ELSEVIER

PII: S0144-8617(96)00129-4

Carbohydrate Polymers 32 (1997) 57–63
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0144-8617/97/$17.00 + .00

Characterization of the cellulosic residues from lithium chloride/*N*,*N*-dimethylacetamide dissolution of softwood kraft pulp

Elisabeth Sjöholm[a], Kristina Gustafsson[a], Bert Pettersson[a] & Anders Colmsjö[b]

[a]*STFI, Swedish Pulp and Paper Research Institute, Box 5604, S-114 86 Stockholm, Sweden*
[b]*National Institute of Occupational Health, S-171 84 Solna, Sweden*

(Received 21 November 1995; revised version received 20 March 1996; accepted 13 April 1996)

In contrast to hardwood kraft pulps, softwood kraft pulps are not completely soluble in LiCl/DMAc. Characterization of the undissolved fraction was made in order to obtain an understanding of the reason for its limited solubility. It was found that the residue consisted mainly of latewood fibers. In comparison with the initial pulp, the residue contains a higher relative amount of mannan, lignin and nitrogen. The nitrogen was assumed to originate from degraded proteins retained in the pulp. In contrast, the softwood pulp xylan seems to be easily dissolved and mainly amorphous structures were present in the residue. On the addition of LiCl/DMAc, gel formation occurs, probably caused by the glucomannan content of the softwood kraft pulp. The gel formation also seems to be the main reason for the limited solubility of pulps with low lignin content. © 1997 Elsevier Science Ltd

INTRODUCTION

Wood is the most important renewable raw material for papermaking. There is an increased interest in improving processing and in designing wood pulps for various paper products. In order to understand and control pulping processes, more direct analytical methods are required for the purpose of determining pulp properties.

One of the most important properties of the pulp is strength. Since there is a correlation between intrinsic viscosity and strength properties of bleached kraft pulps (Rydholm, 1967a), pulp viscosity has been used to estimate the degree of degradation after different process stages. However, the correlation is not the same for unbleached pulps with large amounts of non-cellulosic material. For example sulphite pulps have a higher viscosity than kraft pulps, although they are weaker (Rydholm, 1967b). In addition, kraft pulps cooked with black liquor-pretreated wood chips have an opposite strength–viscosity relationship vs conventional kraft pulps, where strength improves with increasing viscosity (Andrews, 1989). The viscosity depends on the whole pulp sample and, therefore, information concerning specific alterations of the different polymers initiated during pulping are omitted.

An alternative way to study degradation of wood pulps is to characterize the dissolved polymers after separation according to hydrodynamic size by size exclusion chromatography (SEC). One of the most promising solvents for this purpose is lithium chloride/*N*,*N*-dimethylacetamide (LiCl/DMAc). Originally, the solvent was used to dissolve chitin (Austin, 1977) and for the preparation of cellulose derivatives (McCormick & Lichatowich, 1979; McCormick, 1981). This solvent is considered to be non-degrading (Turbak *et al.*, 1981; Turbak, 1983) although a slight decrease in the viscosity of cellulose solutions after 30 days has been reported (McCormick *et al.*, 1985).

Utilizing LiCl/DMAc, the molecular weight distribution (MWD) of cellulose from cotton fibers (Timpa, 1991), purified cellulose samples (Kennedy *et al.*, 1990; Kvernheim & Lystad, 1989) and solutions of wood pulp from the kraft (Kennedy *et al.*, 1990; Westermark & Gustafsson, 1994) and sulphite (Ekmanis, 1986; Kvernheim & Lystad, 1989; Kennedy *et al.*, 1990) processes has been determined by SEC.

In contrast to hardwood kraft pulps, softwood kraft pulps (SWKP) are incompletely dissolved in LiCl/DMAc (Karlsson & Westermark, 1994). The dissolution of SWKP yields two fractions, one of which is dissolved; the other fraction is gel-like, which renders a pellet on centrifugation. Since the main pulp production in

Sweden is based on softwood, it would be of great interest if SWKPs could also be dissolved and characterized by SEC by using LiCl/DMAc as a solvent.

In alkaline pulping of softwoods, such as the kraft process, more than 30% of the raw material is lost. More than half of the xylan is retained in a pine kraft pulp, whereas only about 25% of the original amount of the deacetylated galactoglucomannan remains in the pulp.

The extensive loss of carbohydrates during alkaline pulping is caused by dissolution of the hemicelluloses in the cooking liquor and hydrolysis of the polysaccharide chain at the reducing end (peeling reaction). This reaction continues until the reducing end group has been transformed into a stable carboxylic acid group by a competing reaction. This kind of degradation is more severe for the hemicelluloses, especially mannans, than for cellulose. It is generally considered that the divergence in susceptibility to the peeling reaction is caused by the amorphous state of the hemicelluloses and their lower molecular weight compared to cellulose. The final kraft pulp has a much lower uronic acid content compared to the original wood, partly because the uronic acid groups are easily hydrolysed in alkali. In spite of the severe cooking conditions, there are still traces of arabinose and galactose residues in the xylan respective glucomannan polymer remaining in the kraft pulp. Alkaline hydrolysis of cellulose is a more important degradation reaction than for hemicelluloses, although the loss of cellulose is relatively small, the cleavage of the glycosidic linkages in the cellulose chain results in a decrease in viscosity during kraft pulping (Sjöström, 1981a).

In order to explain the limited solubility of a SWKP in LiCl/DMAc, the chemical composition and the microscopic structure of the residue were examined. Sample preparation and its effect on the amount of undissolved pulp is also briefly evaluated.

EXPERIMENTALS

Materials

All chemicals were of analytical grade. Lithium chloride (Merck, Darmstadt, Germany) was divided into small portions and stored in a desiccator over phosphorus pentoxide. Once withdrawn from the desiccator, the portion was weighed and then immediately added to the DMAc (Sigma-Aldrich, Gillingham, UK) which was filtered prior to use. Dissolution of the salt was carried out under vacuum, with cautious heating and continuous stirring for about 30 min. The LiCl/DMAc solution was stored at +4°C.

An industrial unbleached SWKP with kappa number 18 and viscosity 950 dm^3/kg was used as a starting pulp in the characterization study. Together with this starting pulp, an unbleached SWKP with kappa number 79 and a SWKP pretreated with oxygen and bleached with chlorine dioxide, with 86% brightness and viscosity 610 dm^3/kg was used in the gravimetric study.

Pectinase, Novoferm 26, 33 μkat/ml (Novo Nordisk, Denmark) and mannanase, from *Trichoderma reesei*, 1·5 μkat/mL (VTT, Finland) were used for the enzymatic treatments. Cotton linter with a viscosity of 870 dm^3/kg (AB Klippans Finpappersbruk, Lessebo, Sweden) was used as substrate to examine cellulase activity of the pectinase.

Galactoglucomannan was isolated from softwood by the method described by Berthold (1994) and arabinoglucuronoxylan was isolated from softwood by the method described by Hansson (Hansson & Hartler, 1968). Pulp lignin was obtained by extraction of a softwood pulp (Gellerstedt *et al.*, 1994).

Pulp sample preparation

To obtain sufficient material for the characterization study, a preparative sample dissolution was made, from batches of 250 mg pulp. In the gravimetric study, an analytical sample preparation was made from 15 mg pulp.

The pulps were carefully washed with water to remove any remaining cooking chemicals, after which they were soaked in deionised water at +4°C for 1 h. The pulp was filtered through a glass filter, DMAc was added and the solvent was allowed to equilibrate with the pulp for 30 min prior to filtering. This procedure was repeated three times before 8% (w/v) LiCl/DMAc was added and the solution was allowed to stand for 5 days at +4°C. The final solution was obtained by dilution with DMAc to a final concentration of 0·5% with respect to LiCl and 0·05% with respect to pulp. For the characterization study, the solution was centrifugated at 2700 g for 30 min, and the gel-like pellet was collected, washed with DMAc and finally dried. This part, designated residue, was characterized and compared with the composition of a dried pulp sample withdrawn before the addition of LiCl/DMAc, designated initial pulp.

In the gravimetric study, one of the sample preparations included an additional solvent-exchange step using methanol prior to the replacement by DMAc. The replacement by methanol was repeated three times for 30 min each time, in the same way as for DMAc. The centrifugation was carried out at 87 000 g for 30 min. Since LiCl is highly hygroscopic, the pellet was washed with DMAc and deionised water until the conductance of the water was low and stable, after which the residue was obtained by freeze-drying and then weighed.

Chemical analysis

The kappa number reflects the amount of oxidizable structures in the pulp and is used as a measure of the lignin content. This was determined by the consumption of permanganate according to ISO 302 (1981). Determination of the brightness of the bleached pulp was made according to SCAN-C11:75. The viscosity of pulps dissolved in cupriethylenediamine (CED) was determined according to ISO 5351/1 (1981). To obtain the neutral carbohydrate composition, the samples were first extracted with dichloromethane and then subjected to acid hydrolysis (Theander & Westerlund, 1986). After reduction, the corresponding alditols were acetylated and analyzed by gas chromatography using 2-deoxy-galactose as an internal standard. Separation was performed on a fused silica column DB-1 (J and W Scientific), (25 m×0·32 mm inner diameter × 0·17 μm thick phase). The injector temperature was 260°C and the temperature of the flame ionization detector 290°C. Helium was used as a carrier gas, flow 1·85 ml/min, split ratio 1:20 and the temperature program was: 160°C for 2 min, the temperature being increased by 2°/min up to 250°C. The acid-insoluble part of the pulp sample is designated Klason lignin. Acid-soluble lignin was determined by measuring the absorbance of the hydrolysate at 205 nm, using a correction factor for the degradation products from the carbohydrates (Schöning & Johansson, 1965).

The elemental composition was carried out by Mikro Kemi AB, Uppsala, Sweden and the metal analysis by SGAB, Luleå, Sweden.

Enzymatic treatments

A solution of 1 g substrate/100 ml buffer was treated by pectinase using a 50 mM sodium acetate buffer, pH 3·8 at 40°C for 18 h. The enzymatic activity used for the treatment of the softwood pulp was 70 μkat/100 ml, while the incubation of cotton linter was performed at various activities (see Results and Discussion). After incubation of the linter sample, 5 ml of the buffer was withdrawn and the amount of dissolved carbohydrates was determined by the orcinol method (Vasseur, 1948).

The mannanase treatments were carried out in a 50 mM sodium acetate buffer, pH 5·0 at 40°C for 24 h. The enzymatic activity in the incubation solution was 25 μkat/100 ml and gram substrate (SWKP). The neutral carbohydrate composition of the solubilized carbohydrates were determined as described in the chemical analysis section.

Solid state NMR

The ^{13}C-crosspolarized magic angle spinning (^{13}C-CP/MAS) NMR measurements were performed on a Bruker AMX 300 instrument operating at 75·47 MHz at ambient temperature. Rotor speed was 5 kHz using double air bearing probe and ZrO_2 rotors. Instrumental parameters were: 1 ms contact time, 2 K datapoints filled to 4 K. The chemical shift scale was referenced to the carbonyl peak in glycine, located at 176·03 ppm. Number of scans on each spectra was 3000.

RESULTS AND DISCUSSION

Gravimetric determination

To study the influence of the lignin content and the effect of different treatments on the amount of residue obtained after dissolution in LiCl/DMAc, gravimetric determinations were carried out on various SWKPs.

Preparative sample handling, performed for the characterization study, resulted in a larger amount of residue (43%) in comparison to an analytical preparation (37%), see Fig. 1. Since any water remaining in the pulp may have a negative influence on the dissolution (Turbak *et al.*, 1981), an additional solvent-exchange step using methanol prior to the replacement by DMAc

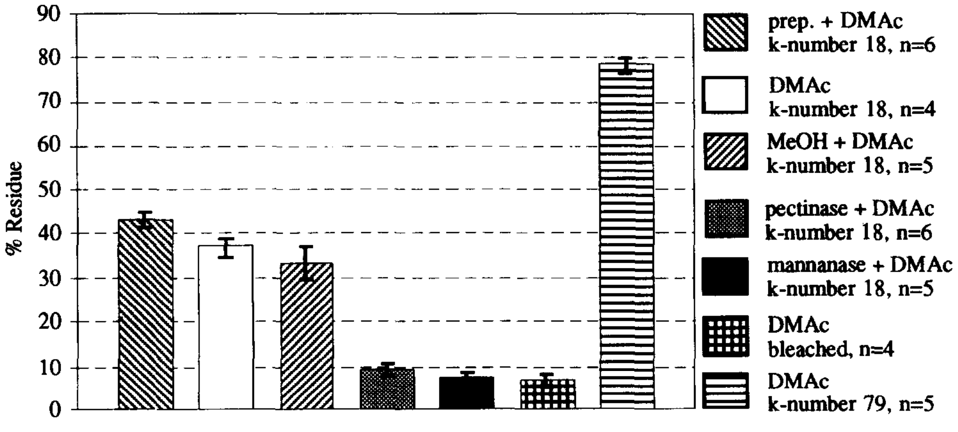

Fig. 1. The influence of the sample preparation and the kappa number on the relative amount of LiCl/DMAc undissolved material from SWKPs according to gravimetric determination. The error bars indicate the standard deviation of the mean, *n* = number of samples and prep. = preparative sample handling.

was performed. However, this seems to be insignificant with regard to the amount of residue obtained.

The results in Fig. 1 clearly show that the kappa number, i.e. lignin content of the starting pulp has a great impact on the amount of obtainable residue. At a kappa number of 18, about 37% of the initial pulp is undissolved, while with a kappa number of 79, the undissolved amount is increased to 78%. In this case, the very high kappa number is, in itself, the most probable explanation for poor solubility. The high lignin content makes the pulp fibers stiff and thereby decreases their ability to swell. However, the limited solubility of SWKPs in LiCl/DMAc cannot solely be explained by the presence of lignin, since 8% of the bleached starting pulp still remains undissolved.

Enzymatic treatments

The positive effect of pretreating the pulp with pectinase before the sample preparation is significant; thus 9% of the pulp was still undissolved. This can be compared with the same starting pulp without enzyme pretreatment, when 37% was undissolved, Fig. 1. The pectinase is a mixture of several pectin degrading enzymes acting by, e.g. random hydrolysation of the 1,4-α-D-galactosiduronic linkages in pectate and other galacturonans. Pectin in softwood is evenly distributed across the fiber wall, but the highest concentration is found in the middle lamella (Parmeswaran & Liese, 1982), where the defibration occurs during pulping. The initial amount of pectin in wood is low (Timell, 1967), and the amount remaining in the pulp is considered to be negligible. Therefore, the increased solubility of the softwood pulp is probably due to enzymatic activity other than that of the pectinase. In order to evaluate the purity of the enzyme with regard to cellulytic activity, cotton linter was treated with various concentrations of pectinase. It was found that the amount of glucose increases with increasing enzyme concentration, which indicates an elevation in cellulose degradation (Fig. 2). The decrease in viscosity of the cotton linter, from 840 to 780 dm^3/kg, was however small at the enzyme concentration with which the softwood pulp shown in Fig. 1 was treated (70 μkat/g pulp).

A considerable drop in viscosity of the SWKP treated by pectinase, from 950 to 705 dm^3/kg, was found. This can be ascribed to the lower crystallinity of the pulp in comparison with cotton linter, which makes enzymatic treatment more efficient. Carbohydrate analysis of the pectinase-treated SWKP revealed a slight decrease in the amount of xylan compared with non-treated SWKP. Degradation of the pulp lignin by the pectinase preparate cannot explain the increased solubility of the treated SWKP, since the decrease in kappa number and Klason lignin after the treatment was low. Altogether, these results indicate that the effect of the extensive treatment by pectinase is caused by other enzymes in the preparation.

The effect of pretreating the SKWP with mannanase is also significant. Only 7% of the pulp remained undissolved after the sample preparation, Fig. 1. The relative composition of neutral monosaccharides in the hydrolysate from the mannanase treated pulp was: 47·8% mannose; 14·2% glucose; 3·5% galactose; 0·4% xylose; and 0·2% arabinose, which corresponds to a ratio of galactose:glucose:mannose of 0.2:1:3.4. This can be compared to the composition of galactoglucomannans in softwood; which is 0.1–1:1:3–4 for the same components (Sjöström, 1981b). The increased solubility of the SWKP after treatment with mannanase may thus be due to degradation of the galactoglucomannans in the pulp.

One important parameter for the efficiency of enzymatic degradation is the pore size of the pulp fiber (Viikari *et al.*, 1990). Because of this, only the surface of the fiber is considered to be accessible for enzymatic modification. Therefore, the reason for the increased solubility of the SWKP pretreated by the pectinase preparate may be due to degradation of polysaccharides

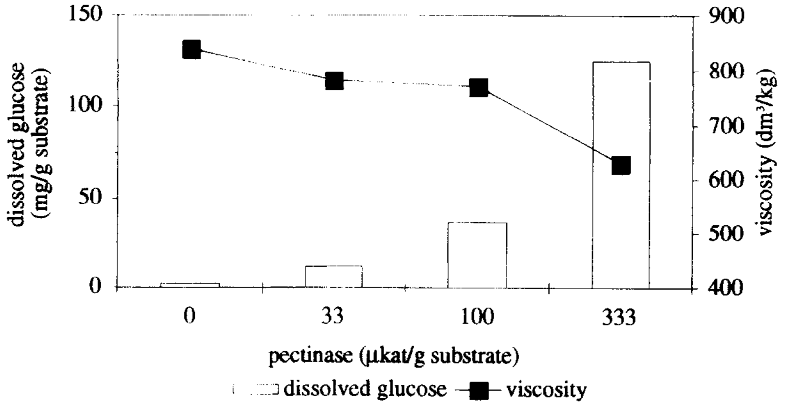

Fig. 2. Presence of cellulase activity in pectinase preparation, using cotton linter as substrate. Viscosity of the cotton linter and total glucose dissolved in the incubation solution was determined after treatment by pectinase at various concentrations.

present on the surface of the fibers, which exhibit gelling properties, probably galactoglucomannans.

Elemental analysis

The nitrogen content of the residue is higher compared to that of the initial pulp, see Table 1; the origin of this nitrogen is probably from degraded proteins remaining in the pulp. Contamination by the nitrogen-containing solvent was excluded, since the initial pulp was also subjected to DMAc. Both the initial pulp and the residue have a similar content of elemental oxygen and ash. If a larger amount of carboxylic groups had been present in the residue, this would have coincided with an increase in oxygen content in the residue as well as in the amount of divalent cations such as calcium, which was not the case according to metal analysis, see Table 2. Also, IR analysis revealed no differences in functionality between the initial pulp and the residue. Altogether, these results suggest that the incomplete solubility is not caused by carboxylic groups in the SWKP.

Monosaccharides and lignin content

The relative distribution of monosaccharides and lignin in the residue differs from the initial pulp, Fig. 3. The most striking observation is the low content of xylan in the residue, which may reflect the high solubility of the xylan in LiCl/DMAc. In contrast, the concentration of mannan is higher in the residue compared to the initial pulp. This divergence in solubility of the hemicelluloses is in accordance to the different solubility of isolated preparations. It was found that arabinoglucuronoxylan was almost completely dissolved after the addition of a small amount of water prior to dissolution, while galactoglucomannan isolated from softwood formed a gel on addition of LiCl/DMAc.

Table 1. Elemental composition of the initial pulp and the residue obtained from LiCl/DMAc dissolution of unbleached SWKP

	C	H	N	O	ash
			(%)		
Initial pulp	44·8	6·3	0·6	48·3	0·5
Residue	45·4	6·8	1·3	46·1	0·4

Table 2. Metal content of the initial pulp and the residue obtained from LiCl/DMAc dissolution of unbleached SWKP

	Ba	Ca	Cu	Fe	Mg	Mn
			(ppm)			
Initial pulp	3·6	350	1·5	10·5	50	10
Residue	<0·9	10	1·9	3·7	<3·5	1·2

The formation of a gel on utilizing LiCl/DMAc in order to dissolve SWKP can be attributed to the chemical modifications of the galactoglucomannan that occurs during pulping. In thermomechanical pulping (TMP) of spruce, where no chemicals are added, Thornton *et al.* found that enzymatic deacetylation of the dissolved galactoglucomannans led to an adsorption onto the TMP fiber (Thornton *et al.*, 1994). Adsorption of deacetylated pine glucomannan onto cellulose has also been observed by Hansson (Hansson, 1970). Gelling and adsorption onto the fibers is favored by low amounts of galactose groups (Overbeeke *et al.*, 1987; Thornton *et al.*, 1994) and is also affected by the ratio of glucose: mannose in the deacetylated galactoglucomannans (McCleary, 1990). It is thus possible that the glucomannan dissolved in the black liquor during SWKP, precipitates onto the fibers and causes the gel formation on dissolution of SWKP in LiCl/DMAc.

Although the lignin content is higher in the residue, an isolated pulp lignin preparation was easily dissolved in LiCl/DMAc. This indicates that the low solubility of pulps with high lignin content is connected with limited swellability of the pulps rather than to the chemical composition of lignin.

Crystallinity

According to ^{13}C-CP/MAS-NMR, Fig. 4, the signals corresponding to crystalline cellulose in the spectrum of the residue are, in contrast to the starting pulp, of low intensity. Cotton linter, which has a higher crystallinity index than SWKP (Lennholm *et al.*, 1994), is completely

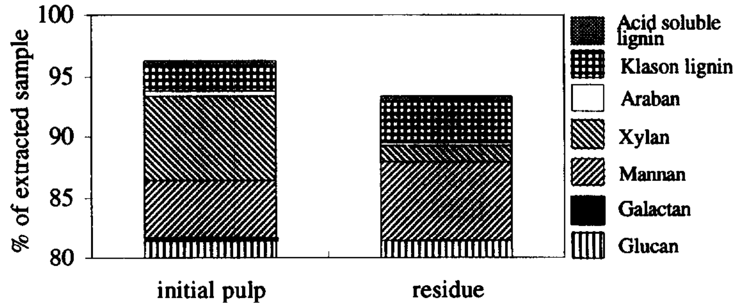

Fig. 3. The lignin and carbohydrate content and composition of the initial pulp and the residue obtained from LiCl/DMAc dissolution of unbleached SWKP.

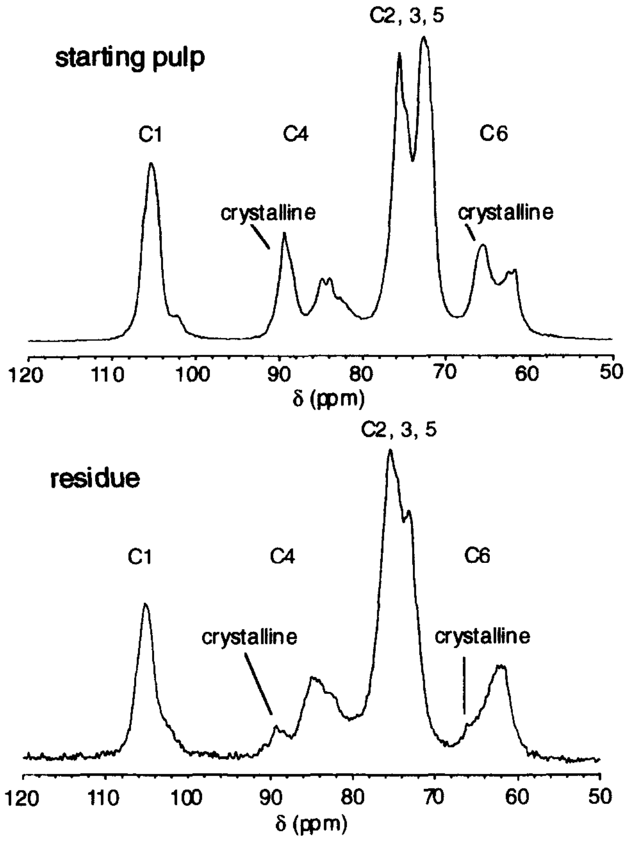

Fig. 4. ^{13}C-CP/MAS-NMR spectra of the starting pulp and the residue obtained from LiCl/DMAc dissolution of unbleached SWKP.

soluble in LiCl/DMAc. This emphasizes that there is no obvious connection between the limited solubility and presence of the crystalline cellulose.

Microscopic analysis

The residue was also studied by microscopy, utilizing the differential interference contrast technique. Apart from some ray cells, the residue was found to consist of latewood fiber fragments. The relative percentage of glucomannan in latewood fibers is higher than in earlywood fibers (Meier, 1962). Latewood fibers are in general difficult to impregnate, since pits are relatively less frequent in the fiber walls of these than of earlywood fibers. The low amount of lithium found trapped in the gel also indicated difficulties for the LiCl/DMAc to penetrate the fiber surface. To examine the importance of impregnation, SWKP was extensively ground prior to dissolution in LiCl/DMAc but no improvement of the solubility could be observed. One possibility is that the formation of the gel, probably initiated by glucomannan, takes place quickly and covers the fibers. In this way, the gel may restrict the accessibility of the LiCl/DMAc. Thus, it is possible that the thick-walled latewood fibers are more difficult to dissolve, partly due to the higher content of glucomannan, and partly because, in order to dissolve, these fibers need to be exposed to the solvent for a longer period of time than the earlywood fibers.

CONCLUSION

The residue obtained from LiCl/DMAc dissolution of SWKPs consists of larger amounts of mannan and lignin but has a diminished xylan content compared with the initial pulp. It was found that the residue, to a large extent, consists of latewood fibers. An enhanced level of nitrogen, probably originating from degraded proteins retained in the pulp, is also found in the residue.

There is no single explanation for the limited solubility of SWKPs in LiCl/DMAc. The formation of the gel, probably due to glucomannan, seems to be the main reason for the incomplete solubility of pulps with kappa numbers below 18. At very high kappa numbers, it seems reasonable that the stiffness of the fibers, i.e. low swellability, restricts the dissolution. It is demonstrated that the crystallinity of the pulp does not influence the solubility in LiCl/DMAc. Enzymatic pretreatment seems to be a promising method for increasing pulp solubility, although it is difficult to draw any specific conclusions about the effect of the pectinase treatment of SWKP, since our knowledge of the enzyme preparation is insufficient. The increased solubility after treatment with mannanase may be due to degradation of galactoglucomannans adsorbed on the pulp fibers. The ratio of galactose:glucose:mannose found in the hydrolysate after mannanase pretreatment of the SWKP is similar to the composition in softwood, indicating that the galactoglucomannans dissolved from the wood fibers are not degraded to any appreciable extent during the kraft cook.

As the chemical composition of the residue differs from that of the initial pulp, it seems to be doubtful if LiCl/DMAc dissolved softwood pulps can be characterized in a reliable way as long as the pulps are incompletely dissolved.

ACKNOWLEDGEMENTS

Philip Wormald is greatly acknowledged for the NMR-analysis and Ann-Chatrin Haglund for the microscopic analysis. Maija Tenkanen is greatly acknowledged for providing the mannanase, Jesper Berthold and Annika Rydlund for the hemicellulose preparations, and Göran Gellerstedt for the residual lignin preparation.

REFERENCES

Andrews, E.K. (1989). *Proc. Tappi Pulping Conf.*, pp 607–625.
Austin, P.R. (1977). Chitinlösung und deren Verwendung, German Offen. 2,707,164.

Berthold, J. (1994). Hydratation et gonflement des constituants polymères du bois, PhD dissertation, L'Universté Joseph-Fourier, Grenoble, France.

Ekmanis, J.L. (1986). *Waters*, **13**.

Gellerstedt, G., Pranda, J. & Lindfors, E.-L. (1994). *J. Wood Chem. Technol.*, **144**, 467–482.

Hansson, J.-Å. (1970). *Holzforschung*, **243**, 77–83.

Hansson, J.-Å., Hartler, N. (1968). *Sv. Pappertidn.*, **719**, 358–365.

Karlsson, O. & Westermark, U. (1994). *Proc. Tappi Pulping Conf.*, **1**, 1–4.

Kennedy, J.F., Rivera, Z.S., White, C.A., Lloyd, L.L. & Warner, F.P. (1990). *Cellulose Chem. Technol.*, **24**, 319–325.

Kvernheim, A.L. & Lystad, E. (1989). *Acta Chem. Scand.*, **43**, 209–211.

Lennholm, H., Larsson, T. & Iversen, T. (1994). *Carbohydr. Res.*, **261**, 119–131.

McCleary, B.V. (1990). In *Enzyme in Biomass Conversion*, eds G.F. Leatham & M.E. Himmel. ACS Symposium Series 460, American Chemical Society, Washington, D.C., pp. 437–449.

McCormick, C.L. (1981). Novel cellulose solutions, U.S. Patent 4,278,790.

McCormick, C.L. & Lichatowich, D.K. (1979). *Polym. Sci., Polym. Lett. Ed.*, **17**, 479–484.

McCormick, C.L., Callais, P.A. & Hutchinson, B.H.Jr. (1985). *Macromol.*, **18**, 2394–2401.

Meier, H. (1962). *Pure Appl. Chem.*, **5**, 37–52.

Overbeeke, N., Fellinger, A.J. & Termorshuizen, G.H.M. (1987). *Proc. 4th Eur. Congr. Biotechnol.*, **1**, 509.

Parmeswaran, N. & Liese, W. (1982). *Holz. Roh. Roh.-Werkst.*, **40**, 145–155.

Rydholm, S.A. (1967a). In *Pulping Processes*. Interscience Publishers, New York, pp. 970–971.

Rydholm, S.A. (1967b). In *Pulping Processes*. Interscience Publishers, New York, pp. 1160–1162.

Schöning, A.G. & Johansson, G. (1965). *Sv. Papperstidn.*, **6818**, 607–613.

Sjöström, E. (1981a). In *Wood Chemistry, Fundamentals and Applications*. Academic Press, New York, pp. 134–138.

Sjöström, E. (1981b). In *Wood Chemistry, Fundamentals and Applications*. Academic Press, New York, pp. 60–61.

Theander, O. & Westerlund, E.A. (1986). *J. Agric. Food Chem.*, **34**, 330–336.

Thornton, J., Tenkanen, M., Ekman, R., Holmbom, B. & Viikari, L. (1994). *Holzforschung*, **48**, 436–440.

Timell, T.E. (1967). *Wood Sci Technol.*, **1**, 45–70.

Timpa, J. (1991). *J. Agric. Food Chem.*, **39**, 270–275.

Turbak, A.F. (1983). In *Wood and Agricultural Residues*, ed. E.J. Soltes. Academic Press, New York, pp. 87–99.

Turbak, A.F., El-Kafrawy, A., Snyder, F.W. & Auerbach, A.B. (1981). Solvent system for cellulose, U.S. Patent 4,302,252.

Vasseur, E. (1948). *Acta Chem. Scand.*, **2**, 695–701.

Viikari, L. Kantelinen, A., Rättö, M. & Sundquist, J. (1990). In *Enzyme in Biomass Conversion*, eds G. Leatham & M. Himmel. ACS Symp. Ser. 460, American Chemical Society, Washington, DC. pp. 13–21.

Westermark, U. & Gustafsson, K. (1994). *Holzforschung*, **48**, 146–150.