

Short communication

CP/MAS ^{13}C NMR study of pulp hornification using nanocrystalline cellulose as a model system

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ABSTRACT

The hornification process of paper pulp was investigated using solid-state ^{13}C NMR spectroscopy. Nanocrystalline cellulose was used to serve as a model system of the crystalline parts of the fibrils in pulp fibers. Characterization of the nanocrystalline cellulose dimensions was carried out using scanning electron microscopy. The samples were treated by drying and wetting cycles prior to NMR analysis where the hornification phenomenon was recorded by spectral changes of the cellulose C-4 carbon signals. An increase of the crystalline signal and a decrease of the signals corresponding to the accessible amorphous domains were found for both paper pulp and nanocrystalline cellulose. These spectral changes grew stronger with repeating drying and wetting cycles. The results show that cellulose co-crystallization contribute to hornification. Another conclusion is that the surfaces of higher hydrophobicity in cellulose fibrils have an increased preference for aggregation.

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1. Introduction

First introduced in 1944 by Jayme, hornification is a phenomenon that occurs in fiber cell walls when subjecting wet delignified paper pulp fibers to drying (Hubbe, Venditti, & Rojas, 2007; Jayme, 1944). Upon sequential rewetting of the paper pulp, the swelling capacity of the fiber walls decreases. This behavior is suggested to be a consequence of increased degree of cross-linking between the cellulose fibrils in the fiber walls during drying (Weise, 1998). Due to a partial collapse of the porous structure in the fiber walls, the internal surface area is reduced, and the pulp fibers turn stiffer and less conformable (Hubbe et al., 2007). In papermaking, the decreased wet fiber flexibility caused by hornification has been shown to decrease the tensile strength of the paper (Paavilainen, 1993). Hornification is an irreversible process and the fiber swelling can only be increased to a certain degree by refining and/or alkali treatment (Zhang, Hubbe, Venditti, & Heitmann, 2004). Understanding the molecular origin of hornification is of

profound interest to the paper pulp industry since such knowledge can provide a way to tailor-make the product to suite the need of the customer.

Hornification is often explained by strong hydrogen bonds formed between the cellulose molecules in the fiber walls (Hubbe et al., 2007). Closely related to the discussion of dissolution of cellulose, brought up by Lindman, Karlström, and Stigsson (2010) and recently discussed extensively (Glasser et al., 2012), it has however been debated if hydrogen bonds solely can be responsible for the hornification phenomenon. Based upon ^{13}C solid-state NMR studies, co-crystallization between cellulose fibrils in pulp fibers has been proposed as a possible reason for hornification (Newman, 2004). When cellulosic material is dried, the NMR signal corresponding to accessible surfaces decreases while the signal of interior crystalline domains increases.

The purpose of this communication is to increase the understanding of the ultrastructural and molecular mechanisms behind hornification. The possibility of co-crystallization is investigated using solid state ^{13}C NMR spectroscopy by using nanocrystalline cellulose (NCC) as a model system. NCC has the same basic structure as the crystalline parts of the fibrils in pulp fibers and any possible co-crystallization of NCC would be due to association of two or several NCC elements.

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2. Materials and methods

2.1. Materials

NCC was produced from Whatman filter paper according to the method (sulfuric acid hydrolysis) described by Hasani, Cranston, Westman, and Gray (2008). The generated aqueous NCC suspension was heated at 80 °C, for 30 min in order to convert sulfate ester groups, on the fibril surface, to hydroxyl groups. Bleached softwood kraft pulp was acquired from Södra Cell, Väröbacka, Sweden, and used without further treatment.

A series of drying and wetting cycles were performed on the NCC and the paper pulp respectively. The material was dispersed in water for 2 h and then dried in an oven at 105 °C for an additional 2 h. This procedure was repeated 7 times and after each cycle a fraction of the samples was removed for solid-state NMR analysis.

Before NMR analysis, the samples were moistened after drying in order to recover all reversible structural changes upon rewetting. Note that the hornification phenomenon, as often defined (Hubbe et al., 2007), only involves irreversible changes after drying and rewetting. An experimental advantage with wet cellulose is the increased spectral resolution of accessible surface signals (Newman, 1998).

2.2. Solid state NMR spectroscopy

All NMR experiments were performed on a Varian Inova-600 operating at 14.7 T and equipped with a 3.2 mm solid-state probe. Measurements were conducted at 298 K with a MAS spinning rate of 15 kHz. The CP/MAS ^{13}C NMR-spectra were recorded using a cross polarization pulse sequence followed by proton decoupling during acquisition. Acquisition parameters included a 2.9 μs ^1H 90° pulse, 1200 μs contact time, 25 ms acquisition time, 5 s recycle delay to allow for complete thermal equilibrium, and 10,000 acquisitions for each spectrum. The solid-state NMR spectra were processed by MestreNova 7.0.3 software. For all spectra a Gaussian apodization of 30 Hz, zero-filling with 8192 points, phase correction and a first order polynomial baseline correction were used in the processing.

2.3. Scanning electron microscopy

A monolayer of NCC was spin coated, using the suspension described in Section 2.1, on QCM-D crystals for electron micrograph analysis (Ahola, Salmi, Johansson, Laine, & Österberg, 2008). AT-cut crystals were purchased from Q-Sense AB, Gothenburg, Sweden. 3-Aminopropyltrimethoxysilane (APTMS) from Sigma was used as an anchoring substance for the NCC. Crystals were cleaned thoroughly in toluene. NCC suspension was spin coated (Spin 150, APT) onto the crystals at 3000 rpm for 45 s, air cured at 80 °C for 10 min, gently rinsed with Milli-Q water and dried with nitrogen gas. The NCC was sputtered with gold for increased contrast. A Leo Ultra 55 FEG SEM was used for electron micrograph analysis and the NCC was observed at 3.0 kV. Dimensions were calculated using image analysis.

3. Results and discussion

In this study, the ambition was to record quantitative information of the intensity from two areas in the CP/MAS spectrum. The NMR resonance of the C-4 carbon in cellulose gives rise to two spectral signals where one is from crystalline cellulose and the other from amorphous cellulose. As the C-4 carbons are chemically equivalent regardless crystalline or amorphous structure, the only possible effect on their relative signal intensity, apart from relaxation recovery during the recycle delay, is the contact time of the cross-polarization pulse. Therefore, an array of spectra, with

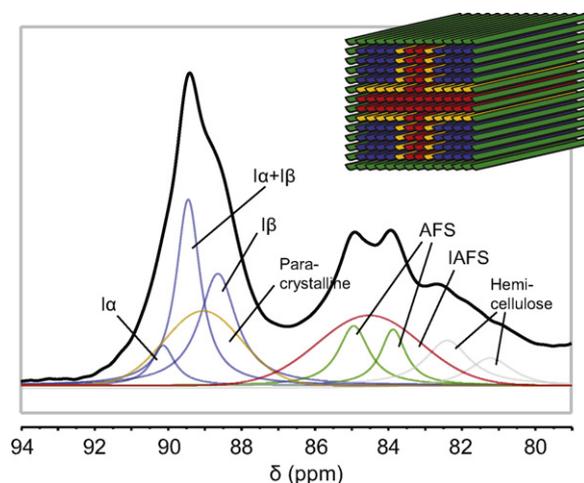


Fig. 1. Square cross-sectional model of a fibril aggregate of four elementary cellulose fibrils (upper right corner). The CP/MAS ^{13}C NMR-spectrum of the C-4 region of never-dried kraft pulp (black) and the deconvolution of crystalline I_{α} and I_{β} signals (blue), paracrystalline signal (yellow), and amorphous signals from accessible (AFS, green) and inaccessible (IAFS, red) fibril surfaces. Hemicellulose C-4 signals are shown in gray. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

different cross-polarization times, was recorded in order to investigate the signal intensities of the two C-4 NMR peaks (Larsson, Wickholm, & Iversen, 1997). We found that the normalized signal intensity of crystalline cellulose is equal to that of the amorphous cellulose when using cross-polarization contact times below 2000 μs . A contact time of 1200 μs was chosen for all samples.

The well-resolved C-4 region, between 80 and 91 ppm, consisting of one amorphous and one crystalline region, was deconvoluted as a sum of seven signals, illustrated by the CP/MAS spectrum of paper pulp and the corresponding cross-sectional model (Hult, 2001) of a cellulose fibril in Fig. 1. The crystalline region was deconvoluted as a sum of four signals where the three narrow ones depend on the crystal allomorphy and the broader, underlying signal, originates from paracrystalline parts of the cellulose (Atalla & VanderHart, 1999). The amorphous region was deconvoluted as a sum three signals where two sharper signals, at 85 and 84 ppm, origin from accessible surface nuclei (Park, Baker, Himmel, Parilla, & Johnson, 2010) and the broad signal at 84.5 ppm corresponds to inaccessible surface nuclei (Wickholm, Larsson, & Iversen, 1998). In samples containing hemicelluloses, e.g. kraft pulp, one or a couple of broad signals were inserted in the deconvolution calculation to account for this material (Hult, Liitiä, Maunu, Hortling, & Iversen, 2002).

Fig. 2 shows the CP/MAS spectra of the Whatman filter before and after the sulfuric acid hydrolysis treatment (Whatman filter, shown in red and final material, NCC, shown in green). The spectrum of untreated kraft pulp (blue) is also shown in Fig. 2 where all spectra are normalized to the signal of the crystalline C-4 carbon. The fine spectral structure of the kraft pulp, compared to the NCC, indicates a higher level of ordering of the fibers (Virtanen, Maunu, Tamminen, Hortling, & Liitiä, 2008). The C-4 carbon spectral region is enlarged, with crystalline signal (87–91 ppm) and amorphous signal (80–87 ppm) clearly separated. Comparing Whatman filter and NCC, a significant change in the signal intensity can be seen between 80 and 87 ppm, corresponding to a decrease of amorphous material in the sample. In the hydrolysis treatment where NCC is produced, removal of easily accessible amorphous cellulose takes place to a significantly larger degree than removal of crystalline material (Habibi, Lucia, & Rojas, 2010). In the paper pulp spectrum, there is additional signal at lower chemical shifts (80–82 ppm) arising from hemicelluloses.

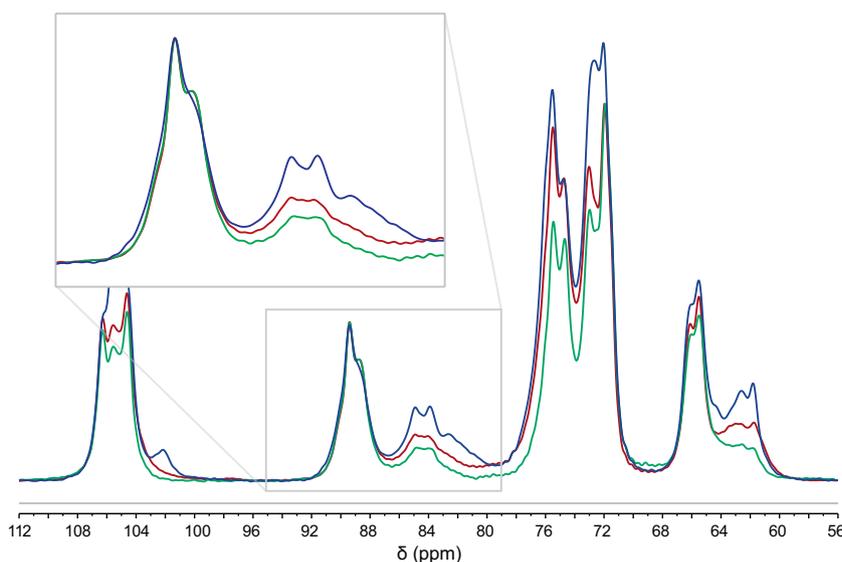


Fig. 2. The CP/MAS ^{13}C NMR-spectra of never-dried kraft pulp (blue), Whatman filter paper (red), and never-dried NCC (green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

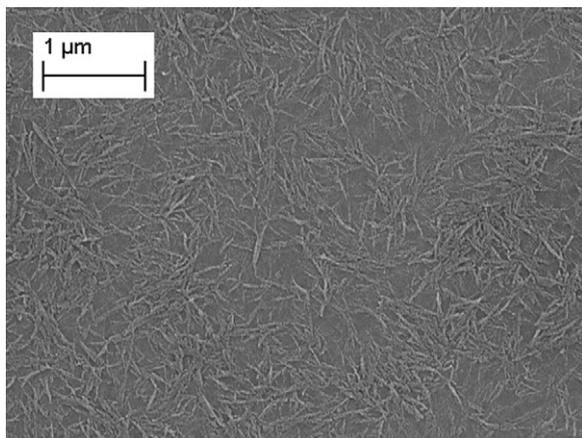


Fig. 3. Electron micrograph of produced NCC.

An electron micrograph of NCC can be seen in Fig. 3. From image analysis, the NCC dimensions were determined with standard deviation to 13 ± 3 nm in diameter and 180 ± 30 nm in length, corresponding well to dimensions of NCC reported elsewhere (Hasani et al., 2008).

Fig. 4 shows the CP/MAS spectra of the pulp subjected to 0, 1, and 7 drying/rewetting cycles respectively. All spectra are here normalized to the signal integral of the entire C-4 carbon spectral region (80–91 ppm). An apparent increase of the crystalline signal and a corresponding decrease of the two accessible amorphous signals correspond to the results by Newman (2004) and this effect can thus be seen as the NMR fingerprint of hornification. The decrease of the two accessible surface signals reveals an aggregation of fibrils. The decreased signal of these nuclei now partly arises as crystalline signals inside the fibril aggregate and partly contributing to inaccessible surface signals.

Fig. 5 shows the CP/MAS spectra of the NCC subjected to 0, 1, 3, and 7 drying/rewetting cycles respectively. Compared to pulp, a similar phenomenon, but to less degree, of signal intensity changes can be seen. Most plausibly, two NCC elements partly associate and co-crystallize. This observation indicates that hornification is, at least to a certain degree, a result of co-crystallization. The NCC is produced by Whatman filter paper, which is treated to drying during manufacturing. The lesser change of signal of the filter paper, compared to paper pulp, could therefore be assigned to the material already being exposed to precedent hornification conditions.

In addition, one of the accessible surface signals (84 ppm) decreased to a larger extent than the other, an effect that was not observed in the kraft pulp samples. Wickholm et al. (1998)

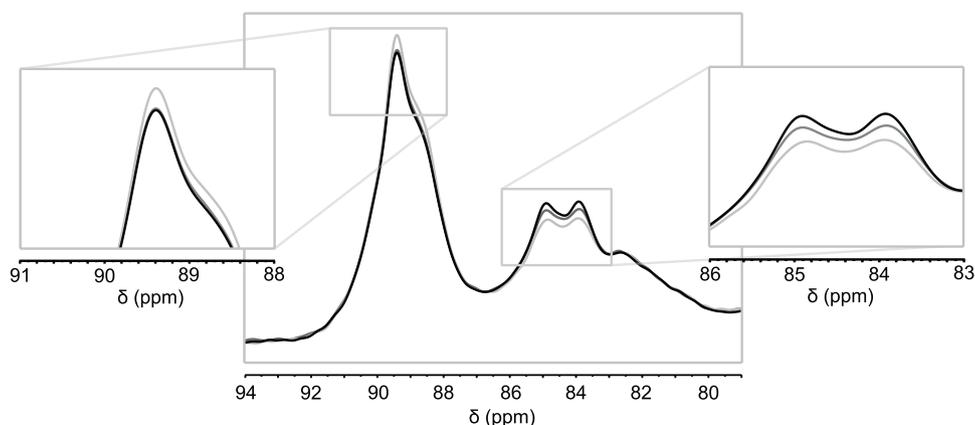


Fig. 4. CP/MAS ^{13}C NMR-spectra of the C-4 region for kraft pulp, dried 0, 1 and 7 times (black, dark gray and light gray respectively). Enlargements show crystalline and amorphous peaks respectively.

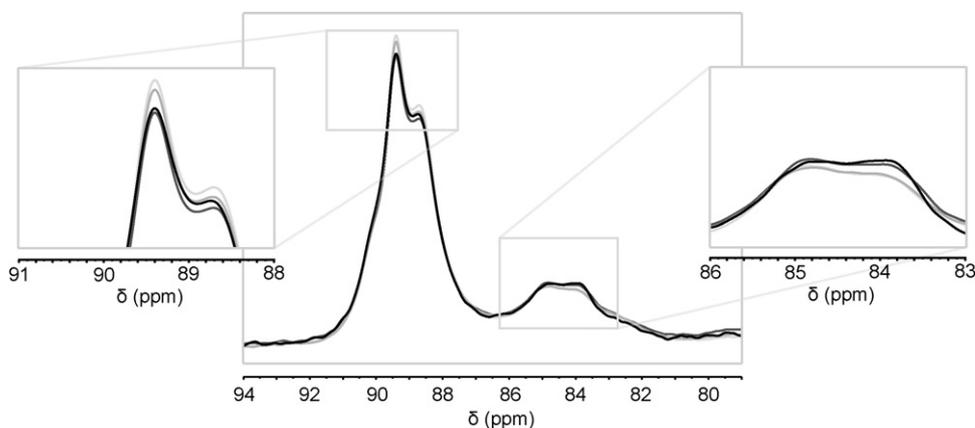


Fig. 5. CP/MAS ^{13}C NMR-spectra of the C-4 region for NCC, dried 0, 1, 3 and 7 times (black, dark gray, gray and light gray respectively). Enlargements show crystalline and amorphous peaks respectively.

proposed tentatively that the two signals at 85 and 84 ppm originate from the two crystal planes 110 and 1–10 respectively. Based upon this theory, we interpret our results as that the 1–10 plane is more influenced by the drying cycles than the 110 plane.

The distance between cellulose chains in the crystal structure differ, being 0.61 and 0.54 nm for 110 and 1–10, respectively (Hult, Larsson, & Iversen, 2001). This would imply that the two crystal planes in elementary fibrils can be associated with different degree of hydrophilicity. Bierman et al. studied hydrophilicity of cellulose I_{β} using molecular dynamics simulations and found a difference between the two crystal planes of cellulose (Biermann, Hädicke, Koltzenburg, & Müller-Plathe, 2001). Both planes essentially being nonhydrophilic, the more narrow 1–10 plane possesses higher hydrophobicity than the wider 110 plane. In view of these findings, our results imply that the more hydrophobic crystalline plane of the cellulose fibril has a stronger tendency to aggregate, when subjected to drying. The reason for not observing this difference in kraft pulp could be that the fibrils in pulp fiber walls are ordered in a restricted structure even in wet state. Furthermore, the presence of hemicelluloses in close association with the fibril surfaces in kraft pulp will influence the rearrangement of cellulose (Köhnke, Lund, Brelid, & Westman, 2010; Oksanen, Buchert, & Viikari, 1997). The NCC elements, on the other hand, have a larger degree of freedom when suspended in water and find a lower energy conformation upon drying.

4. Conclusions

The results presented in this communication indicate that cellulose co-crystallization contributes to hornification. A decrease of accessible surface signals and an accompanying increase of the crystalline signal can be seen for both NCC and paper pulp in CP/MAS ^{13}C experiments. From studies of NCC subjected to repeated drying/rewetting, results suggest that the more hydrophobic surfaces of the crystalline elements in cellulose fibrils have an increased preference for aggregation.

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