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Alkaline degradation of birch and spruce: influence of degradation conditions on molecular mass distributions and fibre strength

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Abstract

The alkaline degradation of birch and Norway spruce during kraft pulping was studied on a laboratory scale by two degradation strategies, by varying the pulping time using the same initial alkali level and by varying the initial alkali concentration using a constant time. The degradation at the molecular level was monitored by determining the carbohydrate composition, intrinsic viscosity and molecular mass distribution (MMD). The influence of the degradation on fibre strength was studied as zero-span tensile index.

The alkaline degradation was to a large extent homogeneous on a molecular level. However, some significant differences in degradation patterns were found. In the case of birch, the two different degradation strategies (increased alkali level and increased pulping time) caused differences in MMD and fibre strength (comparisons made at a given intrinsic viscosity or M_w). For spruce pulps, the decrease in fibre strength and the shift in MMD were the same in both series, regardless of degradation strategy. © 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Spruce; Birch; Alkaline degradation; Cellulose; Hemicelluloses; Molar mass distribution; Size exclusion chromatography; Kraft pulp; Fibre strength

1. Introduction

The purpose of chemical pulping is to degrade and dissolve the lignin in wood. In kraft pulping processes, lignin is degraded in an alkaline solution containing hydrogen sulphide at an elevated temperature. Unfortunately, cellulose and hemicelluloses are also partly degraded and dissolved under these conditions. This decreases the yield and molecular mass of both cellulose and hemicelluloses. A decrease in molecular mass is undesirable, since the mechanical strength of wood pulp, cotton and cellulose derivates decrease with decreasing molecular mass (Gurnagul, Page, & Paice, 1992; Ifju, 1964; Jayme, 1942; Molin & Lennholm, 2000; Rydholm, 1965; Sjöholm, Gustafsson, Norman, Reitberger, & Colmsjö, 2000c; Sookne & Harris, 1945; Staudinger & Reinecke, 1938).

Degradation can be studied at different structural levels. If the degradation on a molecular or ultrastructural level is clarified, the decrease in strength at the fibre level can be better understood. The degradation of cellulose and hemicelluloses can be either heterogeneous or homogeneous. In Fig. 1, models of heterogeneous and homogeneous degradation at the molecular level are shown. In this study, the definition of a totally homogeneous degradation is that the probability of a chain scission is the same at all glycosidic bonds and is not influenced by chain length, crystallinity, fibrillar structure or defects. The degradation is heterogeneous if different glycosidic bonds, within or between cellulose chains, exhibit different reactivities. The heterogeneous degradation of wood fibres can in turn be divided into subtypes with different degradation patterns. Degradation can occur predominantly along weak points throughout the cell wall, i.e. by acid hydrolysis (Battista, 1950; Battista, 1956; Berggren, Berthold, Sjöholm, & Lindström, 2000; Gurnagul et al., 1992) (Fig. 1c) or predominantly at fibre and fibril surfaces, i.e. by ozone degradation which leaves a core of high molecular mass cellulose (Fig. 1b) (Berggren et al., 2000; Zhang, Kang, Ni & van Heningen, 1998).

Alkaline hydrolysis and peeling are the two main alkaline degradation mechanisms of cellulose and

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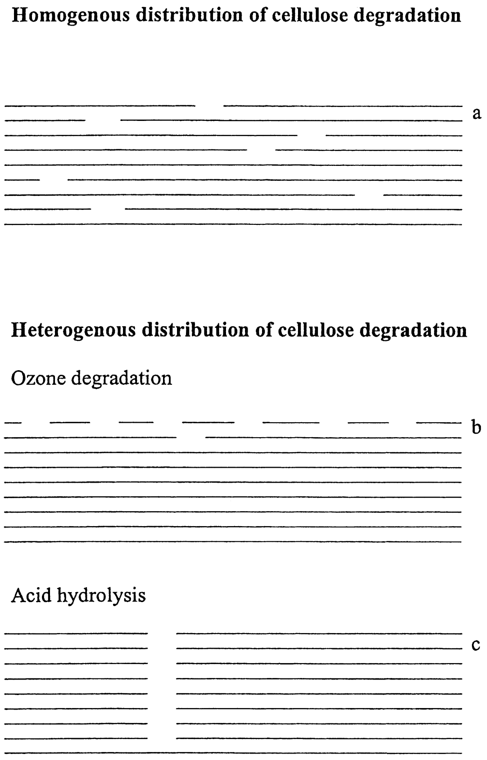

Fig. 1. Model of heterogeneous and homogeneous degradation of cellulose at the molecular level. Lines represent cellulose chains.

hemicellulose during kraft pulping (Fengel & Wegener, 1984). Alkaline hydrolysis causes chain scission of the polymer chain and decreases the average chain length dramatically. Peeling removes one monomer unit at a time from the reducing end of the molecule. This reaction does not influence the molar mass to any appreciable extent unless very long process times are used. Instead, the peeling reaction mainly influences the carbohydrate yield (Fengel & Wegener, 1984).

The decrease in molecular mass during pulping and bleaching is usually described by an intrinsic viscosity average value, measured on pulps dissolved in cupriethylenediamine. More detailed information is obtained by characterisation of the molar mass distributions (MMD) of cellulose and hemicelluloses, measured by size exclusion chromatography (SEC) in a suitable solvent. Today, a commonly used method is based on the dissolution of the fibres in lithium chloride/dimethylacetamide (LiCl/DMAc) (Kennedy, Rivera, White, Lloyd, & Warner, 1990; Schelosky, Röder, & Baldinger, 1999; Sjöholm, Gustafsson, Berthold, & Colmsjö, 2000a; Westermark & Gustasson, 1994). A complete dissolution of softwood pulps in LiCl/DMAc is not possible, due to aggregation (Sjöholm, Gustafsson, Pettersson, & Colmsjö, 1997). In this study, a complete dissolution of the spruce pulp samples was achieved by derivatisation with ethylisocyanate in LiCl/DMAc (Berthold, Gustafsson, Sjöholm, & Lindström, 2001).

The aim of this work was to study the pattern of alkaline degradation of cellulose and hemicelluloses during kraft pulping conditions and how MMD and fibre strength were influenced by different degradation conditions. Degradation of Norway spruce (*Picea abies*) pulps and birch (*Betula verucosa*) pulps was studied either by varying the pulping time using the same initial alkali level, or by varying the initial alkali concentration and using a constant time. By the introduction of modified kraft pulping procedures, alkali concentration profiles of various types can be used during kraft pulping.

2. Experimental

2.1. Pulping

Hand-sawn spruce chips without any chip damage and hand-sorted laboratory-chipped birch chips were used. The pulps were cooked in autoclaves at a liquid/wood ratio of 8:1. The autoclaves were heated in a glycol bath. After the cook, the pulps were washed with deionised water over night and defibrated.

The degradation conditions in the different cooks were varied by changing the pulping time or by changing the initial alkali level. Chemical charges and reaction times are given in Table 1 (birch) and Table 2 (spruce). All spruce pulps were impregnated in the cooking liquor by increasing the temperature from 70 to 170 °C at a rate of 1 °C/min. The temperature was kept at 170 °C for the test of the cooking time. All birch pulps were impregnated at 120 °C for 30 min and then heated at maximum speed (10 min) to 170 °C and kept there for the rest of the cooking time. The initial hydrogen sulphide ion concentration was 0.3 mol/l for all the cooks. The concentration of hydrogen sulphide ions decrease only to a minor extent during kraft pulping.

The residual alkali in the black liquor was determined by titration with HCl to pH 10.7. To achieve a correct value, the black liquor was first diluted eight times and the dissolved lignin and carbonate ions were precipitated with $BaCl_2$. The hydrogen sulphide ion concentration was determined using a potentiometric titration with $AgNO_3$ modified from the method of Chiu and Paszner (1975).

2.2. Dissolution of the samples

The underivatised birch kraft pulps were dissolved according to a procedure described earlier (Sjöholm, Gustavsson, Eriksson, Brown, & Colmsjö, 2000b). Washed pulp samples (15 mg o.d.w. pulp) were swollen in 15 ml deionised water at 4 °C for 1 h. The water was removed by vacuum filtration and 15 ml of methanol was added and removed by vacuum filtration after 30 min. The procedure was repeated twice with methanol and three times with degassed DMAc. A solution of 8% (w/v) LiCl in DMAc was added and gently stirred under a nitrogen atmosphere at 4 °C for five days. The samples were then equilibrated at room

Table 1
Cooking condition for birch

Pulp	Cooking time at 170 °C (h)	[HS$^-$] (mol/l)	[OH$^-$] (mol/l)	Residual [OH$^-$] (mol/l)
BT1	0.85	0.3	1.2	0.56
BT2	2.1	0.3	1.2	0.47
BT3	3.6	0.3	1.2	0.42
BT4	5.2	0.3	1.2	0.37
BT5	7.3	0.3	1.2	0.33
BT6	10	0.3	1.2	0.30
BA1	1.0	0.3	0.8	0.20
BA2	1.0	0.3	1.2	0.52
BA3	1.0	0.3	1.8	1.04
BA4	1.0	0.3	2.5	1.59
BA5	1.0	0.3	3.2	2.19
BA6	1.0	0.3	4.0	2.89

temperature for 30 min and diluted with degassed DMAc to sample and LiCl concentration of 0.05 and 0.5%, respectively. After 2 h, the samples were de-aggregated (Sjöholm et al., 2000b) in a Teflon ball mill for 30 min, filtered through a 0.45 μm PTFE filter and injected on the chromatographic system.

The derivatised softwood kraft pulp samples were dissolved according to a procedure outlined recently (Berthold et al., 2001): 15 mg (o.d.w.) fibres were swollen in water at 4 °C for 1 h. They were then solvent exchanged by vacuum filtration to dry DMAc three times. 1.9 ml of 8% LiCl dissolved in DMAc and 0.2 ml of ethylisocyanate were added, and the samples were stirred under a nitrogen atomosphere for 5 days. Thereafter, 0.5 ml methanol and 27.4 ml DMAc were added, and softwood samples were milled and filtered in the same manner as the hardwood kraft pulps samples before injection.

2.3. Size exclusion chromatography

The chromatographic system consisted of a 2690 Separation Module (Waters Corp.) equipped with a Mixed-A guard column (20 μm, 7.5 × 50 mm, Polymer Laboratories, UK) followed by four Mixed-A columns (20 μm, 7.5 × 300 mm, Polymer Laboratories, UK) connected in series. All columns were thermostated at 80 °C. The mobile phase was 0.5% (w/v) LiCl/DMAc and the flow rate was 1 ml/min. The mobile phase was continuously filtered through a 0.2 μm PTFE inline filter.

Narrow pullulan standards with nominal masses of 738 Da, 5.8, 48, 380 and 1660 kDa (Polymer Laboratories, UK) were used for calibrating the chromatographic system. The hardware was controlled and the data evaluated using the Millennium 3.05.01 software (Waters Corp.). Number average and weight average molecular masses were evaluated using the data over the entire MMD of the samples, i.e. no distinction between cellulose and hemicelluloses was made in the chromatogram.

2.4. Additional analyses

Carbohydrate analyses were performed by a GC-method (Theander & Westerlund, 1986). The pulps were characterised by their kappa number (SCAN-C 1:77), yield and viscosity (SCAN-C 15:99). The fibre length and fibre shape were determined by image analysis with the STFI-Fibermaster (Karlsson, Fransson, & Mohlin, 1999). Laboratory sheets were made according to SCAN-CM 26:99. The fibre strength was estimated both by dry and rewetted zero-span tensile index measurements according to ISO 15361. The

Table 2
Cooking conditions for spruce

Pulp	Cooking time at 170 °C (h)	[HS$^-$] (mol/l)	[OH$^-$] (mol/l)	Residual [OH$^-$] (mol/l)
ST1	1.5	0.3	1.0	0.46
ST2	2.5	0.3	1.0	0.42
ST3	3.75	0.3	1.0	0.39
ST4	5.25	0.3	1.0	0.36
ST5	8.0	0.3	1.0	0.30
ST6	21.5	0.3	1.0	0.18
SA1	2.0	0.3	0.7	0.18
SA2	2.0	0.3	1.0	0.44
SA3	2.0	0.3	1.4	0.75
SA4	2.0	0.3	1.9	1.12
SA5	2.0	0.3	2.6	1.69
SA6	2.0	0.3	3.5	2.21

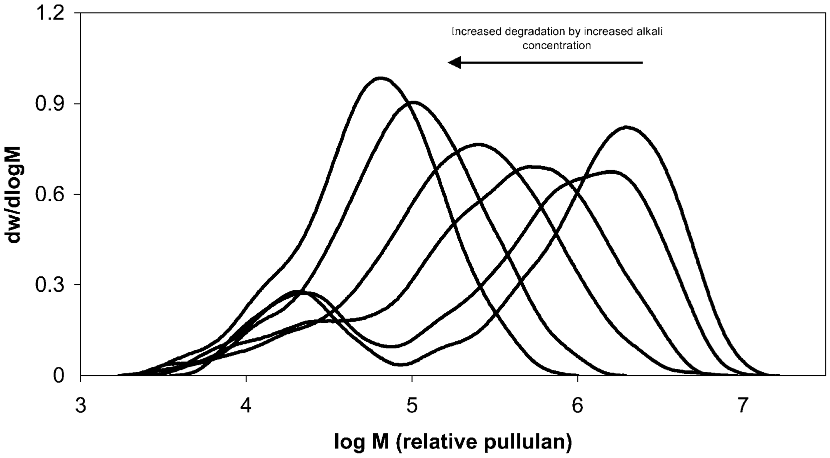

Fig. 2. Molar mass distribution relative pullulan standards of birch pulp, cooked with different initial alkali level (BA). Size exclusion chromatography performed at 80° on four PL Mixed A columns with 0.5% LiCl/DMAc as mobile phase.

two birch pulp series were measured on one occasion and the two spruce pulp series were measured on a later occasion.

3. Results and discussion

Pulping time and alkali concentration are important parameters that strongly influence the rate of degradation of carbohydrates. Both these parameters were varied in this study, to a far greater extent than occurs industrially during kraft pulping. The large span in degradation was chosen to identify trends clearly, not to optimise pulping conditions. To make a comparison possible the pulping temperature was 170 °C for both birch and spruce, although this temperature is higher than is normally used in birch kraft pulping.

3.1. Molecular degradation of birch

In general, the characterisation of hardwood kraft pulp results in a bimodal molar mass distribution (MMD) with two resolved peaks. The smaller, low molecular mass peak corresponds to the hemicellulose and lignin fraction of the pulp. The larger, high molecular mass peak corresponds to the cellulose fraction (Sjöholm et al., 2000a).

Figs. 2 and 3 show the MMD of the two birch kraft pulp series with large spans in molecular mass obtained by a variation in either alkali level (BA) or pulping time (BT). The typical bimodal MMD was clearly seen for pulps with high molecular masses. The bimodality of the MMD for the more severely degraded pulps is less clear, since the degraded cellulose fraction in these cases interfered with the hemicellulose fraction. The cellulose peak moved towards the low molecular mass region in the more degraded pulps, as can also be observed in the decreasing weight average molar masses (M_w) (Table 3).

Various average molar masses ($M_n = \Sigma n_i M_i / \Sigma n_i$, $M_w = \Sigma n_i M_i^2 / \Sigma n_i M_i$ and $M_z = \Sigma n_i M_i^3 / \Sigma n_i M_i^2$) can be determined from the MMD. The average molecular masses for birch and spruce pulps in Tables 3 and 4 are based on the total distribution and not only the cellulose fraction, because no separate cellulose peak was observed for the more degraded pulps, which made it impossible to separate the molar masses of cellulose and hemicellulose.

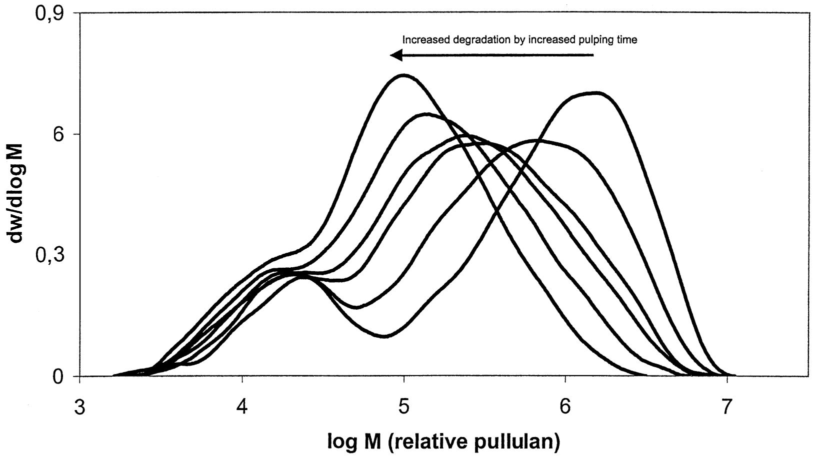

Fig. 3. Molar mass distribution relative pullulan of birch pulps, cooked with different cooking times (BT). Chromatographic conditions as in Fig. 2.

Table 3
Chemical composition and strength data for birch degraded at different times (BT) and different initial alkali concentration (BA)

Pulp	BT1	BT2	BT3	BT4	BT5	BT6	BA1	BA2	BA3	BA4	BA5	BA6
Viscosity (ml/g)	1100	730	510	430	330	250	1260	970	590	380	240	170
M_n (kg/mol)	76	64	52	50	42	36	82	67	68	70	50	33
M_w (kg/mol)	1250	810	540	460	308	190	1740	1170	640	380	160	89
M_z (kg/mol)	2840	2200	1670	1510	1060	580	3660	2750	1560	1080	350	180
Polydispersity (M_w/M_n)	23.4	16.1	12.0	11.7	12.0	7.0	21.2	17.5	9.4	6.0	3.1	2.7
Yield (%)	44.5	41.5	39.3	37.4	34.7	32.5	48.9	44.9	38.9	35.3	31.9	29.6
Kappa number	11	8	7	7	6	7	13	10	8	7	7	7
Arabinose[a] (%)	0.3	–	0.2	–	0.2	–	0.3	–	0.2	0.3	–	–
Xylose[a] (%)	16.1	–	14.3	–	13.5	–	21.2	–	9.7	6.0	–	–
Mannose[a] (%)	0.5	–	0.4	–	0.4	–	0.4	–	0.5	0.6	–	–
Galactose[a] (%)	0.2	–	0.1	–	0.1	–	0.2	–	0.2	0.1	–	–
Glucose[a] (%)	83.0	–	84.9	–	85.6	–	77.8	–	89.3	93.1	–	–
Cellulose[b] (%)	81	–	83	–	84	–	76	–	88	92	–	–
Xylan[b] (%)	16	–	15	–	14	–	22	–	10	6	–	–
Glucomannan[b] (%)	1	–	1	–	1	–	1	–	1	1	–	–
Fibre length[c] (mm)	0.8	–	0.8	–	0.8	–	0.8	–	0.8	0.8	–	–
Shape factor[d]	95.0	–	94.5	–	92.9	–	94.8	–	95.3	95.0	–	–
Dry zero-span tensile index (kNm/kg)	185	179	157	158	131	105	192	179	153	131	107	74
Rewetted zero-span tensile index (kNm/kg)	172	155	139	119	106	82	191	173	147	118	85	56

[a] Relative percentage of monosaccharides.
[b] Calculated to polymer composition according to Janson (1974).
[c] Length-weighted fibre length.
[d] A higher value implies a straighter fibre.

Difference in the MMD of the fibres were observed between the BT and BA series. In the MMD of the BT series, a tail of higher molecular mass material was seen throughout the series (Fig. 3). In the BA series, at high alkali concentrations, all high molecular mass cellulose was degraded and no tail was evident (Fig. 2). This difference between the series can be seen more clearly in Fig. 4, where pulps with similar intrinsic viscosity levels are compared. For pulps in the BT series a tail of higher molecular mass cellulose is clearly apparent.

In addition, the fibres in the BT series had a higher fraction of xylose than those in the BA series, see Fig. 4 and

Table 4
Chemical composition and strength data for spruce degraded at different times (ST) and different initial alkali concentration (SA)

Pulp	ST1	ST2	ST3	ST4	ST5	ST6	SA1	SA2	SA3	SA4	SA5	SA6
Viscosity (ml/g)	1060	850	700	580	410	200	1220	900	680	490	300	170
M_n (kg/mol)	120	118	86	110	64	34	123	169	109	83	61	40
M_w (kg/mol)	1210	1050	713	670	423	140	1450	1110	791	576	265	98
M_z (kg/mol)	3250	2680	7140	1630	1180	350	3250	2570	1950	1620	640	190
Polydispersity (M_w/M_n)	10.1	8.9	8.3	6.1	6.6	4.1	11.8	6.6	7.3	6.9	4.3	2.5
Yield (%)	47	45.5	44.5	43.2	38.3	29.5	48.3	45.5	43.2	41.1	36.9	27.9
Kappa number	23	14	11	9	7	5	19	12	10	8	7	6
Arabinose[a] (%)	0.6	–	0.4	–	0.4	–	0.8	–	0.4	–	0.3	–
Xylose[a] (%)	5.9	–	5.2	–	5.4	–	7.4	–	4.3	–	1.5	–
Mannose[a] (%)	6.3	–	5.6	–	5.1	–	5.8	–	6.4	–	6.6	–
Galactose[a] (%)	0.4	–	0.3	–	0.3	–	0.4	–	0.4	–	0.2	–
Glucose[a] (%)	86.8	–	88.4	–	88.8	–	85.5	–	88.6	–	91.3	–
Cellulose[b] (%)	83	–	85	–	87	–	82	–	85	–	89	–
Xylan[b] (%)	6	–	6	–	6	–	8	–	5	–	2	–
Glucomannan[b] (%)	8	–	7	–	7	–	7	–	8	–	8	–
Fibre length[c] (mm)	2.9	–	2.9	–	2.7	–	2.8	–	2.9	–	2.9	–
Shape factor[d]	91.7	–	90.5	–	89.3	–	92.6	–	91.6	–	90.2	–
Dry zero-span tensile index (kNm/kg)	215	211	211	199	175	110	212	211	209	200	151	87
Rewetted zero-span tensile index (kNm/kg)	212	205	200	188	158	58	212	206	199	192	131	46

[a] Relative percentage of monosaccharides.
[b] Calculated to polymer composition according to Janson (1974).
[c] Length-weighted fibre length.
[d] A higher value implies a straighter fibre.

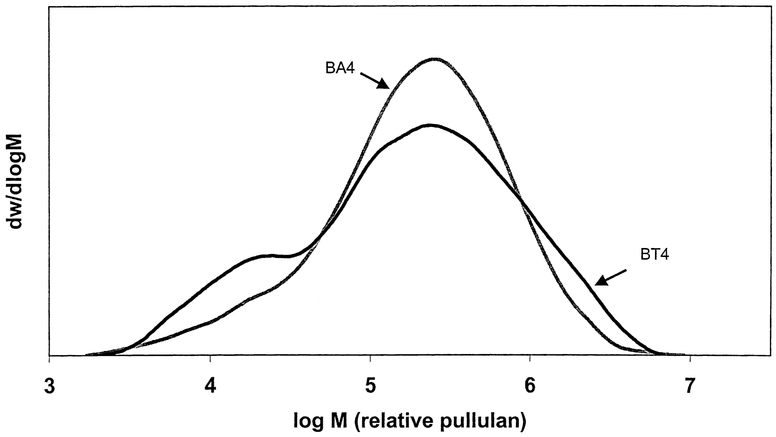

Fig. 4. Comparison of the molar distribution of two birch pulps (BT4) and (BA4) degraded to similar intrinsic viscosity levels. Chromatographic conditions as in Fig. 2.

Table 3. It is well known that more xylan is dissolved in cooks with higher alkali concentration (Aurell & Hartler, 1965; Gustavsson & Al-Dajani, 2000). In the case of the BT series, a distinct distribution of xylan was observed in the MMD of all the pulps, regardless of degradation level (Fig. 3). However, in the MMD of the BA series, the distinct xylan distribution could not be discerned in the more degraded pulps (Fig. 2).

The width of the MMD is often expressed by the polydispersity (M_w/M_n). The difference in MMD already mentioned can also be observed as differences in polydispersity. The polydispersity is shown versus intrinsic viscosity for the two birch pulp series in Fig. 5. The BT series, with a broader distribution, also have a higher polydispersity at a given viscosity than the BA series. This is in accordance with the broader MMD of the fibres in the BT series, due to the larger amount of high molecular mass cellulose and larger amounts of xylan in the fibres. The intersection in Fig. 5 is a result of the cooking conditions. It closely reflects the point where time and alkali charges were the same in both series.

3.2. Molecular degradation of spruce

Spruce pulps were characterised with SEC of samples derivatised with ethylisocyanate. As in the case of birch kraft pulps, the MMD of softwood kraft pulps are bimodal with two resolved peaks. Previous studies have shown that the MMD of derivatised softwood samples may be interpreted in the same way as the MMD of underivatised hardwood samples with respect to the positions of the cellulose and hemicellulose distributions (Berthold et al., 2001).

The MMD of the fibres from the spruce kraft pulp series are shown in Fig. 6 (variation initial alkali concentration, SA) and Fig. 7 (variation in pulping time, ST). The typical bimodal MMD was clearly seen in the case of the spruce pulps with high molecular masses. As in the case of the birch pulps (Figs. 3 and 4), the bimodality of the MMD for the more severely degraded pulps was less clear, since the degraded cellulose fraction in these cases interfered with the hemicellulose fraction. The cellulose peak of the more degraded pulps moved towards the low molecular mass

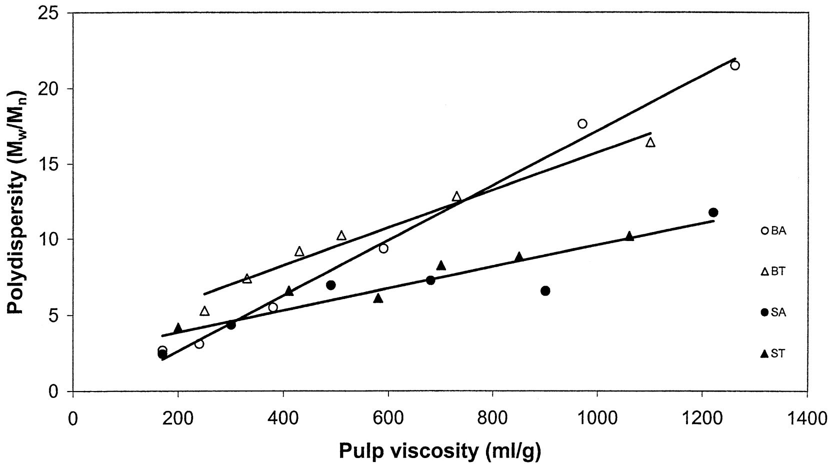

Fig. 5. Polydispersities (M_w/M_n) of birch and spruce pulps as measured by SEC versus intrinsic viscosity.

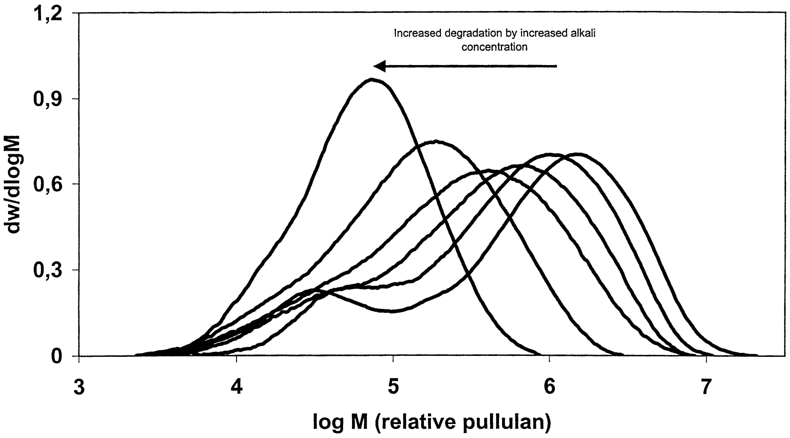

Fig. 6. Molar mass distribution relative pullulan of spruce pulps derivatised with ethylisocyanate, cooked with different initial alkali levels (SA). Chromatographic conditions as in Fig. 2.

region, as is also evident in the decreasing weight average molar masses (M_w), (Table 4).

No differences were observed between the two degradation series in the high molecular mass region of the MMD of the spruce pulps (Figs. 6 and 7), i.e. no tail was evident in the MMD for the ST series in contrast to the BT series. This is also evident in the relation between polydispersity and viscosity in Fig. 5. The same relation is applicable for the two spruce series, regardless of degradation strategy.

Spruce wood has lower amounts of xylan and much larger amounts of glucomannan than birch wood, but only the dissolution of xylan is affected by the alkali concentration in the cook (Aurell & Hartler, 1965; Gustavsson & Al-Dajani, 2000). This resulted in a smaller variation in total hemicellulose content in the spruce than in the birch kraft pulps (cf. Tables 3 and 4). The changes in hemicellulose content were difficult to observe as changed in MMD (cf. Figs. 6 and 7).

Differences in the MMD of fibres degraded by different degradation strategies to similar viscosity levels were found for the birch pulps. These differences were not evident for the spruce pulps. Several possible explanations exist; both the different fibre types with different carbohydrate composition and different morphologies could explain the difference between the spruce and birch pulps. It has been reported (Lagergren, Rydholm, & Stockman, 1957) that the strength of birch wood decreases more than the strength of spruce wood at alkali treatments. The authors interpreted this as alkali causing different swelling in the fibre wall for birch compared to spruce, which also could explain these results. The birch wood and spruce wood were impregnated slightly differently, in similar manner as birch and spruce pulps have been impregnated at earlier experiments at this laboratory. The impregnation should however be sufficient in both cases.

3.3. Mechanical properties

The pulp fibres of both birch and spruce were intact after cooking and defibration. This was concluded by light microscopy (micrographs not shown) and fibre length measurements by image analysis, see Tables 3 and 4. The intact fibres made a strength evaluation possible.

The dry zero-span tensile index is a measure of the

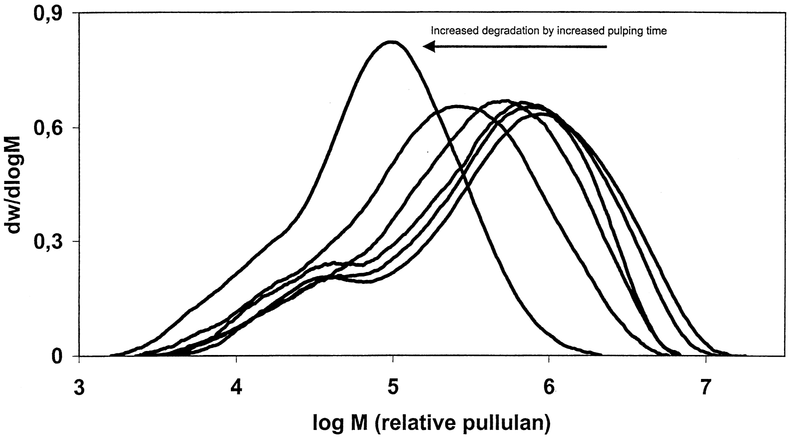

Fig. 7. Molar mass distribution relative pullulan of spruce pulps derivatised with ethylisocyanate, cooked with different cooking times (ST). Chromatographic conditions as in Fig. 2.

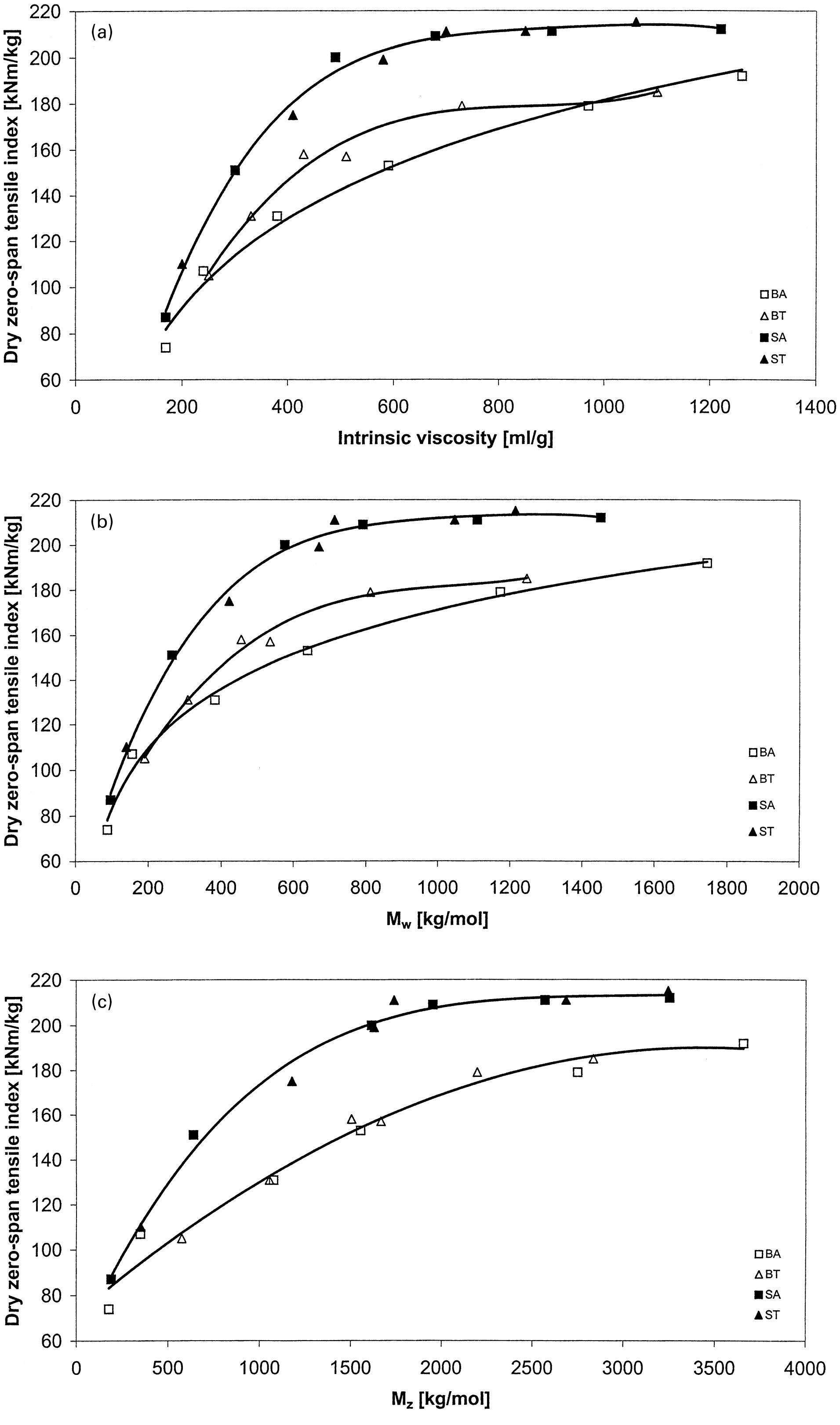

Fig. 8. Dry zero-span tensile index versus intrinsic viscosity (a), M_w (b) and M_z (c) for birch and spruce pulps.

average fibre strength (Seth & Chan, 1999). The dry zero-span tensile index, intrinsic viscosity, M_w and M_z are compared in Fig. 8a–c. For birch, the BT series had a higher dry zero-span tensile index at a given intrinsic viscosity and given M_w, than the BA series. However, the two series had the same relation between dry zero-span tensile index and M_z. M_z is more sensitive than M_w and intrinsic viscosity to the high molecular mass material. The fact that the dry zero-span strength of both birch series followed the same relation with M_z, but not with either M_w or viscosity, implied that the high molecular mass fraction significantly influenced the dry zero-span strength. The presence of high molecular mass material represented by the tail in the MMD of the BT series can thus explain the increase in the dry zero-span tensile index at a given M_w or given viscosity value.

The relations between rewetted dry zero-span strength and intrinsic viscosity, M_w and M_z for spruce kraft pulps (ST and SA series) are also compared in Fig. 8a–c. In contrast to birch, spruce fibres showed similar relations between dry zero-span tensile index and intrinsic viscosity, M_w and M_z for both degradation strategies. This was expected since no MMD of spruce pulp fibres showed any tail.

The relations between zero-span tensile index and intrinsic viscosity, or M_w, were similar for both series, regardless of degradation method for both birch and spruce (Tables 3 and 4). Rewetted zero-span tensile index is more sensitive to local defects (Mohlin & Alfredsson, 1990) than dry zero-span. Apparently these defects were more important for the rewetted zero-span tensile index than the presence of higher molecular mass material.

The dry zero-span tensile index of the spruce pulps was constant at high molecular masses and then decreased rapidly after a limiting molecular mass had been reached, as shown in Fig. 8a–c. This agrees with previous studies (Molin & Lennholm, 2000) and a study focusing on high molecular masses by Seth and Chan (1999). For the birch pulps however, a continuously decreasing trend was evident, especially for the BA series (Fig. 8).

3.4. Homogeneity of alkaline degradation

As discussed in the introduction, degradation can be heterogeneous or homogenous. We suggest that the alkaline degradation of cellulose in spruce and birch has only minor elements of heterogeneity and largely occurs as a homogenous process according to Fig. 1a. One reason for this conclusion is that even very degraded fibres were intact after treatment. Heterogeneous degradation to the same M_w, according to Fig. 1c (acid degradation), results in fragmentation of the fibres (Battista, 1950). Secondly, heterogeneous degradation according to Fig. 1b (preferably surface reactions, i.e. ozone degradation), would leave a core of high molecular mass cellulose, which was not observed in the MMD after extensive alkaline degradation. The homogeneity of the alkaline degradation is expected since alkali can swell cellulose and change its crystal structure (Krässig, 1992), giving a high accessibility of alkali to cellulose.

The BT series contained a fraction of high molecular mass cellulose, which implies a more heterogeneous degradation than was observed in the other series. It is suggested that this heterogeneous degradation was caused by a greater extent of surface reactions (Fig. 1b) leaving a higher molecular mass core. This less degraded cellulose core could explain the observed increase in dry zero-span tensile strength. A heterogeneous reaction at weak points (Fig. 1c) is not probable, because that would have given a lower dry zero-span tensile strength in the BT series than in the BA series.

4. Conclusions

The present work shows that detailed information regarding the alkaline degradation of wood can be obtained from molecular mass distributions in combination with carbohydrate analysis and strength evaluation. Alkaline degradation was to a great extent homogeneous, but significant differences were found between different degradation conditions and different wood species. Birch fibres were found to be more sensitive to the alkaline degradation conditions than spruce fibres. The variations in dry zero-span tensile strength between the two birch series were associated with differences in the MMD. A larger fraction of high molecular mass cellulose at a given intrinsic viscosity could be connected to higher fibre strength, measured as dry zero-span tensile strength.

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