1,2,3,4-Butanetetracarboxylic Acid Cross-Linked Softwood Kraft Pulp Fibers for Use in Fluff Pulp Applications

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ABSTRACT

Cross-linked fluff pulp fibers for use in, for example, acquisition layers in absorption products can be found in the patent literature. Cross-linking improves properties such as the wet resilience of fluff pulp fiber networks. Among the more commonly seen cross-linkers are polycarboxylic acids, such as 1,2,3,4-butanetetracarboxylic acid (BTCA). These acids form ester bonds with the hydroxyl groups in the fiber wall. In this study, softwood kraft pulp fibers were cross-linked with BTCA. The swelling behavior of the fibers and properties related to acquisition in absorption products were studied. It was found that the water retention value (WRV) decreased as a consequence of the introduced cross-linker. After deprotonation of a large part of the introduced carboxylic acids, the WRV increased, but the cross-linker was still able to limit significant swelling of the fiber wall. The wet bulk under load of fiber networks, composed of cross-linked fibers, generally increased with a decrease in WRV. Furthermore, it was found that the property development obtained after a cross-linking reaction with BTCA may be predicted by introducing a relative reaction intensity, RI_{rel}, that takes into account both time and temperature in the curing step. This shows that the time and temperature in the curing step are interchangeable.

INTRODUCTION

Introduction of intra-fiber cross-links in cellulosic fibers is a type of modification that can be applied in order to improve properties, such as wet-strength of paper products [1, 2] and wrinkle resistance of fabrics [3, 4]. In the patent literature, it can also be seen that there is an interest in cross-linked fluff pulp fibers to improve, for example, the wet resilience of high bulk fiber networks. [5, 6]

Reagents for intra-fiber cross-linking of cellulose may be formaldehyde [7], dialdehydes [8] or diepoxides [9, 10]. Polycarboxylic acids can also be used as cross-linkers, and intensive research, especially in the field of cotton textiles, on this type of cross-linker has been conducted in recent decades (cf. e.g. [4,11,12]). Examples of polycarboxylic acids that function as cross-linkers are citric acid and 1,2,3,4-butanetetracarboxylic acid (BTCA). It should be pointed out that even if polycarboxylic acids are often claimed to react with cellulose, they also react with hemicelluloses. In bleached softwood kraft fibers, it might be expected that the hydroxyl groups in the hemicellulose fraction are more reactive than the cellulose hydroxyls. [13] The reaction between BTCA and the hydroxyl groups in the fiber wall leads to the formation of esters and the reaction is thought to proceed via a cyclic anhydride intermediate. [14] To facilitate the reaction, an acid catalyst is needed. Welch [4] has reported that effective catalysts are phosphorous-containing monosodium salts and such catalysts have been used since then in almost all publications related to the cross-linking of cellulosic materials with BTCA.

Fluff pulp is the wood fiber type used in absorption applications. It is dry defibrated and air-laid into absorption cores of, for example, diapers. The function of fluff pulp is mainly to distribute liquid and hold the absorption core together. There is an industrial interest in improving fluff pulp properties and great attention is focused on modification of such pulp. [6, 15, 16]

One of the properties improved when fluff pulp fibers are cross-linked is wet resilience. [17] High wet resilience yields a fiber network that maintains its porosity even when put under pressure. A highly porous fiber network is important in, for example, the acquisition layer of absorption products, and consequently cross-linked fluff pulp fibers are of interest in such applications. [18, 19]

This paper deals with intra-fiber cross-linking with BTCA. In a previous paper, related to this investigation, the reaction kinetics of the modification of kraft pulp with BTCA was studied. [20] The present paper focuses on the property improvement obtained by this type of modification. Special attention is given to the swelling behavior of the modified fibers and properties related to the performance of the pulp fibers in acquisition layers in absorption products.

EXPERIMENTAL
Materials
The pulp used was a never-dried ECF (elemental chlorine free) bleached softwood kraft pulp obtained from a mill in southern Sweden. According to the carbohydrate analysis performed by the manufacturer, the pulp contained 84.5% cellulose, 8.7% xylan and 6.7% glucomannan. 1,2,3,4-butanetetracarboxylic acid (BTCA) was acquired from Merck (Synthesis grade, purity >98%).

Preparation of Pulp and Cross-linking
Preparation of Pulp
The dry content of the pulp was increased from around 20% to around 37% by using two 5 min pressing steps at 200 kPa. The pulp was granulated before it was pressed between two pulp sheets (bleached softwood kraft pulp sheets, grammage ≈ 900 g/m²). The pulp sheets acted as blotting paper that facilitated water removal and were changed between the two pressing steps.

Impregnation with Cross-Linker
Three solutions of BTCA were prepared to obtain three different concentrations of the cross-linker on the pulp. Each solution had a different concentration of BTCA and the ratio of BTCA and NaH_2PO_4 (the catalyst) was 1 in all solutions. The pH of the solutions was 2.8. The pH of the BTCA 5% solution was adjusted with NaOH. A reference solution with only NaH_2PO_4 was prepared as well (pH adjusted to 2.8 with H_3PO_4). The composition of the solutions is shown in *Table I*.

TABLE I. The different cross-linking solutions used in the study.

	BTCA on pulp (weight-%)	BTCA in solution (g/l)	NaH_2PO_4 in solution (g/l)
Reference	0	0	7.71
BTCA 1%	1	7.71	7.71
BTCA 2%	2	15.42	15.42
BTCA 5%	5	38.56	38.56

The cross-linking solution was added to the pulp by spraying into a blender (KMX51, Kenwood) during agitation. The solution was added slowly to ensure an even distribution of cross-linker in the pulp. After impregnation, the pulp had a dry content of 25%. The pulp was then dried at 50° C for 15 hours.

Liberation of Fibers
The impregnated and dried fibers were liberated in a laboratory refiner constructed for mechanical pulp production (Sprout Waldron 12'' single-disc, non-pressurized laboratory refiner). The pulp was fed into the refiner at a speed of 100 g/min and the discs in the refiner were set to 1 mm apart. No steam was used during the refining.

Curing of Fibers
10 g of liberated pulp fibers were dried and pre-heated at 80° C for 10 min before the curing reaction. The sample was then put in an oven (WTC Binder, FDL series) at specific curing conditions, cf. *Table II*.

Analysis
Ion-Pair Chromatography
2 g of cured fibers were leached overnight (16-20 h) in 40 ml water. The fibers were then dewatered and the filtrate, with the unreacted BTCA, was collected.

The BTCA in the filtrate was quantified using HPLC with UV-detection, essentially following the procedure suggested by Daood et al. [21] for the analysis of organic acids. A reversed-phase C18 column (Jupiter™ column, 5 µ C18 300 Å, Phenomenex, Torrance, CA, USA) was used for ion-pair chromatography. The mobile phase consisted of a 93 volume-% buffer solution and a 7 volume-% methanol. 1 ml of 40% tetrabutyl ammonium hydroxide was also added to 1 L of the mobile phase. The buffer solution consisted of 25 mM NaH_2PO_4 of which the pH had been adjusted to 2.75 with phosphoric acid. The detection wavelength was 210 nm.

The error in the measurements was less than 2%.

TABLE II. The different curing conditions used in the study.

Amount of BTCA (weight-%)	Temperature (°C)	Time (min)						
0	-							
0	140	60						
1	105	120	240	480	960			
1	120	15	30	60	120			
1	140	10	20	30	60	120	240	960
1	160	1	5	10	20	30	120	
1	180	2	5					
2	105	120	240	480	960			
2	120	15	30	60	120			
2	140	10	20	30	60			
2	180	5						
5	105	60	120	240	480			
5	120	10	20	30	60			
5	140	10	15	20	25	30		
5	180	5						

Water Retention Value

The water retention value (WRV) was measured according to SCAN-C 62:00. The moist pulp samples were dewatered by centrifugation at 3000 g for 15 minutes. After centrifugation, the sample weight was recorded. The dry weight of the sample was then determined after drying at 105° C (16-20 h in oven). WRV was analyzed with and without prior neutralization with 0.1 M NaHCO$_3$. In the neutralization the pulp fibers (1 g) were treated in a 0.1 M NaHCO$_3$ solution for one hour at a consistency of 0.1%. After neutralization, the fibers were dewatered, displacement washed with 3 L water and then subjected to WRV analysis. Duplicates were made of the pulp fibers that were analyzed without any pretreatment for all measurements (pooled standard deviation = 0.01 g/g). No duplicates were made of the neutralized samples.

Anionic Charge of Pulp

The anionic charge was measured by performing conductometric titration according to SCAN-CM 65:02 (cf. Katz et al. [22]). The pooled standard deviation was 2 µmol/g fibers for 1 weight-% BTCA, 8 µmol/g fibers for 2 weight-% BTCA and 21 µmol/g fibers for 5 weight% BTCA.

Free Swelling Capacity

The free swelling capacity (FSC) was measured according to Edana 440.1-99. The procedure involves soaking a sample in a water solution containing 0.9% NaCl and measuring the uptake of water of the sample at specified intervals. The water uptake in this study was only measured at 1 and 30 minutes, which was a deviation from this standard procedure. The FSC values reported here were the ones measured after 30 minutes.

Compression Test

Before the compression test, test pads were made with a test piece former according to SCAN-C 33:80. Deviations from the SCAN method were a plastic ball (d=37 mm) that was suspended from the lid of the test piece former (improves fiber separation), and a sintered metal plate (pore size = 0.4 mm and 140 pores/cm²) that was used instead of a wire screen. In the SCAN method, 1.2-1.3 g is recommended for test pad preparation. However, when this amount of cross-linked pulp fibers was used, the test pads were too high and not possible to analyze in the compression tester. For this reason only 0.8 g was used for each test pad. After formation, the test pads were pressed at 0.37 MPa before being subjected to the compression test.

The compression test involved a stepwise increase in pressure in both the dry state and the wet state. Each pressure was applied for 2 minutes to reach equilibration and then the height of the test pad was recorded. The equipment used for the compression test has been described elsewhere [10] and the pressures used in the test can be seen in *Table III*. After the compression test, the test pads were dried over night (16-20 h at room temperature) and the bulk was measured again at 2 kPa.

TABLE III. Pressures used in the compression test.

Time (min)	Pressure (kPa)	State
0	0.5	Dry
2	2	Dry
4	6	Dry
6	0	Wetting
16	0	Drainage
18	0.5	Wet
20	2	Wet
22	6	Wet
24	15	Wet
26	0	Wet
31	0.5	Wet

RESULTS AND DISCUSSION
Effect of Cross-Linking on Fiber Swelling

Never-dried bleached softwood kraft pulp fibers were impregnated with a water solution containing BTCA and NaH_2PO_4. The impregnated fibers were dried at 50°C for 15 h, defibrated and then cured at temperatures $\geq$ 105°C. During drying, water is removed from the swollen fiber walls, which induces a closure of pores, leading to the formation of a more dense fiber wall. This means that the cross-links introduced in the fiber wall polysaccharides in the curing step will counter-act swelling during re-wetting. Thus, changes in the pulp's tendency to swell in contact with water can be used to monitor the extent of cross-linking. In the present study, the water retention value (WRV) was used to quantify the swelling. Determining the WRV is a common method in the pulp and paper industry, for example, for investigating the effect of beating on fiber swelling and the influence of drying on the ability of pulp fibers to swell when re-slushed. [23, 24] The analytical procedure involves soaking a sample in water and then measuring the amount of retained water after centrifugation. The water retained after centrifugation is, to a large extent, held within the pores of the fiber wall. The WRV in this study is calculated as:

$$WRV = \frac{m_{water}}{m_{sample} - m_{BTCA}} \quad (1)$$

Where m_{water} is the mass of the water retained after centrifugation, m_{sample} is the dry weight of the sample after oven drying and m_{BTCA} is the mass of BTCA in the fiber wall. This eliminated the influence that the added weight of the BTCA had on the WRV.

Results in *Figure 1* show that BTCA treatment decreased the WRV of the pulp fibers when the amount of reacted BTCA increased, which indicates that the reaction of BTCA involves the formation of cross-links. When comparing the different levels of BTCA added (1, 2 and 5 weight-% BTCA on pulp), it can be noted that a higher amount of reacted BTCA is required to give an equal decrease in WRV when the level of BTCA is increased. Furthermore, a high addition of BTCA seems to decrease the slope of the curve representing WRV as a function of reacted BTCA.
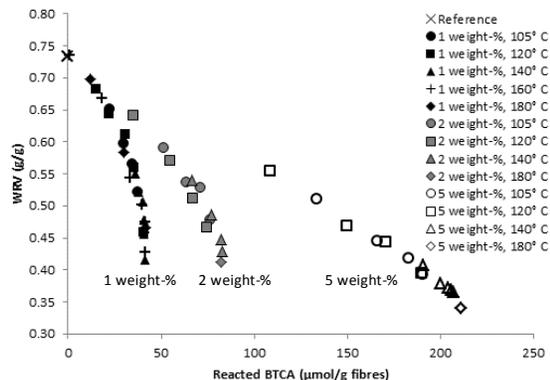

FIGURE 1. Water retention value plotted against the amount of reacted BTCA. For each temperature, several curing times were used.

The different trends seen for the three levels of BTCA could be due to several possible mechanisms, such as:

- Primary and secondary cross-linking reactions

- Charges introduced into the fiber wall

- Mechanisms related to hornification, e.g.

  o BTCA and NaH_2PO_4 acting as spacer molecules in the drying step

  o Reacted BTCA acting as a spacer molecule in the curing step

One BTCA molecule can form one, two or three ester linkages with the fiber wall polysaccharides (the formation of a fourth ester linkage is unlikely in this type of modification [25]). Lowering the WRV at harsher reaction conditions as seen in the 1 weight-% BTCA series might be due to secondary reactions of BTCA (the formation of a second and a third ester linkage). However, an evaluation of the reaction kinetics and quantification of anionic charges in the BTCA-treated fibers (reported in a separate paper, cf. [20]) indicates that the formation of the second ester bond had occurred quite instantly after the first bond had been formed (cf. also [25]). Results in *Figure 2* indicate a linear relationship between the amount of charges and the amount of reacted BTCA, and no deviations based on harsher reaction conditions could be seen (deviations at 5 weight-% BTCA are probably due to the high variance in the measurements of these highly charged fibers).

However, it may also be speculated that slower trans esterification reactions take place [26] and that these reactions can lead to more stable structures than those initially formed.
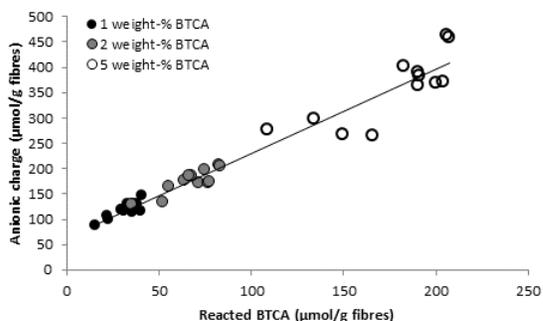

FIGURE 2. Anionic charge of modified fibers plotted against the amount of reacted BTCA. For guiding purposes, a trend line has been included.

The modification introduced carboxylic acid groups into the fibers, but most of these groups were protonated during the WRV test presented in *Figure 1* (due to the low pH required in the curing step). However, there might be a difference in the charge of the fibers, which would influence the swelling of the fibers.

Drying of pulp fibers is known to decrease swelling when re-wetted. This feature of pulp fibers is denoted "hornification". This irreversible closure of pores in the fiber wall is believed to result from hydrogen bond formation and cellulose co-crystallisation (cf. e.g. [27-29]). It has been proposed that hornification may also include the formation of covalent bonds between cell wall components. [30] Hornification involves interaction between polysaccharide chains in the fiber wall. The presence of BTCA and NaH_2PO_4 between the chains in the drying step may influence hydrogen bond formation and co-crystallization, since the molecules could act as spacers and prevent the chains from coming close together. Furthermore, the introduction of cross-linking molecules may prevent rearrangement of the polysaccharides. These effects would become more pronounced as the addition of BTCA increases and may thus account for the differences seen between the three levels of added BTCA.

Results in *Figure 3* show the WRV of the samples after neutralization with 0.1 M $NaHCO_3$ as a function of the amount of reacted BTCA. A pH of around 8 was obtained in the neutralization step, which means that most of the carboxylic acids in the fiber wall were deprotonated. The modification applied gave a substantial increase in the anionic charge in the fiber wall; cf. *Figure 2*, particularly at a 5 weight-% addition of BTCA. An increase in anionic charges increases osmotic pressure which promotes swelling of the fiber wall. [31] Results in *Figure 3* show that the WRV was retained on a low level also after neutralization. Only a small increase can be seen with the addition of 1 weight-% BTCA. A more pronounced increase, but still on a low level, can be seen at additions of 2 and 5 weight-% BTCA. Evidently, the cross-links introduced are capable of withstanding high osmotic pressure. If no cross-links had been present, a substantial swelling of the fiber walls would have occurred. Modification with succinic anhydride, which introduces anionic charges, but no cross-links, into the fiber wall, has been shown to yield fibers that swell extensively when subjected to alkaline conditions. [32]
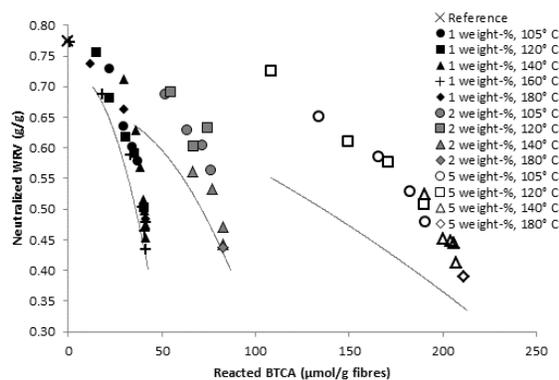

FIGURE 3. WRV for fibers treated with 0.1 M $NaHCO_3$ prior to measurement plotted against amount of reacted BTCA. Grey lines are trend lines for WRV for fibers that had not been treated with $NaHCO_3$ prior to measurement, cf. *Figure 1*. For each temperature, several curing times were used.

Acquisition Layer Properties

It is essential that that the fiber network in acquisition layers is able to maintain a porous structure, even when put under pressure. It is also of interest to determine if the fiber network recovers after a compression, i.e. if it regains a more porous structure. To test these properties, modified fibers were air-laid into test pads that were subjected to a compression test in dry and wet states. The wet bulk at 15 kPa in the compression test was obtained by measuring the height of the test pads when put under load in the wet state, and is a measure of the porosity of the fiber network. The wet spring-back was obtained by releasing the pressure in the compression test (from 15 kPa to 0 kPa) and allowing the test pads to recover for 5 minutes and then measuring the height at 0.5 kPa.

The wet bulk values obtained were found to depend on the addition of BTCA, reaction time and reaction temperature. A variable denoted "relative reaction intensity" was introduced for treating reaction time and reaction temperature as a single variable (cf. e.g. the H factor concept for the calculation of degree of delignification of wood in alkaline cooking at different temperatures [33]).

In calculating the relative reaction intensity, we assumed that the property development of the modified fibers followed the Arrhenius equation, Eq. (2):

$$k = Ae^{-\frac{E_a}{RT}} \qquad (2)$$

This type of equation is often used to describe the influence of temperature on chemical reaction rates. k is the reaction rate, A is the pre-exponential factor, E_a the activation energy, R the ideal gas constant and T is the temperature in Kelvin. The reason for using this type of equation for describing the influence of time and temperature on property development is based on the assumption that the changes in fiber characteristics are dependent on chemical reactions. In Eq. (3), a relative reaction rate, k_{rel}, is calculated as:

$$k_{rel} = \frac{e^{-\frac{E_a}{RT}}}{e^{-\frac{E_a}{378.15R}}} \qquad (3)$$

Where Eq. (2) has been normalized with the reaction rate at 105° C, i.e. the relative reaction rate at 105° C is 1. The activation energy for the reaction of BTCA with kraft pulp fibers was previously determined to be 134.4 kJ/mol [20] and this activation energy was used in further evaluating data. In calculating the relative reaction intensity, RI_{rel}, k_{rel} is multiplied by time of reaction (in minutes), Eq. (4):

$$RI_{rel} = k_{rel} \times t \qquad (4)$$

Results presented in *Figure 4* show that the modification enhanced the wet bulk of the fiber networks as the relative reaction intensity increased.

Similar trends were also seen for the wet spring-back; a higher relative reaction intensity yields a higher wet spring-back. The effect on the wet bulk and the wet spring-back was higher when the level of BTCA was increased. The wet bulk and wet spring-back values formed logical curves when plotted against relative reaction intensity. This implies that the reaction time needed for the development of these properties at different temperatures can be estimated by RI_{rel}. Consequently, temperature and time are interchangeable in the development of these properties.

The modification of kraft pulp fibers with BTCA decreases the WRV of the modified fibers and, in addition, increases the wet bulk under load of fiber networks. These two properties were plotted against each other to see how properties on the fiber level, WRV, and how properties of fiber networks, wet bulk, correlate, cf. *Figure 5*.

The general trend is that the wet bulk increases with a lower WRV. Considering the values for each level of BTCA separately, it can be seen that at a given WRV, the wet bulk tends to be higher when the addition of BTCA is lower. The difference between the three additions of BTCA may be related to differences in fiber form, since this type of modification has been shown to stabilize curl formation. [6] Attempts were made to measure fiber form using a fiber analyzer (Kajaani FS300). However, when modified fibers were analyzed, the fibers also formed flocs in the highly diluted water suspensions used in the analytical procedure, which prevented measurements in the fiber analyzer.

Table IV shows the results obtained at the three different levels of BTCA at two curing conditions. A reference sample is included as a comparison. The table gives the amount of reacted BTCA, the WRV, wet bulk and wet spring-back. The free swelling capacity (FSC) and the dry bulk at 6 kPa are also included. FSC is a measure of the amount of liquid a sample can absorb when allowed to swell without pressure. The dry bulk value at 6 kPa was recorded in the compression test procedure. The trend is that higher relative reaction intensity or higher addition of BTCA, gives:
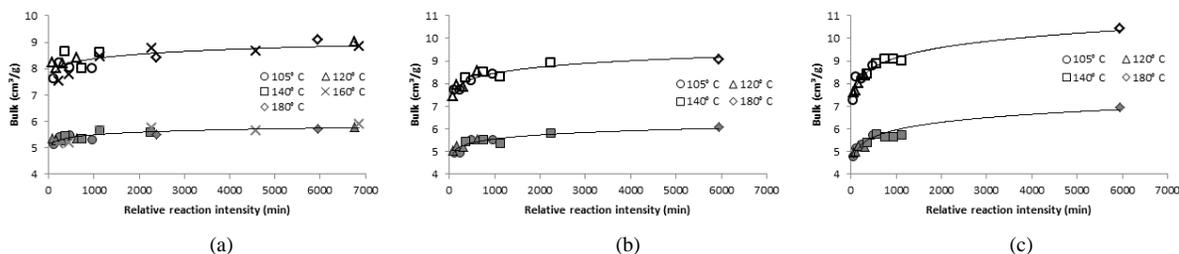
FIGURE 4. Bulk plotted against the relative reaction intensity at (a) 1 weight-% BTCA, (b) 2 weight-% BTCA and (c) 5 weight-% BTCA. Trend lines are shown to guide the eye. No fill = Wet spring-back, Grey = Wet bulk at 15 kPa.

- − A low WRV

- − A high absorption capacity (measured as FSC)

- − A high wet resilience in both the dry and the wet states

- − An increase in wet spring-back

TABLE IV. Results from absorption tests at two different curing conditions.

BTCA addition (%)	Sample Temperature (°C)	Time (min)	RI_{rel} (min)	Reacted BTCA (μmol/g)	WRV (g/g)	FSC (g/g)	Dry bulk at 6 kPa (cm³/g)	Wet bulk at 15 kPa (cm³/g)	Wet spring-back[1] (cm³/g)
0	-	-	-	-	0.73	20.6	6.6	4.9	7.5 (2.6)
1	140	30	1125	38 (90%)	0.52	-	6.7	5.6	8.6 (3.0)
1	180	5	5942	41 (97%)	0.46	26.6	7.3	5.7	9.1 (3.4)
2	140	30	1125	82 (94%)	0.45	25.7	7.8	5.3	8.3 (2.9)
2	180	5	5942	80 (96%)	0.41	27.4	9.2	6.1	9.1 (3.0)
5	140	30	1125	207 (97%)	0.37	26.9	9.5	5.7	9.0 (3.3)
5	180	5	5942	211 (99%)	0.34	27.5	11.5	7.0	10.4 (3.5)

[1]The value in parenthesis is the difference between wet spring-back and wet bulk at 15 kPa.
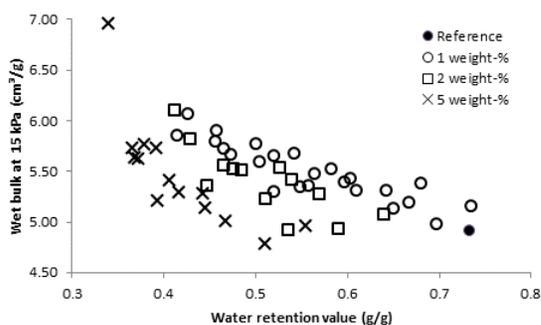

FIGURE 5. Wet bulk at 15 kPa plotted against the water retention value. Test liquid was 0.9% NaCl in water.

These results demonstrate that BTCA modification enhances the suitability of kraft pulp fibers in acquisition layer applications.

CONCLUSION
Results in this study show that the WRV of fibers cross-linked with BTCA decreases. A deprotonization of the introduced carboxylic acids in the modification increased the WRV, but the cross-linker inhibited major increase in swelling. When properties of fiber networks were studied, the wet bulk under load of the fiber networks was found to increase as a result of the cross-linking reaction. It was further found that a relative reaction intensity, including both time and temperature, can be used to predict property development of the cross-linked fiber networks. Thus, time and temperature in the curing step are interchangeable.

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