SEC STUDIES ON HCL TREATED SOFTWOOD AND BIRCH KRAFT PULPS

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Abstract
Unbleached and bleached softwood kraft pulps and six birch kraft pulps were treated with hydrochloric acid and evaluated for molecular weight changes using Size Exclusion Chromatography (SEC-MALLS). In addition the distribution of uronic acids in hemicelluloses relative to molecular weight was analysed applying group selective fluorescence labelling. The goal was to evaluate how cellulose and hemicellulose are affected by acid treatment of these softwood and hardwood pulps. The softwood pulp fibres were strongly cleaved by the acid during hemicellulose degradation and an overall molecular weight decrease was observed. The uronic acid content associated with hemicellulose also decreased. The birch fibres were affected only little by HCl. The SEC results clearly reflect the observed cleavage rates of the used softwood and hardwood pulps. While for the bleached and HCl treated softwood pulp a clear decrease of Mw was observed, the effect on birch pulp was smaller.

Introduction

Fibre deformations are already present in small amounts in naturally grown trees and they increase during pulp cooking and bleaching. These irregularities have been defined as dislocations. This term describes the localized change or distortion of the crystalline cellulose microfibrils in either the S1 or both S1 and S2 secondary cell wall layers (Nyholm et al. 2001). While small dislocations are not considered to be significant and are thought to add to fibre flexibility, large dislocations are considered to be a target for chemical, mechanical or enzymatic attack due to their less ordered or more open amorphous cellulose structure.

Several investigations (Ander et al. 2005; 2008) show that all acid conditions partly cleave fibres in dislocations. Thus, dislocations make the cell wall more susceptible to enzymatic and chemical attack allowing for a stronger penetration of cooking and bleaching chemicals during pulping and this leads to inferior strength of the resulting paper.

In this study it was tried to link the enhanced availability of dislocations that were produced by hydrochloric treatment in the fibres to changes in molecular weight and uronic acid content. In order to shed some light on the effects of HCl on the softwood and birch fibres and possible molecular weight changes of hemicellulose and cellulose, SEC was run on the different pulps before and after acid treatment.

Materials and Methods

Pulps

Unbleached (3.9% lignin) and bleached (0.2% lignin) mixed spruce (*Picea abies*) and pine (*Pinus sylvestris*) kraft pulps were obtained from Karin Sjöström, Södra Cell, Sweden (Common pulp samples COST E54). The ratio of spruce to pine was 79:21. The pulps resulted from a batch cook and were TCF-bleached with the sequence Q - OP - Q+Paa – PO (Q: chelator, Paa: Peraacetic acid). Lignin and carbohydrate composition was determined at Stora Enso, Karlstad, Sweden and given in the paper by Heinemann and Ander (2011).

Six birch (*Betula verrucosa*) kraft pulps from a pulp bleaching line were obtained from Irina Rauvanto, Lappeenranta, Finland.

HCl-treatment

HCl-treatment was done using 100 mg pulp (dry-weight) and 1M HCl pH 0 at 81°C according to Ander et al. (2008). The equipment for making HCl treatment is shown in Heinemann and Ander (2011).

Fibre characterisation

Fibre lengths before and after acid treatment were determined using a FibreMaster at Södra Cell for softwood fibres. For birch fibres a Fiber Tester from Lorentzen & Wettre was used.

Cellulose characterization

Size exclusion chromatography and fluorescence labelling of oxidized cellulose functionalities before and after HCl treatments were done as described in Bohrn et al. (2006).

Results and Discussion

Softwood pulps and HCl method

The results for unbleached and bleached softwood pulp fibres are shown in Table 1 below.

Table 1. Characterization of bleached and unbleached softwood pulp fibres

Pulp type	LWFL (mm) (L_0)	LWFL (mm) (L)	Cleavage per fibre (L_0 / L) - 1	Cleavage per mm fibre
Unbleached pulp	2.73	0.59	3.62	1.33
Bleached pulp	2.60	0.37	6.11	2.35

Cleavage values of 3.6 for the unbleached pulp and of 6.1 for the bleached pulp can be considered typical (Ander et al. 2008). They reflect an increased formation of dislocations and other weak points during pulping and bleaching. HCl releases more xylose than glucose indicating a stronger effect of HCl on hemicellulose. A typical kraft pulp of the same kind as here can give 0.055 g/l of xylose and 0.0075 g/l of glucose for 100 mg pulp (Ander et al. 2008).

Polarized light microscopy (PLM)

Typical appearance of some unbleached and bleached softwood fibres before and after HCl treatment is shown in Figures 1a-d. Some birch fibres and vessels after HCl treatment are shown in Figure 2a-c. The vessels appear to be rather acid stable, and although they appear in only a few percent they may contribute to a seemingly lower acid cleavage of the fibres. See also Table 2.

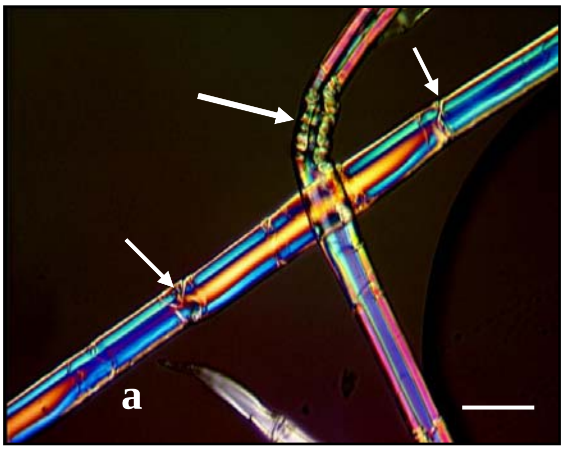

Figure 1a. Latewood (LW) spruce fibres.

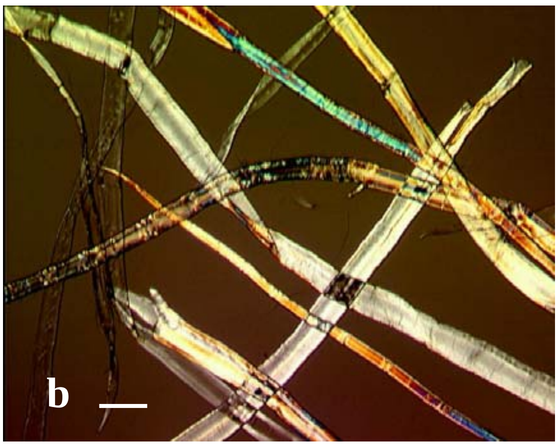

Figure 1b. Grey earlywood (EW) fibres

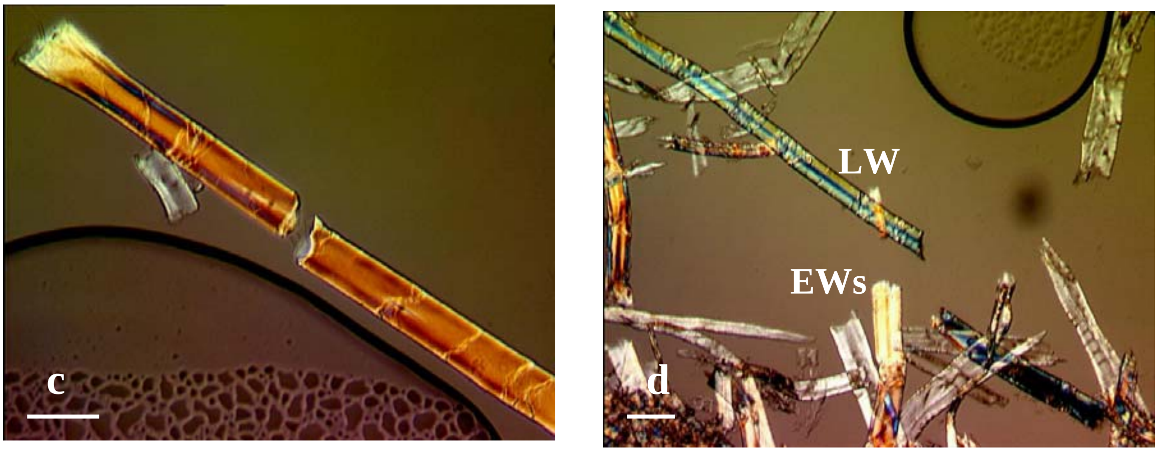

Figure 1a. Latewood (LW) spruce fibres under polarized light microscopy showing dislocations of different sizes. See arrows. Water treated undelignified fibres, 20x
Figure 1b. Grey earlywood (EW) and colored latewood fibres. Some breakages caused by the industrial pulp bleaching are seen. Bleached fibres water treated controls, 10x
Figure 1c. A latewood spruce fibre after cleavage in a dislocation, 20x. Unbleached and HCl treated fibre
Figure 1d. LW and EW fibres cut by the acid treatment are seen. Bleached fibres, 10x. All bars are 30 µm

HCl treatment of birch fibres and PLM

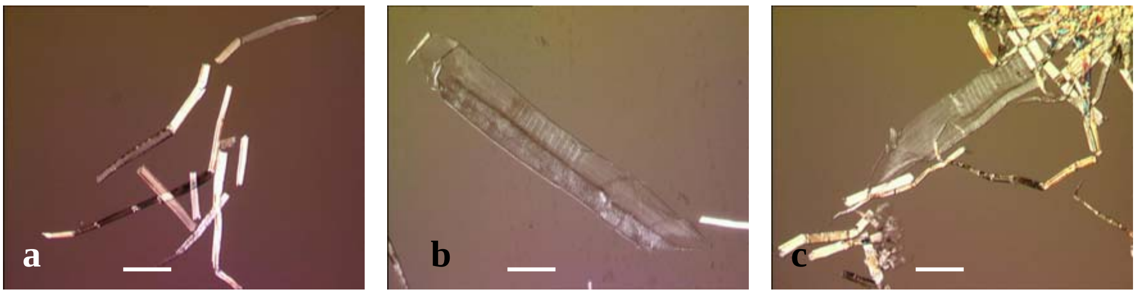

Figure 2a. Birch fibres after HCl cleavage.
Figure 2b with a typical birch vessel. Both figures were photographed at magnification 10x indicating that the width of the vessels are about 7 times larger than the width of normal birch fibres.
Figure 2c with typical difference in size of birch vessels and fibres cut by the acid. The vessels appear to be rather stable against acid cleavage. Figure 2a & b are from fibre line nr 1; 2c from the most bleached part of the fibre line nr 6. Bars are 50 µm

SEC investigations

Figure 3 gives the weighted average molecular weight of the softwood pulp obtained from SEC before and after acid treatment for bleached and unbleached samples.

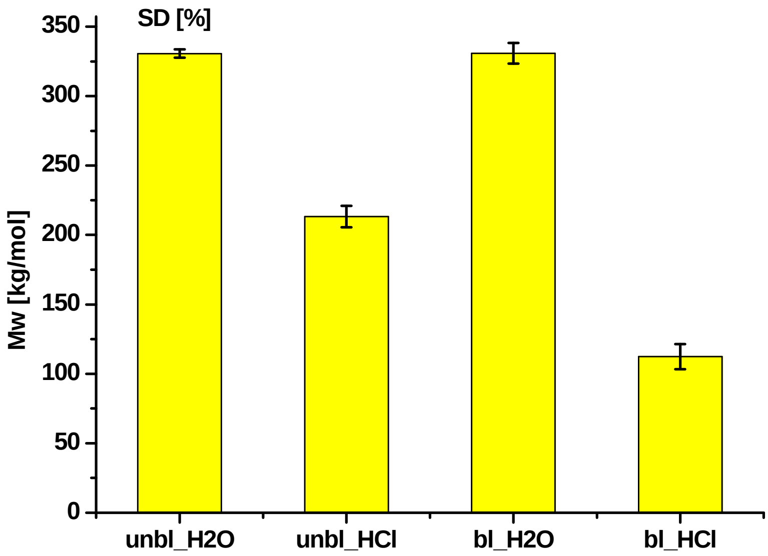

Figure 3. Change in Mw for unbleached and bleached softwood pulps before and after HCl treatment

The observed effect on Mw for the unbleached material was significantly lower compared to the bleached pulp. Bleaching renders the cellulose more accessible, cellulose hydrolysis is more severe. In addition, lignin may serve as a barrier and protects the pulp during the acid treatment.

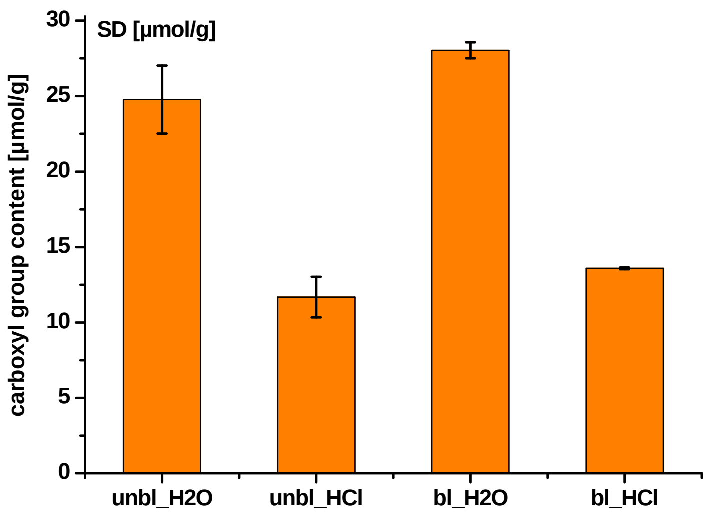

Figure 4. Change in carboyxl group content for unbleached and bleached softwood pulps before and after HCl treatment. Error bars give the standard deviation in µmol/g

The carboxyl group content given in Figure 4 mainly corresponds to the uronic acids, which are not as pronounced in softwoods compared to hardwood. The uronic acids mainly reflect the xylan content of the material. The differences observed between bleached and unbleached pulp is not very pronounced, slightly lower numbers were found for the unbleached pulp.

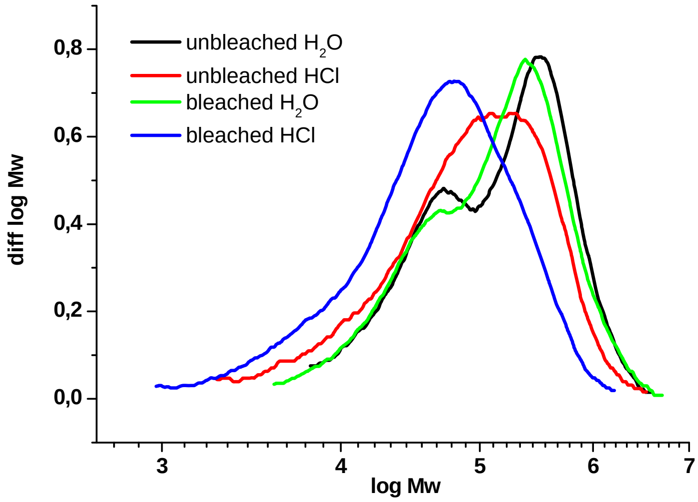

Figure 5. Molecular weight distribution of the unbleached and bleached softwood samples

In Figure 5 it can be observed that the molecular weight distribution of the two starting samples is already different, as one would expect. The water treated samples show a low molecular weight shoulder that was removed by the acid treatment. This low molecular weight shoulder is already affected by the water treatment; even though there is no significant change in Mw, this shoulder is noticeably decreased by the treatment. After HCl-treatment however, the whole MWD shifted towards smaller masses.

Hardwood birch pulp

The results for the HCl test method for the birch pulp fibre line are given in Table 2.

Table 2. Characterization of cleavage of birch pulp fibre.

Birch Pulp sample	Cleavage per fibre 80.5°C & 30 min std stirring	Cleavage per fibre 85.5°C & 30 min std stirring	Cleavage per fibre 85.5°C & 45 min long stirring
1	0.35	0.62	0.56
2	0.28	0.76	0.77
3	0.33	--	--
4	0.305	--	--
5	0.33	--	--
6	0.225	0.54	0.635

Cleavage per fibre (0.225 – 0.35) at the standard temperature 80.5°C was unexpectedly low. At 85.5°C the detected cleavage increased somewhat to 0.54 – 0.76. Longer stirring time had little effect on the acid degradation. One explanation for this result may be the stability of birch vessels in acidic environments, which result in lower overall cleavage (see Figure 2). Protection by hemicellulose is another possibility (Ander and Daniel 2006). Although, another hardwood fibre, bleached eucalyptus also has vessels it was more HCl sensitive and a larger cleavage number was obtained for that fibre (0.835 & 1.17; Ander 2008). More research is needed for hardwood fibres.

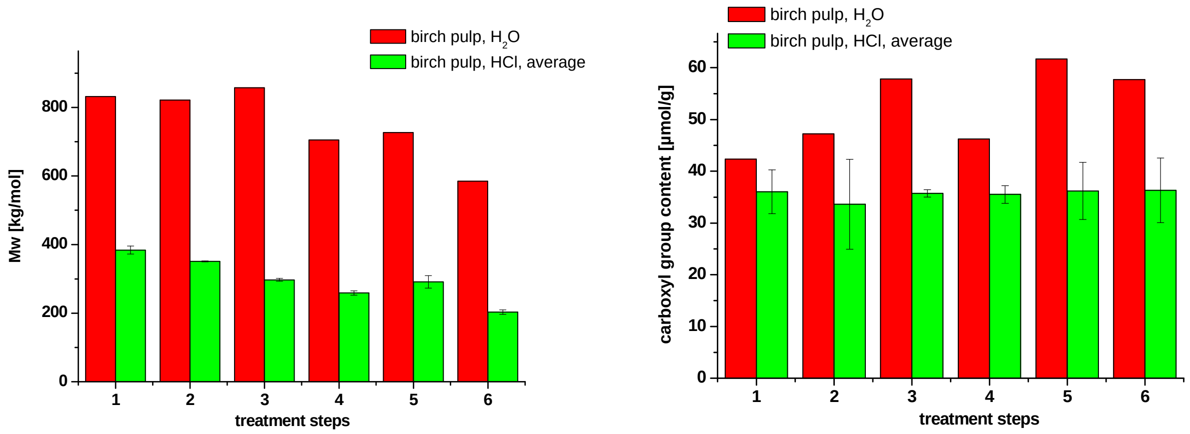

Figure 5a,b. Change in Mw and carboxyl group content for birch pulps before and after HCl treatment.

Regarding birch fibres, Figure 5a shows that high Mw cellulose decreased in the pulp fibre line during bleaching. After HCl treatment, the starting Mw was much lower than for water samples and further decreased for fibre line samples 1 to 4. It appears as if hemicellulose was not degraded so much by HCl in opposite to the softwood fibres. This result is supported by the MWD of the birch samples: the low molecular weight shoulder that reflects the hemicellulose content did not disappear in the course of the bleaching treatment (not shown).
Regarding the uronic acid content (Figure 5b), the trend was not clear for the water samples. For the HCl-treated samples, the uronic acid groups did not change, which may be due low hemicellulose degradation in birch. That result may fit with the low cleavage induced by HCl of the birch fibres reported here in Table 2. With softwood fibres, however, HCl gave strong fibre cleavage (Table 1). Similarly, Ander et al. (2008) have shown that HCl releases the hemicellulose sugar xylose in large amounts and rather little cellulose sugars.

Conclusion

In short, the molecular weight of softwood pulp decreased by the acid treatment due to degradation. The fibre cleavage corresponds in this case to the molecular weight decrease. Bleaching in combination with HCl treatment gave the strongest degradation, but no further decrease in uronic acid content. This is mainly because the hemicelluloses have been removed by the bleaching already, resulting in a decreased uronic acid content. Noticeable degradation by HCl was obtained in all molecular regions; this was most visible for the bleached pulps.

With birch pulp, less fibre cleavage was observed. Hemicelluloses were not affected in the same way as in softwood pulp. So the lower fibre cleavage observed again reflects the higher stability of the samples as demonstrated by SEC-MALLS. This is mainly explained by more protection of the cellulose fibre due to the hemicelluloses in birch pulp that are not easily attacked and withstand the acid treatment as shown in a generally unchanged uronic acid content.

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