Microspheres and Nanorods Produced in the Dissolution of Mildly Carboxylated Cellulose Fibers in Alkaline Solutions

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Abstract

A mild etherification of spruce kraft pulp was performed to introduce 1.3 and 2.5 mmol/g carboxyl groups on cellulose chains. 1.3 mmol/g carboxymethyl fibers (CMF) were dissolved partially in alkaline water to form balloons and collars on the tracheid and their ultra-structure was investigated. Primary wall, expanded S1, swollen S2, wrinkled S3, spiral bands of S1, parallel microfibrils of S2 and their transverse splitting were observed on swollen fibers. It is indicated that balloons, collars and wrinkled S3 were formed due to different cellulose microfibril features in different layers of tracheid cell wall. Microspheres with a size up to about 0.6 μm were observed by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). It is shown that they originated from transverse splitting of S2 microfibrils and contain bundles of well-known cellulose nanocrystals (CNC). After homogenization and sonication of an aqueous dispersion of 2.5 mmol/g CMF, electroacoustic spectroscopy showed the presence of nanorods with a size distribution of 18-208 nm. Similar sizes were observed by TEM.

Introduction

The wood cell wall is a heterogeneous structure and is mainly composed of structural polysaccharides of cellulose and hemicellulose, and a non-structured lignin matrix. These materials are distributed in the cell wall with different concentrations in the three main regions of the cell wall: middle lamella (ML), primary wall (PW), and secondary wall (SW). The highly lignified ML acts as a glue between two or more cells in wood. The PW is very thin and indistinguishable from ML so that the term compound middle lamellae (CML) is often used for the ML and two adjacent PWs. However, PW contains cellulose in the form of microfibrils which are interwoven randomly (Rowell 2012) and is made up of mostly cellulose β (Stevanic and Salmén 2008). The SW can be subdivided into three layers: a thin outer layer (S1), a thick middle layer (S2) and a thin inner spiral layer (S3). Cellulose is present in the SW in the form of co-axial microfibrils arranged in parallel lamellae in a number of orientations which have hemicellulose and lignin embedded in them (Roberts 2007). Figure 1 shows a schematic of wood cell wall layers and in Table 1 the chemical compounds, thickness, microfibril angle (MFA) and their patterns in different layers are summarized. The MFA has been reported to have a great influence on mechanical properties of wood (Cave 1968; Megraw 1985; Cave and walker 1994) and paper (Kellogg and WG 1975; Armstrong et al. 1977; Watson and Dadswell 2017) as well as on fibers individually (Page et al. 1977). Furthermore, the shrinkage and swelling differences of wood and individual fibres in different directions is specifically ascribed to the MFA (Harris and Meylan 1965; Barrett et al. 1972; Boyd 1974; Watanabe and Norimoto 1994; Ying 1994).

After kraft pulping and bleaching, almost all the lignin and a great part of hemicellulose are removed leaving cellulose-rich cells (Roberts 2007). Carboxymethylation of such pulp would increase water absorption and swelling of the cell. With increasing the extent of carboxymethylation, the structure of secondary wood cell wall changes, creating features called 'balloons' and 'collars'. The formation mechanism and morphology of balloons have been explained by Sim et al. (Sim et al. 2014; Sim and van

Loading [MathJax]/jax/output/CommonHTML/jax.js diameter increases with an increase in carboxyl charge

density, but at or above 3 mmol/g, balloons break apart into smaller particles and dissolved carboxylated cellulose (Yang et al. 2012).

In this study bleached spruce kraft pulp was chemically analysed, mild etherification reactions were applied, and an X-ray diffraction analysis was performed to determine changes in crystallinity. After dispersing 1.3 mmol/g carboxymethyl fibers (CMF) in alkaline water, the morphology of balloons, collars, PW, expanded S1, swollen S2, wrinkled S3, spiral bands of S1, parallel microfibrils of S2 and their transverse splitting were observed on swollen tracheids and the reasons of their formation are discussed and ascribed mostly to the MFA. The origin and the formation mechanism of microspheres which were observed by SEM and TEM were then elucidated and the particle size was measured by electroacoustic spectroscopy. After dispersing the 2.5 mmol/g carboxymethylated fibers (CMF) in water, the particle size distribution was measured by electroacoustic spectroscopy and carboxylated cellulose nanocrystals (CNCs) were observed by TEM. Nanocellulose particles can be produced solely by mechanical forces (Zimmermann et al. 2004; Hietala et al. 2016; Mendoza et al. 2019), but because this is highly energy consuming, some chemical or enzymatic pretreatments have been established, which decrease the energy consumption, as well as the fiber damage (Jiang et al. 2017; Hu et al. 2018). The most common chemical pretreatment is by applying 2,2,6,6-Tetramethylpiperidine-1-oxyl known as TEMPO-mediated oxidation, which produces carboxylated nanofiber (CNF) with limited carboxyl charges (0.8–1.7 mmol/g), as only the C6 hydroxyl groups are carboxylated (Mendoza et al. 2020; Isogai et al. 2020). For the production of carboxylated nanocellulose, the TEMPO method creates thin nanofibrils with uniform sizes. However, the cost of production is very high (Nelson et al. 2016). In this study it is shown that by a facile mildly etherification reaction, carboxylated nanocrystals (CNC) are produced.

Table 1

Chemical composition, thickness and microfibril features of the Tracheid cell wall layers (Rowell 2012; Huang et al. 2003)

Tracheid layer		cellulose %	hemicellulose %	lignin %	thickness μm	microfibril pattern	microfibril angle °
ML	CML	0.7	1.4	8.4	0.1–0.2	interwoven	-
PW							0–90
S1		6.1	3.7	10.5	0.1–0.3	helical	50–70
S2		32.7	18.4	9.1	1–2 (early wood) 3–5 (late wood)	parallel	5–30
S3		0.8	5.2	-	0.1	helical	+ 70

Material And Methods

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Materials

Bleached spruce kraft pulp from Resolute Forest Products was ground by GlenMills-SM300. Potassium dichromate ($K_2Cr_2O_7$), ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2$), sodium monochloroacetate ($C_2H_2ClNaO_2$), sodium hydroxide (NaOH), sodium bicarbonate ($NaHCO_3$), potassium permanganate ($KMnO_4$), sodium thiosulfate ($Na_2S_2O_3$), potassium iodide (KI), sulfuric acid, hydrochloric acid, ethanol and isopropyl alcohol were purchased from Sigma-Aldrich. Conductometric titrations were done using milli-Q water (resistivity $\sim 18.2 M\Omega cm$).

Cellulose, hemicellulose, lignin, and ash determination

Cellulose and hemicellulose content of the kraft pulp was measured using TAPPI standard, T 203 cm-99. Lignin and ash content were measured by TAPPI standards T 222 and T11 om-02.

Carboxymethylation reaction

Carboxymethylation reaction was performed as reported previously (Moradian et al. 2021) to produce 1.3 and 2.5 mmol/g (DS: 0.25 and 0.56) carboxyl charge densities. Briefly, two set of 20 g ground pulp and 220 g isopropyl alcohol were put into two glass bottles and placed into two 45 °C water bath while stirring (150 rpm). 6.5 and 9.5 g sodium hydroxide dissolved in 12 and 14 g water respectively and added to each bottle and left for 60 min. Then, 5.3 and 7.8 g sodium chloroacetate dissolved in 10 and 12 g water respectively and added to the bottles, and the temperature was raised to 55 °C and left for more 120 min. Afterwards, CMFs were filtered on 20 μm nylon screens, and washed by 300 mL of 50% ethanol two times for 10 min. Lastly the filtered CMFs were air-dried and kept in plastic bags.

Carboxyl content and degree of substitution (DS)

The carboxyl content was calculated by conductometric titration as reported previously (Moradian et al. 2021). DS was measured by the following Eq. (1):

$$DS = \frac{162 \times C \times (V_2 - V_1)}{\omega - (111 \times C \times (V_2 - V_1))} \times 100 \quad (1)$$

where V_1 and V_2 are the volume of NaOH required to neutralise the carboxylic acid, C is the molarity of sodium hydroxide, ω is the weight of dry CMF, and 111 is the molar mass difference of 2,3,6-tricarboxycellulose and anhydroglucose unit (Mendoza et al. 2020).

FTIR and X-ray diffraction (XRD)

FTIR analysis was carried out by a Perkin-Elmer spectrometer (single diamond ATR) ranging from 400–4000 cm^{-1} wave number. The spectrum was obtained by combining 50 scans with a resolution of 4 cm^{-1} .

XRD measurements for the kraft pulp, CMFs powders and regenerated films (after dissolution in

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Advanced diffractometer using CuK α radiation of 1.54178 Å,

with a LYNXEYE linear position sensitive detector (Bruker AXS, Madison, WI), and 5° to 35° 2θ range with a step interval of 0.02° with a 0.200 scanning speed.

Optical, FE-SEM and TEM microscopy

Optical microscopy on swollen fibers was done by Hoffman modulation contrast light microscopy (HMC; Nikon Eclipse TE2000-U). For field emission scanning electron microscopy (FE-SEM) a film of 1.3 mmol/g carboxylated fiber was sputter-coated about 5 nm with Platinum and observed by high resolution FE-SEM (FEI Inspect, F-50) at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) observations of CMF particles were performed with an FEI Tecnai 12 Biotwin operating at 120 kV. For TEM sample preparation, a suspension of 0.05 % CMF was sonicated by an ultrasonic processor (Hielscher UP200H, Germany) for 1 min while in an ice bath. Then, 1 microliter of the suspension was placed on a copper – carbon grid for 3 min, then the droplet on the grid was blotted away with a filter paper (Whatman, Inc., Canada). 1 microliter of 1% Uranyl acetate solution was placed on the copper – carbon grid for 10 second before blotted away by the filter paper.

Electroacoustic measurement

To study the size distribution of particles in suspended CMF, an Acoustic and Electroacoustic Spectrometer DT-1202 (Dispersion Technology, Bedford Hills, NY, USA) was used. The acoustic and electroacoustic sensors of the instrument measure the ultrasound attenuation at 1-100 MHz, sound speed at 10 MHz, magnitude and colloid vibration current, and the colloid particle sizes. This method is described comprehensively by Dukhin and Goetz (Dukhin and Goetz 2017).

Results And Discussion

Composition of kraft pulp

Table 2 shows the chemical composition of the kraft pulp used as well as its initial carboxyl group content. The pulp mostly consists of α cellulose, a low amount of β cellulose (degraded cellulose), a considerable amount of γ cellulose (hemicellulose), very little lignin and ash content, and a very low carboxyl group content.

Table 2
kraft pulp compositions.

α cellulose %	β cellulose %	γ cellulose %	Lignin %	Ash %	Carboxyl group mmol/g
86.8	0.91	12.3	0.14	0.20	0.06

Optical microscopy

Figure 2 shows the optical microscopy of swollen tracheid subjected to 1.3 mmol/g carboxymethylation and partial dissolution in 5% sodium hydroxide. Therefore, some regions along the tracheid cell would swell and form balloons while not-swollen parts remain as collars between them (part a). According to Fig. 2 (b and c), where the primary wall is broken, the secondary wall is able to swell. The membrane of balloons is composed of S1 and the swollen interior component is S2 (part d). When cellulose microfibrils absorb water, they mostly swell perpendicular to their axis. The direction of arrows in Fig. 1 is the direction of expansion layers of a wood cell wall. Despite the fact that the primary wall layer is thin and the cellulose amount is very low, because the microfibrils in this wall are interwoven randomly, it cannot swell considerably and wraps around the SW unless it is broken apart either by a sufficient internal swelling force or by external mechanical action. S1, with 5–20 nm lignin-free voids (Kesari et al. 2021), is also very thin, however it has enough cellulose in the form of helical microfibrils (50–80° in Norway spruce) to render it highly flexible with an enormous expansion capability. Brändström et al. (2003) indicated that the S1 layer of Norway spruce is a homogeneous layer oriented approximately perpendicular to the tracheid axis without a cross fibrillar structure in alternate S (clockwise) and Z (anticlockwise) helices. The transition of microfibril orientation from S1 to S2 is abrupt.

S2 on the other hand, is very thick (represents 80% of total cell wall in spruce (Fengel 1973)) and is composed of several lamellae and a lot of cellulose microfibrils with a very low angle (5–30°); it accounts for most of the physical and mechanical properties of the cell and wood such as shrinkage and swelling. Generally, the longitudinal shrinkage of wood is very low (0.1–0.2%) while the radial and tangential shrinkage of wood are much higher (black spruce has 4.1 and 6.8% shrinkage respectively) which is due to the low S2 angle of microfibrils (Glass and Zelinka 2021). Balloons and more specifically S2 swell transversely for the same reason and the swelling may be so large to cause S1 to break (Fig. 3, d), leading to the dispersion of S2 microfibrils, or when the carboxyl charge is sufficiently high, to their dissolution.

S1 constitutes a small portion of cellulose and, when swollen, appears as a skin and sometimes it has one or more spiral bands of highly crystalline cellulose which are more difficult to dissolve than the rest of secondary layer (Fig. 2, f and g). Spiral bands are also nearly insoluble in Schweizer's solution and do not dissolve in nitrate and acetate and appear in viscose solutions too (Hagglund 1951). S1 in black spruce has three parallel running threads of such spiral bands, connected by delicate membranes consisting of fibrils that are nearly perpendicular to the edge of spirals (Hagglund 1951). A double spiral band of S1 layer without opposite directions was observed in Norway spruce by Brandstrom et al. (Brändström et al. 2003).

The innermost layer of SW is S3 with the highest concentration of cellulose in the form of microfibrils with a more than 70° angle. When the thin S3 expands in the direction depicted in Fig. 1, it has not enough space and would bend and wrinkle in the lumen (Fig. 2, e and h).

Microfibrils of S2, along to the tracheid axis are barely visible in high magnification optical microscopy (Fig. 2, i), while transverse splitting of layers is shown clearly (Fig. 2, d and j). Nevertheless, parallel

microfibrils of S2 are readily observed by FE-SEM (Fig. 3, a). Transverse splitting of microfibrils can create microspheres discussed in the following section.

FE-SEM and TEM microscopy

The scanning electron microscopy images of films made with 1.3 mmol/g CMF are shown in Fig. 3, a, b, and c). To make films, CMF was dissolved in an alkaline solution, casted in molds and regenerated in a 10% sulfuric acid bath, then washed and dried. More details about film making and measuring the undissolved portion of CMF were described in our previous study (Moradian et al. 2021). This CMF contained 6.5% of undissolved fiber particles; an image of a piece of undissolved tracheid cell wall shows S2 parallel microfibrils (Fig. 3, a).

Transverse splitting of microfibrils can create plenty of microspheres observed on the surface of the films (Fig. 4, b and c). After the etherification reaction, fibers can absorb lots of water, balloons form and microfibrils expand transversely while cross splits are created that can be observed by optical microscopy (Fig. 2, j). When the carboxyl charge density is low, some parts of fibers do not swell and appear as collars between balloons. More charge density results in less collars in swollen fibers and hence less undissolved fibers will remain in the suspension. At a charge density of 2.5 mmol/g, no undissolved particles and collars were observed in water dispersed CMF by optical microscopy, while microspheres could be observed by transmission electron microscopy (Fig. 4, d). Microspheres can be broken up in smaller pieces (nanoparticles) by applying a shear force and/or sonication, which can be weaker if the alkalinity is increased. Figure 4, e, shows the TEM image of a homogenized (3 min, 10,000 RPM) and sonicated (2 min, 50 Hz) 1% water solution of 2.5 mmol/g CMF. It can clearly be seen that the microspheres were broken up into nanorods.

FTIR and XRD analysis

The FTIR spectra of kraft pulp, CMFs, and the regenerated film are shown in Fig. 4 (top). For the original kraft pulp, both CMFs and film, the OH and CH absorption bands were appeared in the ranges around 3330 and 2900 cm^{-1} respectively. However, the peaks at 1600 and 1730 cm^{-1} represent carbonyl groups in sodium and proton forms on CMFs and the film respectively proving the successful carboxymethylation reactions. Figure 2 (bottom) shows the X-ray diffraction pattern of kraft pulp, CMFs with 1.3 and 2.5 mmol/g carboxyl groups and the regenerated film. The kraft pulp peaks appear at around $2\theta = 15^\circ$, 16.5° , and 22.5° representing (110), (110), and (200) crystallographic planes of cellulose β , respectively (French 2014, 2020, Yang et al. 2012). After carboxymethylation reaction both CMFs and the regenerated film show cellulose II structure (Langan et al. 2001, Yang et al. 2012). The main peak of CMFs is at $2\theta = 20.4^\circ$ representing (110) crystallographic plane while peak at about 22.5° (020) is most likely too small to be seen. Generally, carboxymethylation would decrease the crystallinity of cellulose, thus 2.5 mmol/g CMF showed less intense peaks than 1.3 mmol/g CMF (Rachtanapun et al. 2012). Presumably the S2 layer (the main component of a fiber) inside the balloons is partially dissolved and when drying into a powder is regenerated into Cellulose II. The regenerated film made with 1.3

mmol/g CMF showed the highest intensity at about 11.5° representing (110) crystallographic plane, similar to regenerated cellulose made by Yang et al. 2012.

Electroacoustic spectroscopy

The size distribution of cellulose nanocrystals with 2.5 mmol/g was measured by acoustic attenuation spectroscopy and it was found that 99% of the particles were in the range 18–208 nm, as shown in Fig. 5 and Table 3. The size distribution of cellulose nanocrystals with 1.3 mmol/g, after separation of undissolved fiber fragments by centrifugation (5 min, 1000 RPM), ranged from 27–613 nm (Fig. 5, Table 3).

Table 3
Cumulative particles size of 1% CMF suspensions with 1.3 and 2.5 mmol/g carboxyl groups

cumulative %		1	3	5	10	50	75	90	95	99
cumulative	1.3 mmol/g CMF	27	36	42	54	126	200	295	384	613
size (nm)	2.5 mmol/g CMF	18	23	26	31	60	86	117	144	208

Microspheres

S2 is considerably thicker than other layers of a tracheid cell wall and consists of a large number of very thin concentric lamellae. The thickness of individual lamella when very much swollen is about 1µm. Mechanical, chemical treatment or a combination of both, would disintegrate lamellae into long fibrils or bundles of fibrils (Hagglund 1951). Dolmetsch et. al (1944) have reported that a transverse splitting of lamellae would happen when acid treatment of fibers is followed by sodium hydroxide treatment. The thickness of transverse cleavage was reported 1–2 µm depending on the wood species and type of cell (Fig. 6). When the cleaved microfibrils disperse in a solution, elliptical and round particles are observed. The diameter of round particles of spruce was reported 0.6 µm (Dolmetsch et al. 1944; Hagglund 1951). Microspheres are micro-units into which the S2 microfibrils can be disassembled.

In our study it was observed that etherification of spruce tracheid and dispersion in water similarly, splits the fibrils transversely and produces microspherical fragments (Fig. 4). Furthermore, microspheres of carboxylated cellulose contain bundles of nanorods that can be dispersed to cellulose nanocrystals by mechanical action and/or by mixing with a sodium hydroxide solution. The higher the carboxyl charge, the less shear force and/or sodium hydroxide is necessary for producing carboxylated CNC.

Conclusions

In this study a mild carboxymethylation of spruce kraft pulp was performed to produce 1.3 mmol/g CMF. After swelling in an alkaline water, some balloons and cell wall components were observed and ultrastructures were investigated. It was concluded that random orientation of microfibrils in the primary wall prevents fiber swelling but instead leads to collars, while S2 swelled greatly at locations where the

primary wall fibrils were broken. S1 forms the membrane of the balloons due to its near longitudinal expansion perpendicular to the orientation of microfibrils. Similarly, S3 has a high microfibrillar angle and expands along the fiber axis, causing folding and wrinkling inside the lumen. Microspheres were observed by TEM and FE-SEM in 2.5 mmol/g CMF solutions and on top of the 1.3 mmol/g regenerated films. The origin of these particles ($< 0.6 \mu\text{m}$) were ascribed to the transverse splitting of S2 layers during carboxymethylation, followed by water absorption. After a mild mechanical force and/or mixing in an alkaline solution, the microspheres are disintegrated to nanorods of carboxylated CNC with the size ranging from 18–208 nm.

Declarations

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Conflict of interest The authors declare no competing interests, or other interests that might be perceived to influence the results and/or discussion reported in this paper.

Consent for publication All authors have read and approved the final version of manuscript for publication.

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Figures

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Figure 1

Tracheid cell wall layers; ML: middle lamella, PW: primary wall, CML: compound middle lamellae, SW: secondary wall (S1, S2, and S3) (Adapted from Rowell 2012)

Figure 2

Optical microscopy images of swollen tracheid, details of which provided in the text. (image h is reprinted from Sim et al. (2014) with permission, where 2.6 mmol/g CMF was subjected to 1 N HCl at 50°C for 2h, then dyed with toluidine blue and imaged)

Figure 3

FE-SEM images (a, b, c) of CMF films with 1.3 mmol/g carboxyl charge groups; a: S2 parallel microfibrils of a tracheid cell wall, b and c: microspheres on the surface of the film, and TEM images (d and e) of in water dispersed 2.5 mmol/g CMF; d: microspheres and e: nanorod particles

Figure 4

FTIR (top) and XRD (bottom) spectra of ground kraft pulp, 1.3 and 2.5 mmol/g CMFs, and 1.3 mmol/g regenerated film

Figure 5

Weight-based size distribution of particles in 1% water dispersed 1.3 and 2.5 mmol/g CMFs

Figure 6

Transverse splits of S2 microfibrils and formation of microspheres and nanorods (the left part is adapted from Hagglund 1951)