

Effects of released organic substances on sizing efficiency – Influence of origin, composition and molecular properties of the organic material

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SUMMARY: The possible detrimental effects of different white waters on sizing efficiency were evaluated. Different white waters (containing varying amounts and categories of dissolved and colloidal substances) were prepared and used in AKD sizing experiments. The substances in the white waters originated from pulps of different origin (hardwood or softwood kraft pulp) that were bleached with different bleaching processes (TCF or ECF). Sizing trials were carried out in (i) white waters produced in the laboratory by slushing and beating of well-washed pulps, and, (ii) white waters prepared by diluting press filtrates from bleaching of pulp. The contents of these white waters were considered to represent substances released from the fibres at stock preparation and substances carried over from the pulp mill, respectively.

The sizing trials carried out in white waters containing released substances showed that the sizing efficiency was significantly inferior in these white waters compared to the white waters containing substances carried over from the pulp mill. The material that was released from the fibres was found to be highly detrimental since even low concentrations interfered with the sizing. The chemical composition and properties of these two white waters differed to a high extent. The detrimental white waters contained mainly high molecular mass xylans released during the mechanical treatment of the fibres. In the white waters containing “carry-over substances” the dissolved organic material was mainly low molecular (below 5 000 g/mole). The total amounts of dissolved organic material, determined as COD, and the anionic charge were, however, similar to those of the more detrimental white waters.

When comparing pulps from different wood species the results clearly showed that the material originating from the hardwood pulp was much more detrimental to AKD sizing than was the material originating from the softwood pulp. The overall chemical compositions of the two different white waters were rather similar but there were significant differences in molecular properties of the hemicelluloses.

There was no significant difference in absolute molecular mass between the materials released during the refining of hardwood and softwood pulp. The weight-average molecular mass of both materials was approximately 6 000-7 000. However, the hardwood xylans have a strong tendency to form aggregates in aqueous solutions of low or moderate pH and ionic strength, and this gave rise to an aggregated xylan fraction of high apparent molecular mass. The corresponding softwood xylan showed no such tendency.

To investigate the influence of the molecular properties of hemicelluloses on sizing efficiency, AKD sizing experiments were carried out in different white waters of the same origin (hardwood kraft pulp) and with almost identical carbohydrate compositions but with different amounts of aggregated xylan. The trials showed that the sizing efficiency differed between these waters. The sizing efficiency was considerably better in

white water in which the molecular mass of the xylan had been reduced by enzymatic hydrolysis, compared to sizing in white water containing high amounts of aggregated material. The xylan aggregates are apparently more detrimental to sizing than the corresponding non-aggregated xylan molecules.

All these results show that the composition and molecular mass of the organic material in the white waters are very important for the sizing efficiency. One possible explanation to the detrimental effects is the occurrence of interactions between aggregated xylan originating from the released organic material and the cationic retention agent. This would result in a poorer retention of the AKD to the fibres.

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In the future, the process water systems of paper machines will be more closed, and this may result in an enrichment of detrimental substances in the white water system. Such an increase in the concentrations of dissolved and colloidal substances may affect the runnability and capacity of the paper machine as well as the quality of the product. The origin of the organic substances found in the white water may differ according to the paper mill process and the pulp used. If the mill is integrated, the pulp is transferred to the paper mill with process water which contains dissolved and colloidal material originating from the pulping and bleaching processes. However, some organic material is also released from the pulp when the pulp is subjected to mechanical treatment, i.e. slushing and beating during stock preparation in the paper mill (Sjöström and Haglund 1963; Lindström et al. 1978; Oblak-Rainer et al. 1997; Sjöström et al. 2000). In a mill using dried pulp there is no carry-over from the pulp mill and the main cause of the release of organic substances is the mechanical treatment of the pulp during stock preparation.

These two sources of organic material in the white water; carry-over and release during mechanical treatment, have been studied in detail for bleached chemical pulps at STFI-Packforsk AB during recent years. The results showed, in summary, that:

- There were significant differences in the chemical composition of the material carried over from the pulp mill compared to the material that was released during stock preparation.
- The amounts, and also the composition, of the organic

material released during mechanical treatment, e.g. slushing and beating, were depending on the bleaching sequence used.

The organic material present in the white waters, and on the fibres, may interact with the chemical additives used in papermaking in different ways. One recent example is the sizing with alkylketene dimer (AKD). Mill experience has shown that the AKD sizing efficiency depends on the pulp used. The sizing of hardwood pulps (birch) that are bleached by a total chlorine free (TCF) process has been considered to be extra troublesome.

The AKD sizing mechanism is quite well understood and comprises three different steps:

- retention of the AKD droplet onto the fibres in the wet-end
- spreading of the AKD size over the fibre (sheet) surface
- reaction between the AKD and the hydroxyl groups of the cellulose.

A number of articles have been published over the mechanisms and especially the reaction step has been discussed by many scientists. The main, desired, reaction is that the AKD reacts with the cellulose by forming a beta-ketoester with the cellulose (Lindström and Söderberg 1986a; Ödberg et al. 1987), but some of the AKD is retained in the sheet unreacted, which is believed to give some, but lower, contribution to the sizing (Lindström and Söderberg 1986a). A part of the AKD is also lost by hydrolysis to a ketone without any sizing properties.

It has been reported that the presence of certain extractives in the sheet affects the sizing efficiency of AKD (Lindström and Söderberg 1986b; Johansson and Lindström 2004; Lidén and Tollander 2004). There are different explanations given to these observations. One reason could be that the extractives prevent the spreading of the AKD during the drying phase; another that the extractives interact with the reaction between AKD and cellulose. In a recent article (Zeno et al. 2005) it has been shown that also surface active substances present in deinked pulp are detrimental to AKD sizing, most probably by an interaction with the reaction between the size and the fibres.

The finding that ECF- and TCF-bleached pulps behave differently with respect to sizing has been further studied in EuroFEX trials at STFI (Laine et al. 2004). Fine paper was produced with different pulps and different white waters. It was shown in these trials that the AKD sizing efficiency was lower with TCF-bleached than with ECF-bleached pulp. It was not, however, possible to separate the influence of the white water from the influence of the properties of the pulps.

The purpose of the present work was to evaluate the influence of chemical substances in the white water on the sizing efficiency. One important aim of the work was to investigate the differences between substances that are carried over from the pulp mill (due to poor washing of the pulp) and substances that are released during mechanical treatment in the stock preparation. Another aim was to investigate the differences between substances originating from different types of bleached pulp.

Materials and Methods

Layout of the trials

Different white waters (containing varying amounts and categories of dissolved and colloidal substances) were prepared and used in AKD sizing experiments:

- White waters produced in the laboratory by slushing and beating of well-washed mill pulps (bleached hardwood or bleached softwood). These white waters were considered to contain mainly “released substances”. Some experiments were also carried out with white water fractions of different molecular mass with the purpose to study the effect of molecular properties of the released substances.
- White waters prepared by diluting press filtrates from the last stage of bleaching of hardwood or softwood. These white waters were considered to contain mainly “carry-over substances”.

The sizing efficiency was evaluated as the Cobb value of the sheets.

Preparation of the pulp used in the sizing trials

The pulp used in the sizing trials (Table 1) was a mill-bleached hardwood kraft pulp. The pulp was TCF-bleached and was collected from the edge-trimmings of a wet lap machine.

The pulp was refined to about 25°SR in an Escher-Wyss laboratory refiner. The beating was made at 45°C and at a relatively high salt concentration (15 mM NaCl and 1 mM NaHCO₃). The fibres and fines in the pulp were converted to sodium form prior to the sizing trials. This was made by treatment with HCl followed by treatment with NaHCO₃ and finally with NaOH to pH 9.

Table 1. The properties of the TCF-bleached hardwood pulp used in the sizing trials.

Pulp	Total charge (µeq/g)	Surface charge (µeq/g)	Fines content (%)	WRV (g/g)
TCF-bleached hardwood	104	10	11	1.7

Preparation of white waters containing mainly “released substances”

White water with a high concentration of released dissolved and colloidal substances was prepared in the laboratory from well-washed mill pulps (TCF-bleached and ECF-bleached hardwood kraft pulps and ECF-bleached softwood kraft pulp, respectively). The pulp was washed with 20–25 L of distilled water before use. The washed pulp was agitated for 1 minute in an Escher-Wyss laboratory slusher with 15 L of distilled water and 1 mM NaHCO₃ (or filtrate) at 23°C and 3.5% pulp consistency. The mixture was then refined at 200 kWh/t in an Escher-Wyss laboratory refiner. The suspension was filtered using a 125 µm nylon wire and the filtrate was recirculated and used in new refinings of new pulp. For the hardwood pulps it was sufficient to recirculate the filtrate 4 times to achieve the desired COD level of about 1200 mg/L. It was needed 10–14 recirculations of the softwood pulp filtrate to reach about 300 mg/L. This filtrate was further concentrated by reversed osmosis (RO filter nanomax 95) to double its concentration. The COD of the final filtrate was 1350 mg/L (for the TCF-bleached hardwood

pulp), 1100 mg/L (for the ECF-bleached hardwood pulp) and 550 mg/L for the softwood pulp.

The final filtrate was centrifuged (3600 g, 15 min) to remove the fines and to give a white water containing only dissolved and colloidal material. Prior to the sizing trials the concentrated white water was diluted to give the desired concentration of COD, the pH was adjusted to pH 8 (with NaOH or HCl) and the conductivity to about 1750 $\mu\text{S}/\text{cm}$ (with NaCl).

For the studies of the influence of molecular properties of the carbohydrates on the sizing efficiency, two different molecular mass fractions were prepared from the bleached hardwood pulp white water.

A white water fraction of *high* molecular mass was prepared by preparative ultrafiltration using a Pro Lab YFROLAB 21 (Millipore Process Systems, Molsheim, France) ultrafiltration system. The filter used was a Prepscale TFF cartridge containing a regenerated cellulose membrane with cut-off $M=30\,000$ (prod. no. SK1P026W3, Millipore, USA). 5 L of the white water was added to the ultrafiltration system. The ultrafiltration was continued until the retentate volume was 1.5 L. The retentate was thereafter diluted to 5 L with pure water and the filtration process was repeated until the retentate volume was again 1.5 L. The retentate and permeate were collected separately, and the whole procedure was repeated with 5 L of fresh white water until 15 L of white water had been processed.

A white water fraction of *low* molecular mass was prepared by subjecting the white water to enzymatic hydrolysis. A commercial enzyme preparation, Ecopulp TX 200C (Röhm, Finland), was diluted with water to 1/1000 concentration and 20 mL of this solution was added to 5 L of white water and the mixture was kept at 50°C for 3 hours.

Preparation of white waters containing mainly “carry-over substances”

Two different mill-filtrates were taken during production of bleached pulp in a pulp mill:

- Press filtrate from TCF bleaching of hardwood kraft pulp (from the last wash press after bleaching). COD was about 2400 mg/L.
- Press filtrate from ECF bleaching of softwood kraft pulp (from the last wash press after bleaching). COD was about 2200 mg/L.

The press filtrate was filtered through a 0.45 μm filter to remove the fines and was then diluted (1:2) to give a COD of approx. 1200 mg/L. Prior to the sizing trials the filtrate was diluted to give the desired concentration of COD, the pH was adjusted to pH 8 (with NaOH or HCl) and the conductivity to about 1750 $\mu\text{S}/\text{cm}$ (with NaCl).

Sizing trials

Sizing trials were carried out using the TCF-bleached hardwood kraft pulp and different white waters. Reference trials were also made in “water” with the same pH and conductivity as the white waters.

The sizing trials were made at 0.35% pulp consistency at pH 8 and with a conductivity of 1750 $\mu\text{S}/\text{cm}$. The AKD

size used was Hydrores 152 MDY and the (C-PAM) retention aid used was Fennopol K3400R. Both chemicals were supplied by Kemira Kemi. The addition of AKD was between 0.2–2 mg/g pulp in most trials. The retention aid was added at a fixed level of 0.5 mg/g pulp.

The pulp suspension was agitated for 3 min at a stirring speed of 700 rpm. At the addition of AKD the stirring speed was decreased to 300 rpm. After a reaction time of 30 sec the retention aid was added. After an additional reaction time of 60 sec the pulp suspension was added to the sheet former and the forming started.

Sheets, with a grammage of 80 g/m^2 , were made in a British sheet former. The British sheet former was used as it allowed the forming of sheets in small fluid volumes, only 1 L.

The sheets were pressed according to standard procedures (SCAN CM 26:99) and then dried over night in a conditioned room (23°C and 50% relative humidity). Finally, the sheets were cured for 15 min at 110°C.

The Cobb60 value was determined for the sheets according to the standard method (SCAN P 12:64).

Chemical characterisation of the dissolved and colloidal material

The amounts and types of organic material in the white waters were characterised by chemical analysis of the aqueous phase (duplicate samples) using the following methods:

COD. The COD was determined using the Dr Lange Cuvette Test LCK 114.

Carbohydrate content. The orcinol method was used to determine the total amount of dissolved carbohydrates. The sample was mixed with the orcinol reagent in sulphuric acid and, after reaction at 90°C for 15 min, the colour formed was measured at 540 nm. Xylose was used as calibration substance. (Vasseur 1948; Sjöström and Rådeström 1996).

Carbohydrate composition. Carbohydrate analysis of lyophilized water samples was performed employing enzymatic hydrolysis and capillary zone electrophoresis (CZE), as described previously (Dahlman et al. 2000).

Low molecular components. Low molecular alcohols were determined by GC using methanol and ethanol as internal standards according to the STFI internal method AH 83-10. Low molecular aliphatic acids were determined by Ion Chromatography using a Dionex DX500 ion chromatograph equipped with a conductivity detector (ED-40) and an IonPac AS11HC anion-exchange column (250 mm X 4 mm I.D.) together with an AG11HC guard column. A membrane suppressor (ASRS-I) was used to convert the eluent and the separated anions to their respective acid forms. The eluent used consisted of 80 % (v/v) water and 20% (v/v) of a mixture of 0.4 mM NaOH and methanol (50% v/v) at a flow rate of 1.4 mL/min. The amounts of aliphatic acids were determined from external calibration curves.

Lignins. The UV absorbance at 280 nm was measured to determine the lignin concentration. A lignin absorptivity of 22 $\text{L}/\text{g} \cdot \text{cm}$ was used in the calculations (Sjöström and Ödberg 1994).

Anionic charge. Polyelectrolyte titration was used to determine the anionic charge. The sample was titrated with a cationic polymer (Polybrene) of known charge density. The equivalence point was defined as the point where the potential passed zero, using the Mutek PCD 03 instrument.

Molecular mass characterisation by ultrafiltration. For fractionation of the dissolved organic material into different molecular mass fractions, ultrafiltration equipment from Sartorius was used. With this equipment, Vivaspin 20, the fractionation is carried out by centrifuging the sample in a specially designed unit consisting of two tubes fitted together. The top tube has an ultrafilter fixed vertically at its base. The low molecular mass substances pass through the ultrafilter to the bottom tube and the high molecular mass substances are retained in the top tube. After the ultrafiltration, the tubes are disconnected and the aqueous phases are removed and analysed. Filters with cut-off values of 5 000, 10 000 and 30 000 were used in the trials.

Molecular mass characterisation by SEC/MALDI-MS. The SEC equipment consisted of three columns of Ultrahydrogel 120, 250 and 500 (Waters Assoc. USA), respectively, linked in series to a refractive index (RI) detector (Waters Assoc. USA). Two different eluent systems were employed; i.e. (i) 50 mM ammonium acetate (pH 7) and (ii) a strongly alkaline sodium acetate/sodium hydroxide solution (0.2 M acetate and 0.1 M hydroxide, pH 13). 100 µL of white water was injected onto the SEC column system. The signal from the RI detector was processed using the PL Caliber SEC software and interface (Polymer Laboratories Ltd., UK) on a standard PC. The SEC system was calibrated using MALDI-MS (matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry) as described previously (Jacobs and Dahlman 2001). At regular intervals during the emergence of peaks from the SEC system, fractions (100 µL) were collected at the outlet of the refractive index detector. The peak-average molar mass (M_p) values of the fractions were determined by MALDI-MS analysis. For each fraction, the logarithm of the M_p value determined by MALDI-MS was plotted as a function of the time required for elution from the SEC system. A linear relationship between $\log M_p$ and elution time was established for the white waters, and these relationships were subsequently employed to determine the number and weight-average molar masses (M_n and M_w) of the entire molecular mass distribution.

Characterisation of the pulp

The *total charge of the pulps* was determined by conductometric titration (Katz et al. 1984).

The *surface charge of the pulps* was determined by adsorption of a high molecular mass PolyDADMAC ($M > 500\ 000$) onto the fibres, followed by a polyelectrolyte titration of the non-adsorbed PolyDADMAC with potassium polyvinyl sulphate (KPVS). (Wågberg et al. 1989).

The *Water Retention Value*, WRV, was determined according to SCAN-C 62:00.

Results and Discussion

Properties of the white waters containing mainly "released substances"

The general composition of the organic material in the different white waters is shown in *Table 2*.

Table 2. The amount of organic material measured as COD, TOC, carbohydrates, lignins, low molecular mass compounds (organic acids and alcohols) and anionic charge in the white waters produced in the laboratory by slushing and beating of hardwood or softwood kraft pulp.

White water	COD (mg/L)	TOC (mg/L)	Carbo- hydrates (mg/L)	Lignins (mg/L)	Low mol. mass compounds (mg/L)	Anionic charge (meq/L)
WW from TCF-bleached hardwood kraft pulp	1100	390	840	20	<4	0.48
WW from ECF-bleached hardwood kraft pulp	1060	340	800	15	<3	0.51
WW from ECF-bleached softwood kraft pulp	550	190	340	20	<3	0.61

About 80% of the total amount of organic material in the white waters from the hardwood pulps was carbohydrates. The contribution of lignins was low, less than 5%. The contribution of low molecular mass compounds was not significant.

The carbohydrates were the major source of anionically charged material in these laboratory-produced white waters. The composition of the carbohydrates is shown in *Table 3*.

Table 3. Carbohydrate content (Total conc, mg/L) and relative carbohydrate composition (in %) in the aqueous phase of the white waters produced in the laboratory by slushing and beating of hardwood or softwood kraft pulp.

White water	Xyl	Glc	Man	Ara	Gal	HexA	4OMe-GlcA	Total conc. mg/L
WW from TCF-bleached hardwood kraft pulp	92.2	0.5	0.1	0.3	0.1	5.2	1.7	749
WW from ECF-bleached hardwood kraft pulp	92.0	0.8	0.3	0.7	0.3	0.5	5.5	753
WW from ECF-bleached softwood kraft pulp	80.7	2.8	3.7	6.0	1.7	2.9	2.2	267

Xyl=Xylose, Glc=Glucose, Man=Mannose, Ara=Arabinose, Gal=Galactose, HexA=Hexenuronic acid, 4OMe-GlcA=4-O-Methylglucuronic acid. Calculated as anhydrosaccharides in %.

The carbohydrates present in the white waters were mainly xylans. Hexenuronic acids were the main charged groups in the xylans originating from the TCF-bleached hardwood pulp. The main charged groups in the xylans originating from the ECF-bleached hardwood pulp were 4-O-methylglucuronic acid residues. Also in the case of the material released from the softwood pulp, the main carbohydrate component was xylan containing hexenuronic and 4-O-methylglucuronic acids.

The molecular mass of the organic material in the white water was determined by the ultrafiltration method described earlier. The molecular mass distribution of the organic material released from the TCF-bleached hardwood pulp is shown in *Fig 1*. Note that the molecular mass distribution is given in % of the total amount found for each "class" of substances. The results show that about 75 % of the total material, determined as COD, had a molecular mass larger than 30 000 g/mole. The

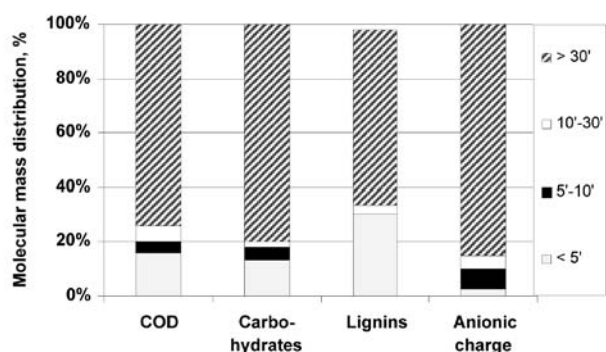


Fig 1. The molecular mass distribution for the total amount of organic material (measured as COD), carbohydrates, lignins and anionic charge in the white water produced from the TCF-bleached hardwood pulp.

carbohydrate material was mainly high molecular with about 80% of the material greater than 30 000 g/mole. It is noticeable that the anionic charged material was also mainly high molecular. This was expected as it is known from other investigations that the carbohydrate material released from pulp during mechanical treatment is mainly high molecular anionically charged xylans (Sjöström et al. 2000).

The molecular mass distribution of the material from the ECF-bleached hardwood pulp was similar to that of the material from the TCF-bleached hardwood pulp.

The molecular mass distribution of the material from the ECF-bleached softwood pulp was, however, significantly different. The molecular mass of the organic material was significantly lower compared to that released from the hardwood pulp. The total organic material, represented by COD, showed a molecular mass distribution of about 30%, 40%, 15% and 15% for the molecular masses $M < 5\,000$, $5\,000 < M < 10\,000$, $10\,000 < M < 30\,000$ and $M > 30\,000$. The results for the distribution of carbohydrates and lignins were similar. For the anionic charge the low molecular fraction, $M < 5\,000$, was lower.

Molecular properties and aggregate formation in the white waters containing released substances

We have previously found when using size-exclusion chromatography (SEC) that certain hemicelluloses, such as hexenuronoxylan from hardwood kraft pulp, aggregate to some extent in aqueous solutions of moderate pH and ionic strength (Jacobs and Dahlman 2001). As a result of this aggregate formation, such polysaccharide solutions often consist of a non-aggregated fraction containing free, completely dissolved polysaccharide molecules and one aggregated fraction exhibiting a high *apparent* molecular mass. Separation on the basis of molecular size can only be achieved using a strongly alkaline sodium acetate/sodium hydroxide solution (0.2 M acetate and 0.1 M hydroxide, pH 13) which is able to dissolve the hemicellulose aggregates (Jacobs and Dahlman 2001). Since the molecular mass determination using the ultrafiltration method described earlier was also performed in aqueous solutions of moderate pH and ionic strength such aggregate formation could possibly explain the differences in molecular mass between the hardwood and softwood white waters described above. The molecular masses of the different white waters were therefore studied by size-

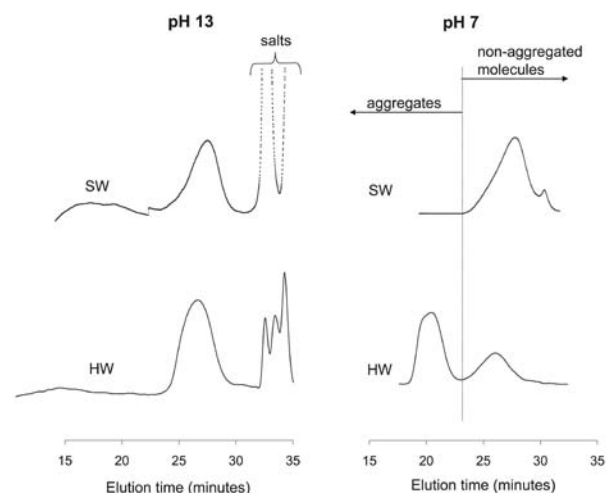


Fig 2. SEC chromatograms obtained upon analysis of xylan in white water employing elution with sodium hydroxide/sodium acetate pH 13 (left) or ammonium acetate pH 7 (right). SW = white water from softwood pulp, HW = white water from hardwood pulp.

exclusion chromatography using two different mobile phase systems:

- (i) a pH 13 sodium acetate/sodium hydroxide solution mentioned above, and
- (ii) 50 mM ammonium acetate (pH 7).

The SEC chromatograms obtained upon analysis of the hardwood and softwood hexenuronoxylans in the different white water preparations employing the two mobile phases are shown in Fig 2.

In ammonium acetate, pH 7, the chromatograms for hardwood xylan exhibit peaks originating from xylan aggregates as well as peaks from the non-aggregated xylan molecules. In sodium hydroxide/sodium acetate, pH 13, only a single peak corresponding to the non-aggregated hardwood xylan is seen. In contrast, the chromatograms for softwood xylan exhibit peaks originating only from non-aggregated xylan molecules in both systems. The molecular masses of the material in the white waters were calculated from the SEC chromatograms after calibration using MALDI-MS. In the ammonium acetate (pH 7) system, the relative amounts of material in the aggregate and non-aggregate fractions were calculated from the peak areas. The molecular mass distributions were also determined by ultrafiltration and subsequent analysis of the fractions obtained. The fractions were analysed with respect to the total organic content by COD. The results of the molecular mass analyses are summarised in Table 4. Since the organic material in the white waters consisted almost exclusively of xylans, the relative molecular mass distributions obtained by SEC could be compared to those obtained by ultrafiltration and COD determination.

Although there was a difference in *apparent* molecular mass (as determined by the ultrafiltration method) between the materials released during the refining of hardwood and softwood pulp, no such difference was found in *absolute* molecular mass. The weight-average molecular

Table 4. Molecular mass and relative amount of non-aggregated and aggregated xylan in white water preparations.

White water preparation	Mw analysed by SEC		Aggregate	Relative amount of COD in fraction after ultrafiltration			
	pH 13 Molecules	pH 7 Molecules		< 5K	5–10K	10–30K	> 30K
Hardwood pulp	7200	5800	45000 ^a	11%	15%	2%	73%
	100%	34%	66%				
Softwood pulp	6200	5900	0%	33%	40%	14%	13%
	100%	100%	0%				

^aApproximate value obtained by extrapolation

mass of both materials was approximately 6 000–7 000, which corresponds to xylan molecules with a degree of polymerisation of 45–55 monosaccharide units. The SEC analyses also showed that the hardwood xylans have a strong tendency to form aggregates in aqueous solutions of low or moderate pH and ionic strength. The corresponding softwood xylan showed no such tendency. A possible explanation is the differences in polysaccharide structure between hardwood and softwood xylan. Although the total amounts of uronic acid residues (i.e. hexenuronic acid and 4-O-methylglucuronic acid) attached to the xylan backbones were similar in the two cases, the structures of the polysaccharide chains are quite different. For example, the uronic acid residues are regularly distributed along the xylan chains in softwood whereas they are irregularly distributed in hardwood xylan (Jacobs et al. 2001). Furthermore, softwood xylans contain arabinose residues which are not present in hardwood xylan. Altogether, these facts imply that fairly long segments of the xylan backbone without any side-groups must exist in hardwood xylan. These linear structural segments are probably involved in the formation of aggregates. Similar aggregated xylans are probably present under the conditions normally prevailing in white water (i.e. moderate pH and ionic strength).

It must be stressed that the molecular masses of the aggregates are approximations obtained by extrapolation of the calibration curves developed for the molecules, and the absolute values must therefore be considered with caution. Nevertheless, these analyses show that the aggregated xylans exhibit apparent molecular masses larger than 30 000.

Properties of the white waters containing mainly “carry-over substances”

The general composition of the organic material is shown in Table 5.

50–60% of the organic material was low molecular mass compounds (low molecular acids and alcohols). The carbohydrates and lignins together contributed to about 20% of the total organic material.

The low molecular mass compounds present in the filtrates are shown in Table 6. The chemical composition of a similar TCF press filtrate has been studied previously (Björklund Jansson et al. 2000) with very similar results.

The composition of the carbohydrates present in the TCF

Table 5. The amount of organic material measured as COD, TOC, carbohydrates, lignins, low molecular mass compounds (organic acids and alcohols) and anionic charge in the mill filtrates used as sources for “carry-over material”.

White water	COD (mg/L)	TOC (mg/L)	Carbo-hydrates (mg/L)	Lignins (mg/L)	Low mol. mass compounds (mg/L)	Anionic charge (meq/L)
Press filtrate (dil. 1:2) from TCF bleaching of hardwood pulp	1200	420	140	40	590	0.41
Press filtrate (dil. 1:2) from ECF bleaching of softwood pulp	1165	455	110	60	700	0.44

Table 6. The low molecular mass compounds in the mill filtrates used as sources for “carry-over material”.

White water	MeOH (mg/L)	EtOH (mg/L)	Hydroxy-prop. acid (mg/L)	Acetic acid (mg/L)	Glycolic acid (mg/L)	Formic acid (mg/L)
Press filtrate (dil. 1:2) from TCF bleaching of hardwood pulp	156	<0.5	147	<0.5	207	84
Press filtrate (dil. 1:2) from ECF bleaching of softwood pulp	65	<0.5	174	<0.5	344	115

press filtrate from hardwood bleaching, was very similar to that in the TCF white water, although the total amount was six times lower. Mainly xylans were present in the filtrate and the charged groups were hexenuronic acids and some 4-O-methylglucuronic acids. It was noticeable that the charged uronic acid groups only contributed to a small part of the anionic charge in the press filtrate. This indicated that not the hemicellulosic material but possibly the lignin was the main source of anionic charge in this filtrate. Small amounts of other carbohydrate components were also found, e.g. galactose, glucose and mannose.

The composition of the carbohydrates in the press filtrate from softwood bleaching was quite different and the xylans contributed only to half of the carbohydrate amount. The charged groups were found in only very small amounts in this filtrate.

The molecular mass distribution in the TCF filtrate is shown in Fig 3.

The results show that about 90% of the total organic material (determined as COD) had a molecular mass

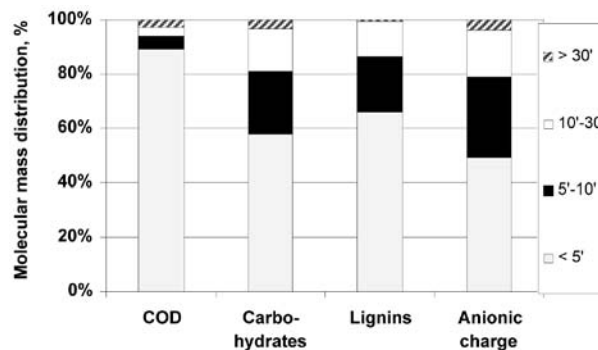


Fig 3. The molecular mass distribution for the total amount of organic material (measured as COD), carbohydrates, lignins and anionic charge in the press filtrate from TCF bleaching of hardwood kraft pulp.

lower than 5 000 g/mole. This result was expected as a main part of the organic material was low molecular mass compounds as shown in *Table 5*.

The carbohydrate material was relatively low molecular with only about 20% of the material larger than 10 000 g/mole. This means that the material that is believed to be most detrimental to sizing, the high molecular carbohydrate material, is present in much lower concentrations in this water compared to the white waters containing released substances.

It was not possible to determine the distribution of the anionically charged material exactly due to an inadequacy of the analytical method, which underestimates low molecular material. The amount of anionically charged material with a molecular mass below 5 000 g/mole has therefore been calculated from the total anionic charge.

Sizing in white waters of different composition

The detailed chemical characterisation showed that the composition of the white waters containing mainly “released substances” and mainly “carry-over substances” was very different. However, it is important to stress that the total content of organic material, measured by COD or TOC, and the total content of anionic charge were quite similar for all the white waters (cf. *Tables 2* and *5*). These two parameters are very often used to characterise waters in mill situations to draw conclusions about the risk for detrimental interactions with additives. The results from our sizing studies below show that such simple characterisations are not sufficient for a conclusion of the “detrimental capacity” of white waters.

Sizing in water with medium amounts of organic material (COD about 500 mg/L)

The sizing efficiency in the white waters containing mainly “released substances” (from TCF- and ECF-bleached hardwood pulps) and mainly “carry-over substances” from TCF bleaching is shown in *Fig 4*. A reference curve (distilled water with salt addition) is also shown in the diagram. The sizing efficiency, measured as the Cobb-value of the hand sheets, is plotted *versus* the amount of added AKD size. It is considered that a good sizing is achieved when the Cobb₆₀ value is close to 25 g/m².

It is evident that it was not possible to obtain a sized paper in the white waters containing released material from the TCF-bleached pulp. Sizing in white water produced from the ECF-bleached pulp gave slightly better results, but the sizing efficiency was still far from sufficient. It seems that the material released from the TCF-bleached pulp was more detrimental than that from the ECF-bleached pulp.

When the sizing was performed in the water containing mainly “carry-over” material, the sizing was better but the amounts of added size needed to obtain a Cobb value close to 25–30 were not at an acceptable level.

Since the anionic charge was almost the same in the white waters (cf. *Tables 2* and *5*), it can be concluded that the anionic charge is not the simple reason for the differences seen in the sizing efficiency. As the pulp type was

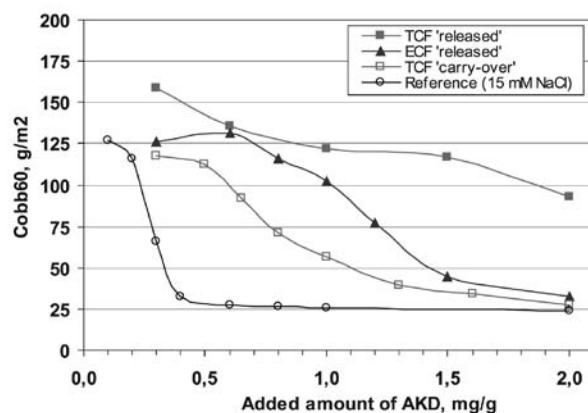


Fig 4. The sizing efficiency (measured as Cobb₆₀) with different amounts of added AKD. The total content of COD was approx. 500 mg/L in the white waters.

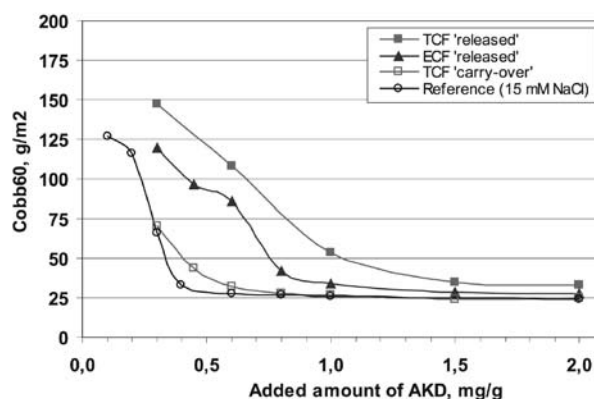


Fig 5. The sizing efficiency (measured as Cobb₆₀) with different amounts of added AKD. The total content of COD was approx. 170 mg/L in the white waters.

hardwood kraft pulp in all cases, the different bleaching sequences apparently resulted in released material of different “detrimental capacity”.

These results confirm the hypothesis that the composition and characteristics of the organic material are very important for the sizing efficiency. This is discussed further in the following sections.

Sizing in water with small amounts of organic material (COD about 170 mg/L)

Sizing trials were also performed in water with a very small amount of organic material. The results are shown in *Fig 5*.

Good sizing was obtained when the sizing was carried out in the water containing “carry-over substances”. Sizing was to some extent also obtained in the white waters containing released material, but the sizing efficiency was hardly acceptable. The sizing threshold level of a Cobb₆₀ value of 25 g/m² was never reached. Also in this case it is evident that the substances released from the TCF-bleached hardwood pulp were considerably more detrimental to sizing than those from the ECF-bleached pulp.

These results show that the composition of the white waters was of a great importance, even when the amount of organic material was very low. It is obvious that material that is released during mechanical treatment of bleached pulp is highly detrimental, even at very low concen-

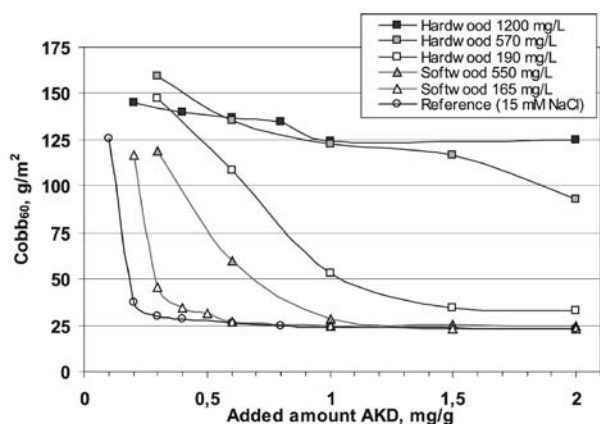


Fig 6. The sizing efficiency (measured as $Cobb_{60}$) with different concentration of organic material originating from two different pulps. The trials were made in white waters produced in the laboratory from bleached hardwood and softwood pulps.

trations, to sizing.

The concentrations of dissolved organic material (COD) in mill white waters will certainly reach the levels tested in our trials. However, in mill white waters the dissolved organic material originates not only from the stock preparation but also from other sources. This means that the concentration of the highly detrimental material that is released in the stock preparation in most cases is lower than in our trials. The results however indicate that even very low concentrations of the detrimental substances may interfere with the sizing.

Sizing in waters containing substances originating from hardwood and softwood pulps

In the previous section, it was shown that the substances released from pulp by mechanical treatment were much more detrimental than substances carried over with the pulp. It was also shown that the bleaching process was important. In the present section, the effect of wood species (hardwood v. softwood) is compared. The trials were carried out using different concentrations of the organic material in the white water during the sizing trials.

White waters containing mainly “released substances”

Fig 6 shows the results for the white waters containing released substances from the mechanical treatment of hardwood and softwood kraft pulps, respectively.

These results clearly show that the material originating from the hardwood pulp was much more detrimental to the AKD sizing. The overall chemical compositions of the two white waters were, however, rather similar as shown in Table 2.

Note that at comparable COD levels the anionic charge was higher for the softwood white water. Nevertheless the softwood white water had a much less detrimental effect. This again shows that the anionic charge as such can not be used as a measure of the detrimental capacity.

Xylans were the dominant sugar in both types of white water. In the hardwood water, they constituted more than 92% of the dissolved carbohydrate material compared to 80% for the softwood. The softwood white water also contained minor amounts of galactoglucomannans in

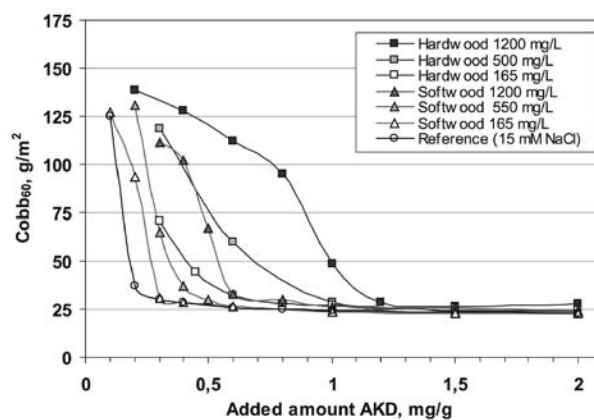


Fig 7. The sizing efficiency (measured as $Cobb_{60}$) at different concentration of organic material originating from two different pulps. The trials were made in white water prepared from press filtrates from production of bleached hardwood and softwood pulps.

contrast to the white water from the hardwood. The total content of uronic acids (i.e. charged groups) was similar for both the white waters. However, the charged groups of the dissolved carbohydrate material, the hexenuronic acids and the 4-O-methylglucuronic acids, were found in very different concentrations. The hexenuronic acid was the dominant uronic acid in the hardwood water, whereas the two acids were present in equal amounts in the softwood water. The fact that the hardwood pulp had been bleached using a TCF-bleaching sequence meant that the hexenuronic acid residues were rather unaffected. In contrast, the softwood pulp had been produced using a so-called ECF-light sequence which destroys the hexenuronic acids to a certain extent.

The molecular mass distributions of the organic material, as determined by the ultrafiltration method, differed greatly between the two cases. The material released from the hardwood pulp was to a very high extent high molecular. About 80% of the material was in the $M > 30\,000$ category. These results were in contrast to the results obtained for the softwood pulp where the molecular mass distribution was skewed towards lower molecular masses.

The results very clearly show that the white waters containing the released material that is high molecular and anionically charged are most detrimental. It is obvious that the composition of the organic material in the white water, especially the hemicellulosic material, is very important for the sizing efficiency and the molecular mass of the dissolved hemicellulosic material and its configuration seems to be a key factor. The relation between the molecular properties (i.e. chemical composition, structure and molecular mass) and their subsequent influence on the sizing efficiency have been studied in more detail and are further discussed below.

White waters containing mainly “carry-over substances”

Fig 7 shows the results for the two press filtrates from the production of hardwood and softwood pulp.

Although the detrimental effects were much smaller in the case of “carry-over substances”, the results also show very clearly in this case that the material that originates

from the hardwood pulp was much more detrimental to the AKD sizing. It is believed that the hemicellulosic material also in this case has an important role for the detrimental effects found.

The total amounts of dissolved organic material, determined as COD, and the carbohydrates and the anionic charge were very similar. This means that the smaller detrimental effect obtained with the filtrate originating from softwood cannot be explained by a smaller amount of anionically charged substances.

In the case of mill filtrates from the production of softwood and hardwood pulp, most of the COD value is caused by the presence of low molecular organic acids and alcohols. The compositions of the low molecular compounds differed slightly.

It should be noted that the content of carbohydrate material (hemicelluloses) was much lower than in the white waters with "released substances", where most of the COD consisted of carbohydrates.

The molecular mass distributions of the organic material (as determined by the ultrafiltration method) also differed to some extent. There seemed to be more high molecular carbohydrates present in the hardwood filtrates. This finding is in accordance with the results for the white waters, which to some extent contained the same types of carbohydrate material, but of much higher concentrations. About 40% of the material was larger than 10 000 g/mole compared to only 20% for the softwood. A similar molecular mass distribution was found for the lignins.

Influence of molecular properties of the dissolved organic material on AKD sizing

To further investigate the influence of the molecular mass of hemicelluloses on sizing efficiency, sizing experiments were performed in different white waters of hardwood origin but with different molecular properties. SEC with ammonium acetate (pH 7) as mobile phase system was used to study the molecular mass distributions of the hardwood white water preparations used in the sizing trials, Fig 8.

The molecular mass distributions were also determined by ultrafiltration and subsequent analysis of the fractions obtained. The results of the molecular mass analyses for the hardwood white water preparations are summarised in Table 7.

As expected, the ultrafiltration and enzymatic treatments affected the molecular mass distribution of the material present in the hardwood white water preparations. As can be seen, the weight-average molecular mass of the hexenuronoxylan molecules as well as the relative amount of aggregated material was changed. The enzymatic hydrolysis reduced the weight-average molecular mass of the hexenuronoxylan molecules from 5800 to 1800; to approximately one third of the initial value. The amount of aggregated material was also reduced by the enzymatic treatment. The results indicate that the aggregated xylan fraction was hydrolysed to a lesser extent than the non-aggregated fraction. The xylanases used for the enzymatic treatment are known to hydrolyse

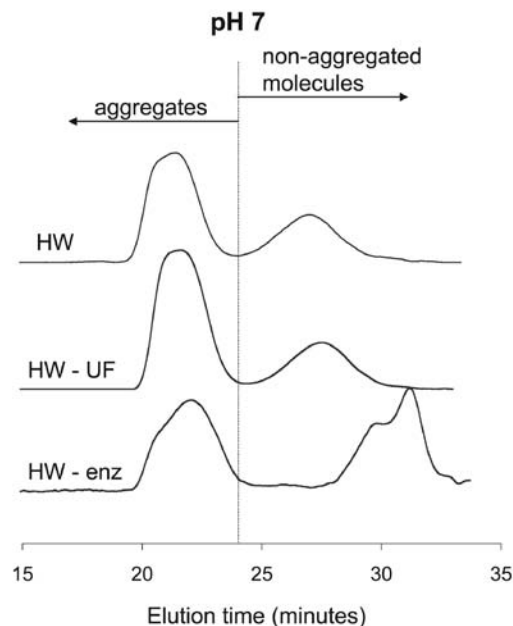


Fig 8. SEC chromatograms obtained upon analysis of xylan in white water employing elution with ammonium acetate pH 7. HW = white water from hardwood pulp, HW-UF = white water from hardwood pulp, $M > 30\ 000$ after ultrafiltration, HW-enz = white water from hardwood pulp after enzymatic treatment giving a decrease of the molecular mass.

Table 7. Molecular mass and relative amount of non-aggregated and aggregated xylan in white water preparations originating from mechanical treatment of hardwood kraft pulp.

White water preparation	M_w analysed by SEC pH 7		Relative amount of COD in fraction after ultrafiltration			
	Molecules	Aggregate	< 5K	5-10K	10-30K	> 30K
Hardwood pulp	5800	45000 ^a				
	34%	66%	11%	15%	2%	73%
Hardwood pulp, after ultrafiltration (high MM)	6300	49000 ^a				
	29%	71%	12%	11%	0%	77%
Hardwood pulp, after enzymatic treatment (low MM)	1800	43000 ^a				
	43%	57%	51%	2%	0%	47%

^aApproximate value obtained by extrapolation

linear, unsubstituted domains in the xylan backbone (Jeffries 1987; Tenkanen et al. 1995). One hypothesis that could explain the fact that the aggregated xylan fraction was hydrolysed to a lesser extent than the non-aggregated fraction is therefore that uronic acid groups are assembled at the aggregate surfaces, thereby hindering the enzymatic attack. This is in agreement with the earlier finding that linear structural segments are probably involved in the formation of aggregates.

Carbohydrate analysis of the white waters showed that the carbohydrate compositions were not significantly affected by the ultrafiltration or enzymatic treatment.

The sizing efficiency in the different white water preparations is shown in Fig 9. A reference curve (distilled water with salt addition) is also shown in the diagram.

The sizing efficiencies obtained in the three different white waters differed considerably, even though the carbohydrate compositions of these media were almost identical, as was the total amount of organic material. The major difference between the white waters studied was the occurrence of aggregated xylan (see Table 7).

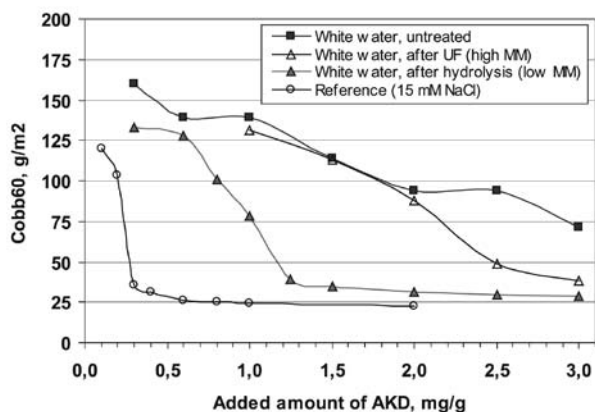


Fig 9. The sizing efficiency (measured as Cobb₆₀) in different white water preparations for different amounts of added AKD. The COD level in the white water preparations is approximately 450 mg/L.

These xylan aggregates were apparently more detrimental to sizing than the corresponding non-aggregated xylan molecules. This conclusion is in agreement with the results from the sizing study where material from hardwood pulps (which contains a large amount of xylan aggregates) was found to be much more detrimental to sizing than the corresponding material from softwood pulps (which contains no aggregated xylan). The detrimental effect of aggregate-containing white waters on sizing efficiency is probably a result of interaction with the cationic retention agent, in this case C-PAM. Ström and co-workers (Ström et al. 1982) studied the interaction between pine xylan and cationic polymers, and found that some retention agents were very sensitive towards the presence of xylan. These authors also suggested (Ström et al. 1985) that xylan molecules which contain unsubstituted domains would present a conformation in water solution in which the linear, unsubstituted domains in the xylan form coils, whereas the domains containing acidic side-groups are extended into the solution. This model can be further applied to explain the nature of the xylan aggregates. Our hypothesis is that linear structural segments are associated, forming the internal of the aggregates, whereas the uronic acid groups are extended into the solution. This implies that the charge density of certain domains in the aggregate surfaces would be higher than could be expected from the gross composition of the hexenuronoxylan. This hypothesis would explain how the materials released during the refining of hardwood and softwood pulp, which do not differ in carbohydrate composition or absolute molecular mass, still behave differently in connection with sizing.

Conclusions

Sizing trials carried out in white waters containing substances released during mechanical treatment of the fibres and white waters containing substances carried over from the pulp mill showed that the sizing efficiency was significantly inferior in the white waters containing "released substances". The material that was released from the fibres was found to be highly detrimental since even low concentrations interfered with the sizing.

When comparing the material released from pulps bleached

with different bleaching sequences, it was found that the material released from TCF-bleached pulp was more detrimental to sizing than that from ECF-bleached pulp. The chemical composition of the two white waters was similar and the carbohydrates present were mainly xylans.

When comparing pulps made from different wood species the results clearly showed that the material originating from the hardwood kraft pulp was much more detrimental to AKD sizing than was the material originating from the softwood kraft pulp. The overall chemical compositions of the two different white waters were, however, rather similar. Although the total amount of uronic acid groups in the dissolved carbohydrate material was similar for hardwood and softwood, the ratio of hexenuronic acid to 4-O-methylglucuronic acid differed between the two white waters, due to different bleaching procedures. The molecular mass distributions of the organic material, as determined by the ultrafiltration method, differed greatly between the two cases. The material released from the hardwood pulp was to a very high extent high molecular. About 80% of the material was in the $M > 30\,000$ category. These results were in contrast to the results obtained for the softwood pulp where the molecular mass distribution was skewed towards lower molecular masses. However, the absolute molecular mass, as determined by SEC, did not differ. In both cases, the weight-average molecular mass of the materials was approximately 6 000.

The hardwood xylans have a strong tendency to form aggregates in aqueous solutions of low or moderate pH and ionic strength, and this gave rise to a xylan fraction of high apparent molecular mass. The corresponding softwood xylan showed no such tendency. Such aggregate formation probably also occurs under the normal conditions of industrial white waters, i.e. at moderate pH and ionic strength.

Depending on the issue, different methods should be used for analysis of the molecular mass of the organic material. In order to study the apparent molecular mass, i.e. the molar mass of the aggregates, SEC in ammonium acetate (pH 7) or ultrafiltration followed by analysis of the fractions obtained should be the method of choice. In order to determine the absolute molar mass of hardwood xylans, SEC employing an alkaline sodium hydroxide/sodium acetate (pH 13) mobile phase should be used.

AKD sizing trials in different white waters with almost identical carbohydrate compositions but with different amounts of aggregated xylan showed that the sizing efficiency differed considerably between the waters. The xylan aggregates are apparently more detrimental to sizing than the corresponding non-aggregated xylan molecules. One explanation to the detrimental effects may be the occurrence of interactions between the aggregates originating from released organic material and the cationic retention agent, in this case C-PAM, which would result in a poorer retention of the AKD to the fibres. It has been reported that interactions between pine xylan and cationic polymers in some cases take place (Ström et al. 1982).

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Literature

Björklund Jansson, M., Reimann, A. and de Sousa, F. (2000): Low molecular mass acids and chelating agents in TCF bleaching filtrates, SCAN FORSK Report 731, STFI, Stockholm.

Dahlman, O., Jacobs, A., Liljenberg, A. and Ismail Olsson, A. (2000): Analysis of carbohydrates in wood and pulps employing enzymatic hydrolysis and subsequent capillary zone electrophoresis, *Journal of Chromatography A* 891, 157-174.

Jacobs, A. and Dahlman, O. (2001): Characterization of the molar masses of hemicelluloses from wood and pulps using size exclusion chromatography and matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry, *Biomacromolecules*, 2(3), 894-905.

Jacobs, A., Larsson, P.T. and Dahlman, O. (2001): Distribution of uronic acids in xylans from various species of soft- and hardwood as determined by MALDI mass spectrometry, *Biomacromolecules*, 2(3), 979-990.

Jeffries, T.W. (1987): Physical, chemical and biochemical considerations in the biological degradation of wood, In: "Wood and Cellulosics: Utilisation, Biotechnology, Structure and Properties", Edited by J.F. Kennedy, G.O. Phillips and P.A. Williams, Ellis Horwood Ltd, Chichester, p. 213-230.

Johansson, J. and Lindström, T. (2004): A study on AKD-size retention, reaction and sizing efficiency. Part 1: The effect of pulp bleaching on AKD-sizing, *Nord. Pulp Pap. Res. J.* 19(3), 330-335.

Katz, S., Beatson, R.P. and Scallan, A.M. (1984): The determination of strong and weak acidic groups in sulfite pulps, *Svensk Papperstidning*, 87(6), R48-R53.

Laine, J., Mattson, R. and Swerin, A. (2004): The effect of bleached pulp type on AKD internal sizing – an EuroFEX experimental paper machine study, *Paperi Puu*, 86(4), 293-297.

Lidén, J. and Tollander, M. (2004): Extractives in totally chlorine free bleached birch pulp and their effect in alkyketene dimers and alkenyl succinic anhydrides sizes, *Nord. Pulp Pap. Res. J.* 19(4), 466-469.

Lindström, T., Ljunggren, S., de Ruvo, A. and Söremark, C. (1978): Dissolution of carbohydrates and lignin during beating of kraft pulps, *Svensk Papperstidning*, 81(12), 397-402.

Lindström, T. and Söderberg, G. (1986a): On the mechanism of sizing with alkyketene dimers Part 1. Studies on the amount of alkyketene dimer required for sizing different pulps, *Nord. Pulp Pap. Res. J.* 1(1), 26-33.

Lindström, T. and Söderberg, G. (1986b): On the mechanism of sizing with alkyketene dimers Part 3. The role of pH, electrolytes, retention aids, extractives, Ca-lignosulfonates and mode of addition on alkyketene dimer retention, *Nord. Pulp Pap. Res. J.* 2(1), 31-38.

Oblak-Rainer, M., Budin, D., Cerne, S. and Lipic, B. (1997): Water soluble substances from bleached pulp fibres, *Cellulose Chem. Technol.* 31, 227-233.

Sjöström, E. and Haglund, P. (1963): Dissolution of carbohydrates during beating of chemical pulps, *Svensk Papperstidning*, 66(18), 718-720.

Sjöström, L., Laine, J. and Thimberg, Å. (2000): Release of organic substances from bleached sulphate pulps at slushing and refining, *Nord. Pulp Pap. Res. J.* 15(5), 469-475.

Sjöström, L. and Rådeström, R. (1996): Überwachung von Rückwasser-Verunreinigungen mit vereinfachten Analyseverfahren – einige praktische Anwendungen, *Wochenbl. Papierfabr.* 124(1), 12-15.

Sjöström, L. and Ödberg, L. (1994): Einfache Charakterisierung von gelösten Stoffen im Kreislaufwasser – Beispiele für Methoden und ihre praktische Anwendung, *Wochenbl. Papierfabr.* 122(8), 302-309.

Ström, G., Barla, P. and Stenius, P. (1982): The effect of pine xylan on the use of some polyocations as retention and drainage aids, *Svensk Papperstidning*, 85, R100-R106.

Ström, G., Barla, P. and Stenius, P. (1985): The formation of polyelectrolyte complexes between pine xylan and cationic polymers, *Colloids and Surfaces*, 13, 193-207.

Tenkanen, M., Hausalo, T., Siika-aho, M., Buchert, J. and Viikari, L. (1995): Use of enzymes in combination with anion exchange chromatography in the analysis of carbohydrate composition of kraft pulps, "The 8th International Symposium on Wood and Pulping Chemistry", Helsinki, Finland, p. 189-194.

Vasseur, E. (1948): A spectrophotometric study on the orcinol reaction with carbohydrates, *Acta Chem. Scand.* 2, 693-701.

Wågberg, L., Ödberg, L. and Glad-Nordmark, G. (1989): Charge determination of porous substrates by polyelectrolyte adsorption, *Nord. Pulp Pap. Res. J.* 4(2), 71-76.

Zeno, E., Carré, B. and Mauret, E. (2005): Influence of surface active substances on AKD sizing, *Nord. Pulp Pap. Res. J.* 20(2), 253-258.

Ödberg, L., Lindström, T., Liedberg, B. and Gustavsson, J. (1987): Evidence for b-ketoester formation during the sizing of paper with alkyketene dimers, *Tappi J.* 70(4), 135-139.

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