ABSORBENT MATERIALS BASED ON KRAFT PULP: PREPARATION AND MATERIAL CHARACTERIZATION

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Today, petroleum-based superabsorbents are widely used, but interest in renewable alternatives is on the rise. This study presents two wood-based absorbent materials suitable for various absorption applications as an alternative to petroleum-based products. Never-dried bleached kraft pulp was treated with TEMPO-oxidation, and new carboxylate and aldehyde groups were introduced. It was found that the aldehyde groups contributed to the wet integrity of the absorbent materials, possibly by the formation of hemiacetal bonds. After oxidation, the pulp fibers were gradually disintegrated, and size analysis showed that the disintegration rate was enhanced by an increase in the charge of the oxidant. Freeze drying produced a porous foam with a large surface area that enabled a rapid absorption rate as well as a reasonably high absorption capacity even for absorption under load. Air drying formed a compact film with a slow absorption rate but with a high final capacity for absorption.

Keywords: Absorption; TEMPO-oxidation; Disintegration; MFC; Foam; Film; Freeze drying

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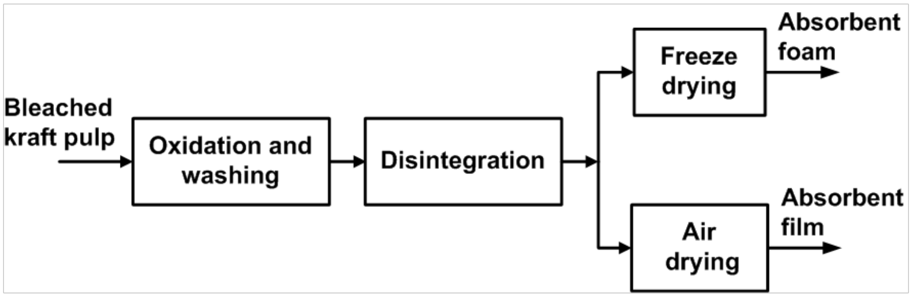
INTRODUCTION

Superabsorbents are important constituents in personal care products including baby diapers, feminine care products, and adult incontinence products. The market for superabsorbents has been growing since the introduction of synthetic, petroleum-based SuperAbsorbent Polymers (SAP) in the mid 80s. This growth is due to an increase in demand for thinner absorbent products, which are obtained by replacing fluff pulp with superabsorbents. A superabsorbent can retain a substantial quantity of liquid, significantly more than what can be retained in a conventional fluff pulp. The first superabsorbents were made from renewable resources such as chemically-substituted cellulose and grafted cellulose or starch, but today more than 95% of superabsorbents come from synthetic SAP, mainly consisting of cross-linked poly-acrylic acids (Staples and Chatterjee 2002). Since the absorption core in a modern diaper often consists of more than 50% of these petroleum-based superabsorbents, there have been recent efforts to develop new high capacity absorbents produced from renewable resources.

MicroFibrillated Cellulose (MFC) is one example of a renewable material that may be utilized as a highly absorbent and retentive material. Methods for producing MFC were first developed by Herrick et al. (1983) and Turbak et al. (1983), who treated dilute slurries of cellulose fibers in a high-pressure homogenizer. Chatterjee and Makoui (1984) obtained a highly absorbent material by freeze drying dilute suspensions of MFC. This material had a retention value of 10 g/g in 1% sodium chloride solution under a load of 3.5 kPa. Later, cross-linking with glutaraldehyde was found to improve the properties of the MFC absorbents and allowed the material to be air-dried. After compression (0.4 g/cm^3), this material had an absorption capacity of 16 g/cm^3 and a retention capacity of 8 g/g (Makoui and Chatterjee 1987).

Since the mechanical treatment in the preparation of MFC has a high energy demand, several different pretreatment methods have been proposed, including acid hydrolysis (Zimmerman et al. 2004; Henriksson et al. 2008) or enzymatic hydrolysis (Paakko et al. 2007; Henriksson et al. 2008). The addition of carboxylic groups has also been used as a pretreatment method. In a study by Wågberg et al. (2008), carboxylic groups were added by carboxymethylation, and it was reported that full homogenization was obtained after only one passage through a dispersing unit. Saito et al. (2006) introduced the use of oxidation with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), NaBr, and NaClO prior to mechanical disintegration. This method resulted not only in an increase in the water retention value, but also in extensive degradation of the cellulose molecule under the alkaline conditions. In another study, a TEMPO/NaClO/NaClO$_2$ system was used, which yielded pulp with a low degradation of the cellulose molecules and almost no aldehyde groups (Saito et al. 2009).

In this study, a three-step process (see Scheme 1) is proposed for the preparation of two types of absorbent materials with wood as the raw material (Theliander et al. 2011; Wernersson and Theliander 2011). In the first step, kraft pulp was oxidized in a reaction system catalyzed with TEMPO and NaBr. NaClO was added as the primary oxidant. The oxidized pulp was disintegrated with a mechanical treatment to obtain a network of liberated fibrils. Finally, drying was performed by either freeze drying or air drying, resulting in two different types of absorbent materials. To study the influence of different process conditions, two different starting pulps, four different charges of primary oxidant, mechanical treatment of various durations, and two drying methods were investigated in this study.



Scheme 1. Process steps for preparation of new absorbent materials.

EXPERIMENTAL

Materials

Industrial softwood kraft pulp produced with a Totally Chlorine Free (TCF) beaching sequence was the main raw material in this study. However, one additional test was performed with an industrial hardwood kraft pulp (Elemental Chlorine Free (ECF) bleaching sequence) to examine the influence of the starting pulp. Both pulps were produced from Scandinavian wood, and the pulps had never been dried prior to the experiments in this work. The chemicals used in the oxidation experiments were TEMPO (purity 98%, Sigma Aldrich), NaBr (purity 99.5%, Scharlau), and NaClO (10-15% available chlorine, Sigma Aldrich).

TEMPO-Oxidation and Washing

12 g of o.d. pulp was oxidized at 1.0% pulp consistency in a reaction that was started by adding NaClO to a pulp slurry containing catalytic amounts of TEMPO and NaBr (see Table 1). The concentration of the sodium hypochlorite solution was determined by iodometric titration. The oxidation reaction was performed at room temperature (21-23 ˚C), and the pH was maintained at 10.0 ± 0.2 by manual additions of 0.5 M NaOH. The oxidation reaction was considered to have ended when no further decrease in pH could be observed. After the reaction, the oxidized pulp was separated from the reaction medium by filtration and was washed with 5 L of deionized water. The washed oxidized pulps were stored in plastic bags at 4 ˚C before further treatment and analysis. The selectivity of carboxylate group formation was calculated according to the equation below, where the formed carboxylate groups (multiplied by two, since two hypochlorite ions are consumed for each carboxylate group) were divided by the charge of the oxidant.

$$\boldsymbol{Selectivity}\,(\%) = \frac{2 \times \left(COO^{-}_{ox\,pulp} - COO^{-}_{non-ox\,pulp}\right)}{ClO^{-}_{charge}} \tag{1}$$

Table 1. Amount of Chemicals in Oxidation Experiments

Wood source	Oxidation level	TEMPO (mmol/g pulp)	NaBr (mmol/g pulp)	NaClO (mmol/g pulp)
Softwood	No	-	-	-
Softwood	Mild	0.1	1.0	0.8
Softwood	Medium	0.1	1.0	2.1
Softwood	Harsh	0.1	1.0	3.2
Softwood	Harshest	0.1	1.0	4.2
Hardwood	Harshest	0.1	1.0	4.2

Reduction of Aldehyde Groups

One batch of the softwood kraft pulp treated with the harshest oxidation was additionally treated with $NaBH_4$ in order to reduce the aldehyde groups in the pulp to hydroxyl groups. 5.0 g of o.d. pulp was suspended in water to 8% pulp consistency, together with 0.303 g $NaBH_4$ and 0.115 g of 0.05 mM NaOH. The suspension was put in a water bath (60 ˚C) for 2 h reaction time. After, the reduced pulp was washed with deionized water and stored at 4 ˚C.

Disintegration of Pulp Fibers

The different pulps were mechanically disintegrated in two series of experiments, as shown in Table 2. In the table, the treatment time shows the duration of the treatment, while the mechanical treatment is a normalized value that was calculated by dividing the treatment time with the amount of pulp in the experiment. In this paper, the results are reported as normalized values to enable comparisons between samples that contained different amounts of pulp.

The equipment used in these experiments was an Ultra-Turrax T 45/N high shear dispersing unit from IKA. All samples were diluted to 1.0% pulp consistency by adding deionized water prior to treatment, and the starting temperature was approximately 20 ˚C. During the mechanical treatment the suspension temperature rose to 40-80 ˚C and a substantial increase in viscosity was observed for pulps with a high oxidation level. In some cases, the samples were diluted to obtain good mixing or were cooled to avoid significant evaporation. After the treatment all samples were stored at 4 ˚C before further treatment and analysis.

In the first series of mechanical treatments (1-15), samples were collected during the disintegration process. Therefore, the starting material of one experiment can be the same as the sample obtained in the latest experiment. The sample sizes were 100 g wet material (1-6) and 80 g wet material (7-14). No samples were taken during Experiment 15. In the second series of mechanical treatments (17-24), the samples were diluted to 0.6% pulp consistency after 1 min mechanical treatment. No samples were taken out during the mechanical treatment, except for Experiment 18 where very small samples of about 2 mL wet material were collected every 30 min. In Experiment 16, the pulp was diluted to 0.6% pulp consistency without any mechanical treatment of the pulp.

Table 2. Experimental Conditions used in the Mechanical Treatments

ID	Wood source/ starting material	Oxidation level	Extent of mechanical treatment	Dry pulp weight (g)	Treatment time (min)	Mechanical treatment (min/g pulp)	Final pulp cons. (%)
1	Softwood	Mild		5.0	5.0	1.0	1.0
2	ID 1			4.0	5.0	2.3	1.0
3	ID 2			3.0	5.0	3.9	1.0
4	Softwood	Medium		5.0	5.0	1.0	1.0
5	ID 4			4.0	5.0	2.3	1.0
6	ID 5			3.0	5.0	3.9	1.0
7	Softwood	Harsh		5.0	1.0	0.2	1.0
8	ID 7			4.2	2.0	0.7	1.0
9	ID 8			3.4	2.0	1.3	1.0
10	ID 9			2.6	5.0	3.2	0.7
11	Softwood	Harshest		5.0	1.0	0.2	1.0
12	ID 11			4.2	2.0	0.7	0.7
13	ID 12			3.7	2.0	1.2	0.7
14	ID 13			3.1	5.0	2.8	0.7
15	Softwood	Harshest	Medium	5.0	15	3.0	0.5
16	Softwood	No	No	-	-	-	0.6
17	Softwood	No	Medium	3.0	9.0	3.0	0.6
18	Softwood	No	Longest	10	240	24	0.6
19	Softwood	Medium	Medium	3.0	9.0	3.0	0.6
20	Softwood	Harshest	Shortest	3.0	1.5	0.5	0.6
21	Softwood	Harshest	Medium	3.0	9.0	3.0	0.6
22	Softwood	Harshest	Long	3.0	30	10	0.6
23	Hardwood	Harshest	Medium	3.0	9.0	3.0	0.6
24	Softwood	Harshest+ $NaBH_4$	Medium	3.0	9.0	3.0	0.6

Drying Procedures

Samples from the first series of experiments (1-14) were air dried. The wet disintegrated pulps were poured on top of a plastic sheet. The samples were dried at room temperature for several days, then stored at room conditions. The dry content of the samples after air drying was 90 to 93%. Sample 15 was dried by both air drying (15a) and freeze drying (15b).

Freeze drying was used for the samples from the second series of mechanical treatments (16-23). 20 g of wet sample were frozen in Pyrex glass beakers (with 47 mm inner diameter) with liquid nitrogen as the freezing agent around the beakers. The drying was performed in a Heto Hetosicc CD 2.5 freeze drier operated at 0.3 mbar for 48 h. After drying, the cylindrical sample pads were put in plastic bags and stored at room temperature. These samples had dry contents after freeze drying that ranged between 93-97%.

Characterization Methods

The amount of carboxyl groups in the pulps was determined by using a method based on the sorption of the cationic dye methylene blue (Davidson 1948; Fardim et al. 2002). 50 mg of o.d. pulp was protonated for 1 h in 100 mL 0.01 M HCl. Thereafter, the pulp was washed with a portion of 50 mL 0.01 M HCl and two 50 mL portions of deionized water. Next, the pulp was added to a beaker with 100 mL of a phosphate buffer solution (pH 7.8) containing 0.04798 g of methylene blue. The sorption time was set to 1 h and was performed in darkness and with continuous stirring. After sorption, the suspension was filtered and the filtrate (diluted 125 times) was analyzed with a spectrophotometer (Hitachi U-3200). The concentration was determined by using standard solutions. The standard deviation of the analysis was ± 0.05 mmol/g pulp.

The amount of aldehyde groups in the pulps was determined after a total oxidation of the aldehyde groups to carboxylate groups using $NaClO_2$ (Saito and Isogai 2004). 0.05 g of o.d. pulp sample was added to a solution (pH 4.6) consisting of 10 mL of 0.5 M CH_3COOH, 5 mL of 0.5 M NaOH, 0.04 g of $NaClO_2$, and 85 mL of deionized water. Reaction time was set to 24 h, and the suspension was continuously stirred. After the reaction, the pulp was washed with 200 mL of deionized water. The amount of aldehyde groups in the pulp was determined by comparing the amount of the carboxyl groups before and after the $NaClO_2$ treatment.

Fiber analysis was performed with a Kajaani FS-300 from Metso Automation. Well dispersed samples were tested for average values of fiber length (length-weighted) and fiber width (number-weighted). The standard deviation of fiber length was 0.1 mm and 0.5 μm for fiber width.

One drawback of the fiber analysis equipment when the sample is a disintegrated pulp is that the sample also contains many objects that are below the detection limit of the equipment (about 0.02 mm in length). Therefore, particle size analysis was performed on the short fraction that was obtained after the removal of a fractionation of long fibers. The long fibers were removed to avoid fiber blockings in the particle analyzer used, a Malvern Masersizer 2000, but also because this type of particle sizer device is designed for measurements of spherical particles. By removing the longest fibers, the quality of the measurements is improved.

The fractionation to remove long fibers from the sample was conducted using a Dynamic drainage jar with a 40 M screen from Paper Research Materials. 10 to 40 g of wet fibrillated material was diluted and dispersed in 0.5 L of deionized water and transferred to the tank. The sample was stirred at a high speed (1500 rpm) for 15 s and then drained at a slower stirring speed (750 rpm). This drained fraction (short fraction) was used to measure the distribution of particle size in the sample. The non-drained fibers (long fraction) were transferred from the screen to a filter paper and dried in an oven at 105 ˚C. The percentage of material in the short fraction was calculated according the equation below, where the dry masses of the total sample and the long fibers are used.

$$\boldsymbol{Short\ fraction}\ (\%) = \frac{m_{total\ sample} - m_{long\ fibres}}{m_{total\ sample}} \qquad (2)$$

Scanning electron microscopy (JEOL JSM-820) was used in order to study the freeze-dried materials. The sample pieces were collected from the bulk of the freeze-dried samples and were prepared by coating the surface of the samples with a thin layer of gold.

The specific surface area was measured by the adsorption of N_2 at the temperature of liquid nitrogen (-196 ˚C) in a Tristar 3000 device from Micrometrics. The samples were pretreated with inert gas at 25 ˚C for 3 h to remove any remaining moisture from the sample. The specific surface area was determined by multipoint BET analysis using ten pressure levels, and the error of the method was less than 1.0 m^2/g.

The pore structure of the freeze-dried materials was studied by using liquid porosimetry, which is a method that has been described by Miller and Tyomkin (1994). The pores were sized according to their effective radii based on the assumption that the pores were cylindrical tubes. By assuming this, the Laplace equation could be used to correlate pressure and effective radius.

$$p_i = \frac{2\,\gamma\,\cos\theta}{r_i} \qquad (3)$$

In the equation, p_i and r_i are the pressure and effective radius corresponding to capillary i, γ is the surface tension of the test liquid, and θ is the contact angle at the liquid-solid-air interface. The pore structure is reported as a Total Cumulative Volume (TCV), which is the total volume of test liquid in the sample pores ($r \leq r_i$) at the measurement pressure p_i. TCV was determined at pressures corresponding to effective radii 400, 350, 300, 250, 200, 150, 100, 75, 50, 25, 10, 5, and 2 µm. The measurement was performed in receding mode, where the test liquid was pressed out of a pre-saturated sample.

Absorption and Retention Analyses

Total Absorption Potential (TAP) was measured for samples from the first series of mechanical treatment experiments. In this test, a sample was put into a beaker with 50 mL test liquid (deionized water or saline solution with 1.0% NaCl by weight) and was allowed to absorb freely. At predetermined times (1, 3, 5, 10, 30, 60, 90, 120, 150, 180, 210, and 240 min), the sample was removed from the beaker and the clock was stopped.

Excess water was allowed to drip off for 5 s and then the sample weight was measured. After measuring the weight, the sample was put back into the beaker, and the timekeeping was resumed. The test continued until no further increase in TAP was observed. TAP was calculated according to the equation below, where m_{wet} is the wet weight of the sample after the absorption time t and m_{dry} is the dry weight of the sample. The error of the analysis was estimated to ± 10% of the TAP value.

$$TAP = \frac{m_{wet} - m_{dry}}{m_{dry}} \tag{4}$$

Free Swell Capacity (FSC) and Centrifuge Retention Capacity (CRC) were measured in saline solution (0.9 weight % NaCl) for freeze-dried samples according to the Edana 440.1-99 and Edana 441.1-99 standard methods with two exceptions (a 2 min drip off time was used before FSC weight measurements, and the sample weight was 0.04 g). The estimated standard deviation for FSC and CRC was ± 5 g/g and ± 0.5 g/g, respectively.

The wet mechanical stability of freeze-dried materials was measured in a compression test in which a wetted sample was subjected to increasing pressures according to the scheme in Table 3. One compression test was also performed on a dry sample before it was wetted. The equipment used in this test has been described by Lund et al. (2011). By measuring the height of the sample at each pressure, the wet bulk (cm^3/g) could be calculated. The wet bulk is the volume of the wet sample divided by the dry weight of the sample at different loads. Consequently, this test provides information about how much liquid a material can retain when subjected to loads according to the test scheme.

Table 3. Testing Scheme Used in the Compression Test

Time (min)	0	2	12	14	16	18	20	22	24	26	28
Pressure (kPa)	0.6	0	0	0.1	0.6	1.3	2.6	5.2	7.7	12.9	19.4
State	Dry	Wetting	Drainage	Wet	Wet	Wet	Wet	Wet	Wet	Wet	Wet

RESULTS AND DISCUSSION

TEMPO-Oxidation

The TEMPO-oxidation treatment introduced new carboxylate groups into the pulp, and the amount of the carboxylate groups in the pulp increased as the charge of the oxidant increased (see Table 4). At the highest charge of the oxidant, the amount of the carboxylate groups increased to 1.38 mmol/g pulp for the softwood kraft pulp, and to 1.64 mmol/g pulp for the hardwood kraft pulp. This difference is large enough to be significant, and it cannot be explained by the amount of carboxylate groups in the starting materials. However, the hardwood kraft pulp was only tested at the highest charge of the oxidant, so further tests are needed in order to verify and explain the difference. It can also be noted that the oxidation is more selective in forming carboxylate groups at a oxidant low charge, but all the added oxidant was consumed and consequently other reactions took place simultaneously. These reactions most likely degraded the cellulose molecule and decoupled the cellulose network. The amount of carboxylate groups and the selectivity of carboxylate group formation are in agreement with the results in earlier studies (Saito et al. 2006, 2007) on the effect of TEMPO-oxidation on chemical pulps.

The amount of aldehyde groups is also shown in Table 4, which shows that the TEMPO-oxidation treatment increased the amount of aldehyde groups in the pulp treated with the harshest oxidation. The amount of aldehyde groups after TEMPO-oxidation was relatively high in comparison to earlier findings (Saito et al. 2006). To investigate how and whether aldehyde groups influence the properties of absorbent materials, the same oxidized pulp was treated with $NaBH_4$ so that most of the aldehyde groups were converted back to hydroxyl groups. The result of the treatment was a pulp with a high amount of carboxylate groups but a low amount of aldehyde groups.

Table 4. Amounts of Carboxylate and Aldehyde Groups in the Pulps

Wood source	Oxidation level	Charge of oxidant (mmol/g)	Reduction treatment	Carboxylate groups (mmol/g)	Selectivity (%)	Aldehyde groups (mmol/g)
Softwood	No	0	No	0.07	-	0.03
Softwood	Mild	0.8	No	0.42	84	-
Softwood	Medium	2.1	No	0.92	82	-
Softwood	Harsh	3.2	No	1.02	60	-
Softwood	Harshest	4.2	No	1.38	63	0.61
Softwood	Harshest	4.2	Yes	-	-	0.14
Hardwood	No	0	No	0.13	-	-
Hardwood	Harshest	4.2	No	1.64	73	-

Fiber Disintegration

In mechanical treatment, the pulp fibers were gradually disintegrated into a fibrillated material that consisted of a mixture of fibers and fibrils. Figure 1 shows that

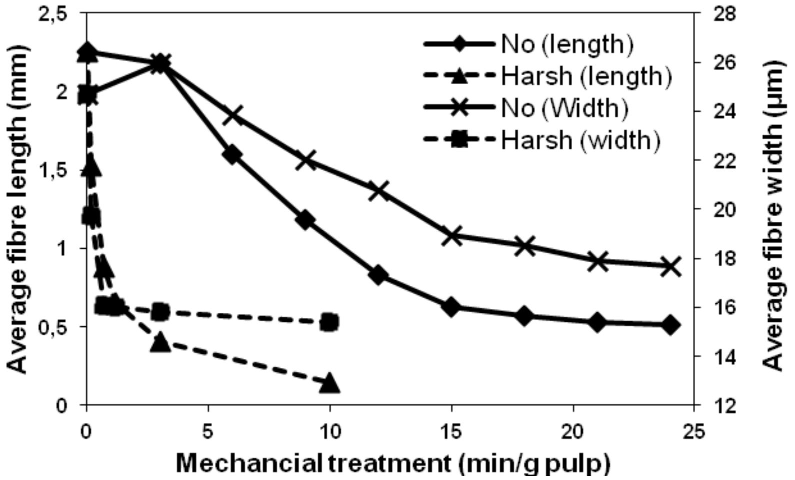


Fig. 1. The average fiber length and average fiber width are plotted versus the amount of mechanical treatment for softwood kraft pulp treated with no oxidation (continuous line) or harshest oxidation (broken line). Mechanical treatment is the treatment time adjusted to the amount of pulp.

the disintegration of pulp fibers is much faster in oxidized softwood kraft pulp than in non-oxidized softwood kraft pulp. The dramatic decrease in fiber length and fiber width was probably a combined effect of the greater amount of carboxylate groups and the decoupling of the carbohydrate network. However, the change in fiber width leveled out after a steep, but not very large initial decrease, which indicates that additional mechanical treatment has a minor influence on the average width of the remaining fibers.

Figure 2 presents the importance of the oxidation level and shows that the higher the charge of the oxidant, the faster and more efficient the disintegration of softwood pulp fibers takes place. The data suggest that the combined effect of a greater amount of carboxylate groups and the degree of the decoupling of the carbohydrate network is more or less proportional to the oxidation level.

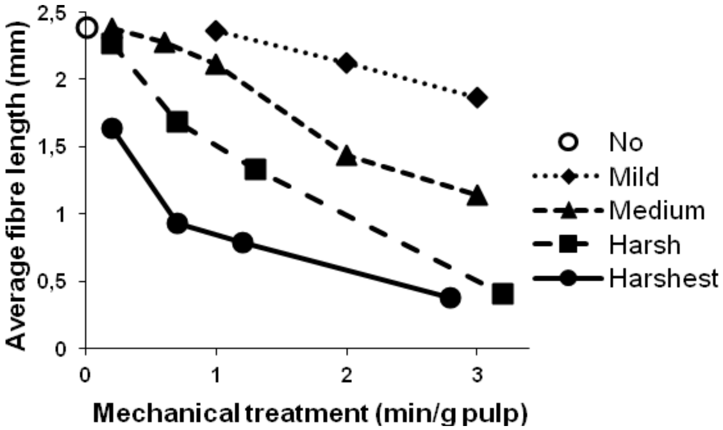


Fig. 2. The average fiber length of four pulps with different oxidation levels is plotted versus the amount of mechanical treatment. The original softwood kraft pulp (No) is included as a reference. Mechanical treatment is the treatment time adjusted to the amount of pulp.

Figure 3A shows the size distribution of the short fraction of non-oxidized pulp. It was found that the average particle size of the short fraction increased as the duration of the mechanical treatment increased. This result can be explained by the fact that the short fraction increased from 5% in the original softwood kraft pulp to 85% after the longest mechanical treatment. Consequently, the total amount of material that is small enough to pass through the fractionation step increased with increasing duration of the mechanical treatment, and the average size of the material in that fraction also increased.

The second peak (at about 500 μm) in the distribution of particle size shows that relatively large fiber parts were present in the short fraction of the non-oxidized pulp even after a long mechanical treatment. The most likely explanation for this peak is that it consists of fragments of larger fibers that had been disintegrated. If longer or more powerful mechanical treatment had occurred, these fiber fragments would have disintegrated into even smaller fragments. Particle size analysis confirmed a more rapid disintegration of the fibers after a powerful oxidation treatment than in non-oxidized pulp or gently oxidized pulp (see Fig. 3B). These findings show that the size distribution obtained with the harshest oxidation treatment followed by the shortest mechanical treatment (with 40% short fraction) was similar to the size distribution obtained with the longest mechanical treatment of non-oxidized pulp. It was also found that after a medium or long mechanical treatment, essentially all the material was small enough to be in the short fraction and the average particle size decreased as the mechanical treatment proceeded. The size distributions together with the fractionation data show that more and smaller elements are obtained when oxidized pulp with a high oxidation level is used.

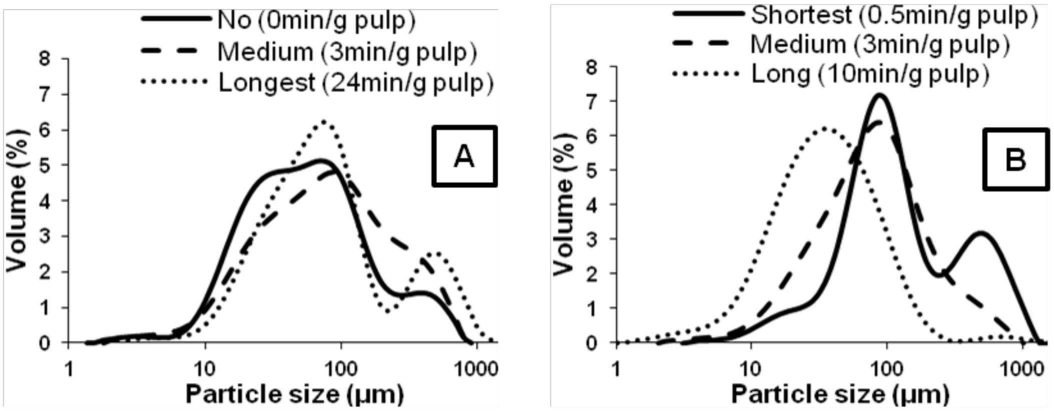


Fig. 3. Particle size distributions plotted versus particle size (logarithmic scale) of **A)** non-oxidized softwood kraft pulp treated with no, medium, or longest mechanical treatment and **B)** softwood kraft pulp treated with the harshest oxidation followed by the shortest, medium, or long mechanical treatment. Mechanical treatment is the treatment time adjusted to the amount of pulp.

Properties of Dried Materials

The two drying techniques used in this study represent two extremes and resulted in two types of absorbent materials. When air drying was used, the fibrillated material was pressed together by capillary forces that were generated between the surfaces in the material during water removal. Consequently, the fibrillated material formed a compact film that was more or less opaque, depending on the charge of the oxidant and the extent of mechanical treatment. The dry bulk densities of the air-dried films were approximately 1.4 g/cm^3 (estimated average value from several measurements of the weight and dimension of samples). This value is approximately the same as the skeletal density of cellulose, which indicates that the films were virtually non-porous solids. If freeze drying was used instead, high porosity was preserved, since water was sublimated from its frozen state. In this case, the material formed a porous foam (dry bulk densities of 0.006-0.008 g/cm^3) if the oxidation was performed with a sufficient amount of oxidant. Since the freeze-dried material was, at this point, considered to be the most interesting material, the main focus of the study was directed to that material. Nevertheless, some interesting data on the air-dried material is presented below.

Freeze-dried samples were studied with SEM in order to visualize the difference between mechanical treatment only and combined TEMPO-oxidation and mechanical treatment. Figure 4A-4D shows some examples: Fig. 4A shows an untreated softwood kraft pulp fiber and is used here as a reference; Fig. 4B is an example of a softwood kraft pulp that has received mechanical treatment only (the longest mechanical treatment); Fig. 4C is an example of a softwood kraft pulp after a mild oxidation treatment followed by a medium mechanical treatment; and finally, Fig. 4D is an example of a softwood kraft pulp after the harshest oxidation treatment followed by a medium mechanical treatment.

It can clearly be seen that mechanical treatment only resulted in a network of fibrils of various sizes, even if the longest mechanical treatment was used. However, a powerful oxidation treatment followed by a relatively short mechanical treatment resulted in a completely different structure (see Fig. 4D). In this case, the structure may be described as a foam, where the fibrillar network is partly covered by thin layers of cellulosic material. These layers build up a system of interconnected pores that has a large available surface area for the absorption of liquids. A comparison of Fig. 4B and 4D shows that it is necessary to have a certain degree of oxidation treatment before the foam-like structure can be formed.

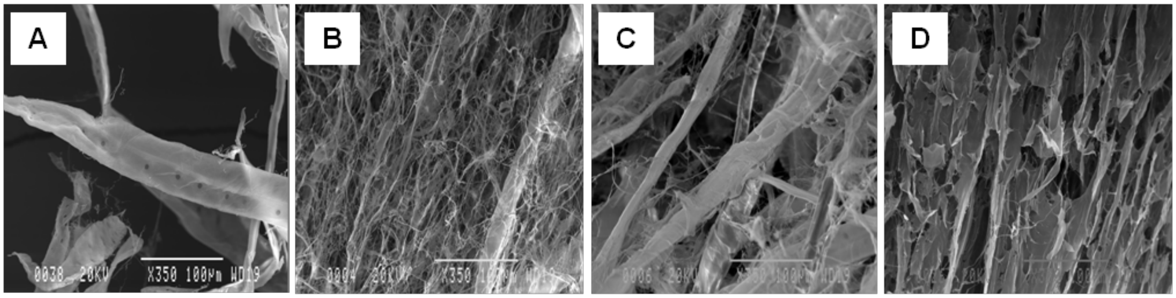


Fig. 4. SEM images of; **A)** Softwood kraft pulp (Sample 16, 350x), **B)** Softwood kraft pulp + longest mechanical treatment (Sample 18, 350x), **C)** Softwood kraft pulp + mild oxidation + medium mechanical treatment (Sample 2, 350x), and **D)** Softwood kraft pulp + harshest oxidation + medium mechanical treatment (Sample 14, 370x).

An interesting property of the porous foam is that it does not disintegrate or disperse when it is soaked in water. This wet integrity was studied in order to determine whether this was related to the oxidation treatment. Therefore, soaking tests conducted with: a) a pulp that was only mechanically treated (Sample 18) and thereafter freeze-dried and b) a pulp that was oxidized in the first stage and then reduced before the disintegration and freeze drying (Sample 24). In both cases porous materials were obtained after freeze drying. However, when these two samples were rewetted they dispersed and formed a suspension. A plausible explanation for the wet integrity of the oxidized samples is that the aldehyde groups formed during the oxidation reacted with hydroxyl groups on the cellulose and formed sufficiently stable hemiacetal bonds during the drying step. It is also possible that these bonds were formed between closely located fibril surfaces, thus introducing wet resistant interfibrillar cross-links into the material. A similar result was obtained by Saito and Isogai (2006), who showed that a greater wet strength was obtained in paper sheets when aldehyde groups were introduced on the fiber surfaces forming interfiber hemiacetal bonds.

The surface area of the air-dried films in Table 5 shows that these compact materials have a much lower surface area than the freeze-dried porous materials. After a more powerful oxidation treatment the surface area decreased, which indicates that these films have fewer small pores available for the absorption of liquids. For the freeze-dried materials, it was found that the surface area increased with increased mechanical treatment. The surface area also increased when the charge of the oxidant was greater. Furthermore, the finding also shows that the hardwood sample (Sample 23) obtained a smaller specific surface area than the softwood sample (Sample 21) after the same treatments. However, this result is based on only one sample, so this finding remains to be validated in future investigations.

Table 5. Specific Surface Area of Air-Dried Materials (AD) and the Freeze-Dried (FD) Materials Calculated According to Multiple Point BET Analysis

ID	Wood source	Oxidation level	Extent of mechanical treatment	Drying method	Surface area (m^2/g)
1	Softwood	Mild	Short	AD	1.22
4	Softwood	Medium	Short	AD	0.72
12	Softwood	Harshest	Short	AD	0.50
16	Softwood	No	No	FD	15.9
17	Softwood	No	Medium	FD	21.7
18	Softwood	No	Longest	FD	24.3
19	Softwood	Medium	Medium	FD	16.1
21	Softwood	Harshest	Medium	FD	64.9
23	Hardwood	Harshest	Medium	FD	27.5

Figure 5 shows the Total Cumulative Volume (TCV) of freeze-dried materials. The findings show that the combination of oxidation and mechanical treatment provided a material after freeze drying that had a large pore volume at small effective radii, which indicates a high content of small pores. It can also be seen that these materials had a high capacity for absorption as shown by the high TCV at large effective radii (low pressures). In a comparison of samples that received the medium mechanical treatment, it is obvious that without the oxidation treatment the material had a low content of small pores, as illustrated by the low TCV values at low effective radii (high pressure). If the longest mechanical treatment was used instead, the content of small pores increases to approximately the same level as in the oxidized samples due to the large amount of liberated fibrils (cf. Fig. 4B).

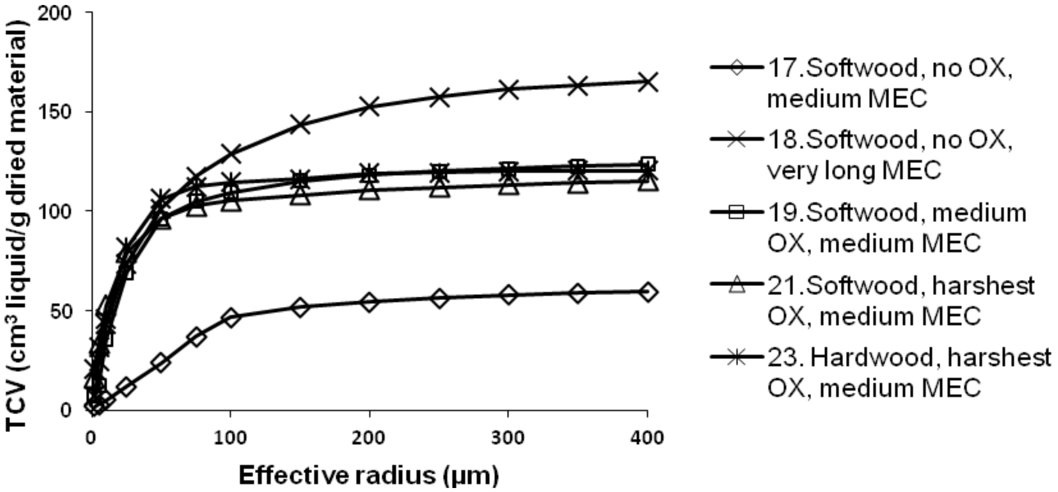


Fig. 5. Total cumulative volume (TCV) plotted versus effective radius of the pores for non-oxidized and oxidized samples after mechanical disintegration and freeze drying. The legend shows sample ID, wood source, oxidation level (OX), and mechanical treatment (MEC). The test liquid is hexadecane.

The small pores are important because of their ability to retain more liquid at higher pressures than larger pores due to greater capillary force. At the smallest pore radii, the hardwood and softwood samples treated with the most powerful oxidation had the highest TCV, which shows that a large amount of small pores was created after medium mechanical treatment and the harshest oxidation treatment. It is important to note that hexadecane was used in the experiments in Fig. 5, which is a non-polar liquid that does not collapse the pore structure of the materials. Consequently, the result should be considered to represent the pore volume of the dried structure without any wetting.

To examine how the pore volumes are affected when the freeze-dried foam is exposed to a polar solvent, the hexadecane results were compared with a water/tenside solution. In Fig. 6, the result shows that the TCV was much lower in for the polar solvent, possibly due to capillary forces that contract the material when wetted and thereby changing the pore structure. After the partial collapse of the pore structure, the retention of liquid in the material was enhanced by both capillary and osmotic forces which provided a similar TCV for both test solutions at the smallest effective radius (highest pressure).

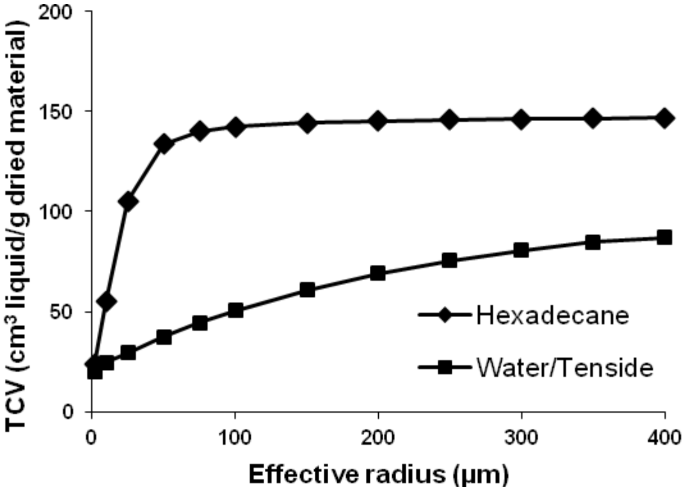


Fig. 6. Total cumulative pore volume plotted versus effective radius of the pores for two different test solutions. Sample 15b was used in these tests and is prepared from softwood kraft pulp with the harshest oxidation, medium mechanical treatment (Sample 15b), and freeze drying.

Absorption Properties of Freeze-Dried Materials

Figure 7 shows the Free Swell Capacity (FSC) of the freeze-dried materials. It can be seen that the absorption rate was very rapid and that the main part of the liquid (saline solution) was absorbed during the first minute. The high absorption rate is likely due to the open structure of these freeze-dried materials (cf. Fig. 4B-4D). The highest FSC was found in oxidized samples when the mechanical treatment of the oxidized pulp was moderate. This finding suggests that the presence of some long fibres in combination with water resistant bonds, possibly hemiacetal bonds, are important factors to obtain a high FSC. The non-oxidized samples showed that it is possible to reach a reasonable high FSC also with without oxidation if a long mechanical treatment is employed. However, the lack of inter-fibrillar bonds results in a low mechanical stability, which makes the material disperse when it is soaked in aqueous solutions. Absorption capacities of around 20 g/g have also been reported for other MFC materials (Makoui and Chatterjee 1987). Consequently, the FSC results show that the use of an oxidation treatment prior to the mechanical treatment improves the absorption capacity of the freeze-dried material.

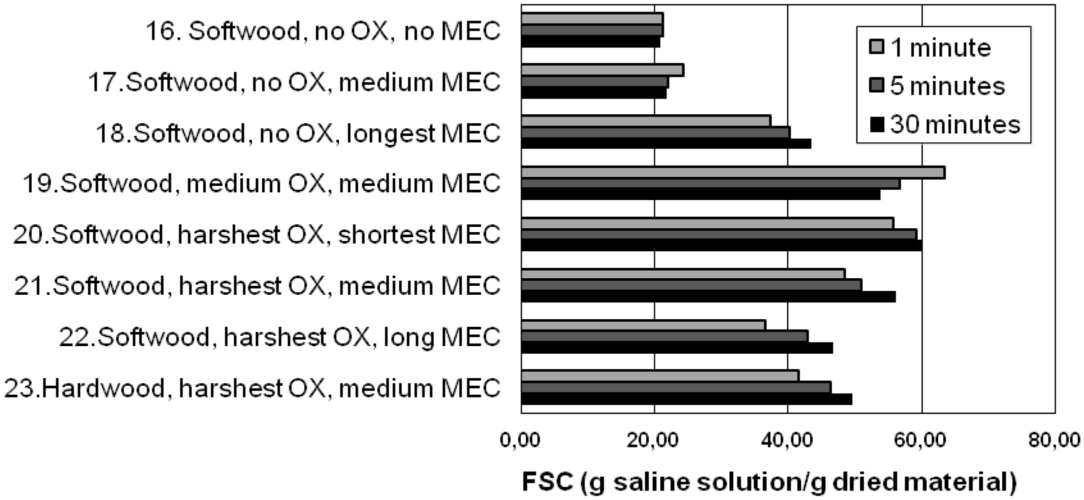


Fig. 7. Free swell capacity (FSC) in 0.9 weight% NaCl solution after 1 min (light gray), 5 min (dark gray), and 30 min (black) of absorption time The legend shows sample ID, wood source, oxidation level (OX), and mechanical treatment (MEC).

In Fig. 8, the Centrifuge Retention Capacity (CRC) is presented for the freeze-dried samples, and the results show that the addition of a large amount of oxidant together with a long disintegration time gives the highest retention capacity (15.8 g saline solution/g dry material). An increase in the charge of the oxidant gives a higher charge density (increased osmotic pressure) and a more efficient disintegration of the fibers (smaller pores), which are both favorable for retention properties of the material.

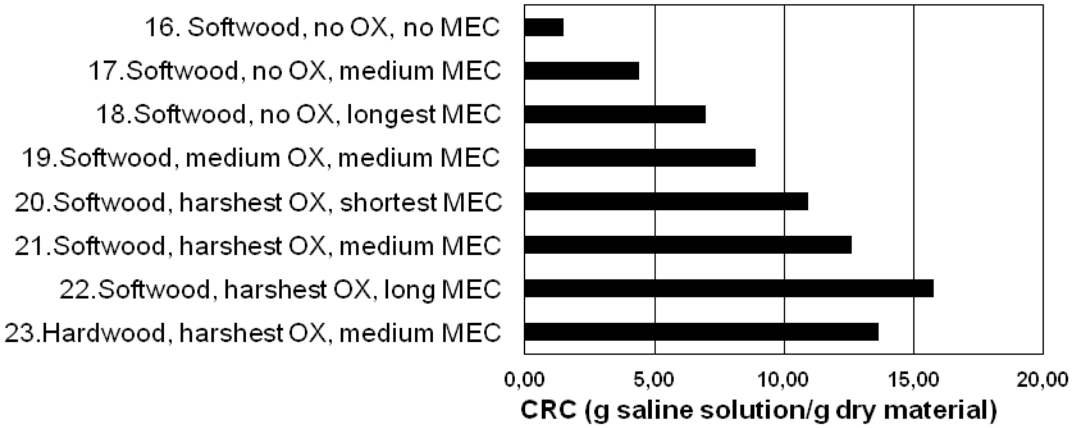


Fig. 8. The centrifuge retention capacity in 0.9 weight% NaCl solution is shown for the freeze-dried materials. The legend shows sample ID, wood source, oxidation level (OX), and mechanical treatment (MEC).

An extensive mechanical treatment (without oxidation) leads to smaller pore sizes only. At their highest capacity, these freeze-dried samples reached about half the capacity of synthetic SAPs, which generally have retention capacities of about 30 g saline solution/g SAP (Nagorski 1994).

In Fig. 9, the wet bulk is plotted versus pressure, and the result shows a rapid decrease in the sample volume at low pressures. This indicates that the freeze-dried materials had weak mechanical stability. This figure also shows that the oxidation level seems to have a greater effect on the wet bulk than the degree of mechanical treatment, indicating that osmotic forces have a large impact on wet bulk. The wet bulk in saline solution (0.9 weight% NaCl) has also been tested (not presented here), showing that immersion in this solution resulted in essentially the same wet bulk as when tested in water (1-2 cm^3/g lower than in water at pressures between 2.6-19.4 kPa). At 3.5 kPa pressure, the wet bulk of the samples treated with the harshest oxidation was about 20-25 cm^3/g, which is about twice as high as the MFC materials produced by Chatterjee and Makoui (1984).

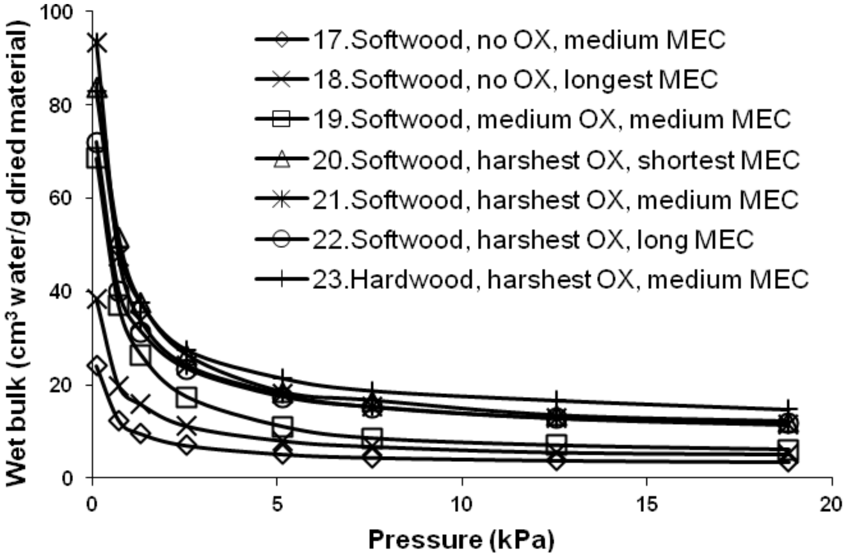


Fig. 9. Wet bulk tested in water plotted versus pressure for freeze dried samples. The legend shows sample ID, wood source, oxidation level (OX), and mechanical treatment (MEC).

Absorption Properties of Air-Dried Materials

From Fig. 10A-10B, where the Total Absorption Potential (TAP) of the air-dried compact films are plotted versus time, it can be concluded that a high charge of oxidant and a long mechanical treatment are favorable to obtain a high absorption rate and a high final capacity. However, the highest absorption rate remains slow and it takes several hours to reach a plateau value. Despite the slow absorption kinetics, the highest final TAP value obtained was 62 g water/g dry material (see Fig. 10B), which is indeed a very high absorption capacity.

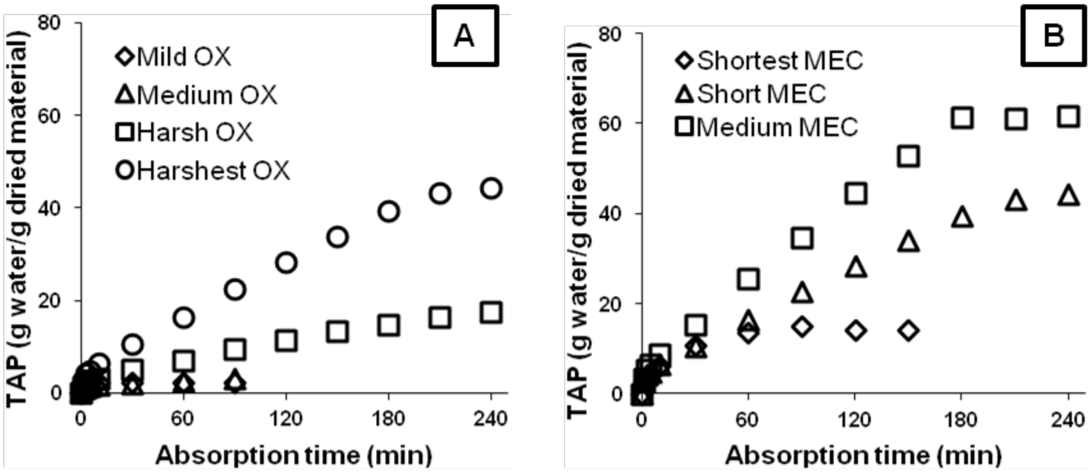


Fig. 10. Total absorption potential (TAP) in water plotted vs. the absorption time of **A)** air-dried samples with different oxidation levels (OX) followed by a short mechanical treatment and **B)** air-dried samples with different extents of mechanical treatment (MEC) after the harshest oxidation.

Figure 11 shows that the absorption rate and the final TAP value of the air-dried films became much lower when they were tested in saline solution compared to absorption of pure water. This result can be explained by the reduction in osmotic pressure due to the presence of ions in the test solution that is to be absorbed. A reduction in osmotic pressure leads to less swelling in the compact film material and, consequently, air-dried films seem not to be suitable as absorbents of saline liquids due to their low absorption rate and low absorption capacity.

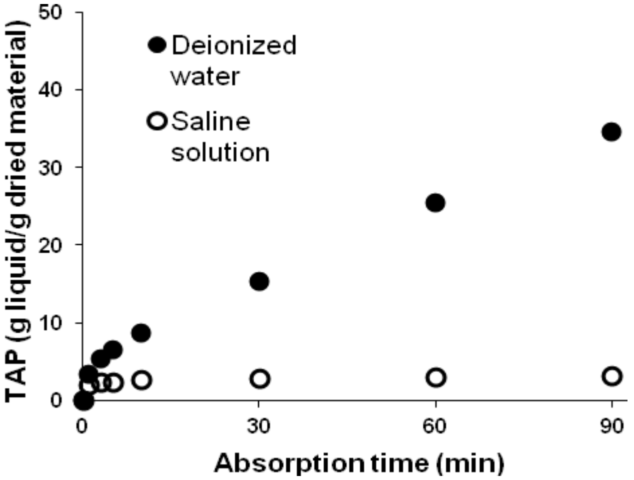


Fig. 11. Total absorption potential (TAP) in water and saline solution (1.0 weight% NaCl) is plotted versus absorption time. The tested sample (Sample 15a) was produced from softwood kraft pulp, subjected to the harshest oxidation, medium mechanical treatment, and air-dried.

CONCLUSIONS

1. TEMPO-oxidation treatment of never-dried bleached kraft pulp provides a pulp with a high amount of carboxylate and aldehyde groups. By increasing the charge

of the primary oxidant (NaClO), more carboxylate groups are introduced, but the selectivity of carboxylate group formation decreases when the charge of the oxidant is high. It has also been shown that the introduction of aldehyde groups provides wet integrity to the material, possibly through the formation of hemiacetal bonds.

2. Fiber analysis and particle size analysis have shown that the disintegration of kraft pulp fibers is facilitated by oxidation treatment, and that the disintegration rate is more or less proportional to the charge of the oxidant.
3. SEM images of freeze-dried materials showed that oxidation treatment is necessary in order to obtain a foam-like material. The porous foam has a large surface area and a high absorption rate, as well as a reasonably high retention capacity. CRC measurements have shown that a powerful oxidation treatment and an extensive mechanical treatment are favorable in obtaining a high retention capacity, while the absorption capacity is favored by less treatment, which preserves some long fibers in the sample.
4. Air drying results in a compact film that has a small surface area and a slow absorption rate as well as a high final absorption capacity in water. The absorption rate and the absorption capacity are enhanced through powerful oxidation treatment and extensive mechanical treatment.

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