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EFFECT OF IONIC FORM ON FIBRILLATION AND THE DEVELOPMENT OF THE FIBRE NETWORK STRENGTH DURING THE REFINING OF THE KRAFT PULPS

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ABSTRACT

The refining of unbleached kraft pulps in their Na^+-form has shown energy saving potential. In this study, the fibre network strength of unrefined and laboratory refined samples of an unbleached never-dried kraft pulp in different ionic forms was studied. The external fibrillation and the fibre flexibility were also studied. The objective was to investigate whether the improved refinability of fibres in the Na^+-form could be related to the floc network strength or to fibrillation characteristics.

The results showed that the rheological properties may not explain the improved refinability of fibres in the Na^+-form, since fibres showed similar rheological properties regardless of their ionic form. Measurements using the MMS (Pulp Measuring System) showed that fibres refined in the Na^+-form have a larger amount of external fibrillation, and microscopic investigation confirmed that the characteristics of the fibrils are different for fibres refined in the Na^+-form from those of fibres refined in the H^+- or Ca^{2+}-forms. The observed differences in fibrillation and improved refinability may be explained by the co-operation of electrostatic interactions of the fibre wall and the mechanical forces applied during refining.

INTRODUCTION

Low consistency refining is an important feature of papermaking. The common view is that the LC-refiners mainly treat fibre flocs and that the fibre flocs are trapped between the bars of the refiner (Ebeling, 1980; Page, 1989). Fibre suspension characteristics, such as floc size and floc strength, have constituted a vast research area due to their profound impact on the formation of paper, and earlier research has shown that both chemical and mechanical factors influence the degree of flocculation and the floc strength (Wågberg, Lindström, 1987; Swerin, 1995; Beghello, 1998; Kerekes, 2006). It has been shown that an increase in fibre length increases the floc size (Jokinen, Ebeling, 1985; Kerekes, Schell, 1992; Beghello, 1998; Yan, 2004) and this can be described by a crowding factor (Kerekes *et al.*, 1985; Kerekes, Schell, 1992) which is proportional to the square of the fibre length. The fibre network can also be described with the "fibre centre span number" Ncs, which is defined as the number of fibre centre spans within the reach of a single fibre (Björkman, 1999). Fibre length and fibre consistency are the most important parameters for floc strength, measured as the apparent yield stress (Kerekes, Schell, 1995; Dalpke, Kerekes, 2005).

Beghello (1998) and Yan (2004) found that an increase in the number of charged groups led to a decrease in the floc size, and they interpreted this as indicating that an increase in the electrostatic repulsion between the charged fibres leads to a decrease in the coefficient of friction between the fibres, and also to a reduction in the network strength. Horvath recently (2006) showed that an increase in the surface charge of the fibres results in a lower apparent yield stress of the fibre suspension, as evaluated by rheological measurements. Horvath also performed a study in which the number of contact points was changed by fibre length fractionation of an unrefined fully bleached laboratory produced pulp and a PFI milled commercial bleached softwood pulp. The results confirmed that an increase in fibre length led to an increase in the network strength measured as storage modulus G′, in agreement with Dalpke and Kerekes (2005). Horvath (2006) also found that the critical strain decreased as the number of contact points increased, but that the flexible refined pulp had a higher critical strain than the unrefined stiffer pulp. This effect may however be explained by a more fibrillated and rougher surface, which increases the mechanical surface linkage. Neither pH nor electrolyte concentration have any great impact on the flocculation and fibre network strength (Beghello, Eklund, 1999; Horvath, 2006).

The swelling ability of fibres is important for the refinability of the pulp and it is known that the counterions to the charged groups in the fibres play an important role for their swelling ability (Lindström, Carlsson, 1978; Scallan, Grignon, 1979; Scallan, 1983; Lindström, Carlsson, 1982; Lindström, Kolman, 1982; Lindström,

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O PAPEL vol. 73, num. 7, pp. 57 - 65 JUL 2012

1992, Hammar *et al.*, 2000, Laivins, Scallan, 2000, Bäckström *et al.*, 2009 a). Electrostatic repulsion of negatively charged groups is the cause of swelling according to the theory of charged electrolytic gels (Flory, 1953). According to Bjellfors *et al.*, (1965), the shear strength and shear modulus of a fibre network are influenced by the counterion to the charged groups, where fibres in the Na^+-form have a lower shear modulus than fibres in H^+-, Ca^{2+}-, Al^{3+}- or Th^{4+}-forms. A tentative explanation is that the cations affect the interaction between fibres and the flocculation process, and thus influence the shear modulus of the network.

It has been shown in the literature that handsheets made from fibres with carboxyl groups in different ionic forms have different tensile indexes, where fibres in the Na^+-form had the highest tensile index and swelling ability, while hydrogen and aluminium counterions gave less swelling and a poorer strength (Scallan, Grignon, 1979). Hammar *et al.*, (2000) separated the effects of counterion on refining and sheet formation by refining pulps in different ionic forms and then converting all the pulps into the Ca^{2+}-form prior to papermaking. Their results showed that the energy required to reach a given WRV (water retention value) or a given tensile index could be reduced by 50% if the fibres were refined in the Na^+-form. The results have been confirmed in a pilot scale study (Bäckström *et al.*, 2009a). Additional energy savings are possible if the sheet formation is performed in the Na^+-form (Hammar *et al.*, 2000).

The objective of the present study was to investigate if the improved refinability - in this case the required refining energy input to reach a given WRV - of fibres in the Na^+-form could be related to changes in floc network strength or if it was related to the fibre, in terms of fibrillation characteristics. The fibre network strength for unrefined and laboratory refined pulp of an unbleached never-dried kraft pulp in different ionic forms was studied using a parallel plate rheometer. The degree of external fibrillation was also studied using three different techniques.

MATERIALS AND METHODS

Materials

Never-dried unbleached kraft pulp from Skärblacka mill, Billerud, Sweden, was used. The kappa number was 31 and the amount of charged groups was 130 mmol/kg. The length-weighted fibre length of the pulp was 2.54 mm.

The pulp was washed with deionized water in order to remove the remaining chemicals from the cooking process; after that, the pulp was centrifuged, homogenized and stored in a cold room.

Ion exchange

The whole pulp was changed to the H^+-form by addition of H_2SO_4 for 2 h at pH 2. The H_2SO_4 was removed by washing with deionized water until the recirculation system reached a low conductivity (close to that of deionized water). Parts of the pulp were then converted into the Na^+- and Ca^{2+}-forms. The chemicals used in the ion exchange process and the washing liquor are listed in **Table 1**. After the ion exchange had been carried out, the ionic form of the pulp was verified by metal content analysis of the original H^+-, Na^+- and Ca^{2+}-forms pulps.

Refining conditions

The refining was performed in an Escher Wyss laboratory conical refiner R 1L at a pulp consistency of 3.5% and at a specific edge load (SEL) of 2 Ws/m at four different specific energy inputs: 50, 75, 100 and 125 kWh/t in deionized water.

Analysis

The total charge of the pulps was determined by conductimetric titration according to Katz (1984). Prior to the measurement, the sample was washed with HCl at a pH 2. Thereafter, the sample was washed with deionized water until the filtrate had a conductivity less than 5 µS/cm and a pH higher than 4.5.

Kappa number was determined according to IS0 302:2004 and the WRV according to SCAN –C 62:00, except that deionized water was used. The WRV is calculated as the wet weight after centrifugation subtracted by the dry weight after centrifugation, and then divided by the dry weight after centrifugation, i.e. weight of water per weight of sample. The °SR (Schopper-Riegler) number according to ISO 5267-1, and metal analysis were performed using plasma emission spectrometry ICP-AES. Fibre dimensions and shape factor were determined using the STFI FiberMaster (Karlsson *et al.*, 1999). Fibre bendability was measured using the FiberMaster where the shape factor of the fibres was measured at two different flow rates (Fransson *et al.*, 1992). The STFI FiberMaster used municipal water in the measuring cell.

Table 1. Chemicals, pH and washing medium employed in the ion-exchange procedure

Ionic form	Chemical in ion exchange	pH during ion exchange	Washing medium	pH (20°C) after refining
H^+	H_2SO_4	2	Deionized water	~5
Na^+	NaOH	10.5	0.0001mol/L $NaHCO_3$, pH9	~8
Ca^{2+}	$CaCl_2$	8	Deionized water	~7

O PAPEL vol. 73, num. 7, pp. 57 - 65 JUL 2012

The external fibrillation measurements were carried out at the laboratory of Paper Technology of the Helsinki University of Technology (now Aalto University). Fines were removed from samples with a BDDJ apparatus. Microscopy samples from the R200 fraction were prepared with gelatin solution as a mounting medium. Images were acquired automatically using a phase contrast microscope with 10x objective. The images having too few or too many fibres were removed automatically by a Matlab program. The number of accepted images was about 100 for each sample. Another Matlab program was used to detect fibres and fibrils in the images. The degree of external fibrillation is calculated as the ratio of fibril area to the fibre area. Based on this data, a fibrillation index was calculated as a weighted average (Kurhila, 2005).

The STFI MMS (pulp measurement system) is based on the detection and measurement of light that is scattered, absorbed and transmitted by a flowing pulp suspension (Karlsson, Pettersson, 1982). In our case, the KFP (fibril-to-fibre ratio) was evaluated. This is a relative measurement of the increase in specific surface due to the presence of fibrils in the pulp. The value is presented as a percentage, and a KFP value of 100% corresponds to no fibrils in the pulp. If the value of the KFP is 200%, the specific surface is doubled due to the presence of fibrils. By removing the fibrils/fines that are not attached to the fibres, a measurement of the external fibrillation is obtained. Light microscopy with a phase contrast objective was used.

Rheological measurements

A parallel plate StressTech® rheometer from Rheologica Instruments AB (Lund, Sweden) was used for the rheological measurements. Oscillatory shear with controlled strain was applied. The sample was held in place by a plastic ring with a diameter of 50.5 mm around the lower plate. The diameter of the upper plate was 40.0 mm. In order to prevent slipping, sandpaper 120 grit was attached to the plates with double-sided adhesive tape. The gap between the plates was 7.06 mm and was checked and readjusted before each measurement. Three samples for each pulp and consistency were studied. All measurements used 1 Hz frequency and the strain range was from $6*10^{-4}$ to 1. The pulp consistency was determined by drying the sample after measurements at 80°C overnight. The shear modulus as a function of strain is retained by small amplitude oscillations under controlled strain. The shear modulus, G^*, was divided into its real and imaginary parts, $G^* = G' + iG''$, where G' is the storage modulus and G'' is the loss modulus. The storage modulus is independent of the applied strain at low strains and G'_0 is defined as the plateau value of the storage modulus in the linear region (Horvath, 2006). Above a critical strain, γ_c, the storage modulus starts to decrease. The critical strain thus marks the onset of breakage of the network structure in the fibre suspension (Swerin *et al.*, 1992) and can be determined from the intersection of the regions according to Horvath (2006).

RESULTS

Refining results

Figure 1 shows the development of WRV for the pulp refined in different ionic forms. At a given specific energy input, the highest WRV was obtained for the fibre refined in the Na^+-form. The other two ionic forms (Ca^{2+} and H^+) did not differ substantially from each other. After refining, the pulp refined in the Na^+-form was converted back to the Ca^{2+} -form and the WRV was determined. A large part of the increased swelling was then lost, but at a given specific refining energy input the WRV was still at a higher level.

Figure 2 shows the °SR number for the pulp refined in the different ionic forms. At a given specific refining energy input, the pulp refined in the Na^+-form had a much higher °SR number than the other two ionic forms.

The fibre length measurements showed that the fibre shortening was somewhat more severe for the pulps refined in the H^+-form, and that the fibres refined in the Ca^{2+}-form suffered least from fibre

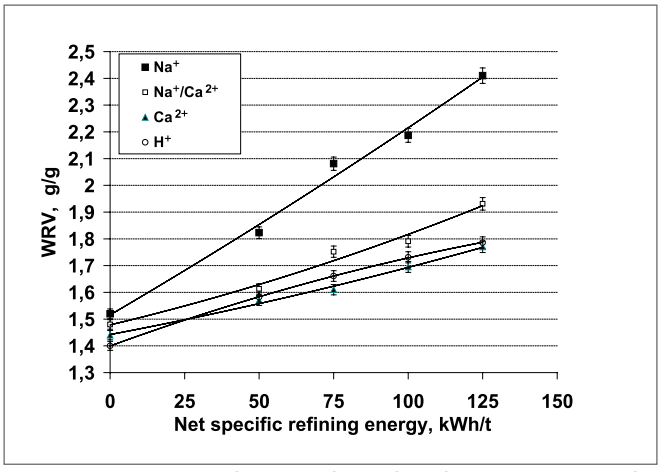

Figure 1. The WRV as a function of specific refining energy input for the pulps in different ionic forms. After refining, the Na^+-form pulp was converted back to Ca^{2+}-form and the WRV was again measured (Na^+/Ca^{2+}). The error bars show the coefficient of variation

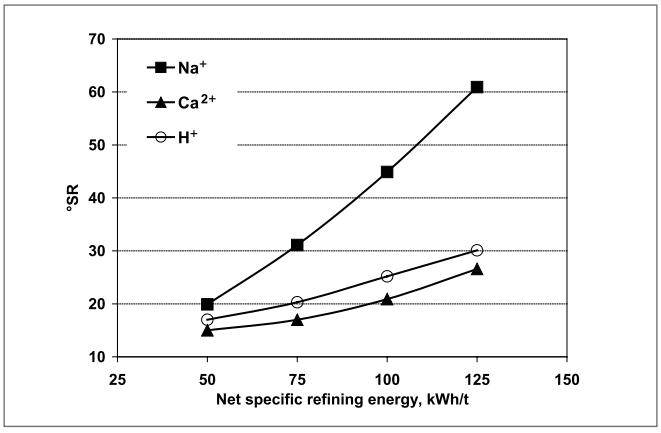

Figure 2. °SR number as a function of specific refining energy input for the pulps in different ionic forms

O PAPEL vol. 73, num. 7, pp. 57 - 65 JUL 2012

shortening, **Figure 3**. At the highest energy input, 20% of the fibres refined in the H^+-form were cut.

At low levels of energy input, the fibres were straightened and an increase in the shape factor was observed. When the energy input was increased the shape factor decreased, especially for the pulp in the Na^+- and H^+-forms, while no significant decrease was observed for the pulp refined in the Ca^{2+}-form, **Figure 4**.

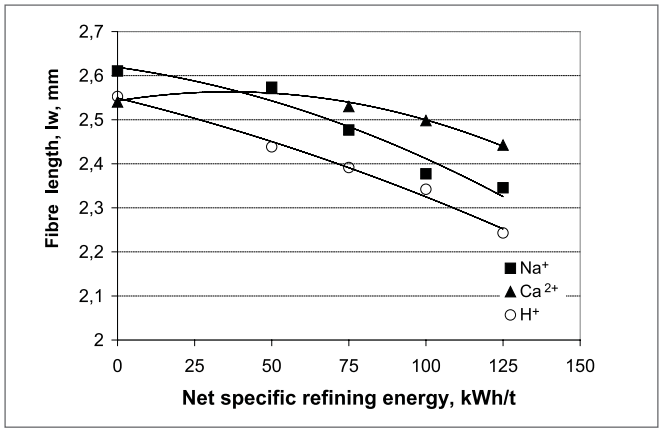

Figure 3. The length-weighted fibre length as a function of specific refining energy input for pulps refined in different ionic forms

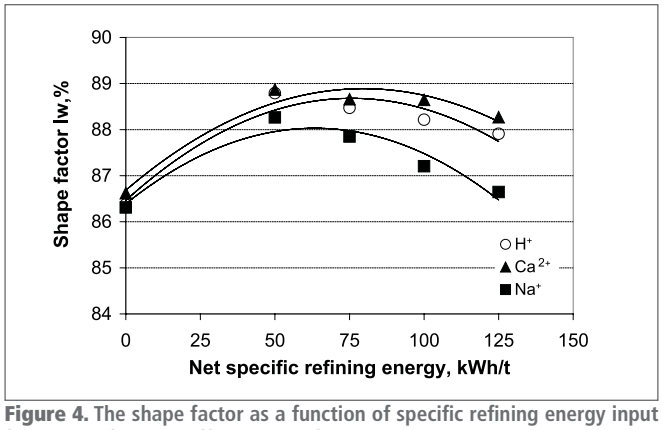

Figure 4. The shape factor as a function of specific refining energy input for pulps refined in different ionic forms

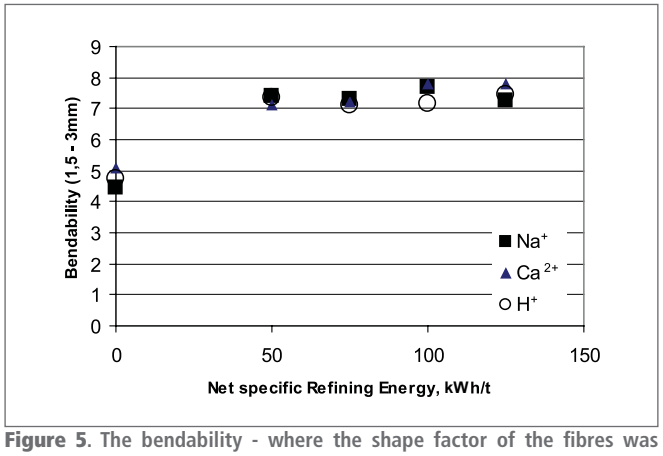

Figure 5. The bendability - where the shape factor of the fibres was measured at two different flow rates for the 1.5-3 mm fraction - as a function of specific refining energy input for pulps refined in different ionic forms

No differences in bendability, i.e. fibre flexibility, were observed between the fibres refined in different ionic forms, **Figure 5**. Since the analysis in the FiberMaster is done in tap water, there is an immediate ion exchange of fibres in the Na^+- or H^+-forms to the Ca^{2+}-form.

Rheological measurements

The unrefined and refined pulp samples were evaluated in a stress plate rheometer at three different pulp consistencies. **Figure 6** shows the storage modulus and the critical strain for the different samples. A higher consistency gave, as expected, a higher storage modulus, the highest value being obtained for the unrefined pulp samples. At the lowest consistency - approximately 1.5% - no difference was observed between the pulp samples regardless of refining energy or ionic form. At higher pulp consistencies, the storage modulus decreased with increasing refining. No significant differences were observed between the different ionic forms, **Figure 6a**.

The critical strain was not as sensitive to pulp consistency, but the critical strain increased with increasing refining, **Figure 6b**. No systematic difference between the different ionic forms could be observed.

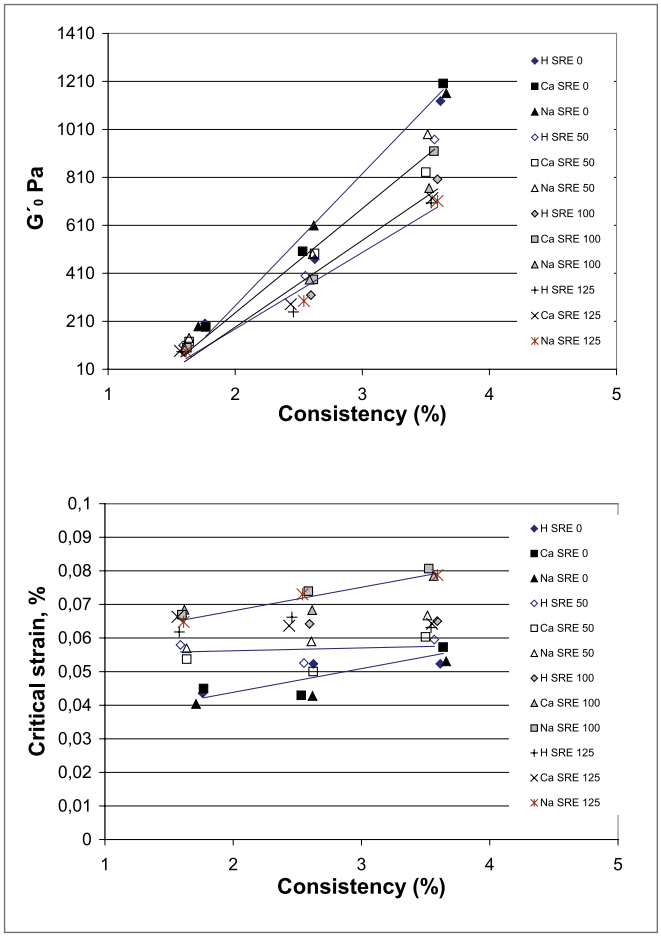

Figure 6. a) The storage modulus and b) the critical strain as a function of pulp consistency for pulps refined in different ionic forms and at different energy inputs

O PAPEL vol. 73, num. 7, pp. 57 - 65 JUL 2012

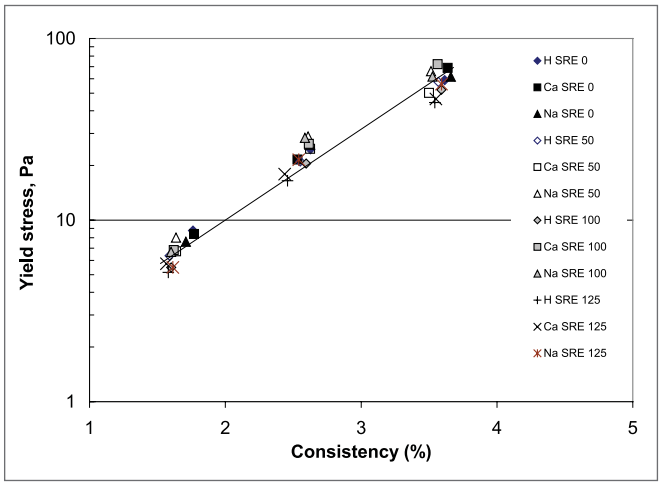

Figure 7. The apparent yield stress as a function of pulp consistency for pulps refined in different ionic forms and at different energy inputs

The apparent yield stress was dependent on pulp consistency as shown in **Figure 7,** but was independent of ionic form of the fibres or of the refining degree.

External fibrillation

The fibrillation of the pulp samples was evaluated by several methods: image analysis to determine the amount of fibrils on the surface according to Kurhila (2005), light scattering (Karlsson, Pettersson, 1982; Pettersson, 2010) and traditional phase contrast microscopy to study the degree of external fibrillation on the fibre surfaces.

The degree of external fibrillation was determined by image analysis and MMS for a limited number of pulp samples, **Table 2**. The results using the image analysis method showed that at a given specific refining energy input (50 kWh/t and 125 kWh/t) the pulp in the H^+-form had the highest degree of external fibrillation. Despite the much higher WRV and higher °SR, the pulp in Na^+-form had a lower degree of external fibrillation than the pulp in H^+-form.

Table 2 includes the crill KFP values based on the MMS light scattering technique. A value of 171% means that 71% of the total surface is made out of crill, with an uncertainty of ±0.5%. These results clearly contradict the results obtained by image analyses.

The external fibrillation was also examined using phase contrast in a microscopy and distinct differences between the samples were observed. The microscopic examination showed that the Na^+-pulp fibres differed from fibres refined in the H^+- and the Ca^{2+}-forms, **Figure 8-10.**

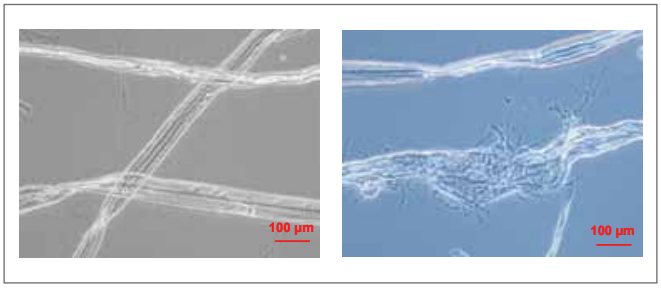

Figure 8. Pulp in the Na^+-form refined at 125 kWh/t. Fines had been removed. WRV was 2.41 when the fines were present in the pulp sample

Figure 9. Pulp in the H^+-form refined at 125 kWh/t. Fines had been removed. WRV was 1.79 when the fines were present in the pulp sample

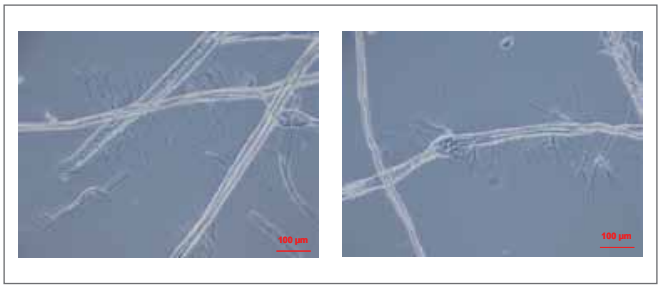

Figure 10. Pulp in the Ca^{2+}-form refined at 125 kWh/t. Fines had been removed. WRV was 1.77 when the fines were present in the pulp sample

Table 2. Degree of external fibrillation of the pulp samples. The refining energy input (SRE), the °SR number and the WRV are also given

Sample	SRE	°SR	WRV	External fibrillation, %	Crill, KFP
Ca50	50	15	1,57	0.7	-
Ca100	100	21	1,70	-	170,5
Na50	50	20	1.82	1	160.4
Na100	100	45	2,19	-	177
Na125	125	61	2,41	3.5	-
H50	50	17	1.58	1.5	157.2
H100	100	25	1,73	-	171.6
H125	125	27	1,79	4.2	-

O PAPEL vol. 73, num. 7, pp. 57 - 65 JUL 2012

The fibre refined in the Na^+-form showed fibrillation to a larger extent with both more fibres and larger regimes of the fibres fibrillated, but the fibrils were tiny and rather short. Tough defibrillation at mechanically damaged fibre walls or at fibre ends was also observed. For the pulp in the H^+- and Ca^{2+}- forms, the fibrils was coarser, longer and more visible than in the case of the Na^+-pulps. Parts of the fibres had fibrils consisting of fibre wall parts.

DISCUSSION

Refining of pulps in the Na^+-form gave, as expected, a faster development of WRV and °SR than pulps in either the Ca^{2+}- or the H^+-forms, as shown in Figure 1. This is in agreement with previous findings (Hammar *et al.*, 2000; Laivins, Scallan, 2000; Bäckström *et al.*, 2009a). The ion exchange also increased the WRV of the unrefined pulp in agreement with several other studies (Lindström, Carlsson, 1978; Scallan, Grignon, 1979; Scallan, 1983; Lindström, Carlsson, 1982; Lindström, 1992). The decrease in WRV after the Na^+- refining was more pronounced than in previous trials (Hammer *et al.*, 2000, Bäckström *et al.*, 2009), but there was a significant remaining effect on the WRV of fibres refined in their Na^+-form.

The reduction of the fibre length during refining was more significant for the pulp in the H^+-form than in the Na^+- and Ca^{2+}-forms (see Figure 2), probably because the H^+-form is more brittle, as has also been reported by Hammar *et al.*, (2000). However, in the present study, the pulp refined in the Na^+-form had the lowest shape factor (see Figure 3), which is contrary to what has been reported by Hammar *et al.*, (2000) and by Bäckstöm *et al.*, (2009a), where the conversion of the pulp into the Na^+-form made the fibres swell, and thus promoted fibre straightening. The pulps used in this study are similar of what has previously been reported, except for the lower shape factor of the pulps refined in the Na^+-form.

Rheology

The fibre network strength of the unrefined and refined pulp samples in different ionic forms was evaluated with the aid of a parallel plate stress rheometer. The result showed that, at a pulp consistency of 1%, the storages modulus did not differ between the pulp samples regardless of refining degree or ionic form, but that at a pulp consistency of 3.5% the storage modulus depended on the refining energy input, Figure 6. As the specific refining energy increased, the storage modulus decreased. No differences between the different ionic forms were observed. The results suggest that fibre properties are more important at high consistency than at low consistency, and that refined fibres are more flexible, so that less tension can be built into the network since the fibres come to rest in a less strained form, i.e. less energy is stored in the network, resulting in a lower storage modulus.

These results are in agreement with results reported by Youn and Lee (2002) and by Horvath (2006). Horvath (2006) used the same experimental setup and observed that refined pulp fibres had a lower storage modulus at a given number of contacts per fibre.

The critical strain marks the onset of breakage of the network structure in the fibre suspension, and the results showed that refining of pulp fibres increased the critical strain, as shown in Figure 6. It can be assumed that the surface becomes more fibrillated and rougher as the refining proceeds and that this affects the mechanical surface linkages and thus increases the critical strain.

The effect on the apparent yield stress follows a power law dependence, $\tau = aC_m^{\ b}$, as described earlier (Dalpke, Kerekes, 2005), where τ is yield stress in Pa, C_m is pulp consistency as a percentage, a is a constant in Pa and ^{b} is also a constant. The values for the constants a and ^{b} obtained in the present study are given in **Table 3**, which includes all the refining pulps. Values for the constant a range between 30.9 and 0.51 and for the constant ^{b} between 2.35 and 3.96 have been reported (Kerekes, 2006). Our values for a and ^{b} correspond well with the values which Horvath (2006) found when studying the effect of CMC grafting on the rheological properties using the same experimental set up.

Our results confirm that pulp consistency is the major parameter that affects the rheological properties of a fibre suspension, and the apparent yield stress being more or less independent of the refining level and ionic form, Figure 7. The effects of refining on the storage modulus and critical strain counteract each other, so that the net result is the same regardless of refining level. The yield stress is the minimum stress required to initiate flow and can be considered to be the stress needed to deform the fibre network. No difference in bendability was observed due to the different ionic forms, which is concordant with the results of Forsström *et al.* (2005) who observed no impact of ionic form on the bendability for unbleached kraft pulps at different pulp yields.

The results of the rheological measurements are in agreement with Horvath´s finding (2006) using a bleached softwood pulp with fewer charged groups than in our case, with an unbleached kraft pulp. When Horvath increased the surface charge by treatment with CMC, fibres in the Na^+-form showed a lower apparent yield stress at a given consistency than fibres in the H^+-and Ca^+-forms. She explained the results in terms of surface

Table 3. Values for the constants a and b for the power law correlation between yield stress and consistency

Pulp	Constant a, Pa	Constant ^{b}	Correlation coefficient R^2
Na	0.21	2.84	0.98
Ca	0.23	2.76	0.99
H	0.22	2,69	0.99

O PAPEL vol. 73, num. 7, pp. 57 - 65 JUL 2012

swelling measured as WRV. In our study, no effect on the apparent yield stress due to differences in WRV was observed, but during refining an increase in WRV involves a swelling of the whole fibre and is not specifically due to the fibre surface effects.

The interpretation of these results is that there are no major differences in rheological behaviour among fibres in different ionic forms measured with a plate rheometer, and that differences in rheology may not be the major factor explaining the improved refinability of fibres in the Na^+-form. It would however be very interesting and informative to study the relation between gap clearance and refining power for fibre suspensions in different ionic forms in a single-stage refiner. A different power gap clearance relationship for fibres refined in different ionic forms would indicate differences in rheological properties of the fibre suspension under realistic refining conditions. The relationship between refining power and gap clearance is a valuable tool for understanding the refining behaviour (Mohlin, 2007; Koskenhely, 2007; Bäckström *et al.*, 2009b).

Fibrillation

The results showed that data regarding the degree of fibrillation can vary a lot depending on the techniques used, and this should be borne in mind when interpreting the data. The fibrillation levels for the pulps obtained by the image analysis methods correspond well with what has been reported by Wang (2006) and Kang (2007) using the same technique. Also, the values for the MMS light scattering method are representative for refined pulps and the method will be developed as an on-line method (Pettersson, 2010). The results showed that the type and characteristics of the fibrils on the fibre surfaces were different, depending on the ionic form. The fibres in the Na^+-form were more fibrillated, but had tiny and rather short fibrils, whereas fibres in the H^+- and Ca^{2+}-forms had coarser and longer fibrils as seen in the microscope, Figure 8-10. These differences could not be detected with the image analysis method, but the MMS light scattering method detected both types of fibrillation and showed that the Na^+-fibres had more fibrils, measured as surface area, than fibres in the H^+-form (Table 2).

Our results indicate that the refinability of fibres in different ionic forms is related more to the fibre and fibre wall than to the rheology of the fibre suspension. Changing the ionic form of fibres changes the swelling behaviour, but also the pores within the fibre wall (Salmén and Berthold, 1997). Forström (2004) has shown that the radii of pores inside the fibre wall is larger in fibres in the Na^+-form than those in the H^+-form. It is not possible, on the basis of our results, to relate the improved refinability of fibres in the Na^+-form to changes in the pore structure of the fibre wall, but the fibres refined in the Na^+-form give a different fibrillation pattern, and this difference is probably due to differences within the fibre wall.

Fibres in the wet state always contain water to some degree, and additional water can be taken up (swelling) if chemical groups attached to the macromolecular network of the cell wall are ionized. To maintain electrical neutrality, the counterions to these groups must be maintained in the wall. This creates a concentration of mobile ions within the wall that is greater than that in the liquor outside the wall, and thus a difference in osmotic pressure arises. Extra water is drawn into the wall to reduce this difference. However, an increasing resistance to expansion of the cell wall is provided by the elastic nature of the wall. Eventually, the osmotic pressure equals the elastic tension in the wall matrix. Gellerstedt and *al*. (2000) showed that swelling - by introducing additional charges onto the fibres with succinic acid - increased the osmotic pressure above the cell wall elasticity and delaminated the cell wall.

Our results can be interpreted as indicating that the reason for the improved refinability of fibres in the Na^+-form is mainly due to co-operation between the increased osmotic pressure in the fibre wall and the mechanical stress. The hypotheses is: as mechanical forces are applied to the fibre and the fibre wall, the electrostatic repulsion due to the ionization provides an additional aid to increase the swelling, and this helps to delaminate the fibre wall. This improves the refinability in terms of an increase in WRV for a given energy input, but also leads to a different fibrillation pattern where smaller fibrils are obtained when the fibres are in their Na^+-form. When refining of fibres in the H^+-form, a large proportion of the charged groups in the fibres are undissociated, which largely means that mechanical energy is transferred to the fibres without any electrostatic interaction. This is not totally true, because at a pH level of 5 some groups are dissociated (Laine, 1994). On the other hand the Donnan equilibrium calculations made by e.g. Grignon and Scallan (1980) show that the pH is much lower within the fibre wall than in the surrounding medium, especially at low ionic strength. When the fibres are transferred into the Na^+-form, the charged groups in the matrix are ionized and, as the mechanical energy is transferred by the refiner, the electrostatic nature of the matrix co-operates to delaminate the fibres, the so called "electrostatic repulsion assisted refining" described by Bäckström and Hammar (2010) and in harmony with the interpretation of Laivins and Scallan (2000) that chemical and mechanical processes are additive under alkaline conditions.

CONCLUSIONS

The results show that the rheological properties, measured with a parallel plate rheometer, may not explain the improved refinability of fibres refined in the Na^+-form, since fibres in different ionic forms showed similar rheological properties.

Fibres refined in the Na^+-form showed, according to measurement using the MMS system and microscopic investigation, a larger amount of external fibrillation and different fibrils characteristics than fibres refined in the H^+- and Ca^{2+}-forms. The observed differences in fibrillation and refinability may be interpreted as being due to a co-operation between electrostatic interactions within the fibre wall as a result of ionization of the charged groups and the mechanical forces applied during refining.

O PAPEL vol. 73, num. 7, pp. 57 - 65 JUL 2012

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O PAPEL vol. 73, num. 7, pp. 57 - 65 JUL 2012

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