ELSEVIER

Polymer 42 (2001) 3309–3314

polymer

www.elsevier.nl/locate/polymer

Cellulose fibril aggregation — an inherent property of kraft pulps

E.-L. Hult, P.T. Larsson, T. Iversen*

Swedish Pulp and Paper Research Institute, STFI, P.O. Box 5604, SE-114 86 Stockholm, Sweden

Received 27 August 2000; received in revised form 17 October 2000; accepted 22 October 2000

Abstract

Changes in cellulose fibril aggregation during kraft pulping and drying of kraft pulps were studied by cross-polarization magic angle spinning carbon-13 nuclear magnetic resonance in combination with spectral fitting. An increase in lateral fibril aggregate dimensions was observed in the initial phase of delignification of the pulping. The increase in aggregate dimensions is attributed to an increased contact between cellulose fibril surfaces as a result of the removal of hemicellulose and lignin. Drying of the pulps results in even larger cellulose fibril aggregates. This process is also shown to be related to the hemicellulose content. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Cellulose; NMR; Fibril aggregation

1. Introduction

Most studies on the effect of pulping on the fibre cell-wall structure have concentrated on the acquisition of more detailed descriptions on a macroscopic or a molecular level [1]. On the other hand, on the intermediate nanoscale, our knowledge is still largely incomplete with regard to important structural features such as the spatial arrangement of hemicelluloses and the assembling pattern of cellulose fibrils in the formation of larger super-structures, and how these features are affected by pulping. It has, for example, been suggested that differences in the assembling pattern of cellulose fibrils must have a major effect on the susceptibility of cellulose substrates to enzymatic hydrolysis [2]. The aggregation of the cellulose fibrils will also, to a large extent, govern the accessibility and reactivity of cellulose substrates in chemical modification reactions [3]. Further, commercial cellulose fibres are often used in a dried form, and it has for a long time been recognized that the drying of pulp fibres results in significant change in their properties.

The loss of swelling capacity of the fibre wall resulting from a drying and rewetting cycle is denoted "hornification" [4]. A reduction in paper strength has been reported for dried pulps compared with never-dried pulps [5]. The phenomenon of hornification is of great importance to papermaking since market pulps are dried before shipment and dry waste paper is used as raw material in the manufacture of recycled papers. Knowledge of the structural changes occurring in the cell wall at the nanoscale level is still incomplete, although many studies have attempted to explain the mechanisms of hornification [6].

Recently, we made a comparative cross-polarization magic angle spinning (CP/MAS) ^{13}C nuclear magnetic resonance (NMR) study of the supermolecular structure of the polysaccharides in native spruce wood and kraft [7]. In this study, we found that distorted wood cellulose were converted to cellulose Iβ during the kraft pulping, i.e. the degree of order was increased. The small initial amount of cellulose Iα was also converted to cellulose Iβ during the kraft pulping. It was also observed that the C4-carbons of hemicellulose chain units contribute significantly to the spectral region representing non-crystalline cellulose (80–86 ppm) in kraft pulp spectra, but much less to the corresponding region in wood spectra. Our interpretation of the spectral behaviour of the hemicelluloses was that changes in their intermolecular aggregation occurred as a consequence of the pulping.

Since cellulose has the property of being an abundant, biodegradable and renewable resource, there is today a renewed interest in developing new cellulosic products, such as sophisticated fibre products based on wood pulps. Softwood kraft pulp is one of the most dominating commercial sources of cellulose fibres and the aim of this study was to elucidate the influence of hemicelluloses on cellulose fibril aggregation during the kraft pulping of spruce wood (*Picea abies*) and the drying of kraft pulps.

* Corresponding author.

PII: S0032-3861(00)00774-6

2. Experimental

2.1. Material

All pulps were made from sorted normal wood of Norway spruce (*P. abies*) that had been manually cut into chips.

2.2. Preparation of the kraft pulps

Conventional laboratory kraft cook: for details consult the papers by Duchesne and Daniel [8] and Hult et al. [9].

Pulp 1: The pulp was cooked in autoclaves that were heated in a polyglycol bath. The chips were pretreated in water at 160°C for 40 min (liquid to wood ratio 4:1). Half of the liquid was then removed. In the second step, the liquid/wood ratio was 4:1, HS^- 0.3 M, OH^- 1.1 M, the temperature was 170°C and the pulp was cooked until H-factor 2000 was reached. The pulp was washed overnight in running deionized water.

Pulp 2: The pulp was an RDH (rapid displacement heating with a black liquor impregnation) pulp made in a laboratory circulation digester with industrial white liquor. The pulp was cooked at 170°C until an H-factor of 1600 was reached. The alkaline concentration during the cook varied between 0.33 and 0.49 M. The HS^- concentration varied between 0.14 and 0.19 M. The pulp was washed overnight in running deionized water.

Pulp 3: The pulp was cooked in autoclaves that were heated in a polyglycol bath. The pulps were impregnated with 1.44 M OH^-, 0.41 M HS^- and 0.36 M polysulfide (liquid/wood ratio of 4:1) at 100°C for 1 h. After the impregnation, half the liquid was removed and chemicals and water added for the second stage with OH^- 0.4 M, HS^- 0.41 and cooking at 170°C until an H-factor of 1300 was reached. The pulp was washed overnight in running deionized water.

Laboratory handsheets were prepared without any prior beating, according to SCAN-CM 26:99 method.

2.3. NMR sample preparation

Cellulose was isolated from the never-dried kraft pulps and from the dried handsheets by chlorite delignification (at 70°C) [7] followed by hydrolysis for 17 h in 2.5 M HCl at 100°C. The samples were cellulose-enriched cell-wall fragments containing >95% glucose.

2.4. NMR spectroscopy

All spectra were recorded on wet samples (water content 40–60% by weight). The CP/MAS ^{13}C NMR spectra were recorded on a Bruker AMX-300 instrument (292 ± 1 K) operating at 7.04 T. A zirconium oxide rotor was used. The MAS rate was 5 kHz. Acquisition was performed with a CP pulse sequence using a 3.5 μs proton 90° pulse, 800 μs contact pulse and a 2.5 s delay between repetitions. Glycine was used for the Hartman–Hahn matching procedure and as external standard for the calibration of the chemical shift scale relative to tetramethylsilane ($(CH_3)_4Si$). The data point of maximum intensity in the glycine carbonyl line was assigned a chemical shift of 176.03 ppm.

2.5. Chemical composition

The relative proportions of the neutral polysaccharide constituents were determined by sugar analysis [10], and the polysaccharide composition according to Janson [11]. Klason lignin was determined according to TAPPI T249, the kappa number was estimated according to SCAN-C 1:77 and the viscosity according to SCAN-CM 15:88. The residual alkali was determined by titration with HCl to pH 10.7 after an eight-fold dilution and precipitation of the dissolved lignin and carbonate ions with $BaCl_2$, Table 1.

2.6. Spectral fitting of NMR spectra

The model and method given by Larsson et al. [12] were used for the spectral fitting.

Table 1
Kraft pulping conditions and the results of chemical analysis of the spruce kraft pulps and black liquor at different stages during the conventional laboratory kraft cook

Pulping phases	Time (min)	Temperature (°C)	H-factor	Yield (%)	Kappa no.	Cellulose (%) on fibre	Viscosity	$[OH^-]$ (mol/l)
Wood	–	–	–	100		44.0		
Initial (1)	19	91	0	99		47.6		0.85
Initial (2)	83	155	50	77		57.6		0.43
Initial (3)	91	162	100	76		58.8	1670[a]	0.39
Bulk (4)	105	170	250	69		63.7	1590[a]	0.35
Bulk (5)	124	168	500	60	88	67.0	1470[a]	0.28
Bulk (6)	158	169	1000	55	47	76.4	1300	0.26
Residual (7)	226	169	2000	52	28	79.0	1140	0.14
Residual (8)	366	169	4000	49	17	81.2	960	0.10

[a] Measured on chlorite-delignified pulp.

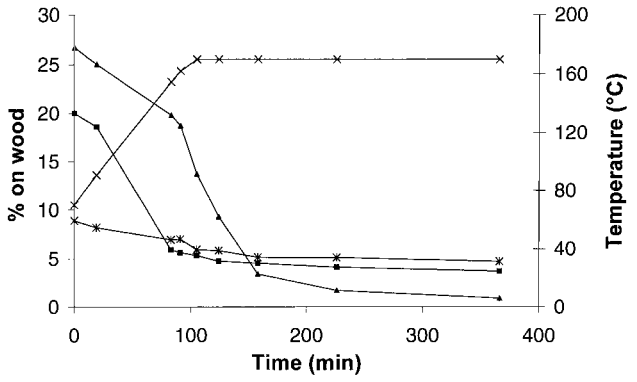

Fig. 1. The variation in chemical composition of wood during the conventional laboratory kraft cook. Left *y*-axis: lignin content (filled triangle), glucomannan content (filled square) and xylan content (star). Right *y*-axis: temperature (cross).

3. Results and discussion

3.1. Determination of average lateral dimensions in kraft pulps

The most informative region in the CP/MAS ^{13}C NMR spectra of cellulose I samples is the cellulose C4-signal cluster with a distribution between 80 and 92 ppm [12–18]. This region contains resolved signals corresponding to the fibril bulk forms (86–92 ppm), cellulose Iα, cellulose Iβ and para-crystalline cellulose, and the fibril surface forms (80–86 ppm), two signals for cellulose at (solvent-) accessible fibril surfaces and one for cellulose at (solvent-) inaccessible fibril surfaces formed due to aggregation. If hemicelluloses are present in the sample, their C4-carbons may give signals in this region, as is typically observed for kraft pulps [7].

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 [7,18–21]. The fraction of the signal intensity from accessible surfaces (calculation of fibril aggregate dimension) or the fraction of the signal intensity from accessible and inaccessible surfaces (calculation of fibril dimension) are both denoted q and are given by the equation: $q = (4n - 4)/n^2$ for these models. In the equation, 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 calculated as the mean value of the repeat distance of cellulose chains in the wide (0.61 nm, monoclinic 110 and triclinic 010) and narrow (0.54 nm, monoclinic 1 − 10 and triclinic 100) surfaces [22–24]. The mean value is used since in the case of the inaccessible surfaces, which is the dominating surface form in the spectra of this study, no assignment can be made to the specific forms, in contrast to the accessible surfaces [18]. In the case of kraft pulps, the calculations of lateral fibril dimensions and lateral fibril aggregate dimensions have to be performed on hydrolysed and chlorite-delignified samples since it is necessary to remove the interfering signals from hemicelluloses and lignin.

3.2. Changes in average lateral fibril aggregate dimensions during kraft pulping

Sorted normal wood chips of Norway spruce (*P. abies*) were laboratory cooked to various yields according to Section 2. The pulping conditions and the results of the chemical analyses of the kraft pulps and black liquor at different stages during the cook are given in Table 1 [8,9]. Fig. 1 shows the change in the fibre chemical composition during the cook. In the figure it is clear that the cook can be divided into three kinetically distinct phases with respect to lignin extraction [25–28]: an initial (up to 91 min), a bulk (91–158 min) and a residual delignification phase (158–366 min).

Fig. 2a and b shows the results of the spectral fitting for the cellulose C4-region of a chlorite-delignified and hydrolysed kraft pulp and of the corresponding kraft pulp [7]. In the ordered C4-region (86–92 ppm), the composite I(α + β) signal at 88.8 ppm is visible, together with the signal from cellulose Iβ at 87.9 ppm and a large signal at 88.7 ppm due to the para-crystalline cellulose. In the less-ordered C4-region (80–86 ppm), two signals assigned to accessible fibril surfaces at 83.3 and 84.2 ppm are visible, together with a large signal assigned to the inaccessible fibril surfaces at 83.8 ppm. In the kraft pulp spectrum (Fig. 2b), the hemicellulose C4-carbons make an intensity contribution in the region of the signal assigned to the inaccessible fibril surfaces and two separate signals at 81.9 and 81.2 ppm [7,29]. In a previous investigation, we showed that the CP/MAS ^{13}C NMR spectra of hemicellulose containing kraft pulps were not quantitative. In order to make the most precise estimate of average lateral fibril and fibril aggregate dimensions, the calculations are therefore performed on spectra recorded on pure cellulose isolated from kraft pulps [7]. However, in the case of spectral fitting, and especially in cases where the individually assigned and fitted lines are used for the determination of average lateral fibril and fibril aggregate dimensions, the quantitativity of the individual lines during cross-polarization becomes an issue of concern. For this reason two spectra recorded on a mixture of wet cotton linters and polyethylene, recorded with two different contact times (600 and 1800 μs), are shown superimposed in Fig. 3. Clearly, this shows that the quantitativity determinations made on this sample [7,30] indicates that both the integrated signal intensity of the cellulose spectra as well as the intensity of the individual lines are quantitative (e.g. representations of relative amounts present in the sample) for a wide range of contact times.

The average lateral fibril dimensions and average lateral fibril aggregate dimensions were estimated for all the used samples; the results are shown in Table 2. The average

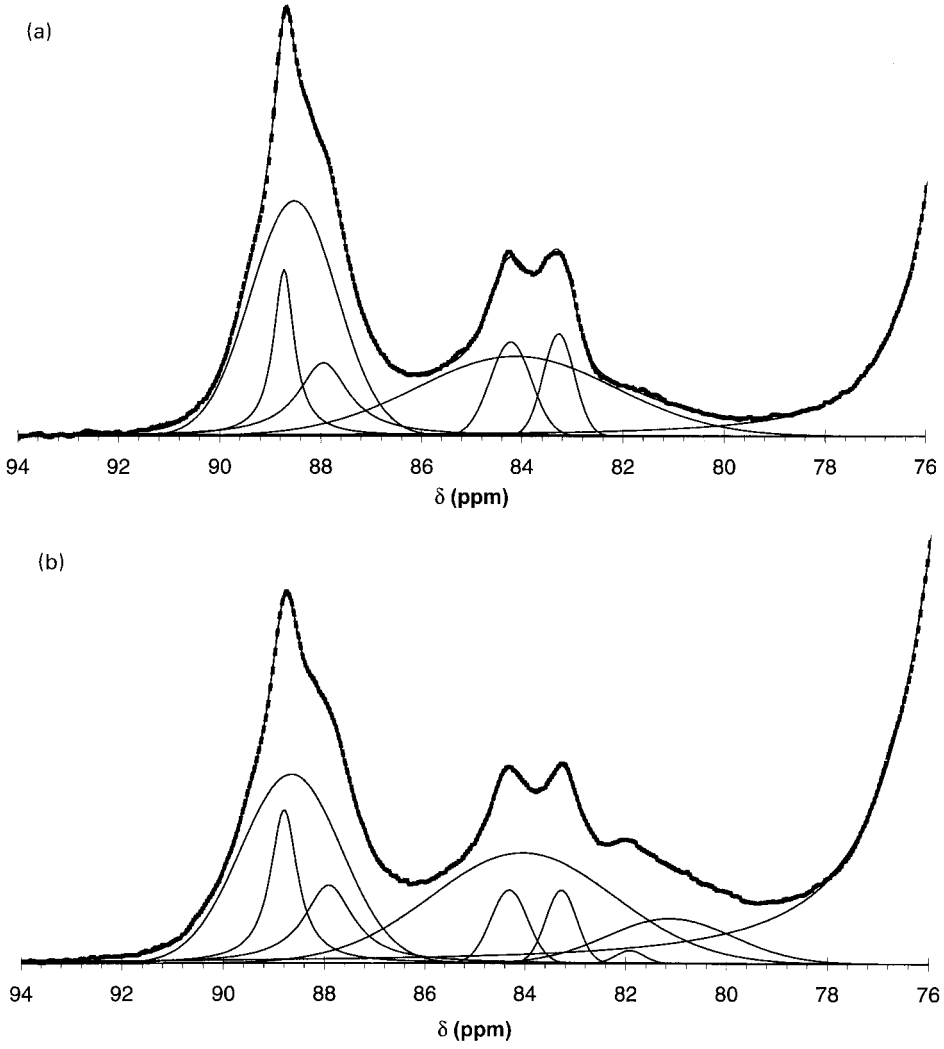

Fig. 2. The results of the spectral fitting of the C4-region recorded on: (a) chlorite-delignified and hydrolysed kraft pulp; and (b) kraft pulp. The broken lines represent the experimental spectrum. The fitted lines and their superposition are shown as solid lines.

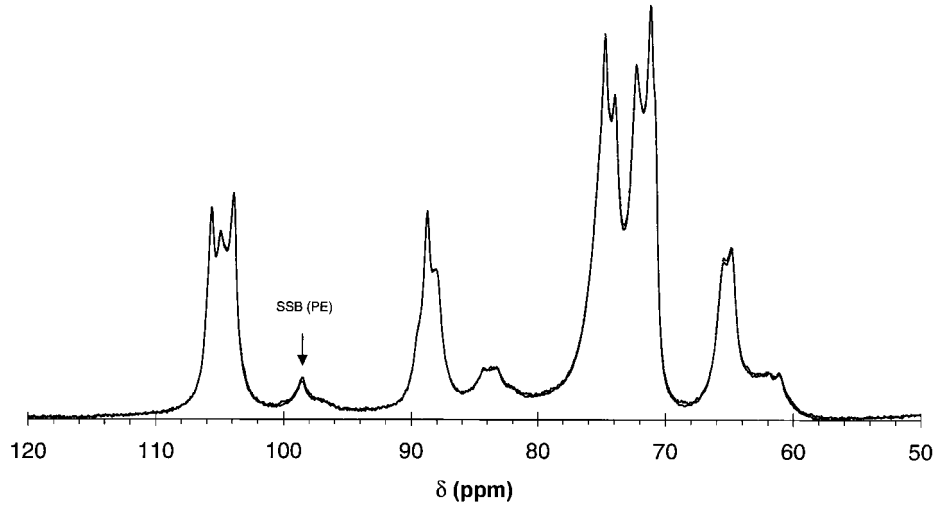

Fig. 3. The CP/MAS ^{13}C NMR spectra of cross-wise quantification of wet cotton linters and polyethylene at 600 μs (broken line) and 1800 μs (solid line). The signals at 98 ppm are the spinning side band (SSB) from polyethylene (PE).

Table 2
The lateral fibril dimensions and the lateral fibril aggregate dimensions for wood cellulose and the kraft pulps taken at different yields during a conventional laboratory kraft cook [8,9]

Sample	Lateral fibril dimension (nm)	Lateral fibril aggregate dimension (nm)
Wood cellulose	4.1 (0.1)[a]	14.9 (0.6)
Cook No. 1	3.7 (0.1)	14.7 (0.5)
Cook No. 2	4.1 (0.1)	19.3 (0.6)
Cook No. 3	4.1 (0.1)	18.6 (0.6)
Cook No. 4	4.2 (0.2)	19.1 (1.4)
Cook No. 5	4.4 (0.2)	17.7 (0.7)
Cook No. 6	4.2 (0.2)	17.5 (0.7)
Cook No. 7	4.8 (0.2)	17.3 (0.7)
Cook No. 8	4.6 (0.1)	18.7 (0.7)

[a] Values in parentheses are the standard errors.

Table 3
The kappa number, viscosity, yield and chemical composition of Pulps 1, and 3

	Pulp 1	Pulp 2	Pulp 3
Kappa number	22	28	28
Viscosity	1150	1190	1290
Yield (%)	44	49	54
Lignin (%)[a]	2.5	3.9	3.1
Cellulose (%)[b]	87.8	78.7	75.0
Glucomannan (%)[b]	4.9	7.5	13.3
Xylan (%)[b]	4.9	9.9	8.4

[a] Klason lignin content.
[b] Percent on fibre.

lateral fibril aggregate dimensions estimated by CP/MAS ^{13}C NMR agree well with the results reported by Duchesne and Daniel [8] based on field-emission scanning electron microscopy. As can be seen in Table 2, the fibril aggregate dimensions increase during the kraft pulping whereas the changes in fibril dimensions are slight. The increase in average lateral fibril aggregate dimension from 14.7 to 19.3 nm occurs in the initial phase of the pulping, i.e. between Cook No. 1 and Cook No. 2, according to Table 2.

During the initial phase of delignification, the dissolution of hemicelluloses is large (Table 1, Fig. 1) [31]. The increase in fibril aggregate dimension coincides with the large dissolution of hemicelluloses and a smaller dissolution of lignin. The present study cannot distinguish the relative importance of the two major spruce wood hemicelluloses *O*-acetylgalactoglucomannan and arabino-4-*O*-methylglucuronoxylan, but the hemicellulose dissolution is most noticeable as a decrease in *O*-acetylgalactoglucomannan content, from 18.6 to 5.9%, calculated on the original wood basis. The concomitant occurrence of the two events suggests that the removal of hemicelluloses and lignin in the initial phase is responsible for a further coalescence of cellulose fibril surfaces, leading to the observed increase in average lateral fibril aggregate dimension.

3.3. Changes in average lateral fibril aggregate dimension during drying

Three kraft pulps with a large span in hemicellulose content (10, 17 and 22%) and with relatively low lignin contents (2.5, 3.9 and 3.1%, respectively) were prepared, Table 3. To observe changes in aggregation of the cellulose fibrils induced by drying, for each of the kraft pulps the average lateral fibril dimension and the average lateral fibril aggregate dimension were determined both on a never-dried and a dried sample (dried handsheet). The lateral dimensions were estimated on the samples following the removal of lignin and hemicellulose, which implies that the dimensional changes observed are irreversible since a rather severe acid hydrolysis (2.5 M aqueous HCl for 17 h at 100°C) was performed after the drying step.

Table 4 shows the average lateral fibril dimensions and the average lateral fibril aggregate dimensions for the never-dried pulps and the pulp sheets. As observed, the aggregate dimensions are larger for the pulp sheets than for the never-dried pulps in the case of all three pulps. Further, a larger increase in aggregate dimension due to drying seems to correlate with a lower hemicellulose content, calculated as the sum of galactoglucomannan and arabino-4-*O*-methylglucuronoxylan, in the original pulp, as shown in Fig. 4.

In addition, the average lateral fibril dimensions increase slightly after drying as seen in Table 4. For Pulp 3, with the highest hemicellulose content of 22%, the increase in fibril dimension is statistically significant, from 3.9 to 4.5 nm after drying. Such an increase could be due to the removal of residual distortions in the interior of the cellulose fibril, i.e. an increase in order, during a drying and rewetting cycle [17].

Recent studies have shown that hornification is a feature of low-yield pulps [32], since in high-yield pulps (mechanical pulps), the interfibrillar spaces in the cell wall are filled with a hemicellulose-lignin gel preventing direct contact between the cellulose fibril surfaces during drying [33–35]. The present

Table 4
The lateral fibril dimension and the lateral fibril aggregate dimension for the never-dried kraft pulps and the dried handsheets

	Average lateral fibril dimension (nm)		Average lateral fibril aggregate dimension (nm)		
Sample	Never-dried pulp	Dried handsheets	Never-dried pulp	Dried handsheets	Hemicellulose (% on dry pulp)
Pulp 1	4.8 (0.2)	4.8 (0.1)	18.1 (0.8)	23.1 (1.0)	10
Pulp 2	4.5 (0.2)	4.8 (0.2)	17.9 (0.7)	21.4 (1.0)	17
Pulp 3	3.9 (0.1)	4.5 (0.1)	15.4 (0.5)	17.6 (0.6)	22

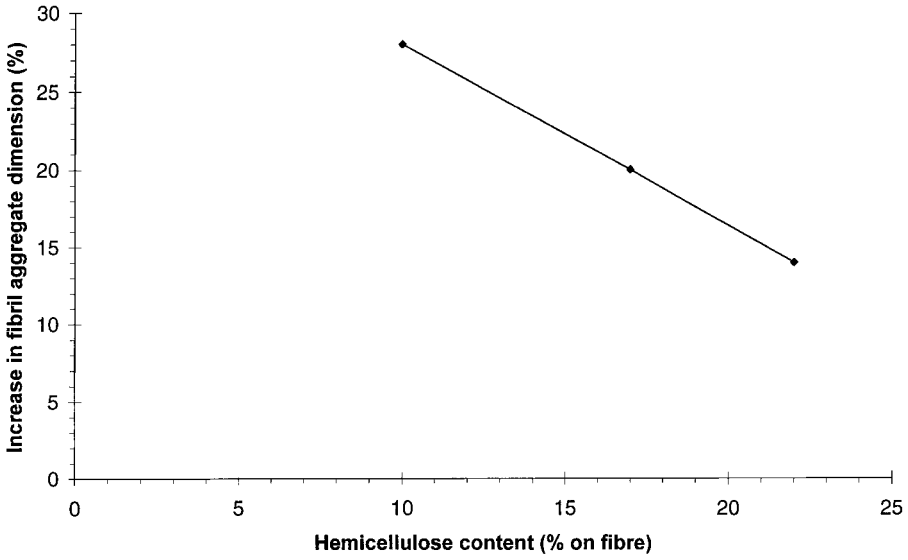

Fig. 4. The increase in fibril aggregate dimension is plotted against the hemicellulose content on the fibre.

study supports such a mechanism. Based on the observations in this study, it is established that an increase in fibril aggregate dimensions due to drying is a common phenomenon in spruce wood kraft pulps and that a higher hemicellulose content in the kraft pulps results in a lower tendency for aggregation.

4. Conclusions

The lateral fibril aggregate dimension increases during the initial phase of kraft pulping. The increase coincides with a large dissolution of hemicelluloses (*O*-acetylgalactoglucomannan in particular) and a smaller dissolution of lignin. The concomitant occurrence of these events suggests that the removal of hemicelluloses and lignin is responsible for coalescence of cellulose surfaces. In addition, aggregate dimensions continue to increase as a consequence of drying. This process was shown to be related to the hemicellulose content of the kraft pulps.

Acknowledgements

This work was carried out within the framework of the Wood Ultrastructure Research Centre (WURC), a NUTEK competence centre at the Swedish University of Agricultural Sciences. The authors thank Ulrika Molin for carrying out the kraft cook.

References

[1] Wågberg L. The fundamentals of papermaking materials, vol. 1. Leatherhead, UK: Pira International, 1997.
[2] Samejima M, Sugiyama J, Igarashi K, Eriksson K-E. Carbohydr Res 1998;305(2):281–8.
[3] Krässig HA. Cellulose. Structure, accessibility and reactivity, Polymer monographs, vol.11. Chemin de la Sallez, Yverdon, Switzerland: Gordon and Breach, 1993.
[4] Jayme G. Wochenbl Papierfabr 1944;6:187–94.
[5] Higgins HG, McKenzie AW. Appita 1963;16:145–64.
[6] Young RA. Cellulose 1994;1:107–30.
[7] Hult E-L, Larsson PT, Iversen T. Cellulose 2000;7(1):35–55.
[8] Duchesne I, Daniel G. Nordic Pulp Pap Res J 2000;15:54–61.
[9] Hult E-L, Larsson PT, Iversen T. Nordic Pulp Pap Res J 2000 (in press).
[10] Theander O, Westerlund EA. J Agric Food Chem 1986;34:330–6.
[11] Janson JOG. Faserforsch Textiltech 1974;25:379–80.
[12] Larsson PT, Wickholm K, Iversen T. Carbohydr Res 1997;302:19–25.
[13] Atalla RH, Gast JC, Sindorf OW, Bartuska VJ, Maciel GE. J Am Chem Soc 1980;102:3249–51.
[14] Earl WL, VanderHart DL. J Am Chem Soc 1980;102:3251–2.
[15] Teeäär R, Serimaa R, Paalkkari T. Polym Bull 1987;17:231–7.
[16] Larsson PT, Westermark U, Iversen T. Carbohydr Res 1995;278:339–43.
[17] Wormald P, Wickholm K, Larsson PT, Iversen T. Cellulose 1996;3:1–12.
[18] Wickholm K, Larsson PT, Iversen T. Carbohydr Res 1998;312:123–9.
[19] Ha MA, Apperley DV, Evans BW, Huxham M, Jardine WG, Remco JV, Reis D, Vian B, Jarvis MC. Plant J 1998;16:183–90.
[20] Smith BG, Harris PJ, Melton LD, Newman RH. Plant Cell Physiol 1998;39(7):711–20.
[21] Heux L, Dinand E, Vignon MR. Carbohydr Polym 1999;40:115–24.
[22] Sugiyama J, Vuong R, Chanzy H. Macromolecules 1991;24:4168–75.
[23] Heiner AP, Kuutti L, Teleman O. Carbohydr Res 1998;306:205–20.
[24] Newman RH. Solid State Nucl Magn Reson 1999;15:21–9.
[25] Wilder HD, Daleski EJ. TAPPI J 1965;48(5):293–7.
[26] Kleinert TD. TAPPI J 1966;49(2):53–7.
[27] Kleppe PJ. TAPPI J 1970;53:35–47.
[28] LéMon S, Teder A. Svensk Papperstidning 1973;76:407–14.
[29] Larsson PT, Hult E-L, Wickholm K, Pettersson E, Iversen T. Solid State Nucl Magn Reson 1999;15:31–40.
[30] Horii F, Hirai A, Kitamaru R. J Carbohydr Chem 1984;4:641–62.
[31] Kondo R, Sarkanen KV. Holzforschung 1984;38:31–6.
[32] Scallan AM, Tigerström AC. J Pulp Pap Sci 1992;18:J188–93.
[33] Spiegelberg H. TAPPI J 1966;49(9):388–96.
[34] Newman RH, Hemmingson JA. ISWPC. Montreal, Canada, 1997. p. O1–1.
[35] Oksanen T, Buchert J, Viikari L. Holzforschung 1997;51:355–60.