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**Sustainpack**

**Innovation and sustainable Development in the Fibre Based  
Packaging Value Chain**

Instrument: **IP**

**D5.28. Improved dimensional stability of pulp fibres to be used in 3D  
thermoplastic composites**

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<b>PU</b>	Public	X
<b>PP</b>	Restricted to other programme participants (including the Commission Services)	
<b>RE</b>	Restricted to a group specified by the consortium (including the Commission	
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Revision [0]

## 1 Introduction

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The aim of this activity was to develop methods for treatment of pulp fibres in order to make them more stable against water and moisture uptake. When selecting solutions to this problem, economical feasibility of investigated methods has been of importance. The main effort has been to combine a cross-linking step with high temperature treatments.

The goal has been to further decrease both water and moisture uptake relative to the fibres of the first generation of fibers and based on the results presented herein a second generation of dimensionally stabilized fibres will be produced.. Both controlled water content during heating, high temperature treatments, salt treatments and alkaline treatments has been investigated.

## 2 Experimental

The following pulps was used in this study: a laboratory made unbleached sulfate pulp, pulp A (kappa (34), a commercial unbleached sulfate pulp, pulp B (kappa 34) and a bleached industrial hardwood pulp (pulp C) supplied by University of Oulu.

### *BTCA treatment*

Approximately 500 g (dry weight) pulp (pulp B) was beaten (2000 rev) at a consistency of 3% (w/w). The pulp was washed once with deionised water and thereafter swelled in 0.02 M NaOH over night. The pulp was washed three times with deionised water to remove NaOH. The pulp was divided into batches of about 70 g fibers that were immersed in 4.5 L BTCA-solution (= consistency 1.5%). The BTCA solution contain 1 % BTCA and 1% NaHPO<sub>4</sub>. The samples were left to soak for 1.25 hours using a vacuum/no vacuum cycle. The solution was removed by filtration and the pulp was dried at room temperature.

Prior to the curing the pulp was put in 40 °C to remove the last water. Curing was performed for 30 minutes at 150 °C. To remove the excess BTCA, cured fibers were washed: first the pulp was beaten at 2 000 rev and thereafter let to stand for 2 hours, washed with deionised water and beaten a second time. The extra beating step was made because of high amounts of knots. Two washing steps were performed after which the pulp was dried in room temperature. Pulps A and C were treated in a similar way as described above.

Table 1. Total carboxylic acid content in tested fibres before and after BTCA treatment. ( $\mu\text{mol/g}$  pulp)

Fiber type	-COOH untreated	-COOH BTCA treated
Laboratory softwood (pulp A)	130	590
Industrial softwood (pulp B)	110	240
Industrial birch (pulp C)	63	380

Sheets with a grammage of 100 g/m<sup>2</sup> were made on a dynamic sheet former. Heat treatment of the sheets was made in a heated lab press, both with and without applied pressure. Four temperatures (200°, 225°, 250° and 300° C) were tried out in combinations with different times (5s, 10s and 30s). Also a 5 minutes sample in 200 °C was made. The sheets were cut into strips with a width of 1.5 cm prior to the pressing/heating.

### *Alkaline extraction*

About 20 g unbleached industrial softwood sulfate pulp (pulp B) was immersed in 10% NaOH for 20 minutes. Thereafter half the pulp was transferred to a solution containing 18% NaOH and extracted for an additional 20 minutes. The extractions were made at 21°C. The pulps were put in deionised water over night, together with a sample of Skärblacka pulp that would serve as reference sample (only water washed). After washing

the pulps were allowed to dry under ambient conditions. BTCA treatment of extracted pulps were performed as described above.

#### *Salt treatments*

Pre-washed Skärblacka pulp was beaten at 2 000 rev. The water was removed by filtration. The pulp was thereafter put in 1%  $\text{ZnCl}_2$  (~pH 3), 1%  $\text{Al}_2(\text{SO}_4)_3$  (~pH 5) or deionised water during stirring. The pulp was recovered by filtration and thereafter air dried. The dry pulp was put in a pre-heated oven at 160 °C or 120 °C for 48 hours. After this time the catalyst-treated pulp samples exhibited a discoloured surface. The likely explanation for this is that salt is transported to the surface of the sample during drying, resulting in high local concentrations in the surface layer.

#### *Acidification of pulp*

The effects of hornification was evaluated under different moist content (25 % and 50%) and pH (pH 3 and deionised water). The pulps where first soaked in either dilute acid (HCl) or deionised water and thereafter filtered with a büchner funnel. The desired moisture content was achieved by letting the pulp air dry in the case of 50% moisture content, and drying in 97% RH in the case of 25 %. The pulps were thereafter put in closed containers in 150 °C for 1 hour and with open lid in the same temperature for an additional hour.

#### *Analysis*

The thickness was measured on an STFI thickness measurement apparatus, but due to problems with the feeding, five points were measured and an average of these values was used. Tensile testing was performed in the MD direction. Standard strips (13\*1,5 cm) were cut from large pressed samples. the tensile properties were determined using an Alvetron TH (Lorentzen o Wettre) standard tensile tester. The gauge length was 10 cm and testing speed 1%/min.

Water and moisture uptake were analysed by moisture adsorption (95% RH) and water retention value (WRV) respectively. Before samples were put in the humid chamber they were put in enclosable containers and dried in 40 °C. The weight increase was recorded on a precision scales. During moisture uptake measurements it was observed that the conditioned vessel was leaking (an RH of about 93% was recorded). However, the results from these measurements can be used for the purpose of comparing the effect of different treatments.

WRV-measurements where performed using the mini-WRV method. However, when the pulp was extremely difficult to beat, only let to stand in deionised water for 3.5 hours before measurement.

The carboxylic acid content of treated fibres was determined in accordance with SCAN-CM65.

### 3 Results and discussion

In an earlier phase of this project different methods to induce hornification was tested. These experiments were all performed at temperatures below 130°. It was thus of interest to see what effects could be achieved at higher temperatures. In this study we looked at the effects of temperatures between 200°C and 300°C. It is well known that such treatments can have a strong effect on the water-pulp fibre interaction (Back 1967, Lyne et al. 1950). The hornification process is to a large part reversible and one main reason for treating the fibres at higher temperatures is to induce cross-linking reactions (auto crosslinking) thus making the achieved stabilization more irreversible in nature. This kind of auto cross-linking reactions has been suggested as responsible for stabilization of fibers treated at high temperatures (Back 1967). Of primary interest is to investigate to what extent we will be able to influence the properties of composites rather than fibres. Therefore the experiments were performed in order to chose the best methods for the production of larger amounts of fibers that can be used in composite production. Because cellulose is susceptible to degradation at temperatures above 200°C, used treatment times were short, between 5 and 30 seconds (in some cases longer). In order to treat fibres for so short periods of time a heatable pressing equipment was used. The pulp was introduced either as dried pulp (experiment 1) or in sheet form (experiment 2 and 3). After pressing/heat treatment the pulps were very difficult to re-slush and due to this it was difficult or even not possible to determine WRV of treated fibers. Both normal and BTCA cross-linked fibres were tested.

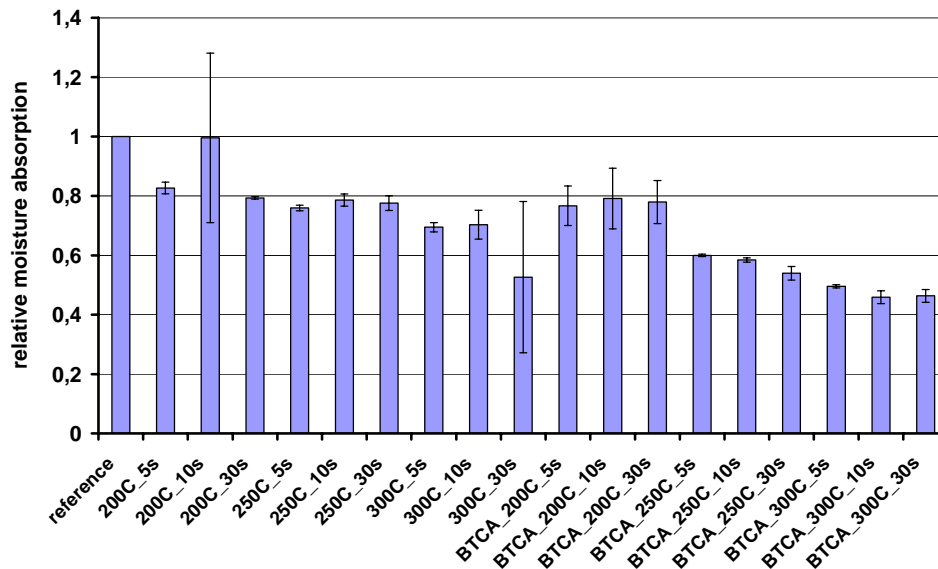


Figure 1. Results from experiment 1. Effects of heat treatment on the relative moisture uptake measured at 95% RH, 21°C. The absorption is related to the absorption of untreated fibers. The treated pulp was a laboratory made unbleached softwood pulp (pulp A). The treatment was performed directly on pulp.

Figure 1 depicts the effect of different heat treatments on pulp. We can see that already a treatment at 200°C for 5 seconds will decrease the moisture uptake of treated fibres. Typically untreated pulp would take up 21-22% water while BTCA cross-linked fibres would take up around 15-17%. When comparing cross-linked and normal fibres we do not observe any difference at this temperature (200°). When going from 200°C to 300°C a slight decrease in the ability to absorb moisture was observed for the untreated fibres. For BTCA cross-linked fibres the effect was much more dramatic and the moisture uptake is halved. The low absolute moisture uptake values recorded in this experiment is probably a little too low because of a leakage in the conditioned chamber. However, all samples were measured at the same time and comparison between treatments are thus possible.

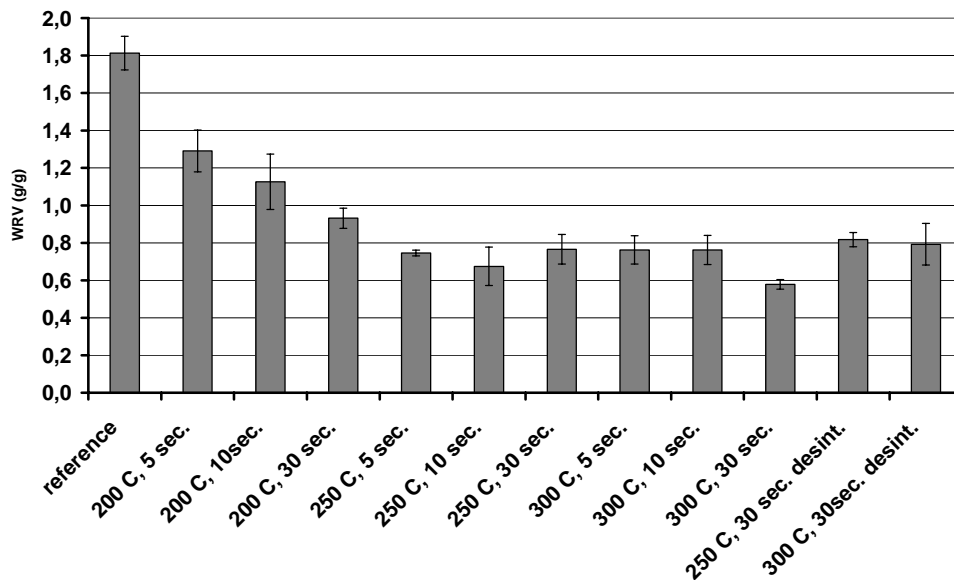


Figure 2. Determined WRV values of heat treated pulp (pulp A) samples. Samples were difficult to re-slush and a further disintegration of samples were tested (denoted desint. in the figure). BTCA cross-linked samples were even more difficult to re-slush and no WRV measurements were therefore attempted on these samples.

Figure 2 show the water uptake of pulp samples after a heat treatment. It is evident that treatments at 250 and 300°C decreased the uptake more than a treatment at 200°C. However, the effect on gain from 250 to 300°C was small. These samples became very dense after the treatment and they were difficult to re-slush. In the case of cross-linked samples, impossible without severe degradation of the samples. Therefore WRV values were only determined for non cross-linked samples.

In the experiment discussed above (experiment 1) the mechanical properties of treated samples were not determined. A second set of experiments were therefore performed in order to determine the effect of high temperature treatment on mechanical properties. A never-dried industrial unbleached softwood pulp (pulp B) and a fully bleached hardwood pulp (pulp C) were used. These pulps were first crosslinked and then hammer milled in

order to separate fibres. Standard test sheets were made from the hammer milled pulps. As is seen in tables 1 and 2 we achieved reduced moisture uptake. Because the pulps were to be used in composite production as well, the crosslinking was performed on 400-500 g pulp. Due to problems with drying and heat treatment of pulp on this scale this might have resulted in lower levels of reaction and thus less stabilization. As is seen in tables 1 and 2 the untreated pulps had very low moisture uptakes. The reason for this is probably that these pulps were repeatedly re-slushed and dried and thus became hornified. This can also lead to poor penetration of the cell wall and a less effective cross-linking. Contrary to what was observed in the first experiment the moisture uptake for both cross-linked and normal fibres decreased in a similar way, again suggesting poor cross-linking. The maximum reduction in moisture uptake was about 25%. For all samples mechanical properties were determined, see figure 3 and tables 1 and 2.

After the hammer milling step fibres were re-slushed in order to produce standard test sheets. A dramatic difference in mechanical properties was observed between sheets made using cross-linked and untreated fibres. We can also observe that the heat treatment did not further decrease the measured mechanical properties of the test sheets. This suggests that this type of heat treatment could be a viable method for the production of very stable fibres. However, it was observed that sheets treated at 300°C and even 250°C at longer times became quite brittle. A marked discoloration of the treated samples was also observed suggesting thermal degradation. It is also difficult to directly deduce fiber mechanical properties from sheet properties. Earlier results has shown that a BTCA treatment slightly decreases the zero-span value (Zhou et al., 1993). It thus remains to be tested if this type of heat treated fibre would contribute to composite mechanical properties.

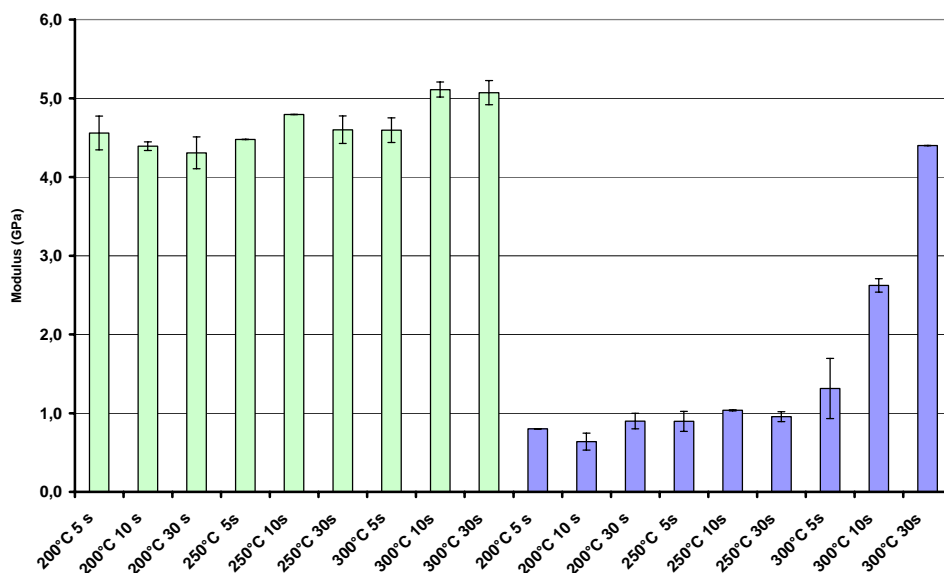


Figure 3. Measured Young's modulus of heat treated pulp B sheets (experiment 2). The sheets were heat treated under pressure. The Light bars – normal fibres, dark bars – cross-linked fibres.

Table 1. Determined mechanical properties and moisture uptake of unbleached softwood pulp treated at high temperatures

	conditions	Strain (%)	Tensile Strength (kN/m)	Tensile stiffness (kN/m)	Tensile stiffness index (MNm/kg)	Young's modulus (GPa)	moisture Uptake (%)
BTCA Not pressed	reference	0,80	0,49(0,02)	113,30(27,4)	1,0	0,2	17,4
	200°C 5s	0,87	0,53(0,03)	142,41(11,3)	1,31	0,26	19,1
	200°C 10s	0,68	0,53(0,03)	150,14(11,29)	1,38	0,28	17,6
	200°C 30s	0,60	0,50(0,10)	197,60(24,79)	1,82	0,37	17,5
	200°C 5min	0,88	0,62(0,02)	136,98(20,51)	1,26	0,25	18,2
	250°C 5s	0,85	0,58(0,03)	129,60(9,74)	1,19	0,24	17,2
	250°C 10s	0,76	0,55(0,02)	148,34(2,25)	1,36	0,28	17,3
	250°C 30s	0,86	0,57(0,05)	155,36(46,32)	1,43	0,29	16,7
	300°C 5s	0,88	0,61(0,03)	162,83(15,16)	1,50	0,30	15,3
	300°C 10s	0,73	0,56(0,06)	140,08(25,83)	1,29	0,26	15,2
	300°C 30s	0,94	0,65(0,02)	123,61(10,35)	1,14	0,23	14,6
BTCA Pressed	reference	0,80	0,49(0,02)	113,30(27,41)	1,04	0,21	17,4
	200°C 5s	0,73	0,72(0,05)	232,94(18,64)	2,14	1,43	17,7
	200°C 10s	0,78	0,55(0,03)	121,05(20,34)	1,11	0,64	16,4
	200°C 30s	0,64	0,55(0,03)	162,01(17,92)	1,49	0,90	13,4
	200°C 5min	0,75	0,55(0,09)	150,26(45,68)	1,38	0,82	16,0
	250°C 5s	0,77	0,65(0,07)	165,13(23,64)	1,52	0,96	16,7
	250°C 10s	0,76	0,60(0,02)	179,23(1,25)	1,65	1,04	17,3
	250°C 30s	0,63	0,57(0,05)	165,24(10,85)	1,52	0,91	15,7
	300°C 5s	0,59	0,74(0,15)	238,17(69,10)	2,19	1,53	14,2
	300°C 10s	0,40	0,93(0,02)	409,35(13,30)	3,76	2,78	14,1
	300°C 30s	0,43	1,73(0,25)	649,12(23,69)	5,97	4,63	12,5
No cross-linking Not pressed	reference	2,04	4,57(0,24)	699,88(12,15)	6,72	3,49	18,3
	200°C 5s	2,16	4,81(0,03)	741,19(21,94)	7,12	3,70	18,2
	200°C 10s	2,14	4,84(0,14)	758,53(9,70)	7,29	3,79	19,3
	200°C 30s	2,12	4,82(0,07)	719,36(7,62)	6,91	3,59	18,6
	200°C 5min	2,28	4,92(0,14)	720,30(8,74)	6,92	3,59	18,6
	250°C 5s	2,05	4,94(0,03)	748,96(15,09)	7,19	3,74	18,5
	250°C 10s	2,08	4,98(0,12)	740,17(5,60)	7,11	3,69	17,8
	250°C 30s	2,17	5,39(0,23)	792,08(36,61)	7,61	3,95	17,5
	300°C 5s	2,01	5,57(0,05)	793,80(6,03)	7,63	3,96	16,6
	300°C 10s	2,02	5,52(0,18)	779,15(11,60)	7,48	3,89	16,0
	300°C 30s	1,51	5,34(0,02)	782,29(8,14)	7,51	3,90	14,3
No cross-linking Pressed	reference	2,04	4,57(0,24)	699,88(12,15)	6,72	3,49	18,3
	200°C 5s	1,66	4,49(0,54)	685,12(32,03)	6,58	4,56	17,9
	200°C 10s	1,67	4,71(0,41)	712,68(8,82)	6,85	4,39	17,1
	200°C 30s	1,81	4,64(0,30)	699,99(32,88)	6,72	4,31	18,5
	200°C 5min	1,50	4,42(0,22)	715,48(22,07)	6,87	4,36	18,4
	250°C 5s	1,99	5,13(0,32)	735,41(0,10)	7,06	4,83	17,2
	250°C 10s	1,76	4,93(0,08)	729,89(0,42)	7,01	4,73	17,1
	250°C 30s	1,62	4,74(0,16)	709,66(26,88)	6,82	4,37	17,7
	300°C 5s	1,63	5,41(0,31)	746,90(25,60)	7,17	5,10	15,5
	300°C 10s	1,55	5,11(0,21)	748,90(13,87)	7,19	5,20	15,7
	300°C 30s	1,37	5,02(0,36)	730,47(22,02)	7,02	5,52	13,7

Table 2. Determined mechanical properties and moisture uptake of bleached hardwood pulp treated at high temperatures

	conditions	Strain (%)	Tensile Strength (kN/m)	Tensile stiffness (kN/m)	Tensile stiffness index (MNm/kg)	Young's modulus (GPa)	moisture Uptake (%)
BTCA Not pressed	reference	0,46	0,29(0,03)	111,6(5,9)	1,1		15,6
	200°C 5s	-	-	-	-	-	15,8
	200°C 10s	0,34	0,33(0,07)	139,5(36,6)	1,4	0,4	14,9
	200°C 30s	0,27	0,25(0,03)	145,6(34,4)	1,5	0,4	14,8
	200°C 5min	0,38	0,36(0,09)	119,6(28,4)	1,2	0,3	12,7
	250°C 5s	0,42	0,37(0,01)	128,3(7,5)	1,3	0,4	14,2
	250°C 10s	0,43	0,41(0,09)	130,8(21,1)	1,3	0,4	13,5
	250°C 30s	0,36	0,35(0,06)	123,3(4,5)	1,2	0,4	13,4
	300°C 5s	0,41	0,31(0,07)	105,7(7,7)	1,1	0,3	10,2
	300°C 10s	0,33	0,24(0,00)	141,24(-)	-	-	11,4
	300°C 30s	0,33	0,18(0,00)	64,4(-)	0,6	0,2	10,1
	BTCA Pressed	reference	0,46	0,29(0,03)	111,6(5,9)	1,1	0,3
200°C 5s		0,30	0,29(0,01)	142,2(4,8)	1,4	1,0	16,8
200°C 10s		0,44	0,29(0,02)	102,9(13,5)	1,0	0,6	16,8
200°C 30s		0,44	0,24(0,03)	81,3(17,7)	0,8	0,5	14,9
200°C 5min		0,18	0,36(0,02)	222,9(95,9)	2,2	1,6	14,8
250°C 5s		0,32	0,37(0,10)	158,6(48,8)	1,6	1,1	14,9
250°C 10s		0,24	0,37(0,08)	182,9(29,5)	1,8	1,3	14,2
250°C 30s		0,23	1,16(0,30)	513,26(51,3)	5,2	4,3	11,9
300°C 5s		0,24	0,51(0,1)	270,6(125,4)	2,7	2,1	12,2
300°C 10s		-	-	-	-	-	12,0
300°C 30s		0,29	1,12(0,14)	453,1(36,2)	4,6	4,2	14,6
No cross-linking Not pressed		reference	1,10	3,80(0,14)	766,7(10,1)	7,6	5,0
	200°C 5s	0,99	4,00(0,05)	786,3(6,8)	7,7	5,2	15,5
	200°C 10s	-	-	-	-	-	14,8
	200°C 30s	1,08	4,03(0,09)	788,7(9,9)	7,8	5,2	14,5
	200°C 5min	1,11	4,28(0,05)	830,3(2,3)	8,2	5,5	14,9
	250°C 5s	0,94	3,93(0,17)	782,2(31,3)	7,7	5,1	16,0
	250°C 10s	1,04	4,01(0,13)	810,4(2,1)	8,0	5,3	15,3
	250°C 30s	1,04	4,00(0,03)	783,1(11,9)	7,7	5,1	14,3
	300°C 5s	0,94	4,15(0,02)	801,3(1,7)	7,9	5,3	11,9
	300°C 10s	0,95	4,06(0,26)	786,0(35,9)	7,7	5,2	13,6
	300°C 30s	0,52	3,22(0,43)	793,6(13,6)	7,8	5,2	10,3
	No cross-linking Pressed	reference	1,10	3,80(0,14)	766,7(10,1)	7,6	5,0
200°C 5s		0,54	2,9(0,07)	754,7(12,0)	7,4	5,8	17,4
200°C 10s		0,68	3,4(0,40)	779,1(22,0)	7,7	5,6	17,1
200°C 30s		0,97	4,0(0,01)	812,0(13,2)	8,0	5,7	17,2
200°C 5min		1,06	4,0(0,05)	785,2(18,7)	7,7	5,7	15,3
250°C 5s		1,00	3,8(0,10)	767,9(26,1)	7,6	5,6	16,5
250°C 10s		1,11	4,0(0,17)	762,1(20,9)	7,5	5,8	15,3
250°C 30s		1,00	3,8(0,16)	747,6(13,1)	7,4	5,8	14,3
300°C 5s		0,73	3,7(0,47)	825,5(20,0)	8,1	6,3	12,9
300°C 10s		0,56	3,1(0,40)	860,5(3,03)	8,5	7,0	13,1
300°C 30s	0,38	2,5(0,53)	749,0(24,3)	7,4	6,3	12,3	

At 300°C a significant increase in stiffness of sheets made from BTCA treated sheets were observed, figure 3, indicating interfiber cross linking. A similar effect was also observed for the normal fibres but to a lesser extent.

Due to the dramatic increase in brittleness a third experiment were performed where the effect of treatments at 200-225°C was studied. Pulp A sheets were placed in the heated pressing equipment without applying any pressure. In order to compensate for the lowered temperature the treatment time was increased to 4 and 10 minutes. As is seen in table 3 a clear reduction of moisture uptake was observed already after 4 minutes at 225°C. The effect when going from 4 to 10 minutes were quite small. The effect was smaller when samples were treated at 200°C. The effect of washing out of unreacted BTCA and catalyst prior to the heating step was studied and as is seen in the table heat treatments of unwashed samples were somewhat more effective. The presence of catalyst might promote auto-crosslinking reactions, see more below. A further reduction of moisture uptake of 20% was seen when comparing untreated and BTCA crosslinked fibres treated at 225°C, 4 minutes.

Relatively small effects on the tensile properties were observed as a result of these treatments. However, a small further reduction in sheet strength was observed for BTCA treated samples if the catalyst were present during the heat treatment. Increased brittleness was observed in all samples. Higher temperature and treatment time both had a negative effect on the mechanical properties. Compared to samples treated at higher temperatures the brittleness was much less pronounced however and if a high degree of moisture stability is important this type of treatment might be one possible route.

Table 3. Sheet properties of samples heat treated in experiment 3.

	Young's modulus (Gpa)	Tensile strength (kN/m)	strain at break (%)	moisture uptake (%)
<b>Ref pulp</b>	8,9(0,5)	6,6(0,3)		22,0
4 min 200dg	5,9(0,6)	7,7(0,5)	1,8(0,1)	16,9
10min 200dg	6,7(0,2)	8,2(0,2)	1,5(0,1)	15
4min 225dg	6,4(0,2)	8,6(0,4)	0,8(0,1)	15
10min 225dg	7,9(0,2)	8(0,2)	1,3(0,05)	14,2
<b>BTCA</b>				
4 min 200dg	6,7(0,2)	9(0,3)	1,3(0,1)	16,2
10min 200dg	7,2(0,3)	7,1(0,3)	1,0(0,1)	13,6
4min 225dg	6,1(0,4)	4,8(0,3)	0,5(0,05)	11,8
10min 225dg	11,6(0,2)	5,9(0,3)	0,5(0,05)	11,6
<b>BTCA washing</b>				
4 min 200dg	6,4(0,1)	7,9(0,8)	1,2(0,1)	13,2
10min 200dg	6,7(0,1)	7,8(1,6)	1,2(0,3)	13,4
4min 225dg	6,2(0,2)	6,5(0,8)	0,9(0,1)	12,5
10min 225dg	10,2(0,4)	6,5(0,8)	0,6(0,05)	12,4

The increased dimensional stability achieved after heat treatment at higher temperatures has been explained as the result of auto-crosslinking reactions involving carbonylic functionalities present in the fiber (Back 1967). In a study by Cohen (Cohen et. al 1959) it was shown that the stabilization using heat treatment could be further enhanced if the sample was treated under acidic conditions or in the presence of certain salts. The effect of acid treatment was tested by treating samples with dilute HCl (pH 3). After adjustment of the moisture content to either 25 or 50% the samples were placed in closed containers and treated at 150°C for 60 minutes. After this the containers were opened and the samples were left for 60 minutes at 150°C. Figure 4 show the effect on moisture uptake measured after 24 h at 95 %RH, 21°C. Under the investigated conditions a reduction in moisture uptake of about 25 % was observed for all cross linked samples. No extra stabilization resulting from the acidic treatment were observed and for the reference samples the acidic conditions even led to decreased stabilization.

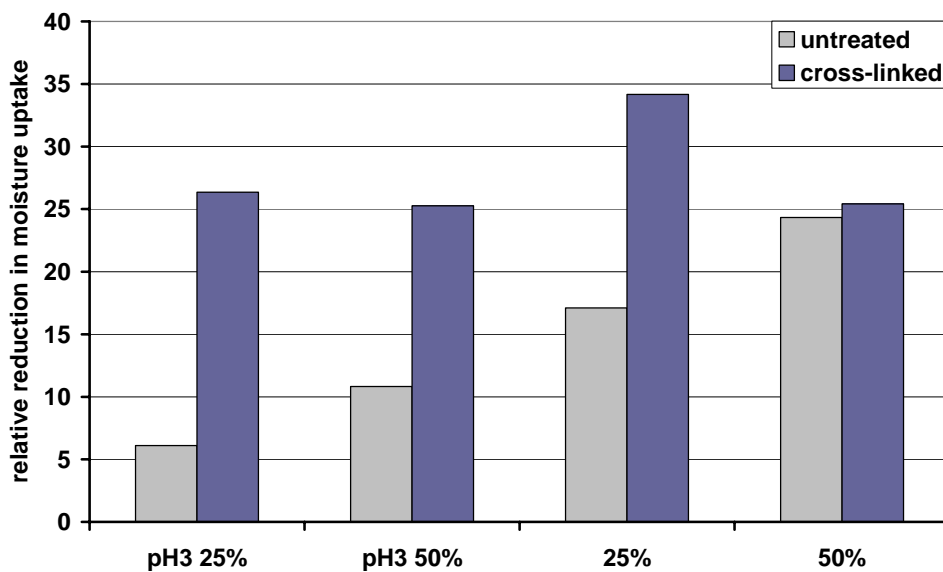


Figure 4. Observed reduction in moisture uptake of untreated and BTCA cross-linked pulp B samples caused by hornification under controlled conditions. The moisture uptake values are calculated relative to non-hornified untreated fibres and cross-linked fibres respectively. Prior to the heat treatment the moisture content of the samples were adjusted to 25 or 50% by drying at 40°C..

For water uptake the acidic treatment had a small positive effect, figure 5, compared to when the hornification was made on neutral samples. Normally cross linking stabilize the fibres more against water uptake than hornification. This suggest that the BTCA treatment in this case was less effective probably as a result of the scale of these treatments (about 500 g).

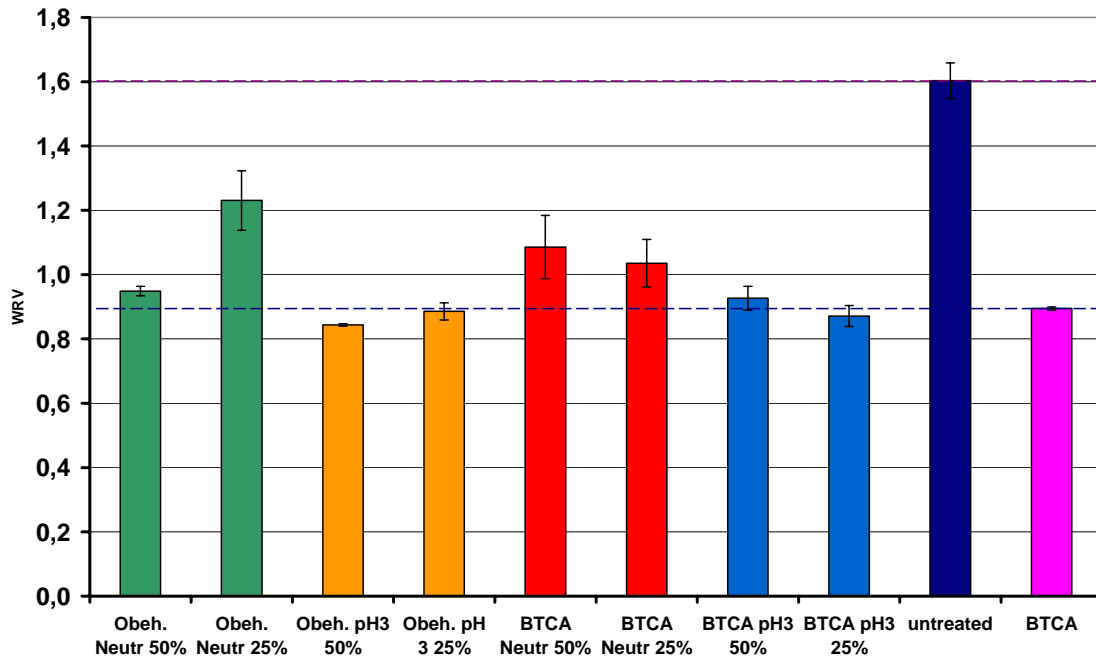


Figure 5. Determined WRV of pulp B samples treated at controlled humidity and under acidic conditions.

Based on the reported results from heat treatments in the presence of different salts (Cohen et. al 1959) we studied the effect of catalyzed stabilization by treating the fibres with 1% salt solutions, either  $ZnCl_2$  or  $Al_2(SO_4)_3$ . Unbleached softwood samples (pulp B) were soaked in the solutions and left to react for 48 h at either 120°C or 160°C. As is seen in figure 6 this treatment resulted in reduced water uptake (WRV) both after treatment at 120°C and 160°C. The treatment at 160°C generally resulted in a further reduction. The effect on water and moisture uptake of reference samples indicated that the treatment temperature played the most important role and that the effect of salt was small. A slight additional reduction in moisture uptake was observed for samples treated at 160°C in the presence of salts. Both tested salts produce acidic conditions and discoloration of samples were observed indicating degradation.

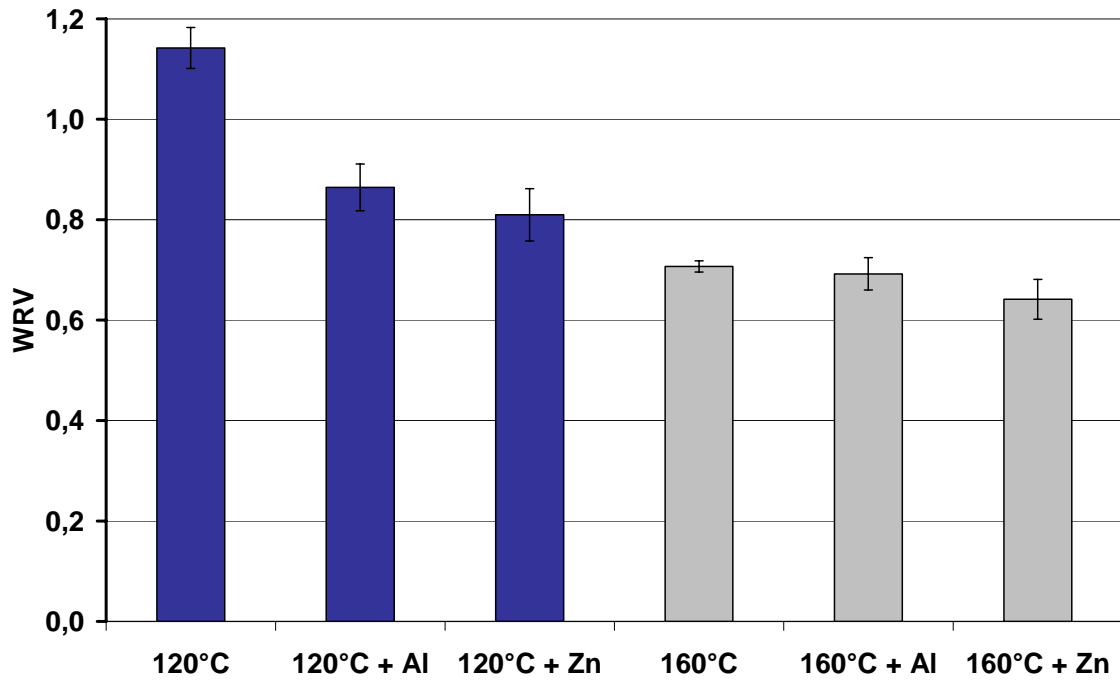


Figure 6. Determined water retention values of samples treated with Zn or Al salts and heat treated for 48 h.

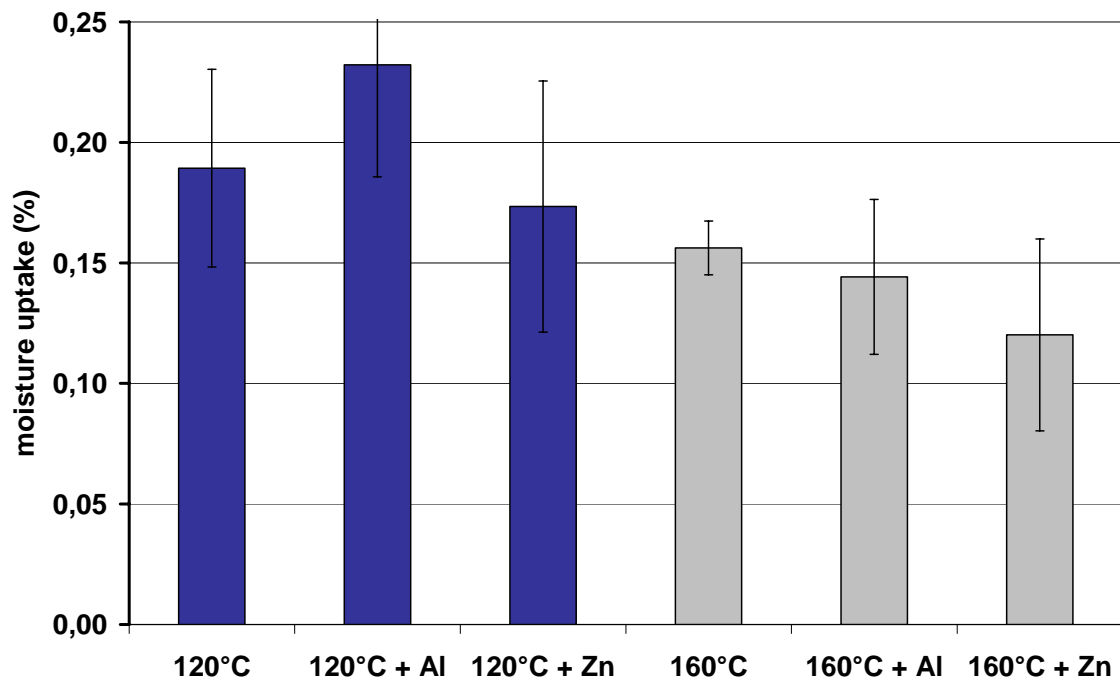


Figure 7. Determined moisture uptake of samples treated with Zn or Al salts and heat treated for 48 h.

The molecular structure of the components building up the cell wall influence the amount of water that can be absorbed. The swelling of cellulose under moist and wet conditions

does not change the crystallinity of cellulose suggesting that water mainly interacts with accessible parts of the cell wall (). The accessible parts, largely made up of hemicelluloses, are characterized by less ordered molecules allowing for easier access for water. In a paper by Oksanen et. al (Oksanen et. al 1997) they showed that by removing hemicelluloses both from hard and softwood it was possible to more effectively hornify pulp fibres. A large part of hemicelluloses and other less ordered material present in the cell wall can be removed using strong alkaline extraction. One method for the removal of this type of material was developed as a method for quality control of dissolving pulp. The pulp is first extracted using 18% NaOH solution, followed by extraction using 10% NaOH solution. However, this type of treatment not only removes hemicelluloses and other amorphous carbohydrates, it can also convert the cellulose into cellulose II (Browning 1967).

Increased crystallinity ratios are also observed in prehydrolyzed pulps where about 50% of the hemicelluloses are removed by an acidic treatment prior to the pulping stage.

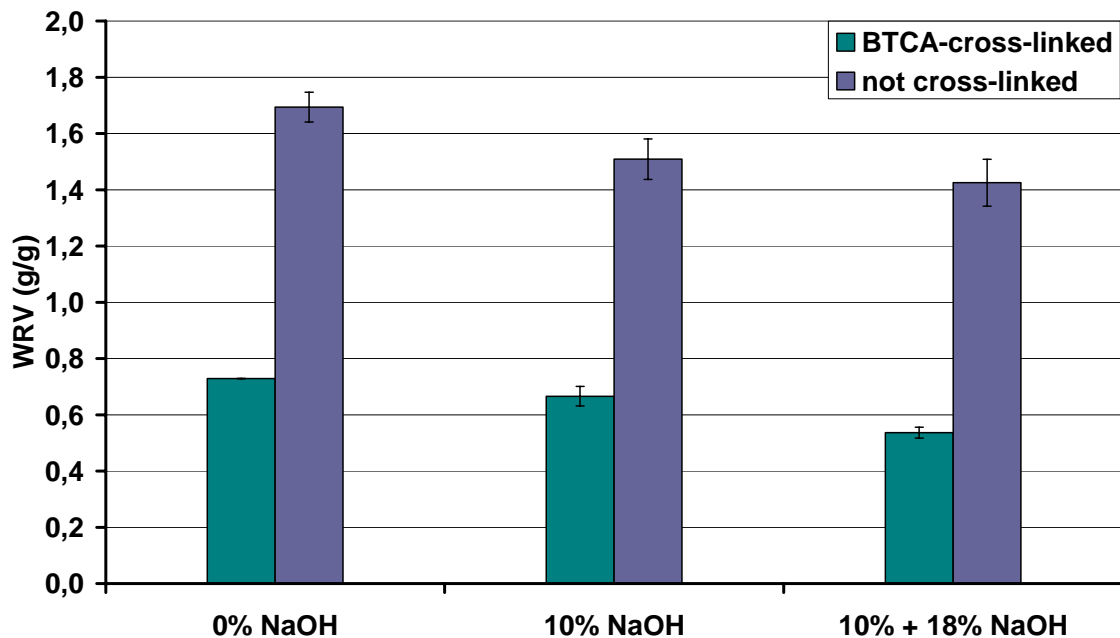


Figure 8. Observed WRV of pulp samples extracted with strong alkali solutions. The BTCA treatment was performed subsequently to the extraction.

By stopping at 10 % NaOH a more crystalline residue is preserved. The extraction need to be performed cold in order to avoid formation of cellulose II. In the traditional extraction procedure of hemicellulose and other less ordered carbohydrates the extraction starts using 18 % NaOH solution followed by 10 % NaOH solution (Browning 1967). By using this procedure not only substantial amounts of hemicellulose is removed from the pulp. The high concentration of NaOH also leads to intra crystalline swelling and conversion of cellulose I into cellulose II. In order to remove hemicellulose without converting the cellulose we therefore performed the extraction using 10% NaOH. This will effectively dissolve hemicelluloses and also some less ordered cellulose without changing cellulose I into cellulose II. In a second step we also treated this sample with 18 % NaOH solution in order to further swell the fibres and convert the cellulose into cellulose II (Krässig 1993).

As is seen in figure 8 decreased WRV values were observed after the alkaline treatments. This was especially evident for crosslinked samples. These samples were dried after neutralization and re-swelled before the crosslinking step. This probably resulted in partial hornification of the samples already after the extraction step, making the following chemical modification less effective.

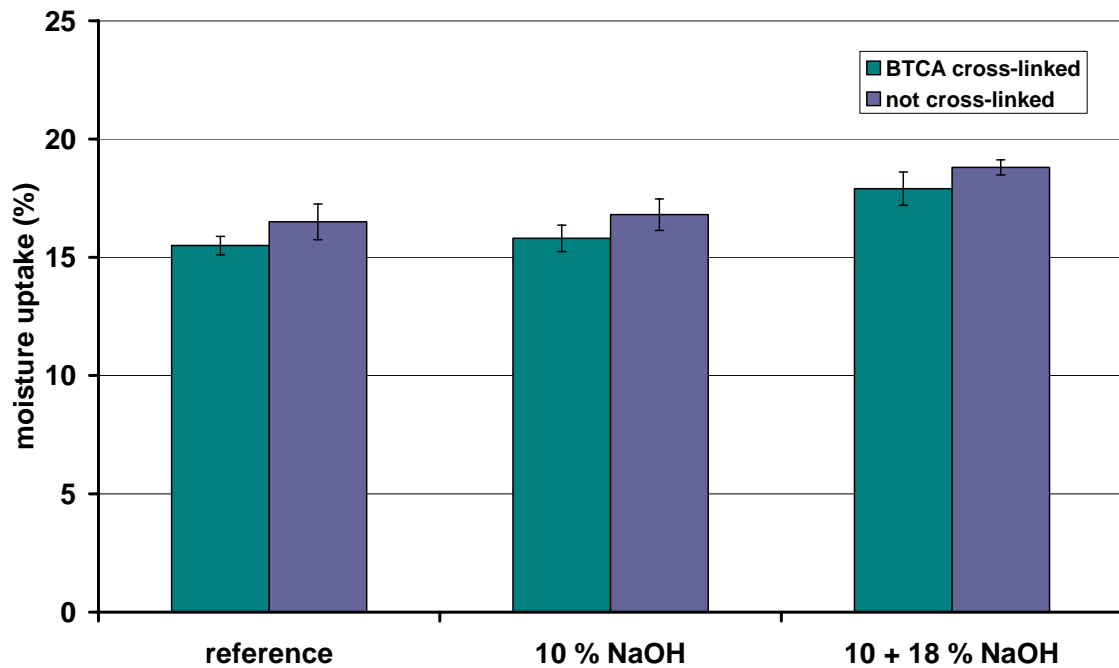


Figure 9. Observed moisture uptake of pulp samples extracted with strong alkali solutions. The BTCA treatment was performed subsequently to the extraction.

In figure 9 the results of these extractions on moisture uptake are shown. Contrary to what was seen for the WRV increased moisture uptake was observed after the extractions. This result suggests that the amount of surfaces available for water adsorption under humid conditions has increased. One action of strong alkali solutions described in the literature is an increased internal surface (Krässig 1993) while hornification leads to the closing of pores in the fiber wall (Stone et. al 1968). This effect is most evident for pores with a diameter above around 30 Å. So taken together, these results suggest that the removal of parts of the components in the cell wall will allow for a more effective collapse of larger pores while the number of very fine pores might increase slightly as a result of this extraction. Also, the mercerization might lead to the formation of material having a less ordered structure that is able to absorb more water as compared to cellulose I.

## 4 Conclusions

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Treatment of fibres at high (200-300°C) temperatures gave a dramatic stabilization of treated fibres. A reduction of 25-35% in moisture uptake was observed in samples treated at 300°C.

The heat treated samples did not lose tensile mechanical properties but became brittle after treatments above 200°C. Fibres treated at 200 and 225°C for 4 minutes showed improved hydro and hydrodynamic properties with only moderate increase in brittleness. By increasing the treatment time it was still possible to achieve substantial stabilization. The results also indicate that BTCA treated samples are stabilized to a larger extent than untreated samples, possibly as a result of auto cross linking.

The addition of salts to the pulp prior to heat treatment gave rise to a small extra stabilization compared to reference samples. However, discoloration of the samples suggested acidic conditions. No further work on this method will therefore be performed.

Sheets made from re-slushed BTCA treated fibres have very poor mechanical properties suggesting a strong debonding effect as a result of the heat/chemical treatments.

Alkaline extraction of the pulp fibres had a positive effect on water retention values while the moisture uptake were slightly increased. One reason for the relatively small effect observed for cross-linked alkaline extracted fibres might be that the fibres were allowed to dry after the alkaline extraction step which slow down or even prevent effective penetration of the cell wall.

## 5 Future activities

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A method for the production of larger amounts of heat treated (200-225°C) fibres will be developed. A possible route would be to form sheets, heat treat those and disintegrate them using a hammer mill. A batch of fibres for composite production will be produced utilizing a treatment temperature of 225 C. Both normal and BTCA treated fibres will be used. Care will be taken to facilitate effective chemical modification at this scale in order to achieve maximum stabilization.

Test the possibilities to heat treat with hot air instead of pressing. This would enable us to treat fibres without having to include a shredding step.

In order to better follow the development of mechanical properties of heat treated fibres, especially cross-linked, zero-span measurements will be performed.

In this study mercerised samples (treated with 18% NaOH solution) were allowed to dry prior to the BTCA treatment. In a further study we will follow the properties of similarly treated fibres where care is taken to preserve the swollen state of the fibres up to the cross linking step. The extraction using strong alkaline solutions will affect the lattice structure of cellulose. This change will be followed in selected samples.

To what extent do the lignin content of pulp influence the achievable level of stabilization? We can observe that fully bleached birch fibres generally take up less moisture as compared to unbleached sulfate pulp. However, in order to better understand this effect fully bleached softwood pulp should be studied as well.

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