containers were measured at the center of the container using suitable probes (Pt100 temperature sensor and pressure transmitter PCE-28 Aplisens Ltd). The samples reached the target temperature in 3 h 30 min and the isothermal times of the samples at the temperature of 150 °C were thus 0.5, 2.5, 4.5, 8.5 and 20.5 h. The pressure was approximately 4.5 bars. After heat treatment, samples were rapidly cooled to room temperature in an ice bath (0 °C) and the pH of the samples was measured after cooling to room temperature.

In the experiments with xylose and glucose, sugar solutions of 10 g/L were prepared using commercial grades of D-(+)-xylose (Sigma Aldrich ≥ 99%) and D-(+)-glucose (VWR, AnalaR Normapur). These monosaccharides were exposed to hydrothermal treatment at 150 °C as for MFC. Blank tests (0 h treatments) were made to check the presence of any indigenous impurities in the starting materials.

Optical microscopy and fibril staining

A small amount of fibrillated material was mixed with 7 drops of Pontamine Sky Blue (1 wt% solution) and 7 drops of Pontamine Orange 6 RN (1 wt% solution).

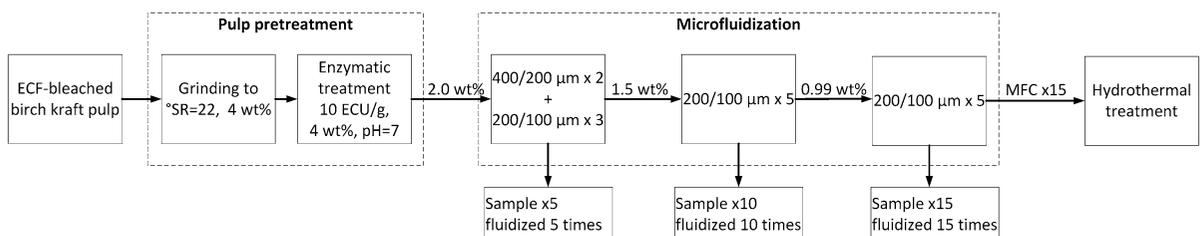


Fig. 1 A schematic flow diagram of the preparation of MFC gels

The mixture was heated in a water bath (75 °C) for 15 min and stirred occasionally using a glass rod. The samples were then cooled for 15 min to room temperature. With coarse MFC grade x5, excess of the staining chemicals was removed by rinsing the gel material with water through a wire with mesh of 70 (210 µm). With finer MFC gels x10 and x15 the rinsing was done only on a glass sheet just before the microscopy imaging using a Leica DM4000 M light microscope.

Rheology

The rheological properties of the gels were measured using a rheometer (Anton Paar Modular Compact Rheometer MCR 302) with a bob-cup geometry (concentric cylinders CC27) and at a temperature of 20 °C. The samples were first pre-sheared at 500 s⁻¹ for 1 min and then allowed to rest for 5 min, and the viscosities of the samples were measured at increasing shear rates of 0.1–1000 s⁻¹. The linear viscoelastic domain was determined using an angular frequency of 10 rad/s (1.59 Hz). A frequency sweep was performed at 100–0.1 rad/s by using a strains of 0.5 and 0.1%.

Water-retention value

The water-holding capacity of the MFC gel before and after hydrothermal treatment was determined using a centrifugal method based on Maloney (2015). Different quantities of MFC (0–13.6%) were mixed with a matrix pulp based on ECF-bleached and ground hardwood pulp from which fines had been removed using a mesh of 200 (75 µm). The matrix pulp had been converted to its proton form by mixing it with 12 mM HCl (pH = 2) for 30 min followed by rinsing with ion-exchanged water until the electric conductivity was <5 µS/cm. The pulp was then converted to its sodium form by mixing it for 30 min with 5 mM NaHCO₃ with the pH adjusted to 9.8 with NaOH. Finally, the pulp was rinsed again with ion-exchanged water in order to remove the excess salt to an electric conductivity was <5 µS/cm.

The MFC and matrix pulp were mixed at 1 wt% total solids content for 30 min. The suspension was then filtered on a qualitative filter paper 401 (12–15 µm) using a Büchner funnel, and the filtrate was recirculated on the filter paper to ensure that all

the MFC was captured in the matrix. The cake was finally rinsed with ion-exchanged water (100 mL). During filtration, the solids content of the filtrate was maintained between 10–15 wt%, which was found to be crucial to obtain reproducible results. The filtered, wet pad (MFC + pulp) was centrifuged for 15 min at 3100 g with constant acceleration and deceleration ramps. The dry grammage of the test pad during the centrifugation step was 1700 g/m² (pulp + MFC). After centrifugation, the samples were oven dried at 105 °C overnight. The water-retention capacity was calculated as:

$$WRV_{total} = \frac{m_{wet} - m_{dry}}{m_{dry}} \quad (1)$$

where m_{wet} is the mass of the centrifuged wet test pad (gel + pulp), and m_{dry} is the mass of the oven dried test pad = total mass of the sample.

UV–VIS spectroscopy and color

UV/VIS absorption spectra of MFC suspensions were obtained at wavelengths of 900–190 nm using a spectrophotometer (Jasco V-670). Ion-exchanged water was used as a blank and all measurements were performed using quartz crystal cuvettes. The concentrations of the different grades of MFC (microfluidized 5, 10 and 15 times) were adjusted to 0.99 wt%. The initial consistency of the gel in the hydrothermal treatment was 0.99 wt% and heat-treated gels were measured as affected by the hydrothermal treatment without any rinsing. All measurements were performed in triplicate.

The colour and brightness of dried MFC cakes were measured with an Elrepho instrument (Lorentzen & Wettre). The MFC cakes were prepared by vacuum filtration and the gels were rinsed with ion-exchanged water to remove water-soluble degradation products. Rinsing was continued until the electrical conductivity of the filtrate was close to that of the ion-exchanged water. The MFC cakes were then frozen and freeze-dried. The colour and brightness of the cakes were measured on a blotter, because the MFC cakes were not fully opaque. The values were calculated using D65/10° illuminant/observer conditions.

XPS

The samples for XPS analysis were prepared as a fibril cake by vacuum filtration. During the filtration, the gels were rinsed with ion-exchanged water in order to remove the water-soluble acids from the heat-treated gels, so that they would not give a signal during XPS analysis. The removal of the acids was monitored by measuring the electric conductivity of the filtrate. Before analysis, the fibril cakes were frozen at -18°C and freeze-dried.

Surface compositions of the dry fibril cakes were evaluated using the AXIS Ultra instrument (Kratos Analytical, U.K.). Samples were mounted on a sample holder using an ultrahigh vacuum-compatible carbon tape and pre-evacuated overnight. A fresh piece of pure cellulosic filter paper (Whatman) was analyzed as an in-situ reference with each sample batch (Johansson and Campbell 2004). Measurements were performed using monochromated Al K α irradiation at 100 W and under neutralization. Wide scans as well as high-resolution regions of C 1s and O 1s were recorded on several locations with a nominal analysis area of $400 \times 800 \mu\text{m}^2$. Analysis depth of the method is less than 5 nm. Data analysis was performed with CasaXPS, and binding energies in all spectra were charge-corrected using the main cellulosic C–O component at 286.7 eV as the reference (Beamson and Briggs 1992).

Polyelectrolyte titration

The surface charge of the MFC suspensions was determined by polyelectrolyte titration as described by Junka et al. (2013). Direct polyelectrolyte titration was chosen because of its better suitability for the material. The MFC gels were dispersed in deionized water at 1 g/l for 1 h and then diluted to 0.5 g/l. The pH and ionic strength were adjusted using 0.1 M NaOH, 0.1 M HCl and 1 M NaHCO₃. A known amount (10–30 mL: 0.1–0.5 g/L) of the MFC dispersion was titrated with a polydiallyldimethylammonium chloride (PDADMAC) solution (MW of 400–500 kDa, CD 6.19 meq/g, 0.25 or 1 meq/L, Sigma Aldrich Oy) or with a hexadimrine bromide (polybrene) solution (MW of 8 kDa, CD 5.34 meq/g, 0.25 or 1 meq/L, Sigma Aldrich Oy). The pH of the MFC dispersion was constantly measured and adjusted if necessary

before titration. Simultaneously, different amounts of the anionic 1 meq/L PES-Na (BTG Group) were titrated with cationic PDADMAC or polybrene in deionized water and solution from which pH and ionic strength had been adjusted to check the concentration of the titrants. The endocluvanase-treated pulps were titrated with the direct method described above. The surface charge of MFC was calculated based on the cationic demand.

Analysis of filtrates

Filtrates of hydrothermally treated samples were prepared by centrifuging the gel samples (30 min, 4900 g) and then filtering the supernatant once through a $0.45 \mu\text{m}$ PTFE syringe filter. It was difficult to separate water from the untreated sample by centrifugation and for this reason the non-heat-treated sample was first filtered through a cellulose fiber filter (12–15 μm) followed by trough syringe filters of $5 \mu\text{m}$ and $0.45 \mu\text{m}$.

Filtrates of MFC were analyzed for hydroxycarboxylic acids, sugars and other non-volatile hydroxy compounds by gas chromatography mass spectrometry (GC/MS), for formic and acetic acids by capillary electrophoresis (CE) and for furfural and its 5-hydroxymethyl derivative by liquid chromatography (HPLC). The hydrothermally treated sugar solutions were analyzed only by GC/MS. The sugar samples were also analyzed for phenolic compounds.

For GC/MS, 2 mL or 4 mL of MFC filtrates and 0.5 mL of xylose and glucose solutions were evaporated to dryness and trimethyl-silylated (Borrega et al. 2013) prior to the analyses with an Agilent 6890 gas chromatograph, equipped with an Agilent 5973 mass selective detector. For the separations, two similar capillary columns (both $30 \text{ m} \times 0.25 \text{ mm i.d.}$, phase thickness $0.25 \mu\text{m}$) were used, an RTX-5MS capillary column for MFC filtrates and DB-5MS column for the sugar samples. The applied temperature program was 1 min at 70°C , $10^{\circ}\text{C}/\text{min}$ to 300°C , and 11 min at 300°C . The injection volume was $1 \mu\text{L}$ and the split ratio was 50:1. The carrier gas was helium. The concentrations were calculated directly from the peak sizes, using xylitol as the internal standard. The MS identifications were based on the use of relevant literature e.g. (Niemelä 1990; Borrega et al. 2013), an inhouse MS library and commercial Wiley database.

For the analysis of the phenolic compounds in the hydrotreated sugar solutions, 5 mL liquor samples were extracted three times with 5 mL of diethyl ether, after addition of salicylic acid as the internal standard. The ether phases were combined, evaporated to dryness, and analysed by GC/MS (after trimethylsilylation), as described for the unfractionated sugar solutions.

For the capillary electrophoresis (CE) analyses, a P/ACE MDQ instrument equipped with a photodiode array UV–Vis detector working by indirect detection at a wavelength of 230 nm (Beckman–Coulter Inc., Fullerton, USA) was used (Keskinen et al. 2018). Commercial electrolyte solutions from Analis (Ceofix Anions 5) were used. A bare fused silica capillary with an inner diameter 75 μm was used, the detector length to the UV detector being 50 cm and the total length 60 cm. A separation voltage of 30 kV and polarity of positive to negative was applied. The samples were injected using 0.5 psi pressure for 8 s. For the quantification of formic and acetic acids, corresponding standard solutions were prepared and analysed prior to the actual samples.

The furfural compounds were quantified from the 0, 12 and 24 h samples using a HPLC-RI (Perkin Elmer, Flexar) system equipped with Aminex column (HPX-87H, 300 mm \times 7.8 mm; Bio-RAD) under isocratic conditions (50 °C) at a flow rate of 0.5 mL/min of 2.5 mM H₂SO₄.

Results and discussion

Optical microscopy

Optical microscopy images of the MFC samples after microfluidization cycles of 5, 10 and 15 times are shown in Fig. 2. The samples were stained with Simons' technique prior to the imaging to increase the contrast between the background and fibrillated material. The applied Simons' technique uses two different staining materials having different molar masses and different affinities to cellulose, causing unfibrillated fibers to stain predominantly blue while fibrils and fiber debris are stained orange (Yu et al. 1995). Figure 2 A shows that after 5 fluidization cycles the gel still contains some unfibrillated fiber fragments appearing with a light blue/green color. The estimated length of the coarse fraction consisting of fibers or

fiber fragments that have not been fully defibrillated was $\leq 200 \mu\text{m}$ and the width $< 15 \mu\text{m}$. Iwamoto et al. (2007), Saarinen et al. (2009) and Lahtinen et al. (2014) have previously stated that several passages are required to obtain a gel free from fibers or fiber fragments. After 10 fluidization cycles (Fig. 2b), the amount and size of fiber fragments are clearly reduced and after the highest number of fluidization cycles (Fig. 2c) unfibrillated fiber fragments are almost totally absent. The stained MFC gels appear as flocs rather than as evenly distributed fibrils. Differences in color density can also be seen and they are most pronounced with the most fibrillated gel. The affinity of the dye to the fibrils is affected by the size of the dye and its solubility to water. It is not clear whether the gel–dye interactions also play a role in the flocculation behavior or whether the different color densities are an artifact caused by entrapped dye molecules.

Rheological properties

Viscosities of the MFC gels determined after 5, 10 and 15 passes through the fluidizer are shown in Fig. 3. The viscosity increased with increasing number of passes through the fluidizer, but the difference in viscosity between 10 and 15 passes was rather small, especially at high shear rates ($>10 \text{ s}^{-1}$). Oscillatory measurements (Fig. 3) showed an increase in storage (G') and loss moduli (G'') between 5 and 10 passes but both the moduli stabilized at certain level between 10 and 15 passes. This confirms the results obtained by Grüneberger et al. (2014) and Colson et al. (2016) who compared viscosities of mechanically fibrillated samples and found a viscosity plateau after a certain number of mechanical fibrillation steps. Grüneberger et al. (2014) reported that the viscosity levelled off after 5–8 passes and Colson et al. (2016) reported a levelling off after 10–14 passes. Colson et al. (2016) also compared the viscosities of fibrillated samples with different fines contents (0–100%) and noticed that the samples having low amounts of fines (0–25%) had the highest viscosities, showing that the fibril length greatly affects the viscosity. It is assumed that the changes in the size, length and intermolecular interactions of the fibrils explain the observed changes in the gel strength also in the current study. It is probable that extended fluidization cycles not only

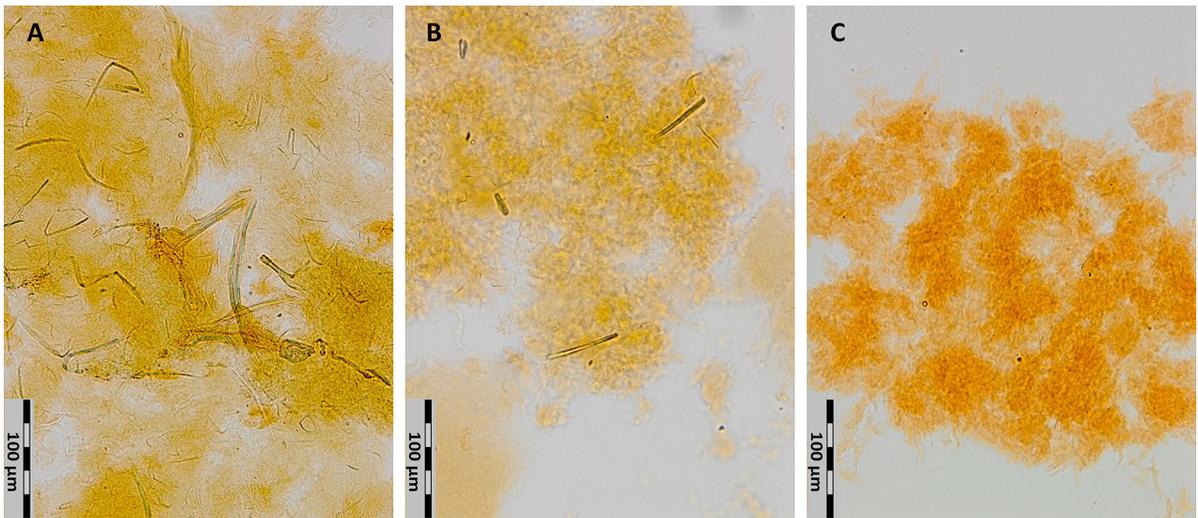
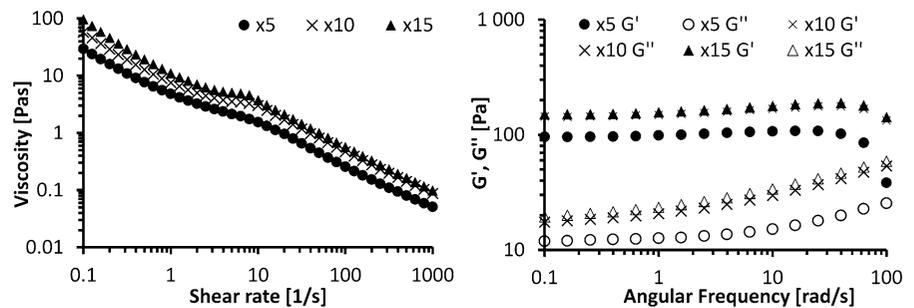


Fig. 2 Optical microscopy images of the gels they had been passed **a** 5, **b** 10, **c** 15 times through the fluidizer

Fig. 3 (Left) Viscosity of the gels as a function of increasing shear rate. The viscosities were measured at 20 °C and at gel consistency of 0.99 wt%. (Right) Storage (G') and loss moduli (G'') of the gels measured at 20 °C and at 0.99 wt consistency. The strain used was 0.5%



fibrillate or delaminate but also affect the length distribution of fibrils, and thus affect the rheology.

Figure 4 shows that the viscosity of the MFC suspensions after hydrothermal treatment at 150 °C decreased with increasing treatment time, and the hydrothermal treatment also caused the intermediate transition region shift to a higher shear rate suggesting

a change in the structure of the gel. Heggset et al. (2017) reported that the viscosity of chemically unmodified MFC decreased as a consequence of hydrothermal treatment, but the exposure time was extremely long (3 days). In our previous study (Hiltunen et al. 2018), the viscosity of fibrillated dissolving pulp remained practically constant even

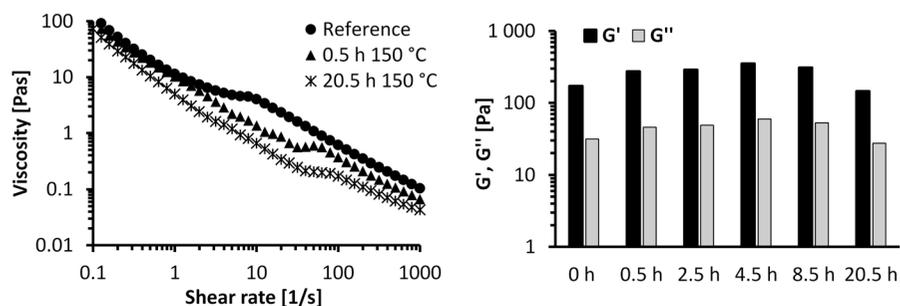


Fig. 4 (Left) Viscosities measured at 20 °C of MFC gels heat treated at 150 °C for 0, 0.5 and 20.5 h. (Right) Effect of hydrothermal treatment on storage (G') and loss moduli (G'') of MFC measured at 20 °C with a strain of 0.1% and angular frequency of 10 rad/s

after several hours at 150 °C. The raw material composition and the amount of hemicelluloses may affect the results. Part of the difference may also be related to consistency, as the interfibrillar network dominates at the higher solids content and small heat-initiated degradation does not cause as great a change in viscosity as at lower consistencies.

Both the storage (G') and loss (G'') moduli of the gels (Fig. 4), increased with treatment times from 0.5 to 8.5 h but had decreased after treatment for 20.5 h. The treatment may induce higher gel strength, because heat initiates hydrolysis of hemicelluloses and the release of degradation products into solution, reducing the electrostatic repulsion between the fibrils and changing MFC gel network behavior and flocculation. Contradictory results regarding the effects of hemicellulose content on MFC gel stability have been reported. Tenhunen et al. (2014) concluded that xylan played an important role as electrostatic stabilizer in dilute suspensions of MFC (0.05 wt%) but that the impact of xylan was less in more concentrated suspensions due to the stronger effect of network structure itself. Arola et al. (2013) found that removal of xylan from the NFC surface by enzymatic hydrolysis increased the storage modulus if the sample was not mixed during the hydrolysis, showing that removal of xylan may enhance the formation of a MFC network but that processing history affects the results. On the other hand, Pääkkönen et al. (2016) found that removal of hemicelluloses by cold alkali extraction gave a weaker and less elastic gel. The floc size may also change because the pH of the gels is lowered due to the formation of acidic degradation products (Tables 3 and 4). The pH of the untreated gel was 6.5 but after thermal treatment for 0.5 h and 20.5 h at 150 °C, the pH of the gel was 4.5 and 3.8 respectively. This may affect the dissociation of the charged groups (hexenuronic and glucuronic acids) and thus the electrostatic stabilization of the gel (Fall et al. 2011). After hydrothermal treatment for 20.5 h the rheological properties decreased, probably due to more extensive degradation of cellulose fibrils which reduced the chain length and entanglement between the fibrils.

Surface charge titration

Polyelectrolyte titrations were made with PDADMAC, MW 400–500 kDa, and polybrene, MW 8 kDa. The charge obtained by polyelectrolyte titration was measured at pH 6.5, 8.5 and 10.5. Figure 5 shows the effects of the number of passes through the fluidizer, the pH, and the choice of cationic polyelectrolyte on the charge values of the gels. The charge is calculated from the amount of accessible carboxyl groups on the surface of the gel sample divided by the total mass of the sample.

The surface charge or accessibility of the cationic polymers on the MFC gel increased initially with increasing number of passages through the fluidizer and is ascribed to the increase in surface area. The largest increase in surface charge was detected after the first five passages. The subsequent five passages (total number 10) also had an effect on the surface charge, but the next five (total 15) had only a minor effect. The surface charge of the untreated pulp before fluidization (0) was 6–11 $\mu\text{eq/g}$ depending on the pH, whereas that of the MFC after passage the fluidizer 15 times (x15) was 58–78 $\mu\text{eq/g}$. Similar observations concerning the effects of multiple passages through a fluidizer on the surface charge of carboxymethylated MFC were made by Junka et al. (2013).

The charge of the bleached birch kraft fibres arises mainly from hemicelluloses, methylglucuronic acid (pKa 3.3–3.5) and hexenuronic acid (pKa 3.1) (Sjöström 1989; Räsänen et al. 2001). Weaker acids such as carboxyls in lignin (pKa 5–6) and phenolic hydroxyl groups in lignin (pKa 8.6) contribute to the charge a lesser extent. The bleaching sequence determines the final charge of the pulp. In Fig. 5, the results for cationic PDADMAC (MW 400–400 kDa) and polybrene (MW 8 kDa) are almost the same, which suggests that both cationic polyelectrolytes can reach the same amount of charges on the fibril surfaces regardless of their different molecular weights. This is in line with the assumption that the charges are located on the fibril surfaces (Fall et al. 2011; Pääkkönen et al. 2016).

At pH 10.5 higher values are obtained for all the different passages through the fluidizer. Methylglucuronic and hexenuronic acid bound to fibrils dissociate in the pH 6.5–8.5 range giving an anionic charge to the fibrils. Theoretical calculations by Wågberg et al. (2008) showed that the surface potential of fibrils

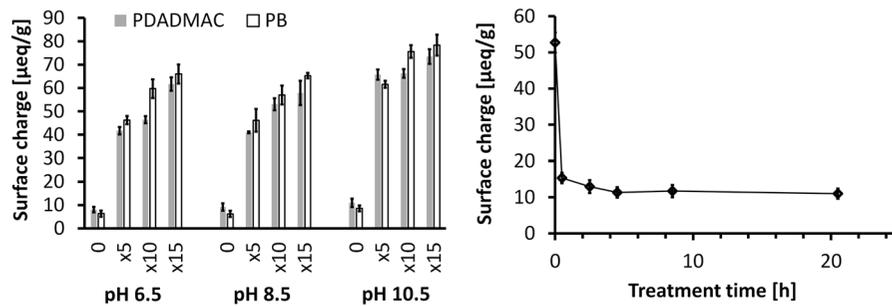


Fig. 5 (Left) Measured surface charges of the gels (after 0, 5, 10 or 15 passes through the fluidizer) at three different pH levels (6.5, 8.5 and 10.5). The NaHCO_3 concentration was 1 mM. (Right) Effect of hydrothermal treatment time on the surface

charge of the cellulose gel (fluidized 15 times). The surface charge was measured at pH 8.5 using 0.01 mM NaHCO_3 buffer. Error bars indicate standard deviation of the measurements

depends on the pH, salt concentration as well as on the size of the fibrils, and that a pH higher than 10 was required to dissociate all the charges of the MFC. In the current study, the excess amount of Na^+ ions from NaOH used to adjust the pH might affect the result but no such effect was seen when cationic PDADMAC was titrated with anionic PES-Na at pH 10.5. The dissociation of hydroxyl groups bound to cellulose could not explain this increase in surface charge, since according to Sjöström (1989), they are ionized only in the presence of strong alkali.

Figure 5 shows the surface charge results for the hydrothermally treated MFC samples. The results indicate that, after the first 0.5 h of thermal treatment, the surface charge was drastically reduced and that increasing the treatment time to 2.5–20.5 h, had no further effect on the surface charge. Due to the high temperature, rather low pH and long treatment times, it is possible that hexenuronic acids were removed from the fibril surface (Vuorinen et al. 2004).

Water retention

The water-retention values of MFC grades that were fibrillated 5 and 15 times are shown in Fig. 6. The water retention was measured using MFC/pulp mixtures and the MFC content varied between 0–13.6 wt%. With the coarser MFC (x5) the water retention increased relatively linearly with increasing MFC loadings but for finer grade (x15) the increase was almost exponential and the samples were difficult to dewater, especially with the highest MFC loadings (8.7 and 13.6 wt%). The water retention of the finer grade (x15) was higher than that of the coarser grade

(x5) in all cases, indicating that increased refining increased the water retention capacity.

The increase in water-retention capacity with increasing fibrillation has been reported in several studies (Turbak et al. 1983; Iwamoto et al. 2005; Spence et al. 2010), and Heric et al. (1983) suggested that water retention could be used as an indirect measure of the success of the fibrillation process. Recently, Gu et al. (2018) confirmed that there is a good correlation between water retention and fibrillation based on SEM- and TEM-imaging. The amount of accessible hydroxyl groups which can form hydrogen bonds with water increases, as well as the amount of accessible hemicelluloses and charges, and this gives rise to increased swelling. Typically, the amorphous parts of cellulose are more swollen than the crystalline parts. Part of the water holding-capability of MFC is related to system properties, as the MFC gel forms an interconnected network structure which can hold water between the fibrils (Maloney 2015).

Figure 6 shows the effect of hydrothermal treatment time on the water-retention capacity of MFC/pulp mixtures with MFC contents of 4.2 wt% and 13.6 wt%. The figure reveals that hydrothermal treatment reduces the water-retention capacity of the MFC/pulp mixtures, particularly with higher MFC loadings. Part of the decrease in water retention capacity is probably related to the decrease in surface charge of the fibrils. A clear correlation in the water-retention capacity of MFC with increasing hemicellulose content was observed by Pääkkönen et al. (2016) who suggested that the hemicelluloses affected the amount of water between the fibrils rather than the particle swelling. The pH is also known to affect the swelling of fibers.

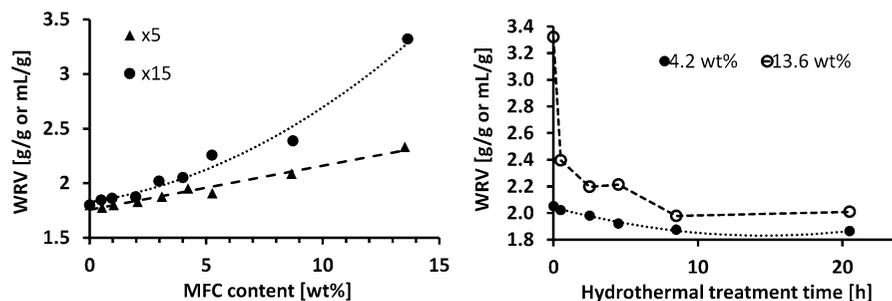


Fig. 6 (Left) Effect of refining on water retention (gels fluidized 5 and 15 times). The water retention was measured using MFC-pulp mixtures with varying MFC content of 0–

13.6%. (Right) Effect of hydrothermal treatment time (0–20.5 h at 150 °C) on water retention capacity with MFC contents of 4.2 wt% and 13.6 wt%

In addition, heat initiated aggregation of MFC that reduces surface area may also affect the water-retention capacity (Pönni et al. 2012, 2013; Silveira et al. 2016).

UV/VIS

Figure 7 presents UV/VIS absorption spectra from 300 to 800 nm of the fluidized samples. The light absorbance through the sample decreased with increasing number of fluidization cycles due to reduced light scattering. Similar results were obtained by Siró et al. (2011) who compared light transmittance of carboxymethylated MFC gels and dried films and noticed that in both cases the opacity (calculated from the UV absorbance spectra) decreased with increasing number of homogenization steps. An increase in light transmittance of carboxymethylated MFC films with increasing homogenization cycles from 1 to 10 was also reported by Aulin et al. (2010).

When the fine MFC gel was exposed to hydrothermal treatment, an increase in light absorbance at 600

nm was observed (Fig. 7). The greatest change in the UV/VIS spectra of the samples was observed between untreated gel (0 h) and the gel treated for the shortest time (0.5 h at 150 °C). This increase in light absorption may be due to changes in the particle size (agglomeration) or to chemical changes introducing light absorbing, functional groups or degradation products.

The discoloration of the gels could not be fully removed by rinsing the samples with ion-exchanged water, indicating that the chromophoric compounds were partly absorbed or chemically bound to the fibrils. Table 1 presents CIELAB color coordinates (CIE standard illuminant D65 and standard observer 10°) and brightness of the MFC cakes after they were rinsed with ion-exchange water and then dried. The hydrothermal treatment increased the yellowness (b^* values) and reduced the brightness.

Heat-initiated discoloration has previously been reported for wood and pulp and has been related to the reactions of hemicelluloses and lignin, but it seems that the discoloration is a result of several reactions, and there is no single factor that can explain most of

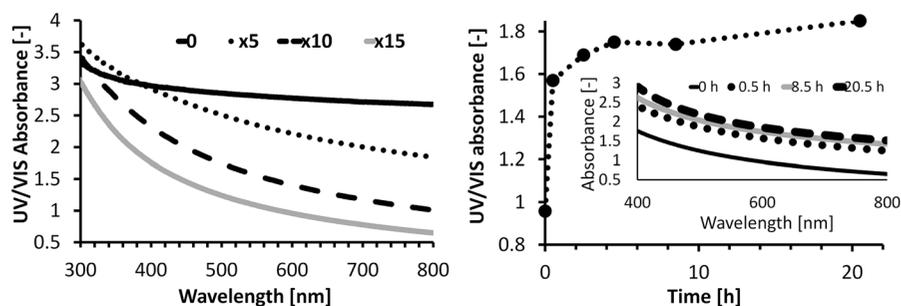


Fig. 7 (Left) UV/VIS absorbance of the fluidized samples (0–15 passes) measured at 0.99 wt% consistency. (Right) UV/VIS absorbance measured at a wavelength 600 nm of the MFC gel as

a function of hydrothermal treatment time at 150 °C and as a function of wavelength for treatment times of 0–20.5 h

Table 1 CIELAB color coordinates (CIE standard illuminant D65 and standard observer 10°) and brightness of the dried MFC cakes

Sample	L*	a*	b*	Brightness
	D65/10	D65/10	D65/10	R457 D65
0 h	95.72	- 0.43	0.68	88.55
0.5 h	94.91	- 0.33	1.5	85.61
2.5 h	94.83	- 0.26	1.73	85.1
4.5 h	94.1	- 0.16	2.28	82.74
8.5 h	92.56	0.34	4.14	77.01
20.5 h	86.61	1.49	6.69	62.06

the discoloration or can be used to control the undesired reactions (Beyer et al. 1999). The exposure of lignocellulosic material to a thermal or acidic stress initiates reactions which may lead to the formation of aromatic or unsaturated structures. For example, residual hexenuronic acids groups may first degrade into different furancarboxylic acids which are then further converted to aromatic structures (Sevastyanova et al. 2006; Rosenau et al. 2017). These chromophoric structures have been identified as bis(furano)-[1,4]benzoquinone and bis-(benzofurano)[1,4]benzoquinone -based mixed oligomers (Rosenau et al. 2017). In addition, hydrothermal treatment leads to degradation products such as sugars with reducing ends, organic acids, furans and aromatic structures which may themselves be chromophoric or the degradation products may act as precursors in the discoloration process (Adorjan et al. 2005; Beyer et al. 2006; Korntner et al. 2015). The degradation products may further go through complicated redox and condensation reactions leading to chromophoric compounds that have been shown to consist mainly of hydroxy-[1,4]-benzoquinones, hydroxy-[1,4]-naftoquinones and hydroxyacetophenones (Rosenau et al. 2004; Korntner et al. 2015). These compounds may bond to the cellulose matrix covalently or by adsorption (Rosenau et al. 2004) and cannot be removed by rinsing with water. Metal ions which are present in pulps may also promote the color formation and transition metal ions in particular have been associated with discoloration. In addition, the amount of oxidized structures in the material, as in the case of TEMPO-oxidated nanocellulose, have been shown to promote

discoloration under hydrothermal treatment (Heggset et al. 2017).

XPS

XPS surface spectra of all samples are shown in Fig. 8, together with the pure cellulose reference specimen. According to this data all treated fibril surfaces consisted of carbon and oxygen only, while similar backgrounds in carbon C 1s and oxygen O 1s indicate uniform and similar depth distributions for both elements (Tougaard 1998). Furthermore, the high resolution carbon C 1s peaks are all nearly identical to the pure cellulose spectra, with strong C–O and O–C–O features at 286.7 and 288.1 (Beamson and Briggs 1992) and no signs of oxidized surfaces or features that could have explained the discoloring. It should be noted that the analysis depth of XPS is less than 5 nm and it characterizes only the surface. Previously it has been reported that some of the chromophores formed from cellulosic materials by thermal or acidic stresses have high discoloration effect despite that they are formed in extremely low quantities and therefore require special methods to be identified (Rosenau et al. 2004; Korntner et al. 2015; Rosenau et al. 2017).

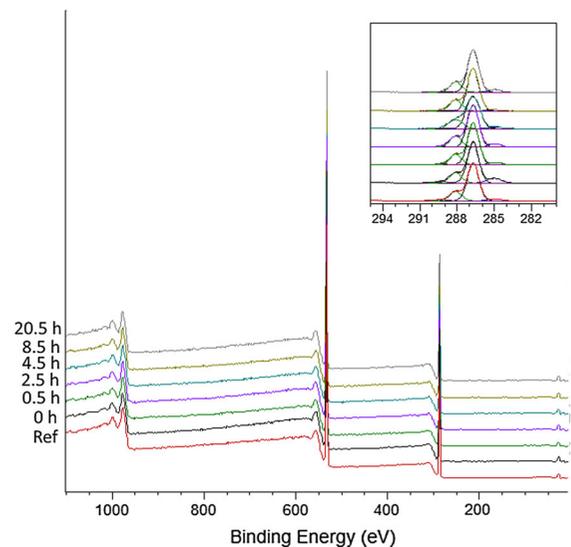


Fig. 8 XPS wide spectra of MFC films after hydrothermal treatment at 150 °C, together with data from a pure cellulose specimen (ash-free Whatman filter paper, used as the XPS in-situ reference also in this experiment). High resolution C 1s regions are depicted in the insert

Low molar mass degradation products in filtrates

The filtrates of the heat-treated gels were analyzed for the low molar mass sugars, carboxylic acids and furans. Sugars were the main hydrolysis products formed, xylose and xylobiose being the most abundant (Table 2), and the amount of sugars increased with increasing treatment time. In addition to the xylose and glucose, their isomerization products i.e. xylulose and fructose, were identified in the filtrates together with a number of sugar-type compounds that could only be partially characterised. Their mass spectra showed many ions characteristic of trimethylsilylated sugars but also ions (e.g. m/z 231 or 243) that suggest the presence of unknown modified structural features. Other typical degradation products identified were acetic and formic acids, furfural and 5-hydroxymethyl furfural, and numerous hydroxyacids including glycolic, lactic, 3-deoxy-pentonic, 3-deoxyhexonic and

xyloxy acids were found in small quantities. Many of these acids were also found after hydrothermolysis of birch wood (Borrega et al. 2013). However, 2-furan-carboxylic acid, 5-formyl-2-furan-carboxylic acid and reductic acid, that could have confirmed the degradation of hexenuronic acid groups, were not found in the filtrates (Teleman et al. 1996; Sevastyanova et al. 2006). In general, the acid concentration in the filtrates was low, which is partly explained by the low solids content of the MFC gel (0.99 wt%) exposed to hydrothermal treatment, and some of the degradation products may have been present in the concentrations below the detection limits. The formation of numerous organic acids explains the observed decrease in pH of the hydrothermally treated gels and the slight decrease in surface tension of the filtrates shown in Table 3.

These analyses reveal that the hydrothermal treatment of cellulosic materials is a complicated process and multiple reactions may occur including

Table 2 The main sugars, acids and furan compounds found in the filtrates (mg/g)

Compound	Treatment time (h) at 150 °C					
	0	0.5	2.5	4.5	8.5	20.5
Xylose	> 0.5	0.5	2.3	3.8	8.1	57.5
Xylulose				tr.	> 0.5	1
Glucose		> 0.5	> 0.5	0.5	0.5	3.1
Fructose					tr.	> 0.5
Other monosaccharides			> 0.5	> 0.5	> 0.5	1.2
Carbohydrate-type unknowns				tr.	> 0.5	1
Xylobiose		> 0.5	0.8	1.4	3.6	12
Xylotriose		tr.	> 0.5	> 0.5	0.9	1.4
Cellobiose	> 0.5	> 0.5	0.5	0.6	> 0.5	1.4
Formic acid		1.1	1.1	1.4	1.6	2.4
Acetic acid	> 0.5	> 0.5	> 0.5	> 0.5	0.5	0.7
Furfural	> 5	n.a.	n.a.	n.a.	> 5	10.3
5-Hydroxymethylfurfural	> 5	n.a.	n.a.	n.a.	> 5	> 5
Glycolic acid		> 0.5	0.5	0.5	> 0.5	1.3
Oxalic acid					tr.	> 0.5
Pyruvic acid						> 0.5
Lactic acid			> 0.5	> 0.5	> 0.5	> 0.5
Glyceric acid			> 0.5	> 0.5	> 0.5	> 0.5
2-Hydroxybutanoic acid				tr.	tr.	> 0.5
2,4-Dihydroxybutanoic acid			> 0.5	> 0.5	> 0.5	> 0.5
Threonic acid			> 0.5	> 0.5	tr.	> 0.5
3-Deoxypentonic acid (2 isomers)			> 0.5	> 0.5	> 0.5	1.4
3-Deoxyhexonic acid (2 isomers)			> 0.5	> 0.5	tr.	0.6
Xyloxy acid	> 0.5	> 0.5	> 0.5	> 0.5	> 0.5	0.8

n.a. not analyzed, *tr.* traces, empty cells indicate not reliably detected

Table 3 pH values of the heat-treated gels and surface tension of the filtrates (mN/m)

Sample	pH	γ (mN/m)
0	6.5	72.1
0.5	4.5	71.6
2.5	4.4	71.3
4.5	4.2	71.4
8.5	4.1	71.3
20.5	3.8	70.8

hydrolysis, degradation, dehydration, isomerization and possibly retro-aldol condensation. Hydrothermal treatment leads to products which can be observed after both acidic and alkaline conditions (Srokol et al. 2004). Hydrothermal treatment of aqueous cellulose suspensions typically leads to the depolymerization of cellulose and hemicellulose chains and the formation of soluble fragmentation products. Furan compounds, such as furfural (from xylose) and 5-hydroxymethyl furfural (from glucose) are well known dehydration products from sugars formed only by acid-catalyzed reactions. Isomerization reactions have long been known to occur in alkaline conditions, but relatively recent studies have found their presence also after severe ($T = 160\text{--}350\text{ }^\circ\text{C}$) hydrothermal treatment (Srokol et al. 2004; Aida et al. 2010; Lü and Shaka 2012; Borrega et al. 2013; Rasmussen et al. 2014). The isomerization of sugars may play an important role in the formation of degradation products as the isomerized forms are less stable than parent xylose or glucose. The organic (hydroxy)acids formed are partly the same as those formed under alkaline conditions but some of the organic acid formation may be through retro-aldol condensation of saccharides into reaction intermediates i.e. glycolaldehyde, glyceraldehyde and dihydroxyacetone and their further conversion into organic acids by benzilic acid type rearrangement, for example (Srokol et al. 2004; Aida et al. 2010).

Although many of the above mentioned degradation products can readily be traced selectively to the reactions of xylose and glucose, further information on the main sources is required for certain identified products. For that, commercial xylose and glucose samples were exposed to hydrothermal treatment as for MFC and the non-volatile degradation products were analyzed with GC-MS. Blank tests (0 h treatments) were made to check the presence of any indigenous impurities in the starting materials. The xylose material contained a small amount of pentoses

and hexoses (c. 1%). The pentoses clearly contained some arabinose, but lyxose or more probably ribose may also have been present. After the 24 h treatment, some lyxose was found, which may have been formed from xylose by isomerisation, via xylulose. The xylose materials also contained some glucose and other hexoses, apparently galactose and mannose. Some xylobiose was detected in the starting material, but not after the 24 h treatment. The glucose material did not contain any detectable amounts of pentoses or other hexoses but some hexose disaccharides (probably maltose) were present. They could not be found after the 24 h treatment.

A large number of degradation products were identified or partially characterised after the hydrothermal treatment of glucose and xylose at $150\text{ }^\circ\text{C}$ with a reaction time of 20.5 h (Table 4). The C2–C4 acids (such as glycolic acid, lactic acid and glyceric acid) were formed from both xylose and glucose, whereas those with five or six carbon atoms were more selectively formed from the different sugars: levulinic, 2-oxoglutaric and 3-deoxy-hexonic acids from glucose and 3-deoxy-pentonic and xylonic acids from xylose. Under alkaline conditions, 3-deoxypentonic acids are known to be formed also from glucose, but under the present conditions only 3-deoxy-hexonic acids were found.

Numerous sugar compounds were detected, the most abundant (apart from the starting materials) being isomerization products i.e. xylulose from xylose and fructose from glucose. The filtrates also contained several unknown sugar compounds, which were classified to different groups on the basis of their mass spectra and retention times. Sugar-type compounds may include anhydroglucoses (excluding levoglucosan) and some sugar-related compounds eluting between mono- and disaccharides, indicating that they contain more carbon atoms and hydroxy groups than normal monosaccharides and are probably condensation products. Alditol-type and other related compounds were formed especially from xylose. From glucose, their amount was very small. Their mass spectra highly resembled those of normal alditols, but in each case the spectra also contained intense ion peaks with the m/z values (e.g. 243) that are unusual for trimethylsilylated normal alditols. The disaccharide-type sugars and “unusual polyhydroxy compounds” eluted before xylobiose and cellobiose, but probably contained one sugar unit and another lower

Table 4 Products detected (mg/g) after hydrothermal treatment of xylose and glucose at 150 °C for 20.5 h

Compound or compound category	Xylose	Glucose
Glycolic acid	1.8	1.1
Oxalic acid	> 0.5	> 0.5
Lactic acid	0.5	> 0.5
Pyruvic acid	tr.	tr.
3-Hydroxypropanoic acid	0.5	> 0.5
Glyceric acid	0.5	> 0.5
2,4-Dihydroxybutanoic acid	> 0.5	> 0.5
Erythronic acid	> 0.5	tr.
Threonic acid	> 0.5	tr.
Levulinic acid	n.d.	0.4
2-Oxoglutaric acid	n.d.	tr.
3-Deoxy- <i>erythro</i> -pentonic acid	1.2	n.d.
3-Deoxy- <i>threo</i> -pentonic acid	2.9	n.d.
Xylonic acid	tr.	n.d.
3-Deoxyhexonic acid (3-4 isomers)	n.d.	5.7
Gluconic acid	n.d.	1.2
Tetroses	tr.	tr.
Xylulose	7	0
Other pentoses	7.1	0.6
Fructose	n.d.	19.8
Other hexoses	0.7	1
Unknown sugar-type compounds	3.9	6.6
Unknown alditol-type compounds	4.7	1.1
Disaccharide-type compounds	0.6	3
Unusual polyhydroxy compounds	0.9	12.7
Reductic acid	1.4	n.d.
5-Hydroxymethylfurfural	n.d.	32.8
2-Furancarboxylic acid	tr.	tr.
Catechol	tr.	tr.
Hydroquinone	n.d.	tr.
Methylcatechol(s)	tr.	tr.
3,4-Dihydroxybenzaldehyde	> 0.5	n.d.
Pyrogallol (1,2,3-benzenetriol)	n.d.	> 0.5
1,2,4-Benzenetriol	n.d.	2.7
Benzenetetrol	n.d.	> 0.5
3,8-Dihydroxy-2-methylchromone	tr.	n.d.
Unknown aromatic/phenolic compounds	0.5	> 0.5

n.d. not detected, *tr.* traces

fragment unit that remains unknown. The mass spectra of these unusual polyhydroxy compounds also contained ion peaks with even *m/z* numbers (548 or 568),

which is not typical for sugars or alditols. Deeper characterisation of most of the above mentioned compounds (as their trimethylsilyl derivatives) is also hampered by difficulties in confirming their molecular weights.

Some other cyclic carbohydrate-derived compounds were also found (Table 4). Of them, reductic acid (2,3-dihydroxy-2-cyclopenten-1-one) is a known product from pentoses and furfural (Feather and Harris 1973) and 5-hydroxymethylfurfural is a well-known product from hexose sugars, but 2-furancarboxylic acid was here found (in trace amounts only) to be formed from both xylose and glucose.

The hydrothermal treatment at 150 °C for 20.5 h led to discoloration of the monosaccharide solutions and an ether extracts were therefore analyzed for possible aromatic compounds. The aromatic compounds from xylose included catechol, its 3- and 4-methyl derivatives, 3,4-dihydroxybenzaldehyde, and 3,8-dihydroxy-2-methylchromone, all formed in trace amounts only. Of these, the chromone compound is a characteristic product from mild acidic treatment of xylose and hexuronic acids (Popoff and Theander 1972). In addition, at least five other (unknown) phenolic compounds were found but no final structures can yet be suggested for them (the molecular weights of their trimethylsilyl derivatives vary from 336 to 472), some of which were also found by Borrega et al. (2013) after birch wood hydrothermolysis. From glucose, the dominating phenolic compound was 1,2,4-benzenetriol which is a well known aromatisation product of 5-hydroxy-methylfurfural (Luijckx et al. 1991). Small amounts of pyrogallol (1,2,3-benzenetriol) were also found, but its route of formation is not that clear. In addition, small amounts of a benzenetetrol were formed, but its full structure could not be established.

Conclusions

Hydrothermal treatment of highly fibrillated MFC leads to relatively rapid changes in the properties of the gel with a decrease in water retention capacity, viscosity and charge of the material. Changes were seen already after the shortest treatment time (0.5 h isothermal time, 4 h total heating time). The charged groups were not thermostable, as a drastic decrease in surface charge was observed. The storage and loss

moduli instead increased with reaction times of 0.5–8.5 h. Most of the changes are probably related to the heat-initiated hydrolysis of hemicelluloses which affect electrostatic repulsion between the fibrils, flocculation and swelling of the fibrils. The pH of the gels also decreased, indicating the formation of acidic compounds. Analysis of the low-molar mass hydrolysis products revealed that numerous degradation products are formed, typically in small or in trace amounts. The main identified products were sugars and numerous (hydroxy)carboxylic acids. The experiments with xylose and glucose showed that C2–C4 acids (such as glycolic, lactic and glyceric acids) were formed from both xylose and glucose, whereas those with five or six carbon atoms were more selectively formed from xylose or glucose. The filtrates also contained trace amounts of sugar-type compounds having more carbon atoms than their parent compounds, indicating the occurrence of condensation reactions that are currently poorly known. Hydrothermal treatment also led to an increase in the UV/VIS absorption spectra of the gels and yellowing of dried MFC cakes, but XPS surface analysis of the cakes did not reveal any significant changes in their surface properties. Part of the discoloration may be due to the formation of aromatic structures such as 1,2,4-benzotriol which were identified in the experiments on xylose and glucose.

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