Hemicellulose Composition in the Outer Cell Wall Layers of Paper Grade and Dissolving Pulp

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Summary: The hemicellulose content of pulp is dependent on different factors, such as the wood species, the conditions with cooking and bleaching harmonised with the application.
In addition to the hemicellulose content, a special interest for the valuation of pulp and the decision of arrangements of the production process is the hemicellulose distribution across the cell wall layers and the influence of several process stages on the hemicellulose distribution across the cell wall layers.
The investigations were carried out on dissolving pulp and paper grade pulp.
For paper grade pulp, the influence of separate bleaching steps and several bleaching sequences on the distribution of hemicellulose across the cell wall were investigated.
Regarding the selected dissolving pulps which were produced according to an acid bisulphite process and a pre-hydrolysis sulphate process the influence of the cooking process on the hemicellulose distribution across the cell wall layers was of a special interest.

Keywords: chromatography (SEM, LC/MS); hemicellulose; morphology

Introduction

The hemicellulose content of pulp is influenced by different factors, such as the wood species used, the pulping with cooking and bleaching harmonised with the application.

It is known that the mechanical strength of paper pulp, especially the tensile and the burst strength, depends strongly on the hemicellulose content[1]. Due to its further chemical processing dissolving pulp should mainly be free of hemicellulose.

In addition to the hemicellulose content, a special interest for the valuation of pulp and the decision of arrangements of the production process is the hemicellulose distribution across the cell wall layers, and the influence of separate process stages on the hemicellulose distribution across the cell wall layers.

There are several methods known for the investigation of the hemicellulose composition across the cell wall such as mechanical peeling[2], chemical peeling and enzymatic peeling[3]. The chemical peeling method was chosen for the investigations, based on good experience in using this method.

The aim of the investigations was to compare the hemicellulose composition of dissolving pulps prepared by several pulping processes, and paper grade pulp bleached by several sequences.

Experimental

The selected dissolving pulps were produced in an acid bisulphite process and a pre-hydrolysis sulphate process.

On the other hand the paper grade pulp is a special bleached spruce sulphite pulp. A spruce sulphite pulp with a kappa number

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of 14.8 and a viscosity of 124.6 cP was selected. This pulp was treated in one stage with either ozone (Z) or peracetic acid (PAA) or in a hydrogen peroxide reinforced oxygen stage (EOP). In this connection the chemical application was chosen to get a comparable kappa number (κ: 7.5 to 8.2). It was also treated in an EOP Z P sequence and an EOP PAA P sequence (κ: 1.9; 2.5).

Residual lignin was removed before peeling and hydrolysis, respectively.

The hemicellulose composition of all samples was determined by gently hydrolysing polysaccharides to monosaccharides with triflouroacetic acid[4]. The hemicellulose composition was then quantitatively determined by a distribution of the sugar in a ReproGel-Pb column using high performance liquid chromatography (HPLC) and a liquid chromatography mass spectrometer (LC/MSD) as detector.

The unbleached and bleached pulps were peeled in order to get different layers of the fibre[5]. These pulps were investigated by scanning electron microscopy, to study the surface of the samples and identify the layers of the cell walls.

The general principle of chemical peeling is shown in Figure 1.

A partial esterification of the fibre under non swelling conditions was carried out. This produces an annular cylinder of ester on the outside surface of the fibre. The acetylation was carried out by using a mixture of benzene, acetic anhydride and sulphuric acid. Afterwards this ester was extracted with methylene chloride to give a solution of ester – called peelings – and an unesterified fibre – called peeled fibre.

Because of the differences in fibre structure (as there are for example size and thickness or the presence of damaged and uncollapsed fibres) the chemical peeling technique could not produce fractions which represent only one location in the cell walls of all fibres in the sample. The samples are attributed to the dominating cell wall layer.

Results and Discussion

Investigations on Paper Grade Pulp

These unbleached, partly bleached and fully bleached pulps were compared with regards to their hemicellulose composition and the chemical penetration into the cell wall.

In order to get more information about the penetration of the chemicals into the cell wall, and their reactions within the cell wall, scanning electronic microscope (SEM) investigations were carried out. With the help of SEM pictures, the different cell wall layers can be identified,

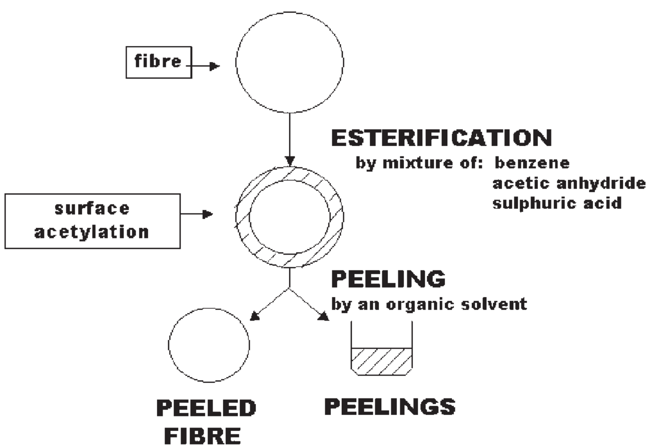

Figure 1.
Chemical peeling flow sheet.

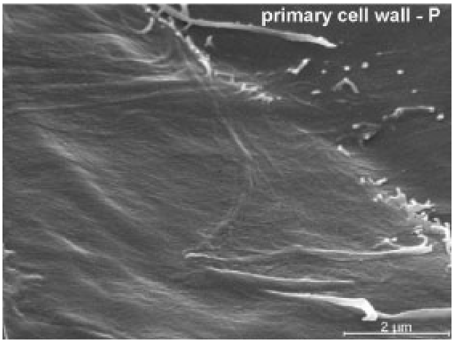

Figure 2.
Fibre-surface of an unbleached spruce sulphite pulp ($\kappa = 14.8$)/primary cell wall.

as each cell wall shows a characteristic structure of the fibrils[6].

These investigations by SEM showed that the surface of the cell wall of this unbleached spruce sulphite pulp consists of primary cell wall (P) and the first secondary wall (S_1). This fact exhibits that parts of the primary cell wall are lost during the sulphite pulping at this kappa number. Figure 2 shows parts of the primary cell wall, seen in the crossing formation of the microfibrils. But for example the structure of S_1 is identifiable in Figure 3. In this case the microfibril formation is perpendicular to the fibre direction. The microfibrils are presented as thin lines. The structures seen parallel to the fibre direction are a result of fibre shrinking drying.

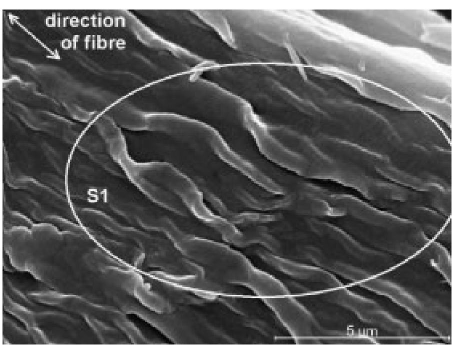

Figure 3.
Fibre-surface of an unbleached spruce sulphite pulp ($\kappa = 14.8$)/secondary cell wall layer.

Table 1.
Hemicellulose composition of the unbleached paper grade spruce sulphite pulp.

	Mannose	Xylose	Arabinose
unbleached pulp	8.3 %	3.4 %	0.01 %

The hemicellulose composition of the unbleached paper grade spruce sulphite pulp are summarised in Table 1.

As expected for a spruce sulphite pulp, a lot of hemicellulose components such as mannose and xylose were found. Traces of arabinose could also be determined.

At first, this starting pulp was alternatively bleached with hydrogen peroxide reinforced oxygen (EOP), peracetic acid (PAA), and ozone (Z).

The investigation of hydrogen peroxide reinforced oxygen bleached pulp (EOP) by SEM showed no further changes in the primary cell wall (P) and the first secondary cell wall (S_1) structures. There was no further chemical penetration into the cell wall (Figure 4).

Even though the surface of the cell walls remained unchanged, hemicellulose losses, especially mannose, were observed (Table 2). The xylose content however remained unchanged.

Fibre surfaces of pulp bleached with peracetic acid also consisted of parts of the primary cell wall (P) and the first secondary wall (S_1). No further cell wall degradation was observed using this treatment (Figure 5).

The PAA bleaching stage caused no change in the hemicellulose composition either. The content of mannose and xylose were observed to be similar to that of unbleached spruce sulphite pulp (Table 3).

Peracetic acid is capable of undergoing nucleophilic and electrophilic reactions due

Table 2.
Hemicellulose composition before and after the EOP stage

	Mannose	Xylose	Arabinose
unbleached	8.3%	3.4%	0.01%
EOP	7.7%	3.5%	0.02%

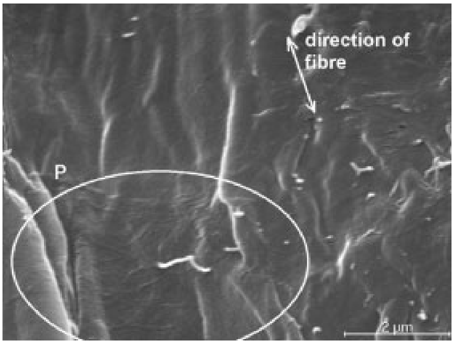

Figure 4.
Fibre-surface of a hydrogen peroxide supported oxygen bleached spruce sulphite pulp ($\kappa = 7.5$)/primary cell layer.

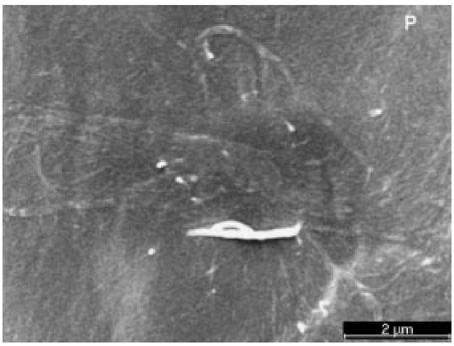

Figure 5.
Fibre-surface of a peracetic acid bleached spruce sulphite pulp ($\kappa = 8.2$)/primary cell layer.

to its structure[7]. The powerful delignification agent does not depolymerise carbohydrates under optimised conditions[8].

On the surface of the ozone bleached spruce sulphite pulp, only some fragments of the primary cell wall could be observed. That means that most of the residual primary wall was removed due to the more intensive chemical penetration into the cell wall during this stage (Figure 6).

During the ozone bleaching stage, all the arabinose was lost. Comparing this stage

Table 3.
Hemicellulose composition before and after PAA stage.

	Mannose	Xylose	Arabinose
unbleached	8.3%	3.4%	0.01%
PAA	8.1%	3.6%	0.03%

Table 4.
Hemicellulose composition before and after Z stage.

	Mannose	Xylose	Arabinose
unbleached	8.3%	3.4%	0.01%
Z	7.3%	2.9%	0.00%

with other stages, ozone caused the highest degradation of mannose and xylose (Table 4).

These partly bleached pulps were also compared with regard to their hemicellulose distribution across the cell wall.

During the peroxide reinforced oxygen stage, a degradation of mannose in the primary and the S_1- wall occurred. The peracetic acid treatment caused nearly no changes in mannose content in the primary and the S_1-layer. There was also a degradation of mannose in the S_1-wall during the ozone stage (Figure 7).

It was observed that there was no further degradation of xylose during the peroxide reinforced oxygen stage and the peracetic acid stage. Ozone caused a small degradation (Figure 8).

The starting pulp was also treated in a EOP Z P sequence and an EOP PAA P sequence.

Comparing these two sequences, there was a drastic removal of mannose and cellulosic substances in the EOP Z P sequence as can be seen in the losses of the S_1- wall. The mannose distribution of the EOP PAA P sequence was preserved in

Table 5.
Hemicellulose composition before and after EOP Z P and EOP PAA P sequences.

	Mannose	Xylose	Arabinose
unbleached pulp	8.3%	3.4%	0.01%
EOP Z P	6.1%	3.8%	0.01%
EOP PAA P	7.1%	3.5%	0.01%

Table 6.
Hemicellulose composition of a pre-hydrolyse sulphate pulp and a acid bisulphite pulp.

	Mannose	Xylose	Arabinose
pre-hydrolyse sulphate pulp	1.16%	0.92%	0.02%
acid bisulphite pulp	0.67%	2.77%	0.01%

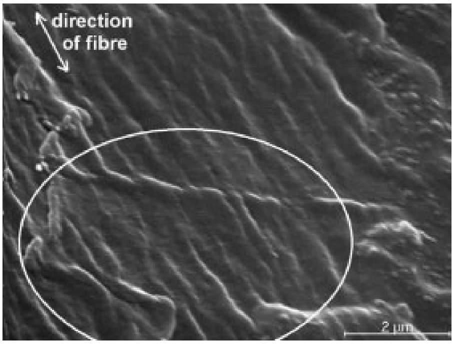

Figure 6.
Fibre-surface of a ozone bleached spruce sulphite pulp ($\kappa = 7.9$)/secondary cell layer.

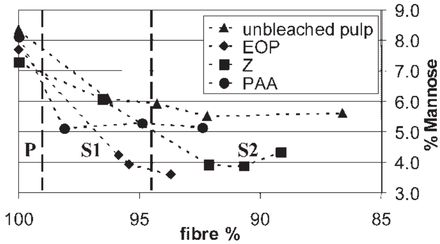

Figure 7.
Mannose distribution across the cell wall as a function of the bleaching agent used in comparison to unbleached pulp.

the cell walls as to see in Figure 9. There was no further degradation of xylose during these both sequences (Figure 10).

Previous studies[9] showed that using EOP PAA P for paper grade pulp in comparison to EOP Z P tenacity increased by 1400 m which is caused by the higher amount of mannose across the cell wall in the EOP PAA P bleached pulp.

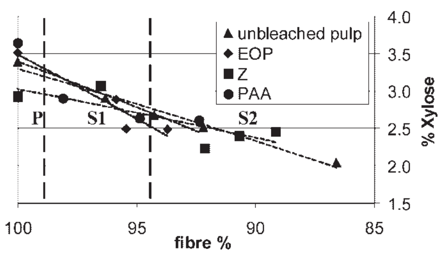

Figure 8.
Xylose distribution in the cell wall as a function of the bleaching agent used in comparison to unbleached pulp.

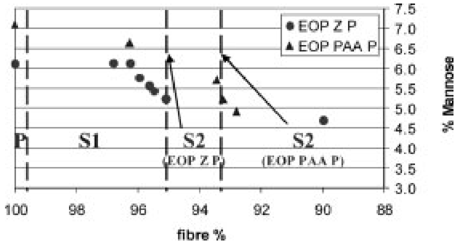

Figure 9.
Mannose distribution across the cell wall in dependence on the bleaching sequence (arrows show the begin of the S_2- wall).

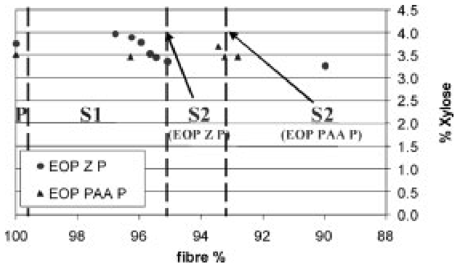

Figure 10.
Xylose distribution across the cell wall in dependence on the bleaching sequence (arrows show the begin of the S_2- wall).

Investigations on Dissolving Pulp

For analysis regarding the hemicellulose distribution of dissolving pulp a pre-hydrolysed sulphate dissolving pulp and a acid bisulphite dissolving pulp were used.

Comparing these pulps regarding penetration of chemicals into the cell wall, it was observed by SEM that the surfaces of both dissolving pulps consist of primary cell wall and first secondary cell wall. Parts of the

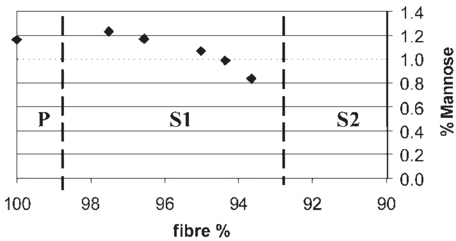

Figure 11.
Mannose distribution across the cell wall of the pre-hydrolysis sulphate dissolving pulp.

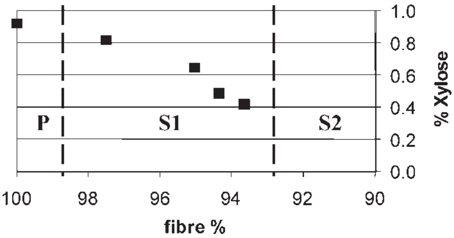

Figure 12.
Xylose distribution across the cell wall of the pre-hydrolysis sulphate dissolving pulp.

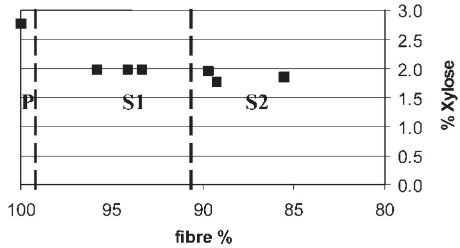

Figure 14.
Xylose distribution across the cell wall of the acid bisulphite dissolving pulp.

primary cell wall were lost during the pulping process.

In pre-hydrolysed sulphate dissolving pulp made from soft wood the highest content for mannose and xylose was measured in the primary wall decreasing towards the S_2- wall (Figure 11, Figure 12).

In dissolving pulp made from hard wood according to the acid bisulphite process the mannose content is on the same level in the residues of the primary wall, the S_1- wall, and deep in the S_2-wall. The xylose content is somewhat higher in the residues of the primary wall (Figure 13, Figure 14).

The effect of interactions between hemicellulose distribution via the cell walls and properties of cellulose derivatives especially with respect to the introduced substituents will be investigated in the future.

Conclusion

When the results of the three non fully bleaching steps (EOP, PAA, Z) were compared, it was observed that during the hydrogen peroxide supported oxygen step (EOP), the outer cell wall layers were not further attacked. A low degradation of mannose in the primary and the S_1-wall was observed, however there was no further degradation of xylose.

Bleaching with peracetic acid is a gentle procedure with regards to the removal of carbohydrates from the cell wall. Its influence on the outer cell wall layers is comparable to that of an EOP stage. The hemicellulose content determined as mannose, xylose, and arabinose is well-preserved.

Using Ozone as bleaching agent causes more attack on the cellulose hemicellulose. This was observed by the loss of most of the primary wall, and parts of the S_1- layer, as well as the highest losses in hemicelluloses.

Considering the dissolving pulps, it was observed that acid bisulphite pulp made from eucalyptus are characterised by a very uniform distribution of xylose and mannose across the cell wall layers. On the contrary, the pre- hydrolysed sulphate pulp showed higher concentrations of xylose and mannose in its outer cell wall layers.

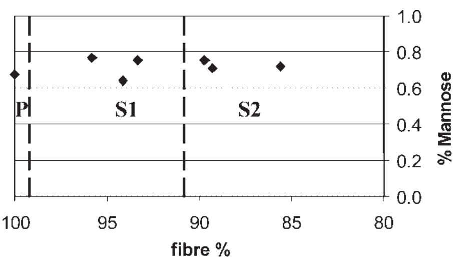

Figure 13.
Mannose distribution across the cell wall of the acid bisulphite dissolving pulp.

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