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Sustainpack

Innovation and sustainable Development in the Fibre Based Packaging Value Chain

Instrument: **IP**

D5.42. Chemical treatments of fibres for improved hygro- and hydrodynamic stability

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PU	Public	
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission	
CO	Confidential, only for members of the consortium (including the Commission Services)	X

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1 Introduction

As a primary strategy for the stabilization of pulp fibres we have explored the use of poly carboxylic acids as cross linkers. Cross linking is one of the most effective ways to achieve a high degree of stabilization. During these treatments the amount of carboxylic functionality covalently bonded in the fibres are increased. In this activity we are pursuing different ways to utilize these functionalities as starting points for further stabilization of the cell wall against water and moisture absorption. All investigated methods has been chosen based on the fact that they can be performed in water phase and under mild conditions.

The following modifications have been tested: Substitute protons/metal ions with quaternary ammonium salt ions having fatty side chains. The idea behind this approach is to make the fiber cell wall more hydrophobic. A second approach has been to esterify the carboxylic acids enabling easy conversion to amides. This would enable us to attach fatty amines onto the cellulose surfaces inside the cell wall.

2 Experimental

The following pulps were used in this study: a laboratory made unbleached sulfate pulp (pulp A), a commersial unbleached sulfate pulp (pulp B), a bleached industrial birch pulp (Pulp C) (received hammer milled from Oulu) and a commercial never dried bleached hardwood pulp (pulp D). All chemicals were purchased from Aldrich or Fluka

Table 1. List of tested ammonium salts

compound	**series**	**Formula**	**MW**
Octadecyltrimethylammonium bromide	C18	$CH_3(CH_2)_{17}N(Br)(CH_3)_3$	392.50
Dimethyldioctadecylammonium chloride	C18	$C_{38}H_{80}ClN$	586.50
Methyltrioctadecylammonium bromide	C18	$C_{55}H_{114}BrN$	869.40
Tetraoctadecylammonium tetrafluoroborate	C18	$[CH_3(CH_2)_{17}]_4N(BF_4)$	1114.76
Trimethyloctylammonium chloride	C8	$CH_3(CH_2)_7N(CH_3)_3(Cl)$	207.78
Octyltrimethylammonium bromide	C8	$CH_3(CH_2)_7N(CH_3)_3(Br)$	252.23
Methyltrioctylammonium chloride	C8	$[CH_3(CH_2)_6CH_2]_3N(Cl)CH_3$	404.16
Tetraoctylammonium chloride	C8	$[CH_3(CH_2)_7]_4N(Cl)$	502.34

Treatment of pulps with ammonium salts

Unless specifically stated all treatments were made using equimolar (total charge) amount of salt . The volumes used were about 2-2.5 l and each batch consisted of about 7 g pulp. The salt was allowed to dissolve in water prior to the addition of pulp. The pH was adjusted to about pH 8. The samples were allowed to soak overnight with stirring after which the solution was filtered off.

Comments to the salts:
Octadecyltrimethyl bromide: difficult to dissolve, emulsion. Gave easily dispersed fibers. Difficult to pH-adjust.
Octyltrimethyl bromide: easily dissolved. Easy to pH adjust. Difficult to stir.
Tetraoctylammonium chloride: somewhat difficult to dissolve. Gives small fiber balls! Also tried without stirring, but instead on a “shake board”.
Methyltrioctyl chloride and Tetraoctadecyl: gave an oily layer.
Methyltrioctadecyl bromide: “Powderly”, difficult to dissolve. Sticks on the plastic ware and other surfaces. EtOH added. Difficult to wash, the salt does not dissolve. Tried to dissolve in propanol with followed fiber modification. Gave a yellow pulp on shaking (could not repeat) and balls with stirring!
: similar as for methyltrioctadecyl.

Moisture adsorption was performed by DVS and or under controlled conditions and water content by the mini-WRV-methods. Total nitrogen content was determined using a chemiluminiscence method calling upon an Antek 7000 apparatus. The amount is calculated using an urea standard curve..

Amidation reaction

A water soluble carbodiimide N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) (Fluka, purum) was used for the cross-linking of carboxylic acid groups in pulp fibres with different amines resulting in amid-linkages and the introduction of a hydrophobic tail.

The pulps used were earlier BTCA cross-linked pulps, one fully *bleached birch pulp* and one fully *bleached* never dried *hardwood pulp*. All pulps were first washed to sodium form before cross-linking.

Following commercially available amines were studied: ethyl amine hydrochloride (Fluka, purum), ethyl diamine dihydrochloride (Aldrich 98%), benzylamine hydrochloride (Sigma), heptyl amine (Sigma) and stearyl amine (Aldrich, tech.).

All reactions, except when using stearyl amine, were performed in water solutions using a MES (2-Morpholinoethanesulfonic acid monohydrate) buffer with pH 5.5 to keep control of the pH during the reaction. For the stearyl amine ethanol-water (1:1 by volume) was used as the amidation medium.

To a 1 % pulp suspension (1,5 g pulp to 150 ml buffer) the desired amine was added during stirring and the pH was adjusted to 5.5. Thereafter the EDC was added to the suspension and it was stirred for 4 h at room temperature. The amidated pulp was finally washed thoroughly with water. For 1 mmol carboxylic acid groups in the pulp 30 mmol amine and 15 mmol EDC was used.

A serie of experiments were performed to find the best conditions for the reaction. Ethyl amine hydrochloride was reacted with a 1% BTCA birch pulp at pH 5, 6 and 7 and also at pH 6 with the addition of sodium chloride (suggested in Hermanson 1996)).

The ethylene diamine was used to investigate if further cross linking could be achieved. Therefore the diamine was added in both large excess (ethyl diamine B), in twice molar amount (ethyl diamine C) and in less molar amounts (ethyl diamine D). These were compared to the reaction of ethyl monoamine in large excess.

The 1% BTCA birch pulp was an earlier treated pulp (june 2006). The 2% BTCA birch and hardwood pulps were reacted with a higher concentration of BTCA and the heat treatment was performed at 170 °C for 20 minutes.

Comments:

In order to avoid the consumption of too large amounts of EDC, rather small batches (1,5 g) were performed. This encountered sometimes problems when analysing the result, therefore some of the moisture absorption studies were performed after the samples were subjected to conductiometric titration (total charge analysis). This is valid for the 1% BTCA birch pulp amidated with heptyl amine and ethyl amine at different pH. For the same pulp reacted with stearyl amine, the moisture uptake is a single measurement, there was not enough sample for a double measurement. For the benzyl amide there was no sample left at all for moisture uptake, but WRV is analysed.

Analyses

In order to determine the outcome of the reaction the total charge of the pulps were determined by an acid-base titration. An FT-IR analysis was also performed on some samples. Thin sheets of pulp were scanned in transition mode (32 scans at a resolution of 8 cm^{-1}) on a FTS 6000 FT-IR spectrometer (Varian Inc., Randolph, MA, USA) with a DTGS-detector.
The effect of cross-linking on moisture uptake was analysed at 95 %RH by placing the samples in a conditioned laboratory for 72 hours and then determine the mass change.
The water retention of the reacted pulp was investigated by a modification of the standard SCAN-C 62:00 to suit small samples (30-50 mg).. The samples were centrifuged at 3000g for 15 min before the water content was determined gravimetrically.

3 Results and discussion

Cross linking of pulp fibres using buyl tetra carboxylic acid will increase the amount of carboxylic acid functionality in the cell wall. The amount of acidic groups in untreated material range from about 100-150 mmol/g for unbleached pulp down to around 40 mmol/g in fully bleached pulp. In our case the unbleached pulp contained about 130 mmol/g acidic groups while the birch pulp contained about 60 mmol/g pulp, as summarized in table 2. In the table the amount of acidic groups before and after a cross linking step (in 1% BTCA solution) are given. Several interesting observations can be made: the treatment led to a four to sevenfold increase in the amount of acidic groups in the pulp (batch 1 to 5). Even higher amounts were introduced when the BTCA concentration was increased to 2%, as presented in table 3. A rather large spread in the amount of introduced charge can be observed. The charge was largelly introduced inside the cell wall rather than on the surface.

Table 2. Example of the amount of charge introduced by BTCA cross linking of a laboratory made unbleached spruce pulp and one fully bleached industrial birch pulp.

Prov	Total Charge	Surface charge	Total introduced charge	Introduced surface charge	COOH Inbunden	Ratio surface/total charge (%)
Spruce (ref)	128	2,3	-	-	-	**1,80%**
Batch1	849	8,5	721	6,2	714,8	**1,00%**
Batch2	522	7,1	394	4,8	389,2	**1,36%**
Batch3	591	10,7	463	8,4	454,6	**1,81%**
Batch4	532	7,1	404	4,8	399,2	**1,33%**
Batch5	642	7,9	514	5,6	508,4	**1,23%**
Batch5 1)	556	3,8	428	1,5	426,5	**0,68%**
Birch (ref)	63	-	-	-	-	-
Birch BTCA	383	-	320	-	-	-

1) not freeze dried

After the cross linking the introduced acid groups are in protonated form so one possible route to furher change the properties of the fibres is to substitute the proton with another counter ion. Prior tests indicated that the effect of going from proton form to Sodium, Calcium and Aluminum form had little effect on moisture and water uptake. Therefore, we wanted to try counter ions carrying larger side groups. One family of positively charged compounds suitable for this is quartenary ammonium salts. Initially we wanted to test the viability of this idea and several commersially available salts were chosen, see table 1.

The results, figures 1 and 2, indicate that in some cases the ion exchange resulted in decreased moisture and water uptake. In all five testes were performed – two on industrial softwood pulp (performed before and after hammer milling, one laboratory made softwood and two on bleached hammer milled birch pulp. All cross linked samples showed decreased water uptake. Results from salts not giving reduced wrv are not shown. As is seen in the figure the general trend is that a further reduction in wrv was observed for samples treated with octacecyl trimethyl ammonium bromide and trtraoctyl ammonium chloride.

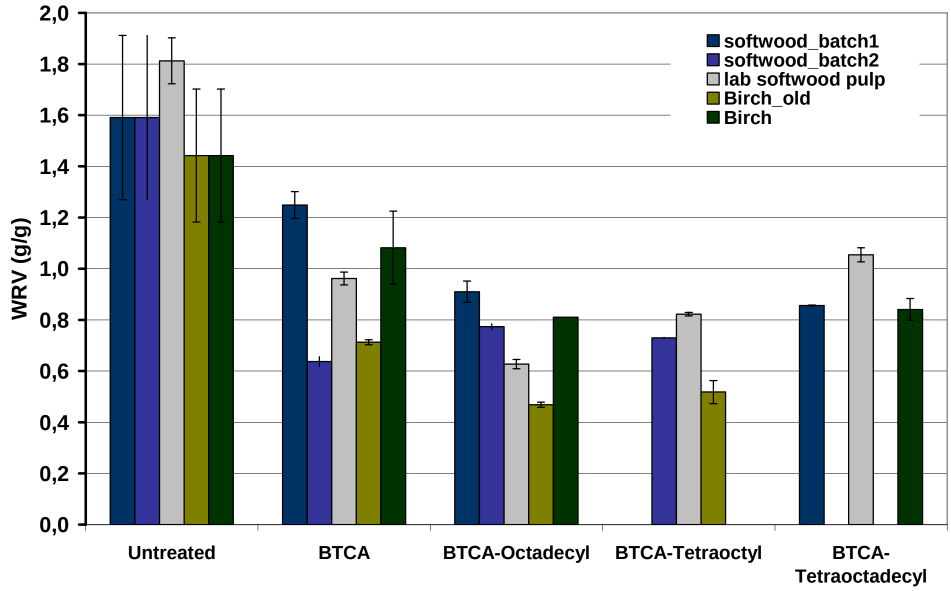

Figure 1. Determined water retention values for a number of pulps treated with quaternary ammonium salts.

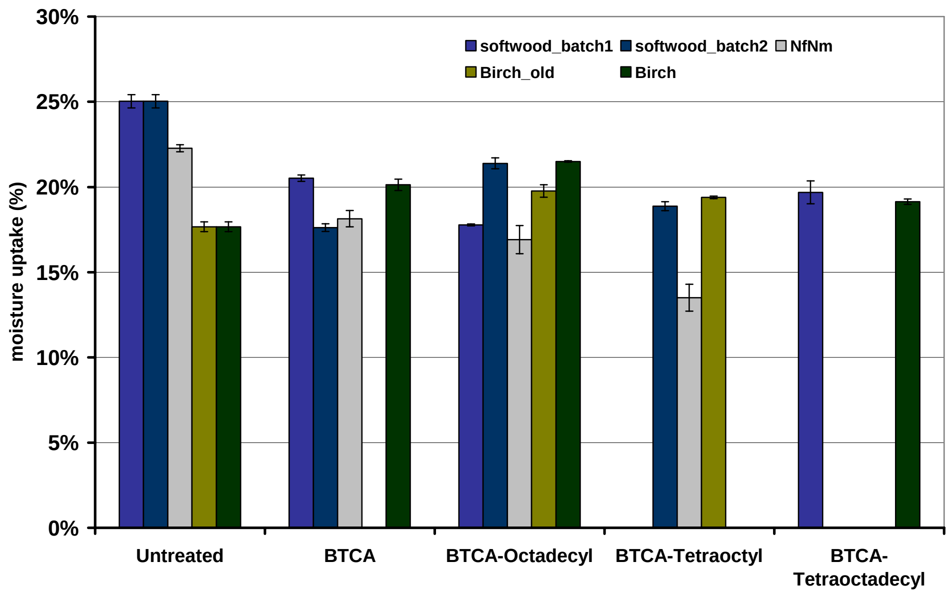

Figure 2. Determined moisture uptake of samples treated with quaternary ammonium salts.

Carbodiimide treatment

Carbodiimides can be used as activators of carboxylic acid functionalities (Hermanson 1996). This has been used to block carboxylic acid groups in pulp (Kitaoka 1995). The activated carboxylic group is susceptible to attack from electron donor groups, see scheme 1. In our case we have used primary amines. This make it possible to attach a hydrocarbon chain or other group to the carboxylic acid under very mild conditions. The change in charge of the cross-linked pulps was used as a measure of the successfulness of the reaction. As can be seen in table 3, most of the introduced groups by the BTCA treatment were reacted in the amidation reaction (the charge decreased to the level of the untreated pulps).

Scheme 1. Activation of carboxylic acid using carbodiimides(*N*-(3-Dimethylaminopropyl)-*N*'-ethylcarbodiimide). Rt=room temperature

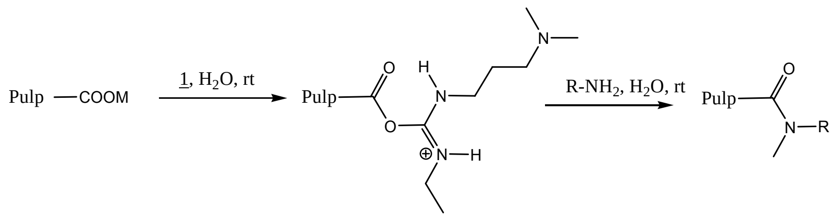

Table 3. Total fibre charge of reference pulps and amidated pulps.

Sample	total fibre charge (μekv/g)
Bleached birch pulp	63
1% BTCA birch	383
Heptyl amine	83
Ethyl amine pH 5	154
Ethyl amine pH 6	108
Ethyl amine pH 7	108
Ethyl amine pH 6 + salt	111
Stearyl amine	111
2% BTCA birch	974
Bleached hardwood pulp	92
2% BTCA hardwood	849

Another way of analysing the performance of the reaction is FT-IR spectroscopy. In figure 3 spectra of a reference birch pulp, a BTCA cross-linked birch pulp and a heptyl amide pulp can be seen for the region 1500 – 1800 cm^{-1}.

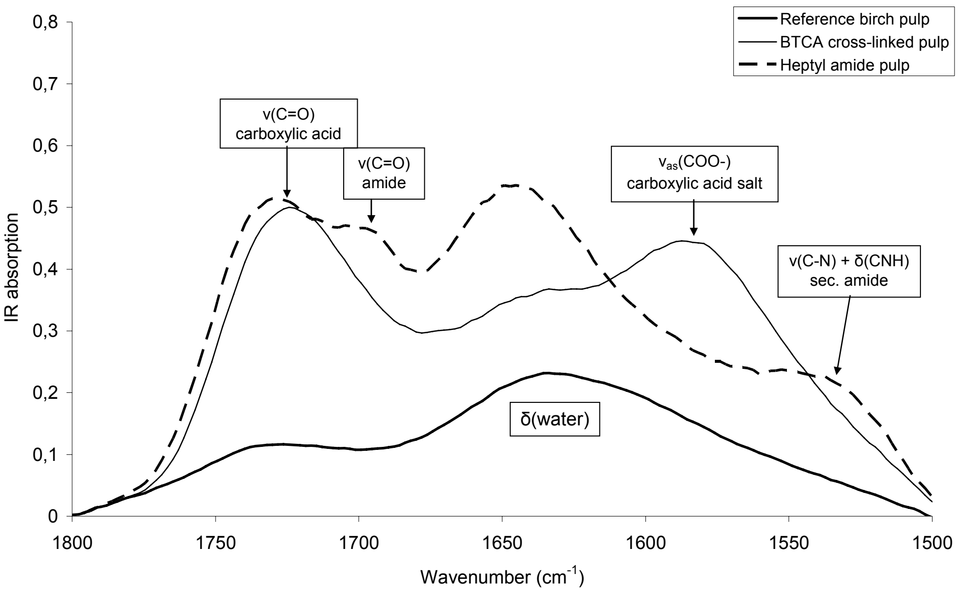

Figure 3. FT-IR spectra of the reference pulps and one amidated pulp.

From the characteristic vibrations of the carboxylic acid and the amide group the reaction steps can be followed. First the introduction of carboxylic acid groups can be seen for the BTCA pulp at wavenumbers 1590 and 1725 cm^{-1}. After the amidation step the appearance of the amide I band at 1695 cm^{-1} and the amide II band at 1540 cm^{-1} can be seen. Except for the reference pulps, following amidated pulps were analysed with FT-IR: heptyl amine, ethyl amine (4 pulps with different pH) and benzyl amine. In all cases the peak from the acid salt disappeared after amidation and the amide bands appeared instead.

Moisture uptake

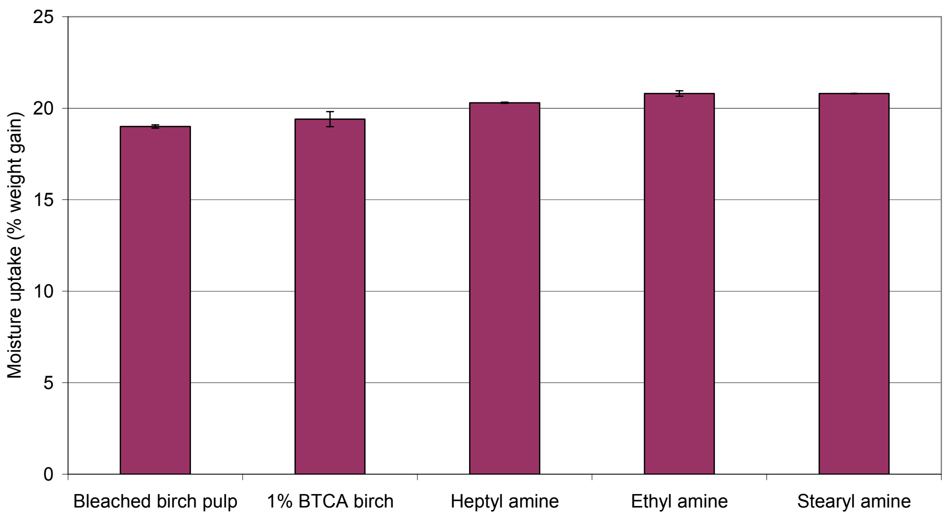

Figure 4. Moisture uptake of amidated pulps and the birch reference pulps.

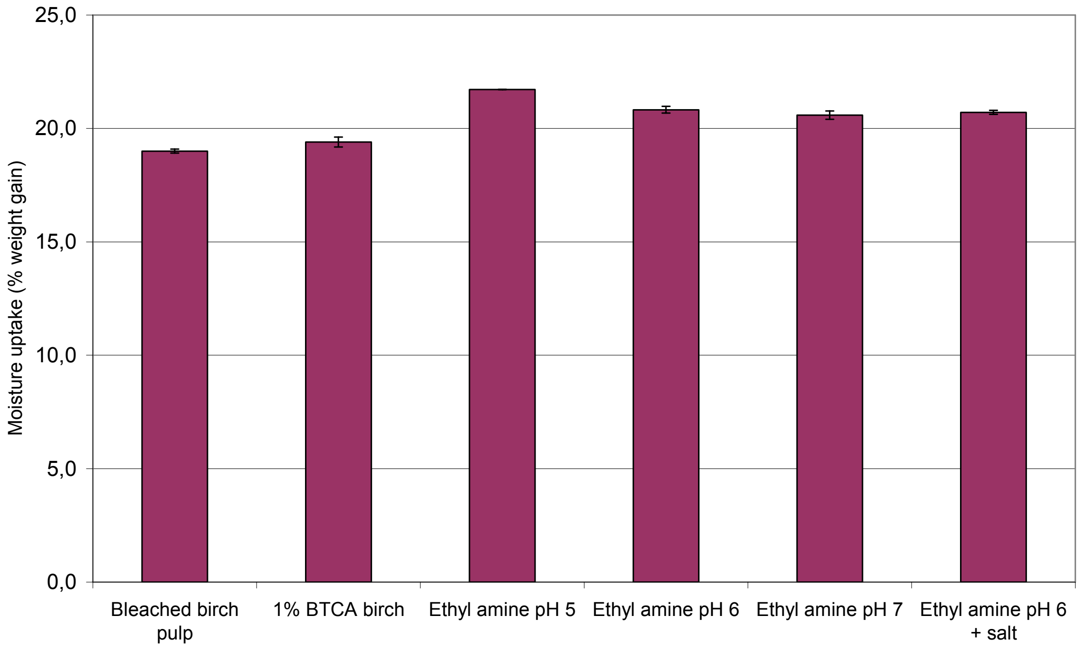

Figure 5. Moisture uptake of ethyl amidated pulps at different experimental conditions.

The effect of pH on the reaction was investigated and the results can be seen in figure 3. It shows no effect of pH between pH 5 and 7.

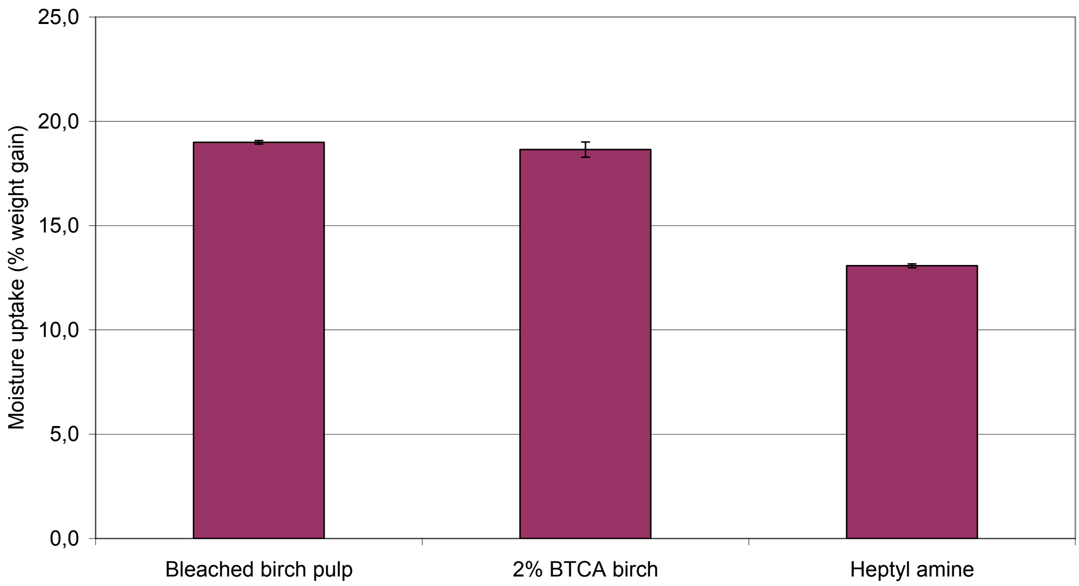

Figure 6. Moisture uptake of the birch pulp (pulp C) cross linked with a larger amount of BTCA (2%) and its heptyl amide.

For both pulps cross-linked with 2% BTCA (Figs 4 and 5) a small decrease in moisture uptake can be seen, which is further decreased by the amidation with heptylamine.

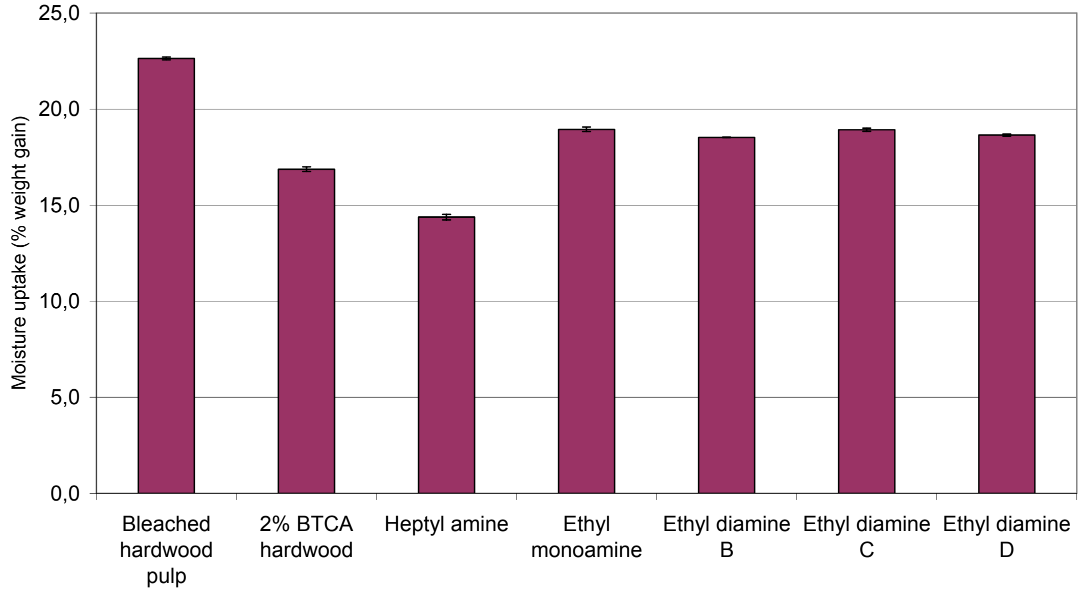

Figure 7. Moisture uptake of the "never dried" hardwood pulp (pulp D), the cross linked pulp and its different amide products.

In figure 5 it is shown that, as expected, the heptyl tail has a better influence on moisture uptake than the ethyl group. The difference between mono- and diamines were also studied (Figure 5). This seems not to effect the moisture uptake. There is yet no data from charge or nitrogen analysis on these samples to confirm the completion of the reaction.

Water retention

Generally speaking the effect of the amidation reaction was larger on water retention compared to moisture uptake. Partly this result might be a result of the way the moisture measurements were performed, see experimental.

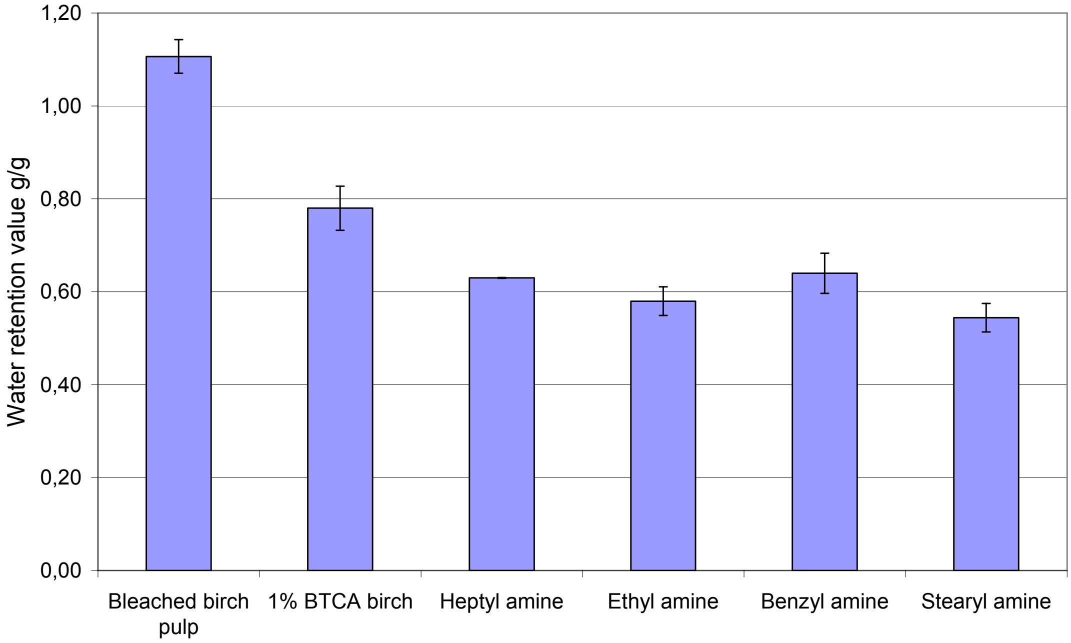

Figure 8. Water retention values of amidated pulps ant the birch reference pulps

No large difference in water uptake between cross linked fibres treated with different amines was observed, figure 8. However, compared to the cross linked fibres a further reduction in water uptake was observed. In the literature the pH of the reaction is claimed to have some impact on the effectiveness of the reaction and this was tested, figure 9. The effect of pH was in our case weak.

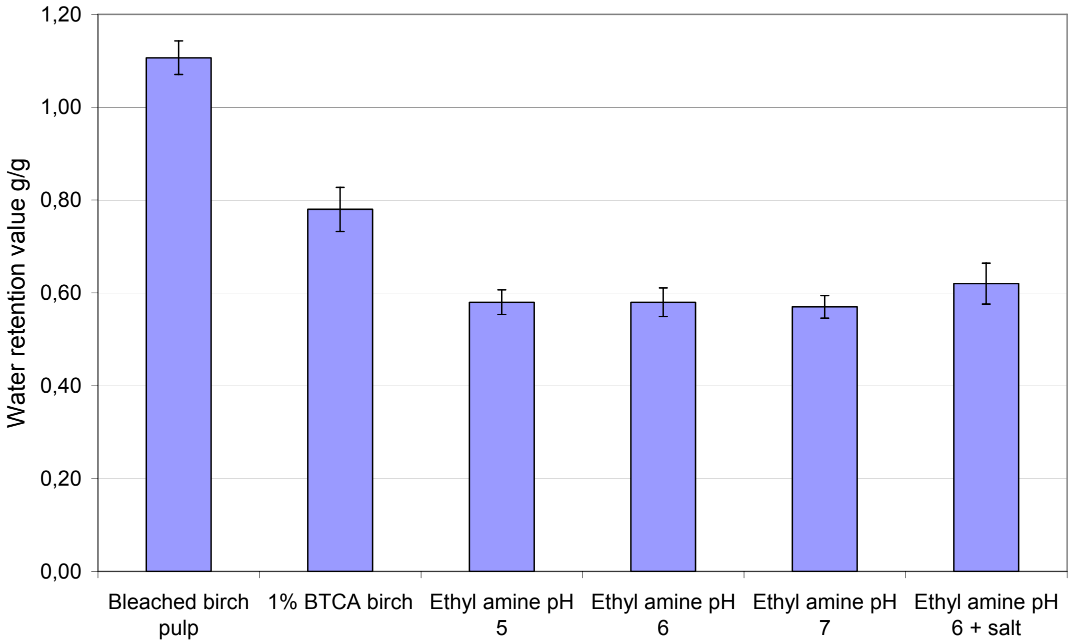

Figure 9. Water retention values of ethyl amidated pulps at different experimental conditions.

Also, the addition of salt (NaCl) was suggested in the literature (Hermanson 1996). In our case salt seem to have a small effect on water retention, figure 9.

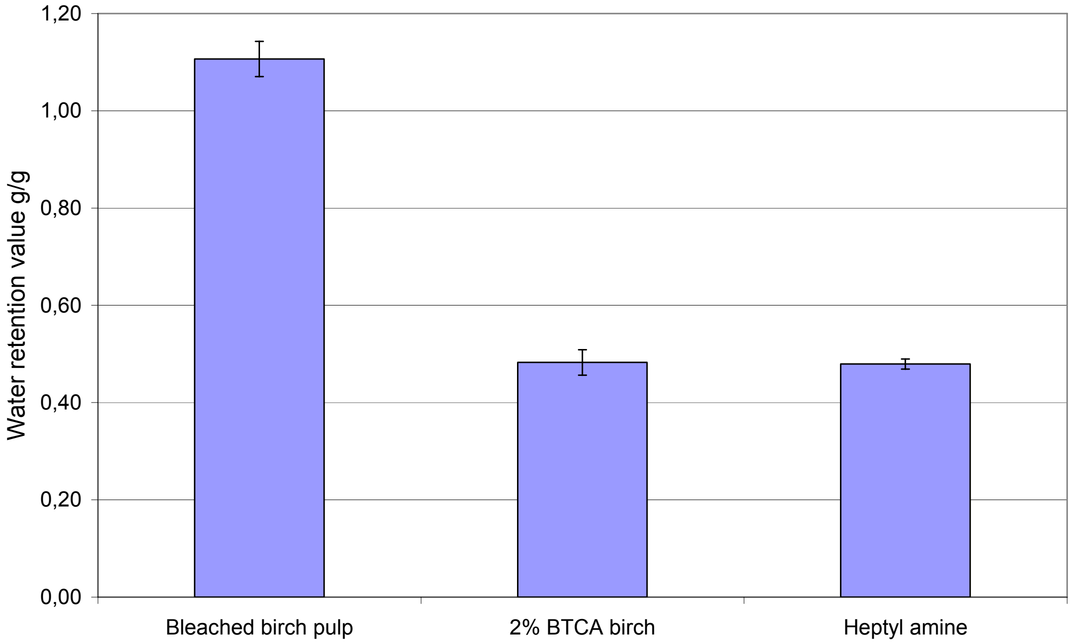

Figure 10. Water retention values of the birch pulp crosslinked with a larger amount of BTCA (2%) and its heptyl amide.

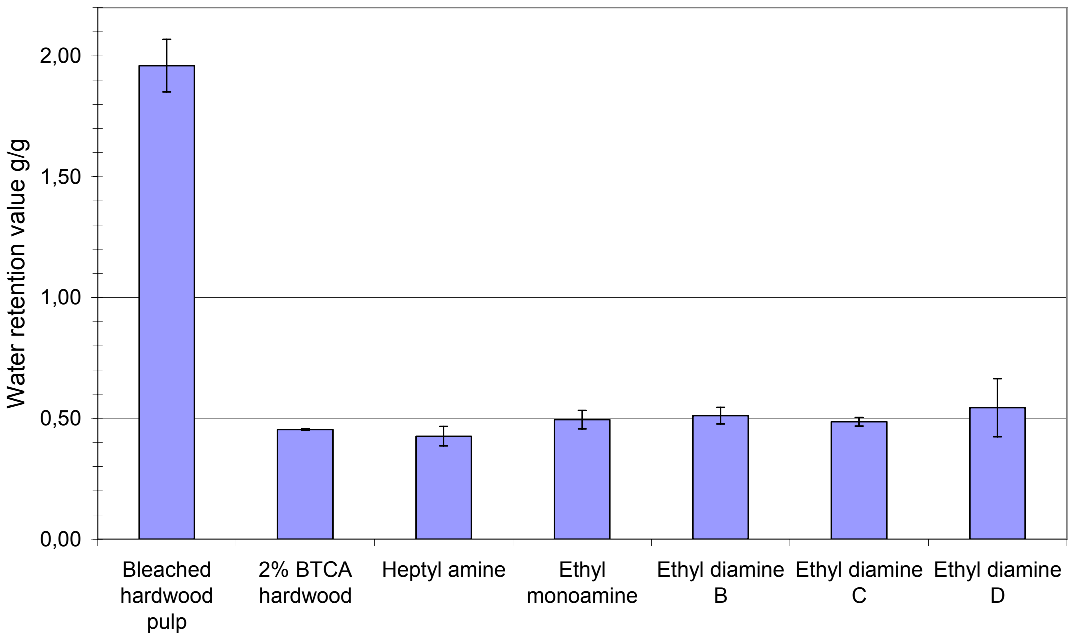

Figure 11. Water retention values of the "never dried" hardwood pulp, the crosslinked pulp and its different amide products.

In figure 11 results from amidation of a pulp treated with 2% BTCA solution are shown. The amount of carboxylic acid functionality was in this case increased compared to earlier studied pulps (table 3). Again, the BTCA cross-linking had a larger effect on water retention than moisture uptake. we can see that the amidation has a larger effect on moisture uptake than water retention (2% BTCA), as illustrated in figures 6, 7, 11. Also, in figure 11 results from the use of a di-amine are shown. The idea was to see weather we could achieve further cross linking using this approach. At the moment we are waiting for analytical results.

There are the moment no charge density analysis of the amidated pulps cross linked with 2% BTCA.

4 Conclusions

This report present results from ongoing activities and no final conclusions can therefore be drawn at this time.

The idea behind the use of quaternary ammonium salts was to substitute the counter ions present in the pulp with moieties carrying hydrophobic functionalities. A number of commercially available salts were screened and based on the results from this screening two candidate salts has been selected: Tetraoctylammonium chloride and Octadecyltrimethylammonium bromide. Both these salts were able to reduce water uptake (measured as WRV) relative to cross linked reference samples. The effects on moisture uptake was more difficult to analyze. In most cases the effect was less pronounced compared to what was seen under wet conditions and in some cases we even observed increased moisture uptake after treatment.

Based on the results so far produced the amidation of carboxylic acids can be a method for further stabilization of pulp. This work was tested on two fully bleached hardwood pulps. One was a birch pulp supplied from Sustainpack and one was a never dried bleached industrial hardwood pulp. Of the tested primary amines heptyl amin showed the best effects and both moisture and water retention values were reduced compared to the cross linked reference. In the case where 2% BTCA solution was used in the cross linking step already the BTCA treated pulps had very low water retention values. This indicate that the pulp fibres have a radically reduced inner surface and the penetration of active chemicals during the derivatization step was in all likelihood quite poor. Nevertheless, a small further reduction in moisture uptake was still observed.

5 Future activities

The behaviour of surface active molecules under dry and wet conditions are very complex, e.g. they can be associated with a surface in a number of ways. In order to gain better knowledge and understanding of observed effects, more careful studies of the adsorption of and interaction between these structures and cellulose are needed.

The amidation of carboxylic acid functionality worked well, especially considering that the modified fibers were heat treated during the cross linking step. At this stage it is also of interest to evaluate the effect of these modifications on fiber mechanical properties and debonding properties. In order to do this we want to produce enough fibres to be able to produce test sheets. If a successful method is achieved, an upscale of the modifications in order to produce composite material would be of interest. As an alternative to modification of introduced functionality we would also like to study the possibility to directly oxidize the fibres in order to produce carboxylic acid functionality. This would enable us to do the amidation on a material that can contain high amounts of acid groups and that is in a never dried state. Such pulp is also of interest when pursuing alternative heat treatment strategies.

6 References

Hermanson G. T., (1996) in " Bioconjugate techniques", Academic press
Kitaoka T., Isogai A., Onabe F., Nordic Pulp Paper Res. J., 10(4)(1995)253