Carbohydrate Polymers 41 (2000) 153–161

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Aggregation of cellulose in lithium chloride/*N*,*N*-dimethylacetamide

E. Sjöholm[a,*], K. Gustafsson[a], B. Eriksson[a], W. Brown[b], A. Colmsjö[c]

[a]*Swedish Pulp and Paper Research Institute, Box 5604, SE-114 86 Stockholm, Sweden*
[b]*Department of Physical Chemistry, University of Uppsala, SE-751 21 Uppsala, Sweden*
[c]*Arrhenius Laboratory, Department of Analytical Chemistry, University of Stockholm, SE-106 91 Stockholm, Sweden*

Received 19 January 1999; received in revised form 21 May 1999; accepted 1 June 1999

Abstract

Hardwood kraft pulps can be completely dissolved in lithium chloride/*N*,*N*-dimethylacetamide (LiCl/DMAc). The cellulose and hemicellulose components can be separated by size exclusion chromatography (SEC). The molecular weight distribution that corresponds to cellulose is extended up to the high molecular weight region and the weight average molecular weight (M_w) relative to pullulan of this distribution is high. Light scattering (LS) measurements were conducted on a cotton linters sample of a similar elution volume as the cellulose portion of the pulp. The true M_w of the cotton linters sample measured by LS was in close agreement with the M_w determined relative to pullulan using SEC. Gaussian curve fitting revealed an additional high molecular weight component, not apparent in the chromatogram of hardwood pulp. Based on this finding the high M_w is suggested to be due to aggregation of cellulose in LiCl/DMAc. The influence of dissolution conditions is discussed and a method for deaggregating the cellulose portion of dissolved hardwood pulps is proposed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Cellulose aggregation; Lithium chloride/*N*,*N*-dimethylacetamide; Size exclusion chromatography

1. Introduction

In order to improve the quality of wood pulp, it is relevant to understand the influence of the process conditions on cellulose, hemicellulose and lignin. In general, the chemical structure and molecular weight are important parameters in relation to the physical properties of polymeric materials (Stevens, 1990). Size exclusion chromatography (SEC) is a suitable technique to obtain knowledge of polymer composition, molecular weight distribution (MWD), and molecular weight averages of kraft pulps. However, the polysaccharides in pulp, particularly cellulose, have a limited solubility in common solvents.

One promising solvent system for SEC characterizations of hardwood pulps is lithium chloride/*N*,*N*-dimethylacetamide (LiCl/DMAc). The latter is a non-derivatizing solvent for cellulose (Nehls, Wagenknecht & Philipp, 1995) and a number of structural models of the solvent and for the solvent–cellulose complex have been proposed and reviewed recently (Morgenstern & Kammer, 1996; Striegel, 1997). The solvent is generally described as a complex between lithium and DMAc with a free chloride anion, $[\mathrm{Li}\cdot x\mathrm{DMAc}]^+\mathrm{Cl}^-$. The dissolution of cellulose is thought to proceed by exchange of one molecule of DMAc by one hydroxyl group of cellulose. Due to its basicity, the chloride weakens the hydrogen bonds of cellulose and thereby participates in the dissolution. Cellulose is dissolved in LiCl/DMAc with no degradation (Turbak, 1983; Turbak, El-Kafrawy, Snyder & Auerbach, 1981) although a slight decrease in the viscosity of cellulose solutions after 30 days has been reported (McCormick, Callais & Hutchinson, 1985). The preparation of sample solutions suitable for SEC is relatively simple but requires activation either in water followed by solvent exchange (Ekmanis, 1986) or by refluxing DMAc (Timpa, 1991). LiCl/DMAc has been used to characterize the MWDs of solutions of birch wood kraft pulp by SEC (Kennedy, Rivera, White, Lloyd & Warner, 1990; Silva & Laver, 1997; Westermark & Gustafsson, 1994).

The size exclusion separation mechanism is based on differences in the hydrodynamic volume of the solutes. Different methods can be used to obtain the molecular weight of the components of chromatographed samples (Jackson & Barth, 1995). Since the hydrodynamic volume is the product of intrinsic viscosity and molecular weight, a universal calibration curve can be established by using

---

* Corresponding author. Tel.: + 46-8-67-67000; fax: + 46-8-411-5518.
E-mail address: elisabeth.sjoholm@stfi.se (E. Sjöholm)

PII: S0144-8617(99)00080-6

Table 1
Designation and characteristics of investigated samples

Designation	Sample	Viscosity (dm^3/kg)	DP_w[a]	Kappa number[b]	Brightness (%)
HP	Unbleached HWKP	1130	–	15	–
BHP	Bleached HWKP	816	–	–	88
BSP	Bleached SWKP	610	–	–	86
CL	Cotton linter	–	7950	–	–

[a] Value obtained from the supplier.
[b] Reflects the amount of lignin in unbleached pulps.

standards of known molecular weight using a viscometer detector together with a refractive index detector. In this way the molecular weight of cotton dissolved and chromatographed in LiCl/DMAc have been determined (Timpa, 1991). To directly measure the molecular weight in each elution slice, a light scattering detector together with a refractive index detector has been used for polysaccharides dissolved in LiCl/DMAc (Striegel & Timpa, 1996).

However, the most common and simplest method to define the relationship between the molecular weight and elution volume is to calibrate the columns by narrowly distributed standards. Since pullulan is the only polysaccharide standard, that is at present commercially available it is frequently used to obtain the MWD of cellulosic samples and has also been used in this study. Pullulan consists of polymaltotriose units linked together by α-(1 → 6)-linkages but because of its linearity it is considered to have about the same relation between molecular weight and hydrodynamic volume as the carbohydrate polymers in wood pulp. One drawback is that pullulan standards do not cover the whole elution range of the cellulose distribution of wood pulp samples, which makes extrapolation of the calibration curve necessary.

Hardwood kraft pulps can be completely dissolved in lithium chloride/*N*,*N*-dimethylacetamide (LiCl/DMAc), whereas softwood pulps have a limited solubility (Karlsson & Westermark, 1994; Sjöholm, Gustafsson & Colmsjö et al., 1997). By differential refractive index detection, two distributions can be discerned in the size exclusion chromatogram of a hardwood kraft pulp. The distribution that appears at the higher molecular weight range of hardwood kraft pulp corresponds to cellulose (Sjöholm, Gustafsson, Berthold & Colmsjo, 1999). This distribution usually extends up in the high molecular weight region and sometimes a shoulder on the high molecular weight part can be distinguished.

In the present investigation the reasons for the high molecular weight relative to pullulan and the uneven distribution profile of the cellulose portion of hardwood kraft pulps were studied. A cotton linter sample was used with a similar elution volume in LiCl/DMAc as the cellulose portion of hardwood pulp. Light scattering was measured off-line to give the true molecular weight of the cotton linter sample dissolved in LiCl/DMAc.

2. Experimental

2.1. Materials

All chemicals were of analytical grade. Lithium chloride (LiCl) (Merck, Darmstadt, Germany) was stored in small portions in a desiccator over phosphorous pentoxide. Once withdrawn from the desiccator, a desired amount of salt was weighed and then immediately added to *N*,*N*-dimethylacetamide (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 50 min. Final solutions of 6, 8 and 10% (w/v) LiCl/DMAc were stored at +4°C, while 0.5% (w/v) LiCl/DMAc was used immediately as mobile phase.

Two industrial hardwood kraft pulps (HWKP), one softwood kraft pulp (SWKP) and a cotton linter sample (Temming) were used. One of the HWKPs was unbleached and the other delignified by oxygen and bleached by ozone. The SWKP was delignified with oxygen and bleached with chlorine dioxide. Sample characteristics and designations are listed in Table 1.

2.2. Chemical analysis

The viscosity of pulps dissolved in cupridiethylenediamine (CED) was determined according to ISO 5351/1 (1981). Kappa number is the amount of structures oxidized by potassium permanganate and was determined according to ISO 302 (1981). Brightness of the bleached pulp was determined according to SCAN-C11:75.

2.3. Standard procedure for dissolution in LiCl/DMAc

The pulps were washed with deionized water to remove any remaining process chemicals. The samples were suspended in deionized water at +4°C for 1 h. The water was removed and was followed by a solvent-exchange procedure including consecutive soaking first in methanol and then in *N*,*N*-dimethylacetamide (DMAc). This solvent-exchange was done thrice for each solvent with an intermediate equilibration with the pulp for 30 min. A number of conditions with respect to salt and sample concentrations as well as dissolution times were studied as shown in Table 3. In the standard procedure, 8% LiCl/DMAc was added to pulp giving a concentration of 0.8% with respect to sample.

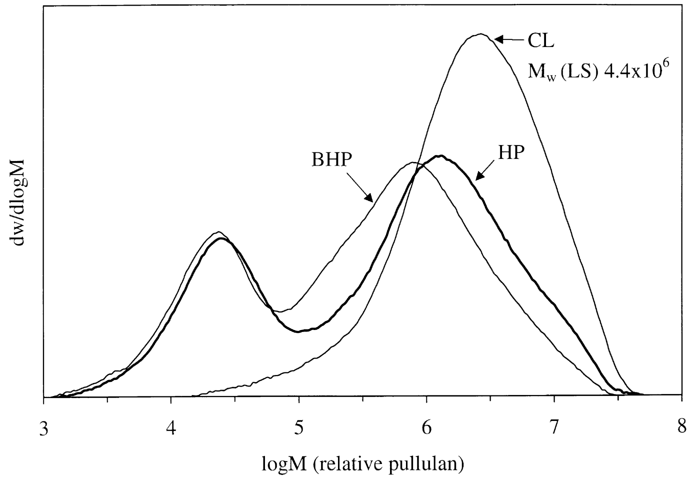

Fig. 1. Molecular weight distributions relative to pullulan of cotton linter (CL), unbleached (HP) and bleached (BHP) hardwood kraft pulps. Sample solutions prepared by the standard procedure. $M_w(\mathrm{LS}) = M_w$ determined by light scattering. Size-exclusion chromatography was performed at 80°C on PL Mixed A columns using 0.5% LiCl/DMAc as mobile phase.

The sample solution was allowed to stand for five days at +4°C. Final solutions were obtained by dilution with DMAc to give a final concentration of 0.5% with respect to LiCl and 0.05% with respect to sample. In order to remove any undissolved material and dust, the final solutions were centrifuged at 87 000*g* for 30 min.

2.4. Mechanical treatment of sample solutions

In order to break aggregates, some sample solutions were treated in a Retsch vibratory mill type MM-2. Sample solutions (3 ml) were treated for 15, 30, 45, 60, 120 or 180 min in a sealed Teflon container using a Teflon-coated stainless steel ball. In order to study the influence of degradation a standard pullulan (853k) dissolved in 0.5% LiCl/DMAc was treated for 30 min. Treated solutions were filtered (0.5 μm, Millex-SR) prior to size exclusion chromatography or light scattering characterizations.

2.5. Size exclusion chromatography

The characterization was performed on a SEC system consisting of an automatic sampler, AS-4000A (Hitachi), with an L-6200A pump (Hitachi) and a refractive index detector, RI-71 (Shodex). The injection volume was 100 μl and the separations were performed at 80°C with 0.5% LiCl/DMAc at a flow rate of 1 ml/min on four 20 μm Mixed-A columns (Polymer Laboratories) preceded by a guard column (Polymer Laboratories). Pullulan standards 1600k, 853k, 380k, 186k, 100k, 48k, 23.7k, 12.2k, 5.8k and 738 Da (Polymer Laboratories), were used to calibrate the columns. The linear coefficient of determination (r^2) between the M_p of the standards and elution time was 0.995. Data acquisition and calculations were carried out with PL Caliber (Polymer Laboratories).

2.6. Static light scattering

The centrifuged samples were filtered (0.7 μm, Whatman GF/F). Static light scattering measurements were made using a Hamamatsu photon counting device with a 35 mW He–Ne laser (633 nm). Toluene was used as the reference ($R_{\mathrm{tol}} = 13.59 \times 10^{-4}$/m at 633 nm). d*n*/d*c* was measured in a differential refractometer with Rayleigh optics at 25°C; d*n*/d*c* = 0.091 ml/g. The weight average molecular weight (M_w) was obtained by measure the angular dependence of the scattered light R_θ of different sample concentrations (c). In the limit as angle (θ) and c goes to zero the following relationship holds:

$$\frac{Kc}{R\theta} = \frac{1}{M_w}$$

where $K = 4\pi^2 n_0^2(\mathrm{d}n/\mathrm{d}c)^2/\mathrm{N_A}\lambda^4$, in which n_0 is the refractive index of the solvent, d*n*/d*c* the refractive index increment measured for the present system at the wavelength used, $\mathrm{N_A}$ the Avogadros' constant and λ the wavelength. R_{90} is the Rayleigh ratio at angle 90° determined using $(I - I_0/I_{\mathrm{tol}}(R_{\mathrm{tol}}(n_s/n_{\mathrm{tol}})^2$. Here n_s is the solvent refractive index and n_{tol} that of toluene. $R_{\mathrm{tol}} = 4.0 \times 10^5$/cm. I is the measured solution intensity, I_0 that of the solvent and I_{tol} that of toluene.

2.7. Curve fitting

The peaks of a hardwood kraft pulp are approximately Gaussian in shape on the log M scale. To estimate the positions (log M_p) and areas of unresolved peaks in a molecular weight distribution (MWD), three Gaussian functions were used as model functions in the curve fitting process. The Gaussian function, g_v, is determined for each component by three parameters: position of peak maximum, p_v, height maximum, h_v, and a parameter $b_v = w_{0.5}/2\sqrt{\log 2}$, where

$w_{0.5}$ is the width at half-height. The $x_k = k/200$ of the elution interval of interest. The model-function, **M**, for the MWD becomes:

$$\mathbf{M}(\mathbf{u}) = \sum_{v}\sum_{k} g_v(x_k) = \sum_{v}\sum_{k} h_v \exp[-(x_k - p_v)^2/b_v^2]$$

$$v = 1, 2, 3 \quad k = 1, 2, 3, \ldots 200.$$

A solution vector of nine elements $u_\sigma = [p1, h1, b1, \ldots, b3]$ was sought such that the three model functions, **M** (a vector of 200 elements) should differ in a least squared sense as little as possible from the MWD, **S** (a vector of 200 elements), calculated by the SEC program. The object function, D, to be minimized is defined as

$$D^2(\mathbf{u}) = \|\mathbf{M}(\mathbf{u}) - \mathbf{S}(\mathbf{u})\|^2$$

$\|\cdot\|^2$ is the Euclidean norm and D is the object function to be minimized with respect to the vector **u**.

A routine curvefit in MATLAB 5.0, was used for the numerical work. This routine uses the Marquardt–Levenberg algorithm to solve the optimising problem. The curvefit routine found a solution within 2 min using a Compaq Deskpro PC. Increasing the number of elements in the MWD data vector increases the optimization time in a cubic fashion.

3. Results and discussion

3.1. The molecular weight distributions of hardwood kraft pulps

In Fig. 1 the MWDs relative to pullulan of unbleached (HP) and bleached (BHP) hardwood kraft pulp are shown. The distribution of the cellulose portion of the BHP has a lower molecular weight compared to that of the HP sample whereas the hemicellulose remaining in the pulp has about the same distribution. For both samples, the distribution of cellulose continues far up in the high molecular weight range. The weight average molecular weight (M_w) relative to pullulan for the cellulose portion of the hardwood kraft pulps is unexpectedly high for both samples, Table 2. A possible explanation for these high values may be that pullulan has a different relationship between molecular weight and elution volume than that of cellulose.

Table 2
M_w relative to pullulan of the cellulose portion of hardwood kraft pulps and of cotton linter. For comparison M_w calculated from the DP_w and as measured by light scattering of the cotton linter is also shown. The samples were dissolved by the standard procedure. Sample designations according to Table 1

Sample	M_w (relative pullulan)	M_w (calculated[a])	M_w (LS)
HP	3.0×10^6	–	–
BHP	1.9×10^6	–	–
CL	4.6×10^6	1.3×10^6	4.4×10^6

[a] From the DP_w specified by the supplier.

To examine if these high values are caused by the use of pullulan as reference, a cotton linter (CL) sample was studied. The advantage of using cotton linter is that it consists solely of cellulose, which makes it possible to determine the true M_w by light scattering (LS). The MWD of the chosen CL sample covers about the same molecular weight range as the pulp cellulose in the LiCl/DMAc system (Fig. 1). However, the M_w relative to pullulan determined by SEC was close to the M_w determined by LS but about thrice that of the M_w calculated from the weight degree of polymerization (DP_w) given by the supplier (Table 2). According to the supplier, the DP_w value is based on viscosity measurements of cellulose dissolved in CED. Using a correlation between the CED viscosity and the M_w as measured by light scattering of tricarbanilated samples, gives a DP_w of about 7950. Obviously the high value observed for the cellulose portion of pulp samples and the CL sample is not solely caused by the use of pullulan for calibration.

Results from SEC of kraft wood pulps dissolved in LiCl/DMAc are almost always presented by showing the MWDs. Silva and Laver (Silva & Laver, 1997) reported the MWD and M_w relative to polystyrene for a number of wood pulps. But since the hydrodynamic radii of polystyrene is smaller than that of pullulan in LiCl/DMAc for the same M_w and the whole distribution was used for the calculation, direct comparison with the results obtained in this study is not possible. However, one of the samples was reported to have a “conspicuous shoulder in the higher molecular weight region”. On a closer inspection of the elution profile of the HP sample shown in Fig. 1, the high molecular end of the cellulose distribution also seems to have a shoulder.

In summary, the distribution of cellulose in pulp samples continues to the very high molecular weight region and its distribution has a high molecular weight shoulder. For cotton linters of about the same elution volume as the cellulose of the pulps, the M_w relative to pullulan is in agreement with results from LS but about thrice that of the value from the supplier. Taken together, these observations indicate either the presence of aggregation of high molecular weight cellulose when dissolved in LiCl/DMAc or the DP provided by the supplier is in error. Henley performed macromolecular measurements on cellulose samples dissolved in cadoxen (Henley, 1961) by several techniques. Cadoxen [tris(ethylenediamine) cadmium dihydroxide] is a clear colourless solvent and forms stable solutions of cellulose (Brown, 1967). By LS, a chlorite bleached native cotton sample dissolved in cadoxen was found to have a M_w of 0.95×10^6 (Henley, 1961), i.e. much lower than the linter sample used in the present study. On the other hand, LS studies have been reported for linters having a M_w of about 1.3×10^6 (DP_w 8000) dissolved in cuoxam (Seger & Burchard, 1994).

The hydroxyl groups of cellulose forms hydrogen bonds within the cellulose molecule i.e. intramolecular bonds, and between adjacent cellulose chains, i.e. intermolecular hydrogen bonds (Krässig, 1993). To obtain molecularly

Table 3
Initial and final concentrations of LiCl (C_{LiCl}) and sample (C_{sample}) and dissolution time for samples used in this study. The final concentrations were achieved by diluting dissolved sample. The bold row corresponds to the conditions in the standard procedure

Initial concentration (%)		Time (days)	Final concentration (%)	
C_{LiCl}	C_{sample}		C_{LiCl}	C_{sample}
6	0.8	1	0.5	0.07
8	**0.8**	**5**	**0.5**	**0.05**
8	0.8	1	0.5	0.05
8	0.8	1	8	0.05
10	0.5	1	1	0.05

dispersed solutions of cellulose the intermolecular hydrogen bonds have to be broken. In general aggregate-free solutions of polysaccharides are difficult to prepare (Rinaudo, 1993) without degrading the cellulose. The aggregates indicated in this study may thus be due to unbroken intermolecular bonds present in the initial sample and/or have been formed during dissolution in LiCl/DMAc. Urea is used to disrupt noncovalent interactions between polypeptides (Stryer, 1981). Attempts to break the hydrogen bonds by addition of urea either during dissolution or to the final solution of the CL sample failed. Factors that may influence the preparation of molecularly dispersed solutions of high molecular weight cellulosic samples were therefore examined. The influences of sample and salt concentration, dissolution time and temperature were examined since we consider these to be the most important factors in this respect.

3.2. Influence of LiCl concentration during dissolution

The solubility of cellulose increases as the LiCl concentration increases (McCormick, et al., 1985). McCormick reported that at LiCl concentration above 6% complete dissolution of a cellulose sample (M_w 0.182×10^6) with a concentration of 0.5% is achieved. Various concentrations of LiCl (C_{LiCl}) and sample (C_{sample}) were studied (Table 3). Our standard procedure is marked by bold figures in the table. The concentration of LiCl in the mobile phase was the same as in the final sample solution.

The MWD obtained for the HP sample by our standard procedure was resolved by applying a curve fitting procedure (Fig. 2). The distributions of the hardwood kraft pulps are approximately Gaussian in shape on the log *M* scale. To estimate the positions and areas of unresolved distributions, three Gaussian distributions were used as model functions. The results shown in Fig. 2 reveals three distributions. One at the low molecular end of the distribution corresponding to the hemicellulose, the main distribution that corresponds to cellulose and an additional distribution, at the highest molecular weight range, which, we suggest, is due to aggregates of cellulose. The HP sample was also dissolved according to the standard procedure with the exception that the sample was diluted with 8% LiCl. Light scattering measurements on the solution gave about the same M_w as with the standard procedure. The MWD obtained for the HP sample was the same when the dissolution time was decreased to one day. Thus the dissolution time does not seem to be of importance for the MWD. When the initial C_{sample} was lowered to half of that of the standard procedure and dissolved for one day in 10% LiCl/DMAc a clear shoulder appears at the high molecular end of the distribution (Fig. 3). In line with this, the relative area of the distribution of the aggregates increases as revealed by curve fitting. The results in Fig. 4 demonstrate that using an initial C_{LiCl} of 6% decreases the amount of aggregates. It was not possible to obtain complete dissolution of the HP sample with a lower C_{LiCl}. Although the area of the distribution that corresponds to aggregated cellulose gets smaller with decreasing LiCl concentration, the position of the distribution on the log *M* scale is about the same. It can be noted that the ratio of the peak value (M_p) between aggregates/cellulose is about seven irrespective of

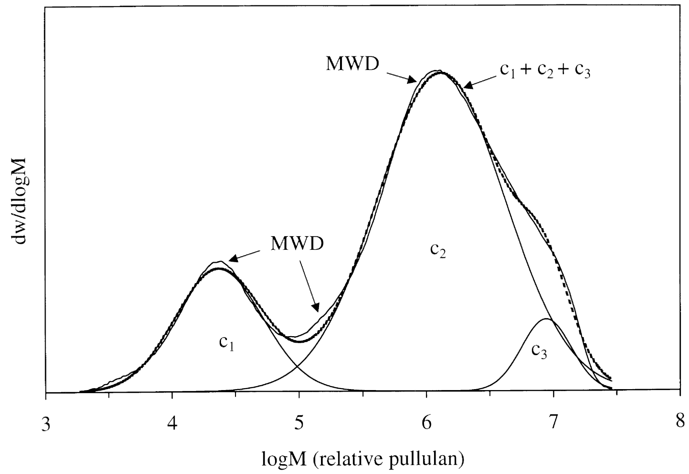

Fig. 2. Molecular weight distribution (MWD) (normal line) and Gaussian curves deconvoluted from the MWD of unbleached hardwood kraft pulp (HP) dissolved by the standard procedure, using an initial LiCl concentration of 8%. c_1, c_2, $\mathbf{c}_3$ are components deconvoluted from the MWD (normal line), $c_1 + c_2 + c_3$ is the sum of the deconvoluted curves (bold broken line).

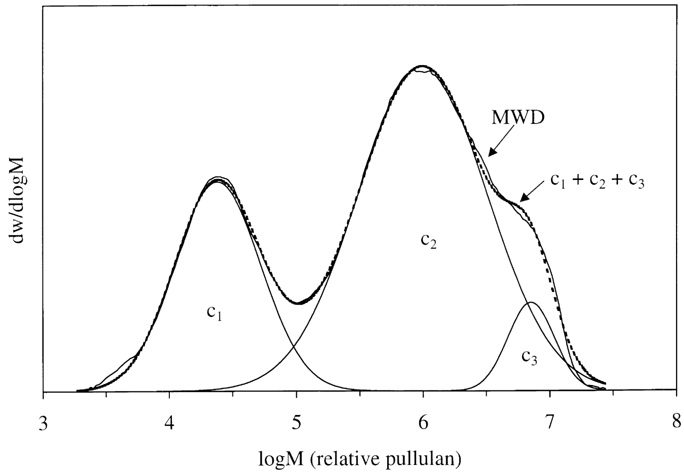

Fig. 3. Molecular weight distribution (MWD) (normal line) and Gaussian curves deconvoluted from the MWD of unbleached hardwood kraft pulp (HP) dissolved by using an initial LiCl concentration of 10%. c_1, c_2, c_3 are components deconvoluted from the MWD (normal line), $c_1 + c_2 + c_3$ is the sum of the deconvoluted curves (bold broken line).

salt concentration used. In a study of cellulose solutions by viscosity and LS measurements (Terbojevich, Cosani, Conio, Ciferri & Bianchi, 1985), stable aggregates consisting of about seven fully extended cellulose molecules with side-by-side organization was reported.

3.3. Influence of temperature and mechanical treatment of the final solution

Cellulosic samples can also be dissolved at elevated temperatures. In the method used by Striegel and Timpa (1996), and Silva and Laver (1997) the sample is activated for 2 h by hot DMAc (at 150°C). LiCl is added after cooling to 100°C. After 1 h the temperature is decreased to 50°C and let to stand for at least 12 h. The initial and final C_{sample} and C_{LiCl} is about the same as in our study. We have not found any difference in the MWD between samples prepared at elevated temperature and our standard procedure.

To study the influence of temperature on the MWD, a CL sample was prepared by the standard procedure omitting ultracentrifugation. This sample solution was kept at 120°C for 2 h followed by a temperature of 80°C for 20 h.

The influence of mechanical treatment was also studied on the CL sample by shaking an uncentrifuged solution in a vibratory mill (see Section 2) for 60 min. In Fig. 5 the influence of thermal and mechanical treatment on solutions of CL sample prepared by the standard procedure is demonstrated. The latter is shown as a reference. The M_ws inserted in the chromatograms were measured by LS. The distribution profile and the M_w were changed considerably by both treatments compared to the reference. As a result of extensive degradation, the chromatogram of the thermally treated sample tails into the low molecular weight range and the M_w

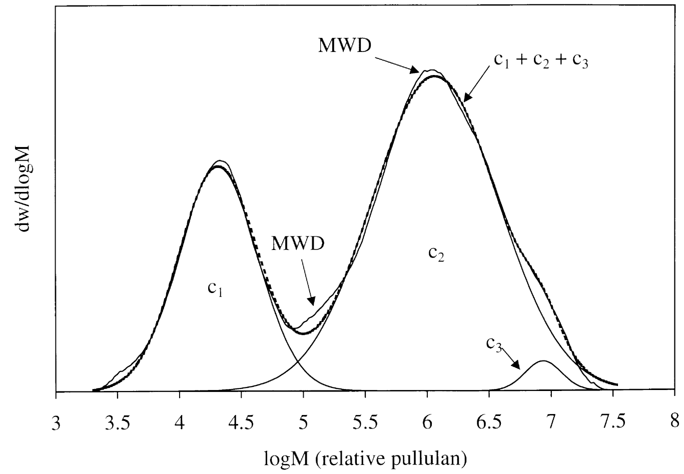

Fig. 4. Molecular weight distribution (MWD) (normal line) and Gaussian curves deconvoluted from the MWD of unbleached hardwood kraft pulp (HP) dissolved by using an initial LiCl concentration of 6%. c_1, c_2, c_3 are components deconvoluted from the MWD (normal line), $c_1 + c_2 + c_3$ is the sum of the deconvoluted curves (bold broken line).

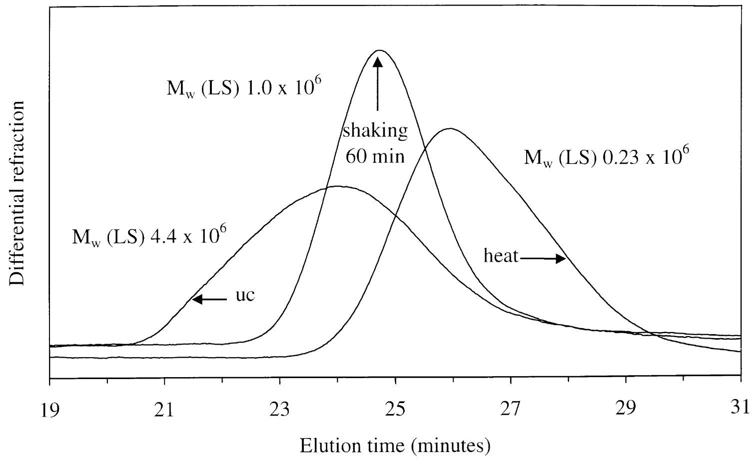

Fig. 5. Chromatograms of reference, thermally and mechanically treated cotton linter sample solution. uc = reference i.e. sample dissolved by the standard procedure including ultracentrifugation. M_w(LS) = M_w determined by light scattering. Chromatographic conditions as in Fig. 1.

is decreased to about one-twentieth of that of the reference. The combination of high temperature and high concentrations of LiCl during dissolution has been reported to degrade cellulose. Degradation at 150°C can be minimized if the sample is purged with N_2 prior to heating (Dawsey & McCormick, 1990) or avoided if temperature is kept below 100°C (Turbak, et al., 1981). According to our results even lower concentrations of salt (0.5%) cause severe degradation at high temperature. On the other hand mechanical treatment of the sample solution seems to affect the higher molecular range of the sample preferentially (Fig. 5). This gives a narrower distribution with a nearly Gaussian shape. The low molecular end of the distribution coincides with that of the reference solution. However, the M_w was found to be lower compared to that calculated from the DP_w (Table 2). Mechanical treatment of polymer solutions can cause degradation, i.e. breakage of covalent bonds between the constitutive units. It is thus possible that, besides of breakage of the hydrogen bonds between cellulose molecules, degradation of the CL sample also occurs during the shaking. Since the shaking was performed for 60 min additional experiments were made to optimize this treatment i.e. to achieve deaggregated sample solutions with a minimum of chain scission.

3.4. Optimization of the mechanical treatment

Various mechanical treatment times of the cellulosic solutions were studied and evaluated by SEC and LS measurements. In Fig. 6 M_w relative to pullulan versus treatment time is shown for LiCl/DMAc solutions of CL and of the cellulose portion of HP and BHP samples. The M_w of the CL solutions as measured by LS is also shown for untreated and some of the treated samples.

The M_w decreases rapidly and levels out after 30 min. No difference in M_w between the CL sample treated for 30 or

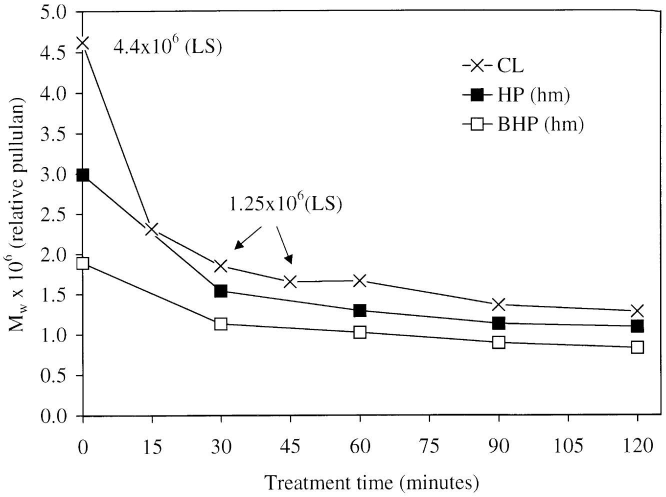

Fig. 6. Influence of the time of mechanical treatment on the M_w (relative pullulan). CL = cotton linter, HP(hm) = the high molecular weight distribution of unbleached kraft wood pulp and BHP(hm) = the high molecular weight distribution of bleached kraft wood pulp. The M_w(LS) = M_w determined by light scattering.

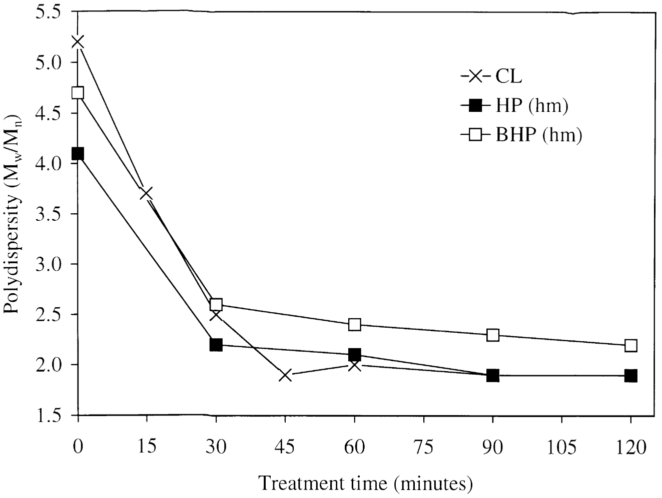

Fig. 7. Influence of the time of mechanical treatment on the M_w/M_n. CL = cotton linter, HP(hm) = the high molecular weight distribution of unbleached kraft hardwood pulp and BHP(hm) = the high molecular weight distribution of bleached kraft hardwood pulp. The M_w(LS) = M_w determined by light scattering.

45 min could be detected by LS. After 30 min shaking of the CL sample solution the M_w according to LS determination agrees fairly well with the M_w calculated from the DP_w obtained from the supplier (Table 2). The hardwood kraft pulp sample solutions, HP and BHP, respond in a similar way as the CL solution (Fig. 6); M_w decreases and levels out after 30 min.

The polydispersity, defined as M_w/M_n where M_n is the number molecular weight average, of the MWD declines with the M_w for the high molecular portion of the hardwood kraft pulps during shaking (Fig. 7). Because the BHP sample has been degraded during the bleaching process, it has a smaller M_w and larger initial polydispersity compared to the HP sample. The CL sample has the largest initial polydispersity of the samples studied, but after 45 min treatment time the dispersity is lowest and levels out.

From these results it seems that a treatment time of 30 min in a vibratory mill is adequate to deaggregate the cellulose portion of hardwood pulps dissolved in LiCl/DMAc. In Fig. 8, the MWD of HP and BHP solutions prepared by the standard procedure and the corresponding samples after 30 min treatment is shown. The high molecular shoulder that can be discerned in the MWDs prepared by the standard procedure is removed by the treatment. The high molecular weight distribution of cellulose is narrower and its peak value (M_p) higher for both samples compared to their untreated counterparts. The increased M_p may be an indication that the hydrogen bonds that keep aggregated cellulose chains together are preferentially broken during treatment for 30 min. In contrast, the low molecular weight distributions are hardly affected at all. This means that the M_w of the hemicelluloses in the pulp samples is essentially preserved during the treatment. The treatment also improves the resolution, which ultimately improves the precision in the molecular weight determinations of cellulose. The RSD of the M_w relative to pullulan for the cellulose portion of the HP sample treated for 30 min is 2.2% ($n = 3$).

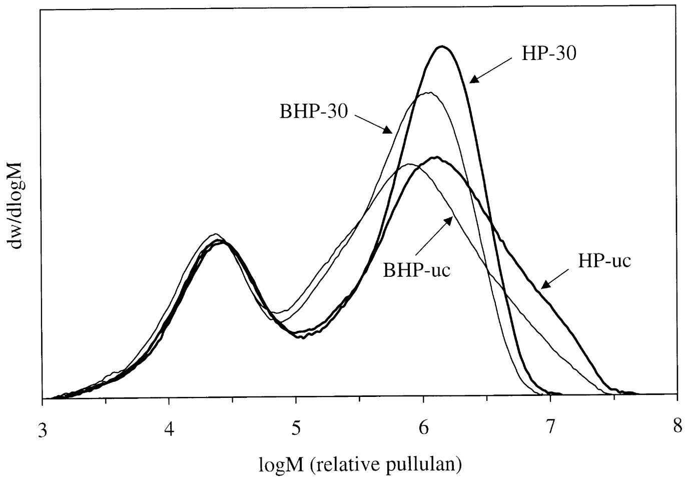

Fig. 8. Molecular weight distributions relative pullulan of unbleached (HP) and bleached (BHP) hardwood kraft pulps. uc = solutions prepared by the standard procedure including ultracentrifugation, 30 = solutions prepared by the standard procedure with 30 min mechanical treatment (omitting ultracentrifugation). Chromatographic conditions as in Fig. 1.

The bond strength of intermolecular hydrogen bonds in cellulose is about 25 kJ/mol (Krässig, 1993) and that of a covalent bond such as CO about 350 kJ/mol (Petrucci, 1982) i.e. the energy required for disrupting hydrogen bonds within aggregated cellulose is considerably lower than for breaking covalent bonds. The M_w (relative to pullulan) of a standard pullulan (853k), dissolved in 0.5% LiCl/DMAc decreases by about 10% when mechanically treated for 30 min. This result indicates that breakage of covalent bonds in the cellulose during treatment may only represent a small fraction of the decrease in the M_w observed for the cellulose of HP and BHP samples. Although a certain degradation of the cellulose cannot be ruled out, the suggested mechanical treatment of the solution seems to be a preferred way to deaggregate high molecular weight cellulose samples dissolved in LiCl/DMAc.

4. Conclusion

The principal results can be summarized as follows:

- The distribution profile of cellulose has a slight shoulder on its high molecular end and, based on calibration with pullulan, the M_w was found to be high. These phenomena were also observed for a cotton linter (CL) sample having about the same elution range. The high M_w was confirmed by LS measurements of the CL, and an aggregate of the cellulose portion of unbleached kraft pulps can be visualized by curve fitting.
- Changing the dissolution conditions does not prevent aggregation.
- Deaggregation cannot be achieved by addition of urea or by thermal treatment of the solution.
- By mechanical treatment of the solutions, it seems possible that deaggregation of the cellulose portion of wood pulps occurs preferentially.

Acknowledgements

Dr Sczostak, Buckeye Cellulose Gmbh (earlier Temming AG) is greatly acknowledged for providing the cotton linters sample and for valuable information about the sample. Dr Fredrik Berthold is greatly acknowledged for valuable discussions.

References

Brown, W. (1967). The cellulose solvent cadoxen. *Svensk Papperstidning*, *70* (15), 458–461.

Dawsey, T. R., & McCormick, C. L. (1990). The lithium chloride/dimethylacetamide solvent for cellulose: a literature review. *Reviews of Macromolecular Chemistry and Physics*, *C30* (384), 405–440.

Ekmanis, J. L. (1986). Gel permeation chromatographic analysis of cellulose. Polymer Notes, Waters Chromatography Division, Millipore Corp., US, 1(3).

Henley, D. (1961). A macromolecular study of cellulose in the solvent cadoxen. *Arkiv Kemi*, *18* (20), 327–392.

Jackson, C., & Barth, H. G. (1995). Molecular weight sensitive detectors for size exclusion chromatography. In C.-S. Wu (Ed.), *Handbook of size exclusion chromatography*, (pp. 103–146). New York: Marcel Dekker.

Karlsson, O., & Westermark, U. (1994). Condensation reactions between wood polymers during kraft pulping. *Proceedings of Tappi Pulping Conference*, *1*, 1–4.

Kennedy, J. F., Rivera, Z. S., White, C. A., Lloyd, L. L., & Warner, F. P. (1990). Molecular weight characterization of underivatized cellulose by GPC using lithium chloride–dimethylacetamide solvent system. *Cellulose Chemistry and Technology*, *24*, 319–325.

Krässig, H. A. (1993). *The fiber structure*. *Cellulose: structure, accessibility and reactivity*, (pp. 6–42). Singapore: Gordon and Breach.

McCormick, C. L., Callais, P. A., & Hutchinson Jr, B. H. (1985). Solution studies of cellulose in lithium chloride and *N*,*N*-dimethylacetamide. *Macromolecules*, *18*, 2394–2401.

Morgenstern, B., & Kammer, H. W. (1996). Solvation in cellulose–LiCl–DMAc solutions. *Trends in Polymer Sciences*, *4* (3), 87–92.

Nehls, I., Wagenknecht, W., & Philipp, B. (1995). ^{13}C-NMR spectroscopic studies of cellulose in various solvent systems. *Cellulose Chemistry and Technology*, *29*, 243–251.

Petrucci, R. H. (1982). *Chemical bonding I: basic concepts*, 3. *General chemistry. Principles and modern applications*, (pp. 196–228). New York, USA: Macmillian.

Rinaudo, M. (1993). Polysaccharide characterization in relation with some original properties. *Journal of Applied Polymer Science: Polymer Symposium*, *52*, 11–17.

Seger, B., & Burchard, W. (1994). Structure of cellulose in cuoxam. *Macromolecular Symposium*, *83*, 291–310.

Silva, A. A., & Laver, M. L. (1997). Molecular weight characterization of wood pulp cellulose: dissolution and size exclusion chromatographic analysis. *Tappi Journal*, *80* (6), 173–180.

Sjöholm, E., Gustafsson, K., & Colmsjö, A. (1997). Characterization of the cellulosic residue from lithium chloride/*N*,*N*-dimethylacetamide dissolution of softwood kraft pulp. *Carbohydrate Polymers*, *32*, 57–63.

Sjöholm, E., Gustafsson, K. Berthold, F., Colmsjö, A. (1999). Influence of the carbohydrate composition on the molecular weight distribution of kraft pulps, *Carbohydrate Polymers*, submitted for publication.

Stevens, M. P. (1990). *Chemical structure and polymer morphology*, *Polymer chemistry: an introduction*, (pp. 70–109). New York, USA: Oxford University Press.

Striegel, A. M. (1997). Theory and applications of DMAC/LICL in the analysis of polysaccharides. *Carbohydrate Polymers*, *34*, 267–274.

Striegel, A. M., & Timpa, J. (1996). Size exclusion chromatography of polysaccharides sin dimethylacetamide-lithium chloride. In M. Potschka & P. L. Dubin (Eds.), *Strategies in size exclusion chromatography*, (pp. 366–378). *ACS Symposium Series 635*. Washington, DC: American Chemical Society.

Stryer, L. (1981). *Immunoglobulins*. *Biochemistry*, (pp. 789–814). San Francisco, USA: W.H. Freeman and Company.

Terbojevich, M., Cosani, A., Conio, G., Ciferri, A., & Bianchi, E. (1985). Mesophase formation and chain rigidity in cellulose and derivatives. 3. Aggregation of cellulose in *N*,*N*-dimethylacetamide–lithium chloride. *Macromolecules*, *18*, 640–646.

Timpa, J. D. (1991). Application of universal calibration in gel permeation chromatography for molecular weight determinations of plant cell wall polymers: cotton fiber. *Journal of Agricultural Food Chemistry*, *39*, 270–275.

Turbak, A. F. (1983). Newer cellulose solvent systems. In E. J. Soltes (Ed.), *Wood and agricultural residues*, (pp. 87–99). New York: Academic Press.

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

Westermark, U., & Gustafsson, K. (1994). Molecular size distribution of wood polymers in birch kraft pulps. *Holzforschung*, *48*, 146–150.