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Reactivity of Dissolving Pulp for Processing Viscose

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Summary: Pulp reactivity is a kinetic term and is always connected with a certain derivatization process. The quality and hence the market value of the pulp is determined by such characteristics as α- cellulose content, solubility, brightness, ash content, as well as the amount of soluble material in dichloromethane. However, solubility data, especially S_{18} and S_{10} values do not characterise dissolving pulp reactivity. These are indicative of pulp solubility and provide some information regarding losses of material during pulp processing. One way by which the pulp reactivity for viscose making can be characterised is the investigation of the mercerisation step. Following the mercerisation kinetics by help of the molecular weight distribution of cellulose II the behaviour especially of the high molecular weight cellulose gives information regarding the accessibility and therefore, about the reactivity of the pulp aside from losses in low molecular weight cellulose. This behaviour will be shown on different pulps and the physicochemical background will be discussed in relation to results obtained from wide angle X-ray scattering and Raman investigations. The influence of the behaviour of the pulp during mercerising on the viscose process, and the molecular weight distribution of the viscose including the distribution of the xanthogenate groups along the chain was investigated and will also be discussed.

Keywords: hemicellulose; molecular weight distribution; pulp; Raman spectroscopy; WAXS

Introduction

Dissolving pulps are sold on the international market according to parameters such as solubility in sodium hydroxide the so-called S_{18} or S_{10} values, content of impurities such as resin components and inorganic material such as silica, calcium oxide, magnesium oxide, copper, manganese, iron, degree of polymerisation, brightness, copper number etc.

Pulp producers are able to adjust most of these parameters to suit the requirements of costumers. Despite of the tailor-made pulp characteristics such as the level of the S_{18}-value and impurities, high brightness at a low level of the copper numbers and the required degree of polymerisation a lot of problems can still occur during processing of such pulp to cellulose derivatives and regenerated cellulose. ‘‘Pulp reactivity’’ is a general term that is often used to summarise all the problems described above. However, it should also be borne in mind that ‘‘pulp reactivity’’ is a kinetic term and is always related to the end use of such pulps.

The aim of our investigation was to characterise the reactivity of dissolving pulp with regards to the viscose process. Therefore the way of the cellulose was followed from the pulp throughout the intermediate steps until viscose fibres were obtained. That means samples were collected during mercerisation and ageing steps and from the viscose itself.

Two sulphite pulps were selected with similar S_{18}-values and impurity levels. However, a different behaviour during the processing of viscose on a large scale

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was observed. This was recognised by a severe filtration of the viscose as well as the formation of a high amount of trash during spinning. The pulps were named as ‘‘low reactive’’ and ‘‘high reactive’’.

Experimental Part

Pulp

Two commercial dissolving sulphite pulps (Eucalyptus sulphite and Spruce sulphite), which showed different behaviours during viscose processing were used.

Analyses

Hemicellulose distribution across the cell walls was determined using a chemical peeling method.[1] The hemicellulose composition was determined by a gentle hydrolysis of the polysaccharides using trifluoroacetic acid.[1]

The molecular weight distribution of the pulps and the regenerated alkali cellulose samples was measured on its nitrates by using SEC.[2]

Wide angle X-ray scattering spectra were measured using a Siemens D 5000 diffractometer with primary multilayer using Cu Ka radiation in transmission technique and the evaluation was carried out using the full width at half maximum at a constant value after separation of the overlapping peaks by help of the Pearson VII function. The crystallite dimensions (D) were calculated according to the Scherrer equation.[3]

FT Raman spectroscopy was carried out according to Fischer et al.[4]

The molecular weight distribution of viscose samples was determined according to Fischer et al.[5]

Results and Discussion

Table 1 summarises the data for the solubility of the selected pulps in a 18% aqueous sodium hydroxide solution (S_{18}) and the hemicellulose composition of the pulps.

Table 1.
Solubility and hemicellulose composition of dissolving pulps.

	S_{18} [%]	Xylose [%]	Mannose [%]
Eucalyptus sulphite	4.8	2.15	0.58
Spruce sulphite	4.7	1.3	1.9

The concentrations of xylose and mannose measured did not correspond to the solubility of the pulps in 18% sodium hydroxide. This means that the solubility of the pulps was affected both by hemicellulose and short chain cellulose. The distribution of the hemicelluloses across the cell walls is presented in Figure 1 and Figure 2.

Mannose was more evenly distributed over the cell walls which can both be seen on the Eucalyptus pulp and the Spruce pulp. Only the concentration of mannose was higher in the spruce pulp. The results presented in Figure 1 and 2 further show that the highest concentration of xylose was found in the outer layer of the primary wall (P). Remarkable differences between the two pulps can be seen in the thickness of the outer cell wall. The primary wall of the Eucalyptus dissolving sulphite pulp was drastically smaller than the one observed for the spruce dissolving sulphite pulp. Consequently the swelling process during mercerisation connected with the leaching of hemicellulose was supported at that pulp possessing the very small primary wall.

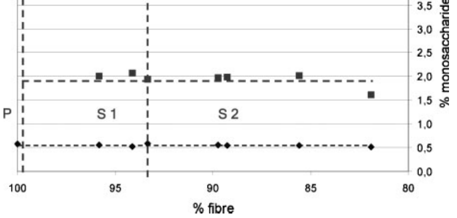

Figure 1.
Distribution of hemicelluloses across the cell walls (Eucalyptus sulphite pulp) P – primary wall; S1 – secondary 1 wall; S2 - secondary 2 wall.

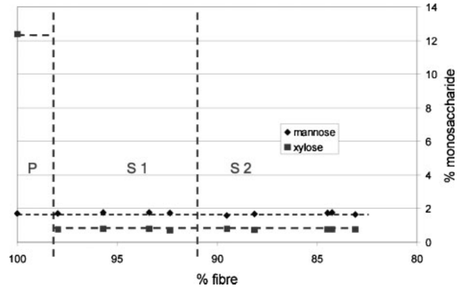

Figure 2.
Distribution of hemicelluloses across the cell walls (Spruce sulphite pulp).

It is well known that in a heterogeneous reaction such as the mercerisation of dissolving pulp the degree of conversion and its reaction rate depend strongly on the availability of the hydroxyl groups which means from the accessibility of the reactants to the hydroxyl groups. In this relation it can be described in terms of the key – lock principle. The highly ordered crystalline region must be accessible for the aqueous alkali to allow the substitution of the CS_2 reactant in the following step.

Considering the changes in the molecular weight distribution of the original pulp in comparison to the molecular weight distributions of regenerated alkali cellulose samples caused by the mercerisation within 15 and 30 min, it can be observed that the curves are nearly parallel shifted towards the low molecular region (Figure 3).

The high molecular weight region of the pulp was degraded during the treatment with 18.5% sodium hydroxide, which means that this region was active and accessible, respectively. In contrast to that the less reactive pulp did not show any changes in the high molecular weight region both after 15 min and 30 min of mercerisation (Figure 4).

Independent on the reactivity and the accessibility of the high molecular weight cellulose low molecular weight material such as short chain cellulose and hemicelluloses was removed during steeping with 18% sodium hydroxide. This can be seen on the left side of the molecular weight distribution curve i.e. the low molecular weight region of the molecular weight distribution curves. Further, it could be observed that about 85 to 90% of the hemicelluloses of dissolving pulps were dissolved during steeping.[6] Therefore, the hemicellulose content in the alkali cellulose itself was very low but nevertheless hemicellulose and short chain cellulose were attached on the alkali cellulose which was caused by the attached lye. These materials can influence the quality of viscose.

In order to get more information regarding the structure and the accessibility pulps and regenerated alkali cellulose samples were investigated by wide- angle X-ray scattering measurements (WAXS). The results obtained regarding the crystallite size of pulps are summarised in Table 2.

The values measured for the pulp samples showed that the sizes of the

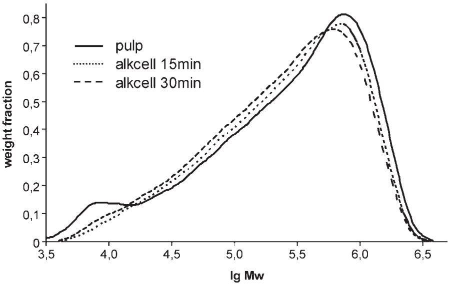

Figure 3.
Molecular weight distribution of pulp and regenerated alkali cellulose samples determined on a high reactive pulp (alkcell – alkali cellulose).

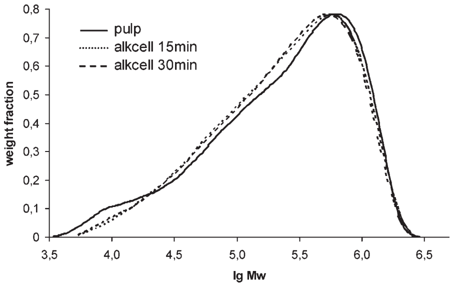

Figure 4.
Molecular weight distribution of pulp and regenerated alkali cellulose samples determined on a low reactive pulp.

Table 2.
Size of crystallites (D) in nm of two sulphite pulps.

	101	$10\bar{1}$	002
high reactive pulp	5.19	5.61	8.71
low reactive pulp	5.35	6.86	8.91

crystallites both in the level 101 and 002 differ only marginal. The value measured for the $10\bar{1}$ level of the less reactive pulp was considerably higher. From that it can be concluded that the crystallites of the low reactive pulp are considerably bigger, which means that the highly ordered regions are larger in the low reactive pulp.

A treatment of cellulose with 18% aqueous alkali solution was responsible for the formation of reactive intermediates which are necessary for the chemical transformation and for swelling the cellulose. This transformation was accompanied by an increase in the size of crystallites in the regenerated alkali cellulose samples and the disorder within the crystalline lattice. Looking at the X-ray spectra in Figure 5 which demonstrate the signals of the regenerated alkali cellulose samples taken away after 30 min of mercerisation, it can be seen that the width of the signals at half maximum obtained from the sample of the low reactive pulp were smaller. That means that these signals coming from that sample reflected a higher crystallinity.

The calculated values summarised in Table 3 were obtained from the separate signal obtained from the 101 level of the crystallite.

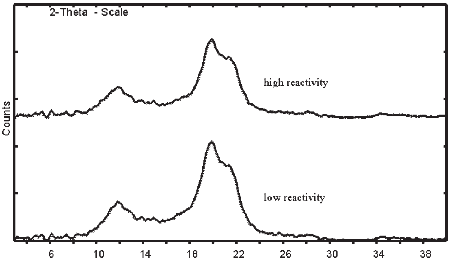

Figure 5.
WAXS measured on the regenerated alkali cellulose samples prepared from the low and high reactive pulp at a retention time of 30 min during mercerising.

Table 3.
Size of crystallites (D) in nm of regenerated alkali cellulose after a retention time of 15 min and 30 min of mercerisation determined at the 101 level.

Time of mercerisation	15 min	30 min
high reactive pulp	6.38	6.55
low reactive pulp	6.66	6.96

Comparing the values in Table 3 especially with those obtained for the 101 level of the pulps (Table 2), it can be seen that the crystallites become bigger when the cellulose has been treated with highly concentrated alkali. The small difference in the size of the crystallites measured between the two pulp samples can also be seen in the regenerated alkali cellulose samples.

The results show that the difference in the size of crystallites occurring in the pulp cannot be compensated during mercerisation i.e. the alkali cellulose having the bigger crystallites are also less accessible for the succeeding process.

FT Raman- spectroscopy has developed to be an excellent method for the determination of molecular conformation and hydrogen bonding patterns of cellulose and cellulose biomaterial.[4,7] Therefore, FT Raman spectroscopy was used for the investigations of pulp and regenerated alkali cellulose samples obtained from the pulps with different reactivity.

Figure 6a shows an example of FT Raman spectra in the range from 3100 cm^{-1} to 2700 cm^{-1} measured on regenerated alkali cellulose samples steeped for 15 and 30 min in comparison to the used pulp in that case the low reactive pulp.

The Raman intensities of the samples which were treated with strong alkali for 30 min using low and high reactive pulp were on the same level. But the Raman intensities of the high reactive pulp rose during mercerisation and a continuous shift towards lower wave numbers was observed in contrast to the results obtained from the low reactive pulp. A shift to lower wave numbers within this region means a splitting off of intermolecular H-bonds

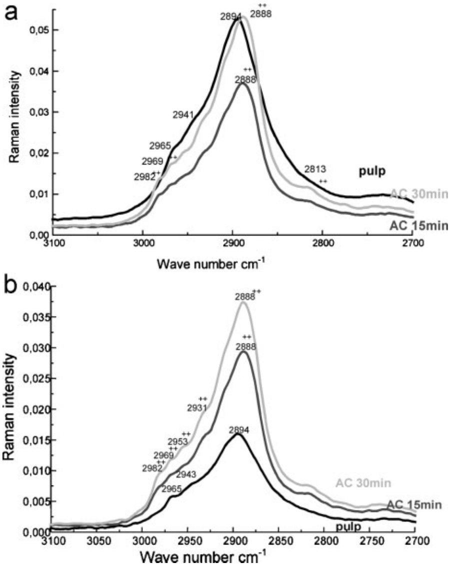

Figure 6.

(a) FT-Raman spectra of regenerated alkali cellulose samples after 15 and 30 min of steeping in comparison to the low reactive pulp. (b) FT-Raman spectra of regenerated alkali cellulose samples after 15 and 30 min of steeping in comparison to the high reactive pulp.

consisting between the macromolecules. Further investigations in order to clarify this behaviour are in progress.

These results are in agreement with the results obtained from the WAXS measurements and the molecular weight distributions of the pulps and alkali cellulose samples.

The worse reactivity of the low reactive pulp influences also the distribution of the xanthate groups along the cellulose chains which can be seen in Figure 7.

Generally, Figure 7 shows that the low molecular weight region of the viscose (left part) is highly substituted than the high molecular weight region. Further, it can be seen that viscose prepared from the low reactive pulp shows a similar degree of substitution in the low molecular weight range but the substitution of the high molecular cellulose in the viscose is lower. That means the higher molecular cellulose is both less accessible for alkali and consequently the alkali cellulose less accessible for carbon disulphide.

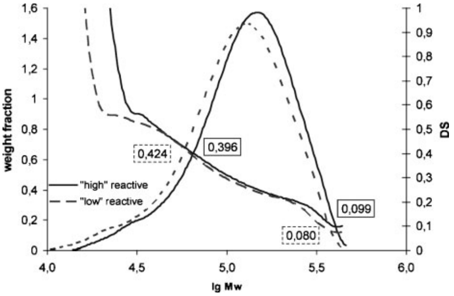

Figure 7.

Molecular weight distribution of cellulose xanthates including the distribution of xanthate groups (DS) along the chain using a low reactive pulp in comparison to the high reactive pulp (DS) – degree of substitution.

Conclusion

Pulp reactivity during viscose fiber processing can be described in terms of the accessibility of the high molecular mass cellulose to sodium hydroxide of a suitable concentration. A thin primary wall or completely removed primary wall improves swelling of cellulose and therefore its accessibility. The distribution of hemicelluloses across the outer cell wall layers seems to have no retarding effect regarding accessibility for dissolving pulps as 85 to 90% of hemicelluloses are dissolved during steeping. Molecular weight distribution of pulp and regenerated alkali cellulose samples taken after a specific time of mercerization can help in the characterization of the accessibility of high molecular weight cellulose evaluating the behaviour of the high molecular cellulose chains. A poor degradation of high molecular cellulose was connected with a higher size of crystallites measured by WAXS. The increased size of crystallites constrains the accessibility of high molecular cellulose during mercerisation and xanthation so that the high molecular cellulose chains of the low reactive pulp possess less xanthate groups which showed the degree of substitution determined on the molecular weight distribution of viscose along the cellulose chains. By help of FT Raman measurements in the range from $3100\,\text{cm}^{-1}$ to $2700\,\text{cm}^{-1}$ a shift to lower wave numbers ($2888\,\text{cm}^{-1}$, $2931\,\text{cm}^{-1}$) was observed. A shift within this region means a splitting off of intermolecular H-bonds consisting between the macromolecules. Therefore, FT Raman- spectroscopy has developed to an excellent method for the determination of molecular conformation and hydrogen bonding patterns of cellulose and cellulose biomaterial.

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