Small-angle x-ray scattering study on the structure of microcrystalline and nanofibrillated cellulose

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Abstract. The effects of different solvents on the structure of microcrystalline and nanofibrillated cellulose (MCC, NFC) were studied using small-angle x-ray scattering (SAXS). MCC was immersed in water, ethanol, and acetone, and NFC was immersed only in water and ethanol, but studied also in the form of foam-like water-NFC-gel in wet, air-dried and re-wet states. The solvent affected the average chord length, which reveals the typical length scale of the structure of the sample: 2.4 ± 0.1 nm for MCC-water, 2.5 ± 0.1 nm for re-wet NFC-gel, 1.6 ± 0.1 nm for MCC-ethanol, 1.2 ± 0.1 nm for NFC-ethanol, and 1.3 ± 0.1 nm for MCC-acetone. The specific surface of cellulose increased strongly when MCC and NFC were immersed in the solvents compared to dry cellulose. The specific surface of cellulose was determined to be larger for NFC-water than MCC-water, and slightly larger for dry NFC powder than for dry MCC, which can be explained by the fact that the width of cellulose crystallites perpendicular to the cellulose chain direction was slightly larger in MCC than in NFC on the basis of wide-angle x-ray scattering results.

1. Introduction
The way to produce microcrystalline cellulose (MCC) from native cellulosic material or pulp by acid hydrolysis has been known already for over 50 years [1]. MCC has become an important material for pharmaceutical industry as a tablet excipient and a binder and filler in dosage forms. It is used as a fat replacer and stabilizer in food industry, and a composite material in wood and plastic industry including for example furniture and sport and leisure items [1, 2, 3]. The production methods, properties, and structure of microcrystalline cellulose have been studied widely. In MCC, the diameter of the cellulose fibres is in the scale of few micrometers. These fibres consist of elementary cellulose microfibrils, whose crystalline parts have a width of about 5 nm and a length of about 20 – 30 nm. [4]

Besides MCC, e.g. cellulose whiskers, nanocrystalline and nanofibrillated cellulose (NFC) can be produced from native cellulose using various preparing methods. In whiskers, nanocrystalline and -fibrillated cellulose the diameter of the cellulose fibres can be in the scale of few nanometers [1, 5]. Because of the nanoscale, the mechanical and optical properties are different, and that is why there exists a large interest in nanocrystalline and -fibrillated cellulose as a raw material.
NFC is more attractive compared to synthetic nanomaterials because of its better availability, biodegradability, and lower cost.

For example, it has been found out that in aqueous colloidal suspensions cellulose whiskers form chiral nematic phases with interesting optical properties. These properties could be used in security and identification papers and iridescent pigments in inks and coatings. [1] It has also been found out that cellulose whiskers can be aligned by a magnetic field and thus they could be used for magnetic alignment of proteins in biomolecular NMR [1]. One more possible application area is in electrolytes. Azizi Samir et al. have studied lithium-conducting nanocomposite polymer electrolytes made from cellulose whiskers and lithium imide salt [6].

We have previously compared the structure of cellulose in native plant material with that of pulp and MCC using x-ray scattering [4]. In that study, MCC was made by mild acid hydrolysis from cotton linter, cellulose from flax fibres and sulphite and kraft cooked wood pulp. Wide-angle x-ray scattering (WAXS) results showed that the width of the cellulose crystallites increased both due to the pulping process and due to the hydrolysis. Furthermore, native spruce wood, flax fibres and cotton linter and the pulp samples made of flax, spruce, pine, and birch wood were immersed in water in order to determine the cross-sectional size and shape and packing of the cellulose crystallites using SAXS. The close range order was the best in the native wood sample, whereas the packing in the other samples was irregular. [4]

Many studies on the effects of various solvents on wood, pulp, and microcrystalline cellulose have been made using chemical methods [7, 8, 9, 10, 11]. The aim of this work was to study the effects of the solvents on the structure of MCC and NFC using small- and wide-angle x-ray scattering. These methods are useful tools for determining the nanostructure of samples. MCC was made of cotton linter by mild acid hydrolysis and NFC was commercial nanocellulose. For SAXS studies dry MCC was immersed in water, ethanol, and acetone, and dry NFC was immersed in water and ethanol. Also foam-like water-NFC-gel in wet, air-dried, and re-wet states was measured by SAXS. The crystalline structures of the dried water-NFC-gel and dry NFC powder were determined by WAXS, so that these structures could be compared with that of MCC.

2. Materials and methods

2.1. Microcrystalline cellulose samples

MCC was prepared from cotton linter with a mild acid hydrolysis in 2.5 M solution of HCl at 105°C for 1 h [12]. Cotton linter was hydrolyzed to the so called level-off degree of polymerization [13]. After hydrolysis MCC was white colored, contained moisture less than 1 mass% and had a powder-like macroscopic morphology. The DP of MCC was 165 [4].

For the SAXS measurements MCC powder was immersed in distilled water, ethanol, and acetone about three weeks before measurements and kept in sealed plastic tubes at room temperature until the measurements were made. MCC-solvent systems were in equilibrium at the time of the measurements because the equilibrium swelling is reached shortly for cellulose-solvent systems [14].

2.2. Nanofibrillated cellulose samples

NFC-gel sample was commercial nanocellulose which was supplied by J. Rettenmaier & Söhne GmbH, Rosenberg, Germany. The product name is Arbocel MF40-10, and it is an aqueous 10 mass% suspension of nanocellulose fibres. The water-NFC-gel had a foam-like macroscopic morphology. NFC-gel was first measured as the original wet suspension, after which the sample was dried in air for 3 hours and measured again. When the gel dried, it formed hard and dry macroscopic aggregates. These aggregates were immersed in distilled water and this mixture was let to swell for one week before a new measurement. So the NFC-gel sample was measured in three states: wet, air-dried and re-wet states.
NFC powder was also produced by J. Rettenmaier & Söhne GmbH. The product name of the powder-like NFC is MF40-100. NFC-water and NFC-ethanol mixtures were prepared by immersing NFC powder in distilled water and ethanol about one week before the SAXS measurements and kept in sealed plastic tubes at room temperature until the measurements were done, so that these samples also reached the equilibrium swelling before the measurements. The carboxyl group content of NFC was 85 mmol/kg [15].

2.3. SAXS

SAXS measurements were conducted at the Department of Physics at the University of Helsinki. A sealed x-ray tube with copper anode and point focus was used. The beam was monochromated with a collimating Montel multilayer to obtain Cu-Kα radiation (wavelength \( \lambda = 1.5418 \) Å). Bruker HI-Star area detector was used, and the distance between the sample and the detector was 52.5 cm. The \( q \)-range (the length of the scattering vector: \( q = 4\pi \sin \theta/\lambda \), where \( \theta \) is the half of the scattering angle) was calibrated with silver behenate and it was 0.03 – 0.4 Å\(^{-1}\).

The MCC- and NFC-mixtures and NFC-gel samples were measured in aluminum rings (diameter 4 mm, thickness 1.6 mm) between two Mylar-foil layers. The measurement time was 60 min. Transmission values for the samples were determined using primary beam values through a semi-transparent copper beamstop. All the 2D SAXS patterns were isotropic, so the data were radially averaged. The absolute intensity scale was determined using the fact, that the maximum of the absolute intensity curve of Lupolen is 5.5 cm\(^{-1}\) around 0.03 Å\(^{-1}\). So the maximum intensity of the scattering curve of Lupolen, which was normalized by time, transmission and optical thickness of the sample and corrected for air-scattering, was set to that value [16]. The intensities of the MCC- and NFC-water and re-wet NFC-gel samples were corrected for water background, but all the other intensities were corrected only for background of an empty aluminum ring with Mylar-foils.

The MCC-water, MCC-ethanol, MCC-acetone, NFC-water, NFC-ethanol, and re-wet NFC-gel samples were weighed before the SAXS measurements in wet state, and after the measurements the samples were dried in air for over 24 hours, and the weights were measured again. Thus the weight fractions of cellulose and matrix (water, ethanol, acetone) could be determined. From these values and known densities of water (1 g/cm\(^3\)), ethanol (0.789 g/cm\(^3\)), acetone (0.122 g/cm\(^3\)), and cellulose (1.26 g/cm\(^3\)), the volume fractions of the phases were calculated. The prepared samples in the Al-rings were weighed, not the mixtures, because the sample preparation could have affected the weight fraction of the solvent phase due to the fact that there were excess amounts of solvents in the mixtures and due to the fast evaporation of the solvent. Thus the weighed amounts were very small and there are large relative errors in the weights, which leads to large relative errors also in the determined volume fraction values. In the case of the NFC-gel, the weight fractions of NFC and water were given by the manufacturer, and it was assumed that the gel was homogeneous enough, so that the known fractions were valid in the measurement.

2.4. WAXS

The WAXS measurements were carried out for the dry NFC powder and dried NFC-gel samples using perpendicular transmission geometry and Rigaku rotating anode x-ray tube at the University of Helsinki. A two-dimensional MAR345 image-plate was used as a detector. The beam was monochromated with a Si(111) crystal and a totally reflecting mirror and focused to the detector. The wavelength of the radiation was 1.541 Å, and the \( q \)-range was 0.6 – 3.8 Å\(^{-1}\). Intensities were corrected for absorption, geometry of the detector and the background arising from air-scattering.

The crystallinity and the width of cellulose crystallites from the cellulose reflections 1-10, 110 and 200 were determined from the WAXS patterns of the NFC samples and the analysis was
made exactly in the same way as in [4].

### 2.5. Analysis of SAXS results

To set the experimental intensities onto the absolute scale, the measured intensities were divided by the measurement time $t$, the optical thickness $d$, and the transmission $T$ of the sample. The optical thickness $d$ of the sample was calculated using linear absorption coefficient $\mu$:

$$d = \frac{-\ln(T)}{\mu}. \quad (1)$$

All the samples were assumed to consist of two phases: in the case of the dry MCC and NFC samples, the two phases were cellulose and air, in MCC/NFC-water cellulose and water, and in MCC/NFC-ethanol and MCC-acetone cellulose and ethanol and cellulose and acetone, respectively. Here cellulose is denoted as phase 1 and air/water/ethanol/acetone as phase 2. The volume fraction of phase 1 is denoted as $\psi_1$, and that of phase 2 as $\psi_2$.

It was checked, if the intensities would follow a power law

$$I(q) \propto q^{-\alpha}, \quad (2)$$

at some $q$-range in order to obtain information on the nanoscale structure of cellulose in the samples. For example, the value $\alpha = 2$ would arise from lamellar structures, and the values $\alpha < 3$ would indicate that the structures may be described as mass fractals (e.g. crumpled paper). The values $3 < \alpha < 4$ would arise from surface fractals with a dense and homogenous inner structure. The value 4 (Porod law) indicates that the phases have smooth and well-defined interfaces. It is essential that the intensities follow the same power law at a wide $q$-region before such interpretations can be made. [17, 16]

For all the samples a $q$-range was found where the intensity obeyed the Porod law,

$$I(q) = Aq^{-4} + B, \quad (3)$$

where $A$ is called Porod constant and $B$ is a constant for background deviation [18]. Since the intensities could be determined in absolute scale, the specific surface of phase 1 could be computed as

$$S = \frac{KA^*}{2\pi(\Delta \rho)^2 \rho d_1}, \quad (4)$$

where $A^*$ is the Porod constant determined from the experimental intensity curve, which has been divided by transmission and corrected for background, $K$ is a coefficient, that scales the intensities onto the absolute values, $\Delta \rho$ is the scattering length contrast between the phases, $\rho$ is the density of phase 1, and $d_1$ is the optical thickness of phase 1 [16].

For the scattering length contrast ($\Delta \rho$) were used values of $1.44 \cdot 10^{11}$ 1/cm$^2$ (between cellulose and air), $5.0 \cdot 10^{10}$ 1/cm$^2$ (between cellulose and water), $6.8 \cdot 10^{10}$ 1/cm$^2$ (between cellulose and ethanol), and $7.0 \cdot 10^{10}$ 1/cm$^2$ (between cellulose and acetone). The difficulty in the case of the wet samples was to determine the optical thickness of phase 1 (cellulose) reliably.

The intensities of most of the wet samples followed the Guinier law,

$$I(q) = I_0 \exp \left( -\frac{R_g^2q^2}{3} \right), \quad (5)$$

at small $q$ values. Here $R_g$ is the radius of gyration of the particles [19]. For these samples the invariant $Q$ could be determined as

$$Q = \int_0^\infty I(q)q^2dq. \quad (6)$$
For computing $Q$, the intensities were extrapolated to $q = 0$ with the Guinier law (Eq. 5) and to high $q$ with the Porod law (Eq. 3). For these samples, the specific surface of phase 1 was also determined using the invariant $Q$ in equation

$$S = \frac{\pi \psi_2 A}{Q \rho}, \quad (7)$$

where $A$ is the Porod constant, $\psi_2$ is the volume fraction of phase 2, and $\rho$ is the density of phase 1 [20].

For these same wet samples, also the average chord length of the sample could be determined by using $Q$ and Porod constant $A$. The relation between these quantities is [19]

$$l_c = \frac{4Q}{\pi A}. \quad (8)$$

The average chord length can also be calculated using the determined specific surface $S$, but then the volume fractions of the two components must be known:

$$l_c = \frac{4\psi_1 \psi_2}{S \rho}. \quad (9)$$

The average chord length of phase 1 is $l_1 = l_c/\psi_2$ and that of phase 2 is $l_2 = l_c/\psi_1 [19]$.

The average chord length reflects the typical length scale of the phase, which is dominant in scattering contrast. If the typical length scale of phase 1 is $l_1$ and the typical length scale of phase 2 is $l_2$, the average chord length $l_c$ is determined as $1/l_c = 1/l_1 + 1/l_2$. According to Jungnikl et al., the typical length scale for cellulose samples in dry state is the dimension of the collapsed interspace between the cellulose microfibrils, and in wet state $l_c$ reflects the dimensions of the fibrils themselves [21].

For the wet samples cellulose microfibrils were assumed as long rigid rods [22], and the Guinier law for rod-like particles,

$$I(q) = \frac{1}{q} I_{c0} \exp \left(-\frac{R_{gc}^2 q^2}{2}\right), \quad (10)$$

was fitted to the intensities at small $q$ in order to determine the radius of gyration of the cross-section $R_{gc}$ [19].

3. Results

3.1. SAXS

The Porod law (Eq. 3) was fitted to the intensities at about $q = 0.23 - 0.35 \text{ Å}^{-1}$, and the background constant gained from this fitting was subtracted from all the intensities. The corrected intensity curves of MCC-water, MCC-ethanol, MCC-acetone, and dry MCC samples are presented in Fig. 1, and the corresponding results for the wet, dried, and re-wet NFC-gel, dry NFC powder, NFC-water, and NFC-ethanol are presented in Fig. 2. The intensity curve of MCC-water obeyed the Porod law already from $q = 0.09 \text{ Å}^{-1}$, and that of NFC-water from $q = 0.12 \text{ Å}^{-1}$. All the other samples obeyed the Porod law at larger $q$-values (around the mentioned $q$-region of $0.23 - 0.35 \text{ Å}^{-1}$).

The intensity curves of wet NFC-gel and NFC-water correspond to each other very well throughout the studied $q$-range, whereas the intensity curves of dry NFC powder and dried NFC-gel correspond to each other only at large $q$-values. The intensity curve of re-wet NFC-gel is different compared to all the other curves. The power law behaviours of all the samples are given in Table 1. At least two different power law regions were determined for all the samples, including the Porod law.
The result for the average chord length was 2.0 nm for NFC-ethanol, and 2.0 nm for both MCC-ethanol and re-wet NFC-gel samples, because their intensity curves obeyed Guinier law (Eq. 5) at low q-values. The extrapolated curves for the MCC-samples can be seen in Fig. 3. The fitting results for the radius of gyration were 4.0 nm for MCC-water, 4.0 nm for MCC-ethanol, 3.2 nm for NFC-ethanol, and 4.5 nm for both MCC-acetone and re-wet NFC-gel. Also fittings according to the Guinier law for rods (Eq. 10) were made for these samples, and the radii of gyration of the cross-sections were 1.2 nm for MCC-water, 1.5 nm for MCC-ethanol, 1.6 nm for NFC-ethanol, and 2.2 nm for both MCC-acetone and re-wet NFC-gel.

The invariant, and thus the average chord length (using Eq. 8), could be determined for these samples. The result for the average chord length was 2.4 ± 0.1 nm for MCC-water, 1.6 ± 0.1 nm for MCC-ethanol, 1.3 ± 0.1 nm for MCC-acetone, 1.2 ± 0.1 nm for NFC-ethanol and 2.5 ± 0.1 nm for re-wet NFC-gel.

The specific surface of cellulose was determined from Eq. 4 and the results are shown in Table 2. The volume fraction of cellulose was needed for this, and it was determined from the weight fractions, which were measured for all the wet samples. The calculated values for the volume fractions of cellulose were small and included large relative errors. Even a small change in this value causes a large difference in S, and thus the values of S have large error margins (even 50%) in the case of the wet samples. Using the measured volume fractions and the determined invariants for the wet MCC-samples, S values were calculated also using Eq. 7 and these results

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### Table 1. The power law behaviour of the MCC and NFC samples. At least two different power laws were found for each sample, so two rows are given for the same sample. Porod law region was found for all the samples, and in some cases the given second power law is directly the Porod law. In any case the Porod law holds always for all the samples in q > 0.25 Å⁻¹. FD=fractal dimension (for surface fractal: surface fractal dimension), SF=surface fractal, MF=mass fractal.

| Sample            | α    | q [Å⁻¹] | FD    | SF/MF |
|-------------------|------|---------|-------|-------|
| 1. MCC-water      | 1.2  | 0.03 – 0.05 | 1.2   | MF    |
| 2. MCC-water      | 3.9  | 0.09 – 0.35 | 2.1   | Porod |
| 1. MCC-ethanol    | 1.2  | 0.03 – 0.06 | 1.2   | MF    |
| 2. MCC-ethanol    | 3.2  | 0.10 – 0.23 | 2.8   | SF    |
| 1. MCC-acetone    | 1.5  | 0.03 – 0.06 | 1.5   | MF    |
| 2. MCC-acetone    | 3.0  | 0.11 – 0.24 | 3.0   | SF/MF |
| 1. MCC (dry)      | 2.7  | 0.03 – 0.08 | 2.7   | MF    |
| 2. MCC (dry)      | 3.5  | 0.09 – 0.25 | 2.5   | SF    |
| 1. NFC-water      | 2.7  | 0.03 – 0.12 | 2.7   | MF    |
| 2. NFC-water      | 4.0  | 0.12 – 0.31 | -     | Porod |
| 1. NFC-ethanol    | 1.6  | 0.03 – 0.11 | 1.6   | MF    |
| 2. NFC-ethanol    | 4.0  | 0.22 – 0.31 | -     | Porod |
| 1. NFC (dry)      | 3.5  | 0.03 – 0.09 | 2.5   | SF    |
| 2. NFC (dry)      | 4.0  | 0.23 – 0.31 | -     | Porod |
| 1. NFC-gel (wet)  | 2.9  | 0.03 – 0.11 | 2.9   | MF    |
| 2. NFC-gel (wet)  | 3.8  | 0.13 – 0.25 | 2.2   | SF    |
| 1. NFC-gel (dried)| 1.9  | 0.03 – 0.14 | 1.9   | MF    |
| 2. NFC-gel (dried)| 4.0  | 0.20 – 0.40 | -     | Porod |
| 1. NFC-gel (re-wet)| 1.6  | 0.03 – 0.07 | 1.6   | MF    |
| 2. NFC-gel (re-wet)| 4.0  | 0.25 – 0.30 | -     | Porod |
differed strongly from the previous values for all three samples, which can be explained by the error margins. However, the specific surface of the dry MCC and NFC powders and the dried NFC-gel could be determined reliably using equation 4, because for these samples the measured optical thickness was straightforwardly that of cellulose. The results were 4.9 m$^2$/g for MCC, 6.4 m$^2$/g for NFC powder and 7.0 m$^2$/g for dried NFC-gel.

**Table 2.** The specific surface of cellulose ($S$), the average chord length ($l_c$), the average chord length of the cellulose phase ($l_1$), and that of the solvent phase ($l_2$), and the diameter of gyration of the cross-section ($2R_{gc}$) of the studied MCC and NFC samples. $S$ was calculated according to Eq. 4 and $l_c$ according to Eq. 8.

| Sample        | $S$ [m$^2$/g] | $l_c$ [nm] | $l_1$ [nm] | $l_2$ [nm] | $2R_{gc}$ [nm] |
|---------------|---------------|------------|------------|------------|----------------|
| MCC-water     | 240           | 2.4        | 3.0        | 11         | 2.4            |
| MCC-ethanol   | 430           | 1.6        | 1.8        | 20         | 3.0            |
| MCC-acetone   | 110           | 1.3        | 1.7        | 5.4        | 4.4            |
| MCC-dry       | 5.0           | -          | -          | -          | -              |
| NFC-water     | 660           | -          | -          | -          | -              |
| NFC-ethanol   | 180           | 1.2        | 1.8        | 3.4        | 3.2            |
| NFC-dry       | 6.4           | -          | -          | -          | -              |
| NFC-gel wet   | 420           | -          | -          | -          | -              |
| NFC-gel dried | 7.0           | -          | -          | -          | -              |
| NFC-gel re-wet| 370           | 2.5        | 3.3        | 8.6        | 4.4            |

**Figure 1.** Integrated intensities of dry MCC, MCC-water, MCC-ethanol, and MCC-acetone. Both axis are in logarithmic scale and the intensities are given in absolute units [cm$^{-1}$].

**Figure 2.** Integrated intensities of NFC-water, NFC-ethanol, dry NFC and wet, dried and re-wet NFC-gel. Both axis are in logarithmic scale and the intensities are given in absolute units [cm$^{-1}$].

### 3.2. WAXS results of the NFC samples

According to the WAXS results, the crystallinity of the NFC powder and the dried NFC-gel was the same, 56 ± 3 %. The widths in the cross-sectional directions of the cellulose crystallite
were 4.5 ± 0.4 nm (1-10), 4.9 ± 0.4 nm (110) and 5.3 ± 0.2 nm (200) for dried NFC-gel, and 4.1 ± 0.4 nm (1-10), 5.1 ± 0.4 nm (110) and 5.4 ± 0.2 nm (200) for dry NFC powder. So also the width of the crystallites was about the same in these samples. These results were very close to the corresponding values of the MCC samples made of wood pulps [4].

4. Discussion
According to the WAXS results, the crystallinity of NFC was smaller, 56 %, than that of cotton based MCC, 65 % [4]. Also the cross-sectional size of cellulose crystallites was smaller in NFC compared to MCC, for which values of 5.2 nm (1-10), 7.4 nm (110) and 8.8 nm (200) were obtained [4]. This can be explained by the fact that MCC was made of cotton linter, which has large crystallites and high crystallinity already in native state [4]. However, the specific surface of cellulose was only slightly larger for dry NFC powder than for dry MCC powder.

The fact, that the specific surface of cellulose \( S \) was larger in NFC-water than in MCC-water, indicated that water has been able to affect more the cellulose structure in NFC than in MCC. \( S \) was always smaller in the samples immersed in ethanol or acetone than in the samples immersed in water, except in the case of MCC-ethanol. So it was assumed that the volume fractions of ethanol and cellulose were not determined reliably for that sample, and thus the conclusion was made according to the results of all the other samples, that water could diffuse inside the cellulose microfibril bundles more effectively than ethanol and acetone, and the strongest effect occurred in the case of NFC.

Wet NFC-gel and NFC-water did not obey Guinier law like all the other wet samples (Fig. 1 and 2), which may be related to the swelling of the cellulose structures. Water has the ability to alter cellulose structure by interactions on the surfaces of the fibrils causing swelling of the surface chains [23, 11]. The lack of Guinier region at small \( q \) values may indicate that in these samples the cellulose microfibril structures are less compact and more heterogeneous than in the other wet samples. However, it is also possible that for wet NFC-gel and NFC-water the Guinier region could be found at smaller \( q \) values than measured in this study.

The different average chord length values in MCC-water, MCC-ethanol and MCC-acetone indicated that there were differences between the structures of MCC in various solvents. The diameter of gyration of the cross-section, \( 2R_{gc} \), was largest in MCC-acetone. The \( 2R_{gc} \) value was smallest in MCC-water, and it was exactly same as the average chord length value of MCC-water (2.4 nm), whereas for all the other immersed samples \( 2R_{gc} \) values were larger than the average chord length values. In MCC-ethanol \( 2R_{gc} \) was about two times the average chord length value, and in MCC-acetone it was about three times that value. Comparing the WAXS results and the diameter of gyration values, water has the largest effect on the cellulose microfibrils among the studied solvents.
Jungnikl et al. gained similar results for the average chord length of their cellulose samples as we gained in this study for MCC and NFC [21]. We gained the average chord length values of 1.3 nm for MCC-acetone, 1.6 nm for MCC-ethanol, 1.2 nm for NFC-ethanol, 2.4 nm for MCC-water, and 2.5 nm for re-wet NFC-gel. Jungnikl et al. studied cellulose samples made of spruce wood, which was extracted with sodium chloride (NaClO$_2$) for delignification and with sodium hydroxide (NaOH) for extraction of hemicellulose. For native spruce wood and the sample delignified with NaClO$_2$, they got as an average chord length 2.1 nm, for NaOH treated samples 2.7 – 3.3 nm, and for the sample treated with H$_2$O$_2$ acetic acid 3.9 nm. All the mentioned values were gained from the samples measured in water. [21] The $l_c$ values of the re-wet NFC-gel and MCC-water samples were between that of the native spruce and the NaOH treated cellulose samples, and the NFC/MCC-ethanol and MCC-acetone samples resembled clearly none of the wet samples measured by Jungnikl et al.

However, the $l_c$ values of NFC-ethanol and MCC-acetone agreed very well with the never-dried and re-wet lyocell fibres, which Vickers et al. [25] studied. They determined for the average chord length of the never-dried and re-wet samples 1.3 and 1.2 nm, respectively. For the dry fibres they gained much higher values, from 7.5 nm to 117 nm. For the average chord lengths of water and cellulose phases in the never-dried fibres they gained 5.9 nm and 1.7 nm, respectively, and 2.9 nm and 2.0 nm in the re-wet fibres. [25] The crystalline structure of lyocell is cellulose-II [26], whereas that of cotton-MCC and the studied NFC was cellulose-I, but the characteristic length scales can be compared even if the crystalline structure of cellulose is not the same.

Ishii et al. [27] studied the effect of the sequential immersion in water, acetone, and DMAc on the pore structure of cellulose (softwood pulp and Whatman CF11) and its dissolution in lithium chloride/N,N-dimethylacetamide (LiCl/DMAc). They observed a difference between the DMAc treated and the untreated celluloses only when acetone was used as a medium. According to the specific inner surface and the average chord length values, the amount of small pores was increased due to the DMAc treatment in acetone exchanged cellulose. When water was used as a medium, no difference between the results of untreated and DMAc-treated cellulose was detected, which they explained by the fact that the sorption of the DMAc-treated cellulose in water spoils the effect of the solvent exchange. According to the interaction parameter, which they calculated, acetone is not adsorbed onto cellulose. [27]

Wet NFC-gel, NFC-water, and dry MCC and NFC obeyed power laws with the exponents $-2.9$, $-2.7$, $-2.7$ and $-3.5$, respectively, at $q = 0.03 - 0.09$ Å$^{-1}$. Ishii et al. [28] studied the power law behaviour of untreated, solvent-exchanged, and milled softwood pulp samples using SAXS. Solvent-exchanging included the sequential immersions in water, in acetone and finally in DMAc. At $q = 0.016 - 0.034$ Å$^{-1}$, the SAXS-curves of the untreated, solvent-exchanged and milled cellulose samples obeyed power laws with exponents $-3.5$, $-2.9$ and $-3.7$, respectively. So the solvent-exchanged sample was the only mass fractal, whereas two other samples were surface fractals. [28] Dry NFC powder behaved like untreated and milled softwood pulp of Ishii et al., and wet NFC-gel, NFC-water, and dry MCC behaved like the solvent-exchanged softwood pulp of Ishii et al. But all the other studied MCC and NFC samples had the exponents in the first mentioned $q$-region between $-1.2$ and $-1.9$.

Stromme et al. have studied the fractal dimensions of different cellulose powders including MCC (Avicel) by multilayer BET adsorption of water and nitrogen. They obtained by water adsorption a fractal dimension of 1.43 for MCC (at the length scale of about 0.1 – 10 nm), whereas by nitrogen adsorption the fractal dimension of MCC was 2.41 (at length scale up to 100 – 1000 nm). Their conclusion was that the water adsorption altered the structure of highly crystalline cellulose by water interactions on the surface of the fibrils without actual swelling of the material. [24]
5. Conclusions

The effects of water, ethanol, and acetone on the nanostructure of microcrystalline and nanofibrillated cellulose were studied using SAXS and WAXS. The specific surface of cellulose increased strongly when both MCC and NFC were immersed in water, ethanol, or acetone (only MCC) compared to dry cellulose, which indicated that the fibre bundles opened in all the studied solvents. The largest effect was detected with water on NFC. The scattering intensities of the immersed samples differed from each other and the same structural parameters could not be determined for all the samples, which makes the direct comparison of the results difficult, but on the other hand, gives information on the differences between the samples. However, important conclusions on the morphology of cellulose microfibrils can be made: Differences between the radii of gyration, crystallite diameters (determined by WAXS) and average chord lengths indicate that the cellulose microfibrils have heterogeneous structure when immersed in the solvents. On the basis of the different average chord length values, the solvents affected the structure of MCC and NFC, and the effect depended on the used solvent. The average chord length was smaller for MCC-acetone, MCC-ethanol, and NFC-ethanol than for MCC-water and re-wet NFC-gel. These differences could arise from the better ability of water to diffuse inside the cellulose microfibril bundles than ethanol and acetone. This same conclusion was made also according to the values of the specific surface of cellulose.

Acknowledgments

We would like to thank J. Rettenmaier & Söhne GmbH for providing the nanocellulose samples and Hans-Peter Hentze for support and comments on the manuscript. K.L. thanks the National Graduate School of Materials Physics for the financial support.

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