ASPECTS OF FIBRE WALL SWELLING IN HIGH-YIELD PULP

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ABSTRACT

When producing mechanical pulps the fibre separation will take place in the weakest part of the wood matrix. A prerequisite to swelling in wood and mechanical pulps is that the wood matrix is softened. The position of where the weakest part of the wood matrix is situated can to a large extent be controlled by adjustment of the swelling and softening properties of each of the wood polymers (lignin, hemicelluloses and cellulose). Most probably the efficiency of the external and internal fibrillation of the fibre walls is also influenced by how the swelling and softening properties are controlled. The combination of position of fibre-fibre separation together with the efficiency of the external and internal fibrillation will to a large extent determine the energy demand to produce mechanical pulps. Refining of wood chips with different state of softening and swelling will give rise to fibres with different optical and physical properties. The most important parameters that influence the wood matrix and wood fibres' ability to swell are temperature, pH, ionic form of and the amount of charged groups in the hemicelluloses and lignin of the cell walls. In order to improve the level of knowledge on how to influence the degree of wood matrix and fibre wall swelling of mechanical pulps we have undertaken to study the swelling properties of wood and fibres produced by means of different mechanical pulping processes.

It was found that pulps not containing sulphonic acid groups need to be heated above the softening temperature of lignin in order to be able to swell to their full capacity. Introduction of sulphonic acid groups also opens up the rigid structure of lignin which lowers the softening temperature and increases the swelling potential even at lower temperatures. The effect of valence of the counter ion was also shown to be more pronounced after adding more carboxylic acid groups to a pulp. Depending on the number and type of anionic acid groups in the fibres, high-yield pulps will have different combinations of properties in different ionic conditions. The preliminary conclusions from this study are that the ability to control swelling properties of mechanical pulps is an important feature to take into account when producing pulp and paper.

Keywords: Swelling; Fibre Wall; Water Retention Value; High-Yield Pulp; Ionic Form.

INTRODUCTION

The swelling properties of the wood matrix play an important role when manufacturing high-yield pulps. When wood is water-saturated in room temperature, the fibre wall is able to swell only to a certain extent. Increasing the temperature[1,2] leads to further fibre wall swelling due to the softening behaviour of lignin that also will give room for the swelling potentials of cellulose and hemicelluloses. Softening of lignin is also influenced by chemical treatments, such as carboxylation and sulphonation[3,4]. Defibrating wood chips at different states of swelling will produce fibres/pulps with different combinations of qualities and at different energy demands[5,6]. This is explained by the fact that the fractures will occur in different areas of the fibre walls depending on where the weakest position is situated. The position of the weakest point will be influenced by the degree of swelling and softening of the wood polymers in the fibre wall[7,8].

Native wood contains carboxylic acid groups positioned predominantly in the hemicelluloses[9,10]. Carboxylic acid groups and sulphonic acid groups can be added to the lignin via oxidative treatments and sulphonation respectively[9-12]. The softening temperature of lignin decreases when increasing the amount of carboxylic and sulphonic acid groups in the lignin[3,4]. The sulphonic groups are relatively strong acids having a pK_a value of ~1.5, while carboxylic groups are weak acids having a pK_a value of ~4.8. This means that sulphonic groups are fully dissociated at much lower pH than carboxylic groups. When acid groups are dissociated, i.e. are in their ionized form, the proton can be exchanged for other counter ions. The type of counter ion will also influence the swelling ability of the fibre wall[4,6,13,14]. A proposed order of swelling for pulp fibres containing carboxylic groups depending on type of counter ion for carboxymethylated, sulphite and Kraft pulps is: $Al^{3+} < H^{+} < Ca^{2+} < Mg^{2+} < Li^{+} < Na^{+}$[15,16]. Monovalent counter ions give more swelling than divalent and trivalent ions. Protons are an exception as they form very strong intermolecular bonds i.e. hydrogen bonds. Addition of soluble salt, which increases the ionic strength, has a negative effect on the fibre wall swelling due to screening of the electrostatic repulsion between the charged groups[6,17].

Increasing the knowledge regarding swelling of the fibre wall matrix of wood and mechanical pulps will further open up the possibilities to control the fibre separation process and modify the fibre/pulp properties. In this study the effect of temperature, carboxylic acid groups, sulphonic acid groups and ionic counter ion on high-yield pulps is by means of measurements of their water retention values at elevated temperatures.

EXPERIMENTAL

Materials

Three commercial spruce pulps, unbleached TMP, peroxide bleached TMP and peroxide bleached HTCTMP, were used in the trials. Prior to the experimental work, the pulps were washed with DTPA and then the fine material of the pulps was removed according to SCAN-CM 66:05. The total acidic group content of the pulps was determined by conductometric titration (SCAN-CM 65:02).

Methods

In addition to their reference form, all pulps were ion exchanged into H^+, Na^+, Ca^{2+}, Mg^{2+} and Al^{3+} form. All pulps were first converted to the proton form by treatment with 0.1M HCl for one hour. It should be emphasized that it is of uttermost importance to wash chemimechanical pulps that contain sulphonate groups at low enough pH, as in this case with 0,1 M HCl, in order to ensure that the sulphonate groups to their proton form. Excess acid was then gently washed out using deionised water. The sodium form was obtained by treatment of 0.1M NaCl for one hour at pH 8.5, followed by gentle washing. In the case of calcium and magnesium the pulps were soaked in 0.1M of the metal chloride and the pH was adjusted to 9.5 with the metal hydroxide or the metal oxide. After soaking for 24h the pulps were washed with deionised water. The aluminium form was obtained by treatment with $AlCl_3$ for 24h followed by washing with deionised water.

The fibre samples were combusted to ash and analysed for several metal ions at the same time using inductively coupled plasma-optical emission spectrometry (ICP-OES). A fibre sample (5-15g o.d.) was transferred to a porcelain crucible and ignited in an oven for two hours at 300°C and then for three hours at 575°C. To the ash, nitric acid (HNO_3, 5ml, 8M) was added and the mixture was concentrated to ~2.5ml by heating on a hot plate. A few drops of hydrogen peroxide (30%) were added and the solution was heated until the hydrogen peroxide was decomposed. After cooling the solution was filtrated and transferred to a 25ml calibrated flask and diluted to the mark. After filtration, the water samples were analysed by SCA R&D Centre AB (Sundsvall, Sweden).

It was not possible by means of the methodology used here to achieve pulp samples with pure metal ion or proton forms. The method should be looked upon as a way to achieve a dominating ion form rather than a pure ionic form. The total charges were 93mmol/kg for TMP, 162mmol/kg for BTMP and 233mmol/kg for BHTCTMP. The total charge measurements were performed by means of conductometric titration[18].

Water retention value (WRV) was measured according to SCAN-C 62:00 with exception that the methodology was further developed in order to take the influence of temperature level into consideration and also to keep temperature constant during the measurement. The experiments were performed in the temperature interval from 25°C to 95°C with a 10°C steps. The pulp suspension, sample holders and rinsing water were heated to the actual temperature before the centrifugation.

RESULTS AND DISCUSSION

A prerequisite to swelling in wood and mechanical pulps is that the wood matrix is softened. Modification of the swelling and softening properties of each of the wood polymers (lignin, hemicelluloses and cellulose) can to a large extent control the position of where the weakest part of the wood matrix will be situated. Moreover, the weakest part of the wood matrix is where the fibre separation will take place when producing mechanical pulps. Most probably the efficiency of the external and internal fibrillation of the fibre walls is also influenced by how the swelling and softening properties are controlled. The energy demand to produce mechanical pulps is to a great deal determined by the combination of position of fibre-fibre separation together with the efficiency of the external and internal fibrillation. The most important parameters that influence the wood matrix and wood fibres' ability to swell are temperature, pH, ionic form of and the amount of charged groups in the hemicelluloses and lignin of the cell walls.

Water retention value (WRV) is a measure of a pulp's capacity to hold water during centrifugation and is strongly correlated to the swelling ability of wood fibres. Water retention value of pulps is according to standard, measured at 23°C. The lignin polymer though, has a softening temperature of ~75°C. High-yield pulps are normally defibrated and fibrillated at temperatures above the softening temperature of lignin, so in order to take account of the contribution to swelling from lignin, water retention measurement were made in an interval of 25-95°C. Increasing the temperature leads to a decrease in water retention value due to that the viscosity of water is reduced with increasing temperature and most probably also due to increased compressibility of the fibre pad. When rising the temperature, the viscosity of water is lowered, thus the water is transported out of the fibres more easily.

Fig. 1 shows the water retention values of an unbleached thermomechanical pulp as a function of temperature. The water retention value is decreased with increasing temperature (up to 85°C) as discussed above. However, at a temperature of 95°C, the water retention is increased in spite of the decreasing water viscosity; this can probably be referred to the softening of lignin which allows further fibre wall swelling. The order of swelling depending on type of counter ion is consistent with earlier findings[p,q].

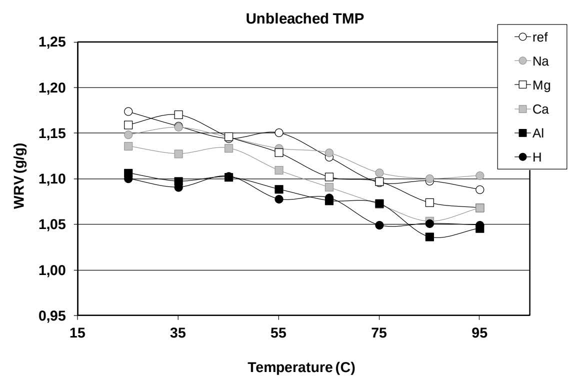

Fig. 1. WRV as a function of temperature for unbleached TMP in different dominating ion forms.

Peroxide bleaching of TMP introduces carboxylic groups in the lignin. The effect of this is seen in **Fig. 2** as a larger increase in water retention at 95°C compared to the increase for unbleached TMP (**Fig. 1**). The effect of valence of the counter ion is also more pronounced for the bleached thermomechanical pulp (see **Fig. 2**), especially with sodium as counter ion.

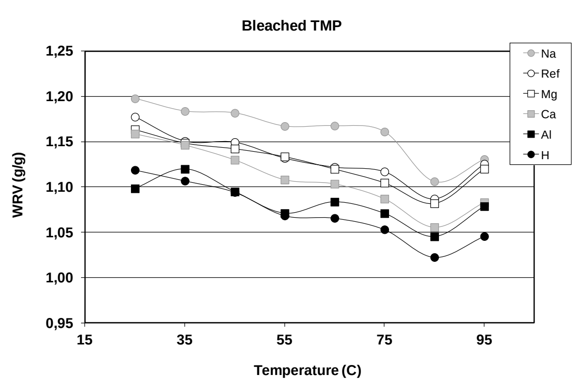

Fig. 2. WRV as a function of temperature for peroxide bleached TMP in different dominating ion forms.

In addition to carboxylic groups, peroxide bleached high temperature chemithermomechanical pulp (HTCTMP) also has sulphonic acid groups in the lignin as a result of sulphonation in the impregnation step. Sulphonation does not add as many acidic groups as peroxide bleaching, but it opens up the rigid lignin structure. Consequently, sodium as counter ion gives a more swollen fibre wall even at lower temperatures than the divalent and trivalent counter ions, and the effect of softening of the lignin due to temperature is not as prominent, see **Fig. 3**.

Proton as counter ion implicates a low pH. Carboxylic acids groups are not dissociated at low pH and therefore do not contribute to the swelling. This is one of the reasons that thermomechanical pulps with proton as counter ion displays the same swelling behaviour as with trivalent counter ions (**Fig 1** and **Fig. 2).** The sulphonic acid groups present in HTCTMP are dissociated at low pH, and can therefore even with proton as counter ion contribute to the swelling to some extent. This is seen in **Fig. 3** as higher water retention for proton as counter ion (at temperatures below 75°C) compared to the divalent and trivalent counter ions. At temperatures above 75°C, where the lignin is softened, the effect of counter ion to the carboxylic acid groups overrides the effect from the sulphonic acid groups.

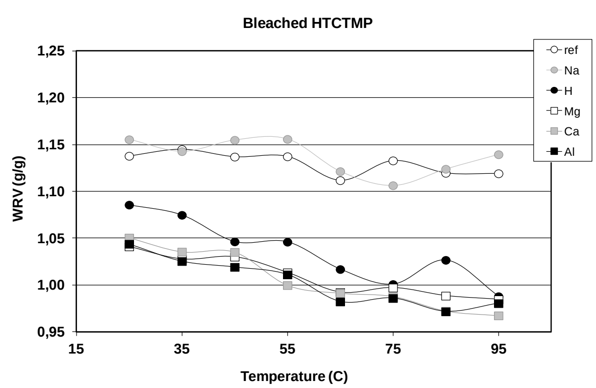

Fig. 3. WRV **as** a function of temperature for peroxide bleached HTCTMP in different dominating ion forms.

Fig. 4 shows the relative water retention value of bleached HTCTMP and unbleached TMP in different counter ion forms. The relative WRV is the value of the ion-exchanged fibres divided by the WRV for the reference sample, i.e. the sample which was not ion exchanged. The results show that the fibres containing more ionisable groups (bleached HTCTMP) are more sensitive to the ionic form (divalent, trivalent) than those fibres which possessed less number of ionisable groups (unbleached TMP).

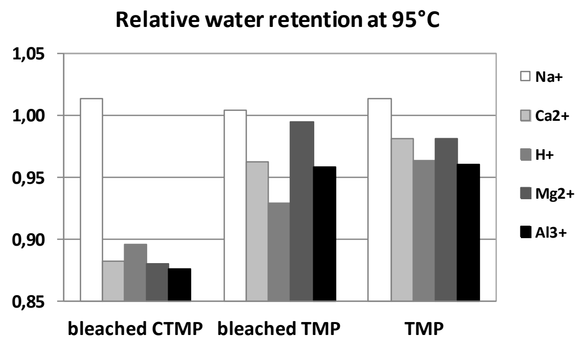

Fig. 4. Relative WRV with different dominating ionic forms for TMP, BTMP and BHTCTMP at 95C. Relative WRV is defined as WRV of ion-exchanged pulps divided by WRV of reference pulps.

CONCLUSIONS

Thermomechanical pulp and peroxide bleached thermomechanical pulp i.e. pulps where no sulphonic acid groups have been introduced; need to be heated above the softening temperature of lignin in order to be able to swell to their full capacity. The effect of valence of the counter ion is more pronounced when more carboxylic acid groups are introduced in the pulp. Introduction of sulphonic acid groups opens up the rigid structure of lignin, thus increasing the swelling potential with the monovalent sodium ion as counter ion even at low temperatures. Due to the low pK_a value of sulphonic acid groups, the proton form displays better swelling ability than divalent and trivalent counter ion at temperatures below the softening temperature of lignin. Depending on the number and type of anionic acid groups in the fibres, high-yield pulps will behave differently in various ionic surroundings. This is important to take into account when producing pulp and paper. Further investigations at higher temperatures and with cleaner counter ion forms will be necessary to perform in the future.

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