Hemicellulose in Dissolving Pulp and its Behaviour during its Processing to Viscose

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Summary: The amount of ''hemicellulose'' in pulps varies according to wood species, and the pulping processes including their bleaching agents.
Making viscose cellulosic and non-cellulosic material is removed during mercerisation which is the first processing step. Low molecular weight material is also formed during the reduction of the degree of polymerisation in order to fit the alkali cellulose for xanthation and dissolving, respectively.
In this work commercially available dissolving pulps with respect to their behaviour during the preparation of viscose fibres shall be discussed. For these investigations a Eucalyptus sulphite and a Eucalyptus pre- hydrolysed sulphate pulps were selected.

Keywords: hemicellulose; molecular weight distribution; pulp

Introduction

The amount of ''hemicellulose'' in pulps varies according to the wood species, and the pulping processes including their bleaching agents.

The quality of dissolving pulp is more or less determined by its content of ''hemicellulose'' i.e. the content of non- cellulosic saccharides such as mannan and xylan and the amount of short chain cellulose. A traditional method used for determining pulp quality is the determination of pulp resistance (R-value) or solubility (S-value) in sodium hydroxide according to standardised procedures.

The interaction of dissolving pulp with aqueous sodium hydroxide is of practical relevance as the first step in esterification or etherification of cellulose, especially in xanthation, carboxymethylation, and methylation is an alkaline treatment.

During the preparation of viscose fibres ''hemicellulose'' is partly removed during mercerisation, but low molecular weight materials are also formed during the reduction of the degree of polymerisation in order to fit alkali cellulose for xanthation and dissolving, respectively.

In this work, the behaviour of two commercially available dissolving pulps with respect to preparing viscose fibres is discussed. For these investigations, a Eucalyptus sulphite and a Eucalyptus pre-hydrolysed sulphate pulps were selected.

On each pulp, the distribution of the non-cellulosic sugars was investigated across the different cell wall layers.[1] During viscose fibres processing the behaviour of ''hemicellulose'' was monitored during mercerisation by wet chemical and spectrometric methods such as chemical oxidation, HPLC[2] and SEC[3] and on laboratory spun fibres.

Results and Discussion

Pulps are ordinarily sold according to their solubility and their alpha-cellulose content, respectively. In order to investigate the influence of the alkali soluble material on the processing of pulp to viscose fibres two pulps prepared from Eucalyptus species with different solubility as determined by different pulping processes were selected.

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Table 1.
Solubility of the investigated dissolving pulps.

	% S_{18}	% α-cellulose
pre-hydrolysed sulphate	2.6	96.1
sulphite	4.6	92.2

The investigations focussed mainly on the hemicellulose components xylose and mannose starting from pulp to viscose fibre.

Table 1 summarises the data for the alpha- cellulose content and the solubility of the selected pulps in an 18% sodium hydroxide solution (S_{18}).

The pulp processed according to the pre-hydrolysed sulphate process showed a higher alpha- cellulose content and a lower solubility, respectively, as compared to an ordinary sulphite pulp. Table 2 shows that the observed amounts of hemicelluloses do not correspond to the results of the solubility analyses. The observed amounts of xylose and mannose did not vary so much between the two pulps. The value for the solubility in 18% sodium hydroxide solution was nearly doubled for the sulphite pulp. This implies that hemicellulose and short chain cellulose determined the solubility of this pulp in nearly equal proportions.

The higher amount of short chain cellulose in the sulphite pulp was also observed in the molecular weight distribution (MWD) of the pulps. The distribution curves of the 96% alpha Eucalyptus pre-hydrolysed sulphate pulp showed significantly less short chains in comparison to the 92% alpha sulphite pulp (Figure 1).

The higher load in press soda measured after the mercerisation is due to the higher amount of low molecular weight material or short chain cellulosic and non-cellulosic material of the sulphite pulp. The results are summarised in Table 3. It is obvious

Table 2.
Hemicellulose composition of the pulps.

	% xylose	% mannose
pre-hydrolysed sulphate	2.16	0.36
sulphite	2.10	0.58

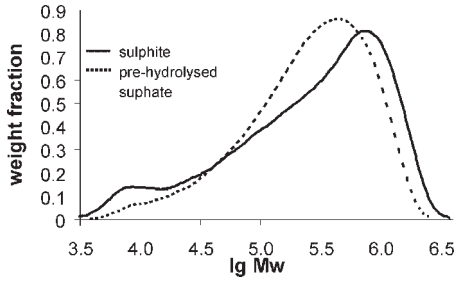

Figure 1.
Molecular weight distribution of Eucalyptus pre-hydrolysed sulphate and sulphite pulps measured on their nitrates.

that the dissolved matter in mercerisation (see Table 3) corresponded very well to the solubility values determined on pulp (Table 1).

Not only the amount of dissolved matter from the two pulps differ, but also the dissolved matter differed significantly in its molecular weight distribution (see Figure 2).

The material dissolved during steeping of the pre-hydrolysed sulphate pulp showed a much higher molecular mass than the material dissolved from the sulphite pulp. That means that under comparable conditions higher molecular weight material was lost during mercerisation of the pre- hydrolysed sulphate pulp.

The losses in low molecular weight material or short chain cellulosic material were also seen in the molecular weight distribution of the regenerated alkali cellulose sample (alkcell) compared with the pulp sample (Figure 3).

Observing the behaviour of the pre-hydrolysed sulphate pulp during mercerisation in Figure 3 it is clear that the chain length was degraded over the whole range and the loss of low molecular weight material was rather small.

In contrast the sulphite pulp reacted much more sensitive against the strong hot alkali. It was much more degraded over the whole chain length range and the losses in the short chain range were extremely high. The composition of the hemicellulose in the

Table 3.
Dissolved material during steeping.

	% dissolved during mercerisation on pulp
pre-hydrolysed sulphate	3.24
sulphite	5.10

alkali cellulose samples was changed drastically (Table 4).

The losses caused by the mercerisation step, especially in xylose were quite enormous. It was observed that more hemicelluloses were removed from the sulphite pulp during mercerisation than from the pre- hydrolysed sulphate pulp.

This can be attributed to the distribution of the hemicellulose across the cell walls determined on pulp.

The results presented in Figure 5 and 6 show that the content of xylose in the S2 wall both in the sulphite pulp and in the pre-hydrolysed sulphate pulp is comparable. The xylose content in the S1 wall of the pre-hydrolysed sulphate pulp is a little bit increased. But the highest concentration of xylose was found in the outer layer, the primary wall, both in the sulphite and in the pre- hydrolysed sulphate pulps.

The concentration of mannose in the different cell wall layers was much lower. It was only in the primary wall of the pre-hydrolysed sulphate pulp where it showed a slight increase.

The primary wall of the sulphite pulp was drastically smaller than that one of the pre- hydrolysed sulphate pulp. That

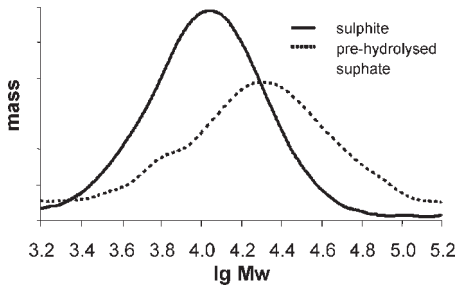

Figure 2.
Molecular weight distribution of matter dissolved during mercerisation measured in press lye.

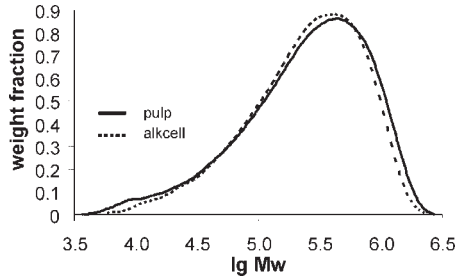

Figure 3.
Molecular weight distribution of pulp and the regenerated alkali cellulose sample (alkcell) made from Eucalyptus pre-hydrolysed sulphate pulps measured on their nitrates.

means that the swelling process during mercerisation and also the leaching of the hemicellulose was hindered in the pre-hydrolysed sulphate pulp. Scanning electron microscopic pictures showed that the primary wall was not removed during mercerisation.

Investigations of viscose fibres spun from standard viscose made from sulphite and pre- hydrolysed sulphate pulps showed that residues of mannose and xylose were also within.

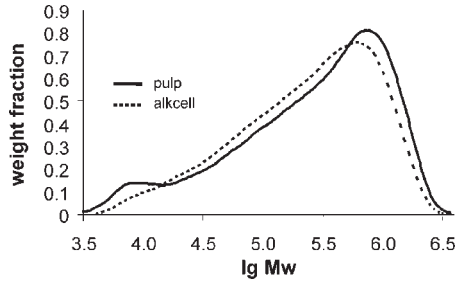

Figure 4.
Molecular weight distribution of pulp and the regenerated alkali cellulose sample (alkcell) made from Eucalyptus sulphite pulps measured on their nitrates.

Table 4.
Hemicellulose composition of Eucalyptus pulps before and after mercerisation.

	% mannose	% xylose
pre-hydrolysed sulphate		
pulp	0.36	2.16
alkali cellulose	0.25	0.35
sulphite		
pulp	0.58	2.10
alkali cellulose	0.24	0.19

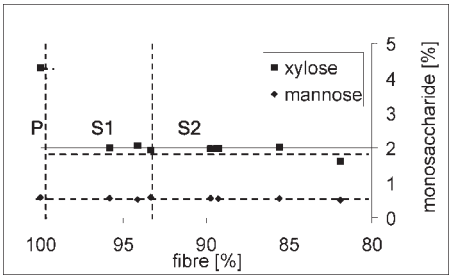

Figure 5.
Distribution of hemicelluloses across the cell walls (Eucalyptus sulphite pulp).

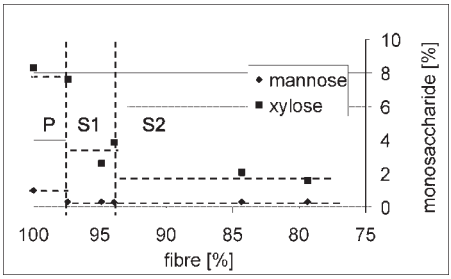

Figure 6.
Distribution of hemicelluloses across the cell walls (Eucalyptus pre-hydrolysed sulphate pulp).

The results in Table 5 show that on the way from alkali cellulose to fibre especially mannose was lost. The residues of xylose seemed to be very stable on the other hand.

The relation of the content of xylose in the fibres corresponded to the relation of the amounts found in the alkali cellulose samples. The values themselves were not only dependent on the hemicellulose bound in alkali cellulose. They were both dependent on the press rate after mercerisation as the attached sodium hydroxide also contained dissolved matter and from the conditions of the spinning bath as especially material having very short chains is not re-precipitated in it.

Table 5.
Hemicellulose composition of fibres made from Eucalyptus pre-hydrolysed sulphate and sulphite pulp.

fibres from	% xylose	% mannose
pre-hydrolysed sulphate	0.82	0.04
sulphite	0.39	0.09

Conclusion

During preparation of viscose fibres ''hemicellulose'' is mainly removed during the first processing step, i.e. the mercerisation step. Under comparable conditions hemicellulose can be more easily removed when Eucalyptus sulphite pulp is used for fibre processing than when the fibres are prepared from Eucalyptus pre- hydrolysed sulphate pulp despite of the higher alpha cellulose content of the latter.

[1] M. Freese, I. Schmidt, K. Fischer, *Macromol. Symp.* **2006**, *232*, 13.
[2] I. Schmidt, K. Fischer, D. Weightman, *Macromol. Symp.* **2006**, *232*, 137.
[3] K. Fischer, R. Koch, I. Schmidt, *Papier* **1999**, *53*, 722.

