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Short Communication

A CP/MAS ^{13}C-NMR study of cellulose structure on the surface of refined kraft pulp fibers

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Abstract

The average lateral fibril and fibril aggregate dimensions and the crystallinity of the cellulose in a spruce kraft pulp were investigated by CP/MAS ^{13}C-NMR spectroscopy in combination with spectral fitting. Cellulose isolated by chlorite-delignification and acid hydrolysis from fines fractions enriched in surface material and long fiber fractions enriched in bulk material exhibited no major differences in either lateral dimensions or crystallinity index.

Keywords: CP/MAS ^{13}C-NMR; Cellulose; Fiber surface; Kraft pulp; Supermolecular structure

1. Introduction

The molecular composition, structure and supramolecular association are expected to vary more at the surface than in the interior of unbleached kraft pulp fibers. Fines enriched in surface material can be isolated from pulp fibers by refinement followed by subsequent sieving (Krause, 1967). The isolated fractions exhibit not only different morphological features but also different lignin and carbohydrate compositions (Hardell, Leary, Stoll & Westermark, 1980; Krause, 1967). The molecular composition of the outer part of the fiber cell wall is characterized by an enrichment of lignin and resorption of xylan from the cooking liquor at the end of the kraft pulping (Laine, Stenius Larsson & Ström, 1994). The surface of a kraft pulp fiber material will also contain fragments from the primary wall (Duchesne & Daniel, 2000). It is known that primary cell wall cellulose from other plant sources may have small fibril widths, in the range of 2–3 nm, compared to secondary cell wall (S_2) cellulose from spruce wood which has fibril widths in the range of 4–5 nm (Chanzy, Imada, Mollard, Vuong & Barnoud, 1979; Ha, Apperley, Evans, Huxham, Jardine, Viëtor et al., 1998).

Several investigators have studied the crystallinity of cellulose in isolated fiber fractions. Leary, Morgan and Newman (1986) found by ^{13}C CP/MAS NMR that fines isolated from spruce wood exhibited lower cellulose crystallinity than the whole wood. Similar results were obtained also in recent studies when fines and long fiber fractions of spruce kraft pulp were compared (Liitiä, Maunu & Hortling, 2000, 2001). On the other hand, Wistara, Zhang and Young (1999) found, using FT-IR, that the crystallinity of cellulose in fines was higher than that in the whole pulp.

During kraft pulping there is an increase in lateral cellulose fibril aggregate dimensions. The change in lateral fibril aggregate dimensions is attributed to an increased contact between cellulose fibril surfaces, as a result of the removal of hemicellulose and lignin. There is also a correlation between fibril dimension and crystallinity (Hult, Larsson & Iversen, 2000. In this paper, we report the use of CP/MAS ^{13}C-NMR-spectroscopy in combination with spectral fitting to compare the crystallinity, lateral fibril and fibril aggregate dimensions of the celluloses isolated from fractions enriched in surface and bulk material from a kraft pulp (Hult et al., 2000; Hult, Larsson & Iversen, 2001; Liitiä et al., 2000, 2001; Wickholm, Larrson & Iversen, 1998.

2. Experimental

2.1. Materials

The kraft pulp was manufactured from spruce (*Picea abies*) chips by cooking at 18% alkalinity and 35% sulphidity at a final temperature of 170°C in a conventional batch reactor. The kappa number of the pulp was 35.7.

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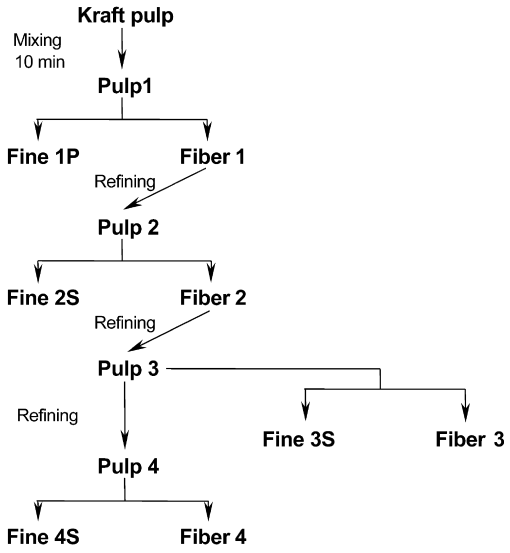

Fig. 1. Scheme for the separation of various fines and fiber fractions after refining in stages (Liitiä et al. 2001).

Refining in stages and the separation of fines and long fibers together with their characterization is described in more detail elsewhere (Liitiä et al., 2001; Tamminen, Jousimaa & Hortling, 2001). To homogenize the pulp suspension (Pulp 1), it was mixed for 10 min, after which the primary fines fraction (Fine 1P) was separated from the long fibers (Fiber 1) with an Attis filter (Fig. 1). The long fibers obtained were refined with a Voith Sulzer laboratory refiner at 4% consistency using a specific edge load of 2.5 Ws/m and an energy of 70 kWh/t to peel the surface material from the fibers. After refining, the secondary fines were separated from the long fibers with an Attis filter and the long fibers were again refined using the same conditions as before. The refining treatment was repeated three times to obtain a fines fractions enriched with fibrillated material from the different surface layers of the kraft fibers. Only primary fines (Fine 1P), two secondary fines fractions (Fine 2S, Fine 4S) and the last long fiber fraction (Fiber 4) were investigated in this study and compared with the original kraft pulp.

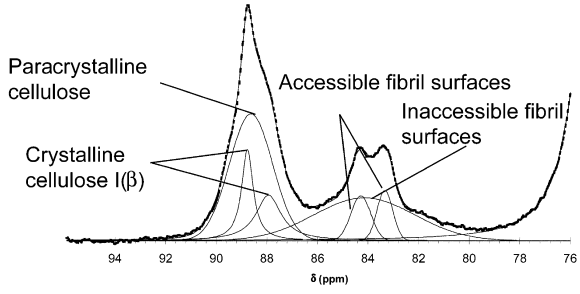

Fig. 2. Results of the spectral fitting of the cellulose C-4 region recorded on cellulose isolated from the long-fiber fraction, Fiber 4. The broken lines represent the experimental spectra. The fitted lines and their superposition are shown as solid lines.

2.2. Sample preparation for NMR analysis

All spectra were recorded on wet samples (water content 40–60 wt%). For the delayed contact measurements, the samples were not subjected to any subsequent treatment. For the spectral fitting experiments cellulose was isolated from the samples by treatment with $NaClO_2$ (0.3 g/g pulp) under acidic conditions (pH 4–5) at 70°C followed by hydrolysis for 17 h in 2.5 M HCl at 100°C (Hult et al., 2000).

2.3. Chemical composition

The total lignin content of the pulp fractions was determined by a method described by Browning (1967), and monosaccharide compositions were determined by an HPLC/PAD system after hydrolysis with strong sulphuric acid (Hausalo, 1995). The relative monosaccharide compositions of the cellulose samples (glucose content $> 96\%$) were determined by sugar analysis according to Theander and Westerlund (1986).

2.4. NMR measurements

Details of the NMR measurements are given by Larsson, Wickholm and Iversen (1997). CP/MAS and delayed contact experiments conducted before chlorite-delignification and acid hydrolysis are described elsewhere (Liitiä et al., 2001).

2.5. Spectral fitting

The procedure for performing the spectral fitting and for the determination of fibril and fibril aggregate dimensions is described in detail elsewhere (Hult et al., 2001; Wickholm et al., 1998). The software was developed and implemented at STFI and is based on the Levenberg–Marquardt method (Press, Teukolsky & Vetterling, 1988.

3. Results and discussion

In Fig. 2 the results of the spectral fitting is shown for the cellulose C-4 region of the cellulose isolated from the long-fiber fraction (Fiber 4). Two Lorentzian lines for the signals from crystalline cellulose Iβ allomorph are visible at 88.8 and 87.9 ppm together with four Gaussian lines for the remaining signals attributed to non-crystalline cellulose forms, para-crystalline cellulose (88.7 ppm), accessible fibril surfaces (84.3 and 83.3 ppm) and inaccessible fibril surfaces (83.8) (Wickholm et al., 1998).

The average lateral fibril and lateral fibril aggregate dimensions are calculated from quantitative spectra of pure cellulose isolated from kraft pulps (Hult et al., 2000; Wickholm et al., 1998). It is possible to calculate average lateral fibril dimensions from the NMR spectra if the fibrils and the fibril aggregates, as a simple approximation, are assumed to have square cross sections (Heux, Dinand, &

Table 1
The crystallinity indexes (CrI) measured by CP/MAS and delayed contact methods (Liitiä et al. 2001) are shown together with the quantification made by spectral fitting of the cellulose C-4 region. The average lateral fibril and fibril aggregate dimensions are shown for the fines fractions, the long fiber fraction and the kraft pulp

Sample	CrI (%)		Spectral fitting						
	CP/MAS	Delayed contact	CrI[a] (%)	Crystallinity (%)[b]	Paracrystalline cellulose (%)[b]	Accessible fibril surfaces (%)[b]	Inaccessible fibril surfaces (%)[b]	LFD[c] (nm)	LFAD[d](nm)
Kraft pulp	49	–	59(3)[e]	20(2)	39(2)	13(1)	28(1)	4.9(0.2)	17.0(0.9)
Fine 1P	38	61(3)	56(2)	21(1)	35(2)	12(1)	31(2)	4.5(0.2)	17.8(1.4)
Fine 2S	41	–	58(3)	18(2)	40(2)	12(1)	30(1)	4.8(0.2)	17.8(1.4)
Fine 4S	44	63(1)	58(3)	17(2)	41(2)	12(1)	29(1)	4.9(0.2)	17.9(1.7)
Fiber 4	51	71(3)	60(3)	23(2)	37(2)	11(1)	29(1)	5.0(0.2)	19.4(1.1)

[a] Fibril interior cellulose (sum of crystalline and paracrystalline cellulose).
[b] Relative intensity.
[c] Lateral fibril dimension.
[d] Lateral fibril aggregate dimension.
[e] Standard error.

Vignon, 1999; Hult et al., 2000; Smith, Harris, Melton & Newman, 1998; Wickholm et al., 1998). The fraction of the signal intensity from accessible and inaccessible surfaces (fibril dimension) and the fraction of the signal intensity from accessible surfaces (fibril aggregate dimension) are both denoted q and are given by the equation: $q = (4n - 4)/n^2$ in these models, where n is the number of cellulose polymers perpendicular to the fibril cross-section along one side of the assumed square fibril or the assumed square fibril aggregate cross-section. A conversion factor of 0.57 nm per cellulose polymer has been used (Heiner, Kuutti, & Teleman, 1998; Newman, 1999; Sugiyama, Vuong & Chanzy, 1991).

Table 1 shows that the crystallinity, average lateral fibril and fibril aggregate dimensions as determined by spectral fitting for the fines fractions and for the long fiber fraction are almost equal within the limits of statistical error. The only significant difference is observed in the case of the long fiber fraction (Fiber 4). A slightly larger average lateral fibril aggregate dimension is observed in the long fiber fraction (19.4 nm) than in the original pulp (17.0 nm). This probably is a result of the extensive multistage refinement of the long fiber fraction. As a result of the refining, the fiber wall is fractured and some of the surface material is removed. This allows a better swelling of the refined long fibers by water, and can lead to further fibril aggregation during the drying (Hult et al., 2001).

In a previous study (Liitiä et al., 2001), the crystallinity index (CrI) determined by CP/MAS and delayed contact methods (Lopez, Sarychev, Pascoal Neto & Gil, 2000; Newman, 1999; Newman & Hemmingson, 1990) was found to be lower in the fines fractions than in the long fiber fraction (Table 1). In the CP/MAS measurements, which were made before chlorite-delignification and acid hydrolysis, residual lignin and hemicelluloses tend to reduce the CrI since these components give a signal intensity contribution in the region of less-ordered (surface) cellulose. In the fines, the amounts of both hemicelluloses and lignin are known to be higher (Table 2), and this could explain the lower CrI observed in the fines.

The delayed contact technique is often used to avoid the effect of interfering lignin and hemicellulose signals on the crystallinity, and to avoid using a chemical treatment, which might cause a change in the nature of the cellulose (Newman, 1999; Newman & Hemmingson, 1990). Since the effect of the prolonged acid hydrolysis used in this study, on the cellulose structure is not known in detail a comparison was made with the crystallinity indexes (CrI) as determined by delayed contact experiments on the original samples (Hult, 2001; Liitiä et al., 2001). As seen in Table 1, there is only one major difference, the long fiber fraction (Fiber 4) has a substantially higher CrI of 71% (delayed contact experiment) as compared to 60% fibril interior cellulose (sum of paracrystalline and crystalline cellulose) as determined by spectral fitting. A content of 71% of fibril interior cellulose would require an unreasonable large kraft pulp cellulose fibril dimension of 7 nm as compared to the 1.5–5 nm reported for similar samples in literature (Fink, Hofmann & Philipp, 1995; Jacob, Fengel, Tshegg & Fratzl, 1995. The CrI as determined by delayed contact technique thus probably more indicates a high sensitivity of the method to changes in the dynamics of the polymer components of the fiber wall.

Table 2
Monosaccharide composition according to sugar analysis (Hausalo, 1995). The values of arabinose, xylose, mannose, galactose and glucose are normalised to a total polysaccharide level of 100%

	Arabinose	Galactose	Glucose	Xylose	Mannose	Lignin
Pulp	0.6	+	83.7	9.2	6.5	4.8
Fine 1P	0.8	1.1	78.7	11.5	7.9	16.9
Fine 2S	+	0.9	83.0	9.0	7.1	10.6
Fine 4S	+	1.1	83.8	8.5	6.6	7.6
Fiber 4	0.7	−	84.6	8.5	6.2	4.3

We conclude that cellulose isolated by chlorite-delignification and acid hydrolysis from fines fractions enriched in surface material and from long fiber fractions enriched in bulk material exhibited no major differences with regard to either average lateral fibril or fibril aggregate dimensions. Some differences may be observed in the CrI determined depending on whether the hemicelluloses and lignin are removed by chemical treatment or by spectral editing techniques (delayed contact experiments).

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