

Preparation of Absorbent Foam Based on Softwood Kraft Pulp: Advancing from Gram to Kilogram Scale

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Absorbent foams were produced at both the gram scale and the kilogram scale by treating bleached softwood kraft pulp fibers to TEMPO oxidation, followed by washing, fiber disintegration, and freeze drying. Two reaction temperatures and three different dosages of primary oxidant were evaluated to find suitable oxidation conditions. It was found that the absorption and retention capacities were 50 to 70% lower for kilogram-scale foams than for gram-scale foams. SEM studies showed that the kilogram-scale foams had larger pores than the gram-scale foams; this explains the major differences in absorption and retention. The oxidation treatments performed in both scales resulted in a major increase in the amount of carboxylate groups and a major decrease in DP_v , but only minor differences in these factors were found in a comparison between pulps from gram- and kilogram-scale experiments. However, the kilogram-scale dispersing equipment appeared to cause more fiber cutting, while the equipment used in the gram-scale experiments promoted the liberation of microfibrils to a greater extent. Furthermore, in both the gram- and kilogram-scale samples, a high dosage of primary oxidant and a low oxidation temperature were found to maximize the retention of liquid.

Keywords: Microfibrillated cellulose; Laboratory scale; Scale-up; TEMPO oxidation; Centrifuge retention capacity; Free swelling capacity; Absorbent foam; Morphology

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INTRODUCTION

Many of the products that are used in our daily life today have a high content of materials originating from crude oil (*e.g.* polyethylene, polypropylene, and polyvinylchloride). Since crude oil is a non-renewable resource, at least with respect to the current rate of extraction, and even though it can be assumed that recycling and reuse of materials will increase, there will be an increasing demand for materials based on renewable raw materials. Utilization of biologically-sourced raw materials such as wood, straw, and vegetable oil will be increasingly important, and among these wood is by far the most available resource. There are two main concepts for converting bio-based raw materials for potential applications. The first concept involves processes for breaking down the polymers of the biomaterial into various types of monomers, *e.g.* sugar monomers in a liquid solution or CO and H₂ in a syngas, in a first phase of the process. And in a second process stage, often involving several reaction steps, both chemical and biochemical, these monomers are used in the production of various chemicals including different polymers. The main drawback of this concept is that the overall energy efficiency and material yield tend to be relatively low. The second concept is to utilize

the polymeric structure of the bio-material, thus, reducing the need for energy-demanding breakdown and buildup processes. Research activities for finding solutions for utilizing renewable resources in accordance with the second concept are on the rise. The outcome of this research has the potential to provide solutions that are more sustainable than conventional petroleum-based materials and the solutions from the first concept.

Some of the materials that need to be replaced in the future are SuperAbsorbent Polymers (SAPs), which today are almost exclusively produced from petroleum-based resources. The SAPs have become important constituents in baby diapers and incontinence products, and the demand for SAPs has increased rapidly since their introduction in the late 1980's. Currently, absorbent materials based on renewable raw material have only a very limited use compared to the petroleum-based SAPs. Thus, there is a need to improve existing alternatives or to find new absorbent materials based on renewable resources.

Recently, an absorbent material based on softwood kraft pulp was successfully prepared at a gram scale (Brodin and Theliander 2012). Furthermore, a process for preparing this absorbent material has been proposed (Theliander *et al.* 2011; Wernersson and Theliander 2011), which is shown in Fig. 1. In this process, oxidation is used as a pre-treatment method. After removing the spent oxidation chemicals by means of a displacement washing step, the pulp is disintegrated, thus forming microfibrillar cellulose (MFC). The last process step is freeze drying where the absorbent foam is formed.

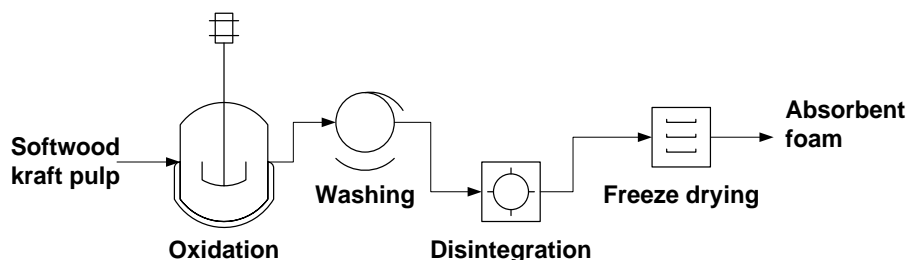


Fig. 1. A simplified scheme for the production of absorbent foam

Various pre-treatments have been suggested to improve processability or to reduce the energy demand of the preparation of MFC such as mechanical cutting (Herrick *et al.* 1983; Turbak *et al.* 1983), acid hydrolysis (Pääkkö *et al.* 2007; Henriksson *et al.* 2007), enzymatic treatment (Pääkkö *et al.* 2007; Henriksson *et al.* 2007), TEMPO oxidation (Saito *et al.* 2006), and carboxymethylation (Wågberg *et al.* 2008). In the preparation of the cellulose-based absorbent material in this work, the pulp was treated with TEMPO oxidation to introduce new carboxylate and aldehyde groups onto the cellulosic microfibrils. TEMPO oxidation is a selective oxidation method that can be used to oxidize water-soluble (De Nooy *et al.* 1995) and water-insoluble (Chang and Robyt 1996) polysaccharides. In TEMPO oxidation, catalytic amounts of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) mediates the oxidation of the cellulose, with or without NaBr as co-catalyst (Bragd *et al.* 2000). Throughout the reaction TEMPO is regenerated by a primary oxidant. A more comprehensive description of the chemical reactions involved can be found in the recent reviews by Isogai *et al.* (2011) and Bragd *et al.* (2004). In our process, the oxidation treatment is followed by a washing step in which the spent reaction chemicals are separated from the oxidized pulp by means of displacement washing with water.

In the next process step, disintegration, the intention is to break up the fiber morphology and liberate microfibrils to further enhance the absorption properties of the material. Microfibrillar cellulose (MFC) can be obtained by treating pulp fibers mechanically in, for example, a high pressure homogenizer (Herrick et al 1983; Turbak *et al.* 1983; Nakagaito and Yano 2004; Zimmermann *et al.* 2004; Pääkkö *et al.* 2007), a ceramic grinder (Taniguchi and Okamura 1998), or a high-speed dispersing unit (Brodin and Theliander 2012). The sizes and yield of microfibrils/nanofibrils depend upon the treatments used, as well as on the raw material. The dimensions of the fibrillar threads can typically have diameters of 2 to 20 nm and lengths of up to several tens of μm , depending on the raw material (Helbert *et al.* 1996). Many published works have described methods for producing MFC on a small scale (*e.g.* Siro and Plackett 2010), but very little is known about scaling up this process or production in larger scale.

Freeze-drying, also known as freeze casting, is used in our process to dry the wet fibrillar suspension and produce a porous foam. The technique involves the steps of freezing a liquid suspension/solution and subsequently sublimating the solidified phase from the solid to the gas phase under reduced pressure (Deville 2008). During the freezing operation, particles in the suspension are rejected from the moving solidification front and are squeezed together between the growing solvent crystals. This technique has mainly been utilized on inorganic particles (Deville 2008), but it has also been used for polymers to generate porous polymer nanocomposites (*e.g.* Zhang *et al.* 2005; Köhnke *et al.* 2012).

Scaling up a process is often a demanding challenge, since a large number of conditions must be considered, including both chemical and physical aspects of the produced material. Also, the exchange to larger process equipment may influence the obtained product. Since most laboratory equipment has a design not even close to more industrially adapted equipment, the scale up from laboratory (gram) scale to bench (kilogram) scale is especially challenging. There are often many conditions (*e.g.* temperature gradient, mixing conditions, flow conditions, and turbulence) that differ between small laboratory scale (or “gram scale”) and the slightly larger bench scale (or “kilogram scale”). It may, thus, be necessary to change some process conditions or equipment design in order to obtain the same process outcome. Additionally, a decrease in usage of resources, *e.g.* water, chemicals, and energy may also be included in the frame of scale-up, which further increases the degree of complexity.

In this study, the aim has been to evaluate process equipment and product performance when advancing from gram scale to kilogram scale. Characterization of chemical and physical properties, as well as absorption has been performed to better understand the influence of equipments and process conditions. The study involved kilogram-scale production in the process steps of oxidation, washing, and disintegration, while the freeze drying operation was performed only on the gram scale to produce test pads for absorption tests. Moreover, a reduction in the use of water has been an important aspect of this work in its aim to approach industrial-like conditions.

EXPERIMENTAL

Materials

Never-dried bleached softwood kraft pulp from a Scandinavian pulp mill was produced in a Totally Chlorine Free (TCF) bleaching sequence.

The following chemicals were used as received: TEMPO (2,2,6,6-tetramethyl-piperidine 1-oxyl, free radical) 98% pure (from Sigma-Aldrich), sodium bromide (99.5% reagent grade, Scharlau), sodium hydroxide (99% reagent grade, Scharlau), hydrochloric acid (solution 1 M reagent grade, Scharlau), sodium hypochlorite (solution 15% w/v extra pure, Scharlau).

Deionized water was used in all process steps.

Oxidation

TEMPO-oxidation was used to introduce new functional groups into the pulps. Gram-scale (“laboratory-scale”) experiments were performed in a cylindrical glass vessel ($\text{\O} = 10$ cm) without baffles and a pitched blade impeller ($\text{\O} = 4.4$ cm, 900 rpm). This glass vessel was mounted in a temperature-regulated water bath to enable temperature control.

The kilogram-scale (“bench-scale”) reactor was 100 times larger in volume. To ensure good mixing conditions in this larger reactor, we chose a reactor ($h = 0.65$ m, $\text{\O} = 0.45$ m) with four fixed baffles (0.6×0.042 m) and a Rushton turbine ($\text{\O} = 0.15$ m, 300 rpm). The jacketed reactor tank was made of stainless steel and had oil as the heating media, which was circulated from a temperature-regulated oil bath. A pH stat (Titroline Alpha with a 50 mL column) was used in experiments on both scales for pH control. More concentrated NaOH was used in kilogram-scale experiments to minimize the need for extra manual additions of NaOH. Manual addition was, however, necessary in the early stage of the reactions in the kilogram-scale experiments, since the pumping capacity of the pH-stat was too low. The specifications for the reactors are summarized in Table 1.

Table 1. Reactor Specifications and pH Control

	Gram-Scale Experiments	Kilogram-Scale Experiments
Working volume (m^3)	0.5×10^{-3}	50×10^{-3}
Reactor material	Glass	Stainless steel
Heating method	Temperature-regulated water bath	Oil circulation in jacketed reactor
Mixing	Four pitched blade impeller	Rushton turbine
Baffles	no baffles	Four baffles
pH – control	pH – stat	pH – stat
NaOH addition	Automatic (0.5 M NaOH)	Automatic + manual (2 M NaOH)

The mixing in the kilogram-scale reactor was tested before the oxidation experiments were carried out in order to ensure that efficient mixing would be achieved under the conditions used for the subsequent tests. A pulp suspension, 2% pulp consistency, was prepared and heated to 30°C . To this pulp suspension 10 mL of 2 M NaOH was added, and the response in pH was followed by logging the pH using a pH-meter. As can be seen in Fig. 2, the time to obtain a fairly stable pH in the vessel was about 10 s, which is indeed a short time compared to the total reaction time.

At both the gram scale and kilogram scale, two conditions were varied; (a) the reaction temperature and (b) the dosage of primary oxidant (NaClO). These and other reaction conditions are shown in Table 2. The pulp consistency was different in experiments at the two scales. Maximum pulp consistency was 1% in the gram-scale experiments but was considered to be too low for industrial applications. Therefore, we chose to use 2% pulp consistency (*i.e.* reducing the water content by 50%) in the kilogram-scale experiments, still with good mixing of the pulp suspension, as seen in Fig. 2.

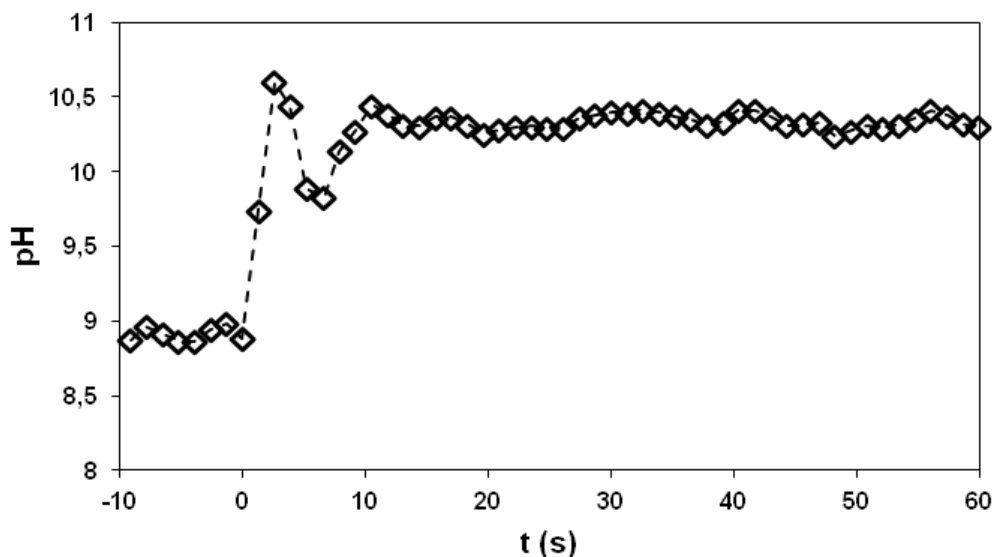


Fig. 2. pH response in kilogram-scale reactor

Table 2. Oxidation Conditions

	Gram Scale	Kilogram Scale
Pulp (kg/batch)	5×10^{-3}	1
Pulp consistency (%)	1	2
Temperature ($^{\circ}\text{C}$)	30 and 50	30 and 50
Reaction pH	10 ± 0.2	10 ± 0.5
NaClO at pH 10 (mol/kg pulp)	2.5, 3.8 and 5.0	2.5, 3.0 and 5.0
NaBr (mol/m^3)	10	10
TEMPO (mol/m^3)	1	1

Many of the oxidation parameters were kept constant in all experiments, such as pH and the concentration of the catalytic compounds (TEMPO and NaBr). However, as can be seen in Table 3, the total residence time at pH 10 and the predefined temperature varied. In general, the total residence time was longer in the kilogram-scale experiments. Before the reaction began, the temperature of the pulp suspension was heated to the predetermined reaction temperature and the catalytic compounds were added. The reaction was initiated by the addition of primary oxidant. In order to maintain pH 10, a NaOH solution was added until no further decrease in pH was observed, thus indicating the depletion of the primary oxidant.

Table 3. Total Residence Time (min) in Reactor Vessel (oxidations at 30°C / 50°C)

Dosage of NaClO (mol/kg pulp)	Gram Scale	Kilogram Scale
2.5	30/ 15	-/ 300
3.0	-/ -	220/ 180
3.8	120/ 40	-/ -
5.0	180/ 40	120/ 90

Washing

In this operation, the pulp was separated from the liquid with spent oxidation chemicals using filtration followed by displacement washing with deionized water. Table 4 summarizes the data of the washing operation. In the washing of the pulps, a large amount of wash water was used. On the gram scale a wash ratio (total wash liquid/ liquid in pulp cake before washing) of 40 was used, and on the kilogram scale the wash ratio of 12 was selected. In both scales an excess of wash water creates a very efficient one-step separation process. The details of filtration and washing of TEMPO-oxidized pulps have been investigated in a separate study (Brodin *et al.* 2013).

Table 4. Washing Equipment and Conditions

	Gram Scale	Kilogram Scale
Filter name	Buchner funnel	Larox Pf 0.1
Filter area (m ²)	9.5 x 10 ⁻³	0.1
Filter cloth	Nylon web	Tamfeld S-2108-L1
Pulp per batch (kg pulp)	7-12 x 10 ⁻³	0.35
Washing liquid (m ³ /kg pulp)	0.40	0.12

Gram-scale filtration experiments were performed in a Buchner funnel with a nylon web. The filtrate was returned once through the filter cake followed by displacement washing. The liquid was distributed over the filter cake with a small spoon to avoid breakage of the filter cake. In the kilogram-scale experiments, each washing batch started by pumping the pulp suspension into the filter at 5 bar pressure under a gradual buildup of filter cake on the filter cloth. After cake formation, the pulp was displacement-washed with deionized water. After the washing step, compressed air at 5 bar pressure was used to dewater the pulp cake to about 16 to 20% of pulp consistency.

Disintegration

In the disintegration step, the pulp fibers were subjected to disintegration treatment in order to liberate the microfibrils from the fiber wall of the pulp fibers. The disintegration equipment and conditions used for the gram-scale and kilogram-scale experiments are presented in Tables 5 and 6.

Table 5. Disintegration Equipment and Conditions

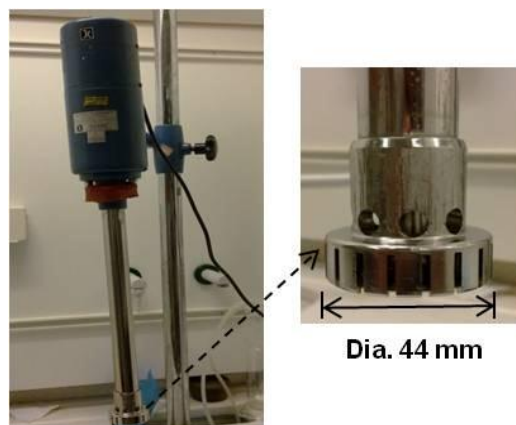
	Gram Scale	Kilogram Scale
Equipment name	IKA Ultra Turrax T45/N	Ystral Z 80-3
Energy input (kW)	0.39	7.5
Rotation speed (rpm)	10000	5000
Chamber volume (L)	0.049	0.55
Stator/rotor slots (mm)	(2/2)	(4/6), (3/5) and (2/4)
Pulp consistency (%)	0.6	2.0
Batch size (kg pulp)	0.002	0.4
Vessel type (size)	Plastic beaker (0.5 L)	Two plastic cans (25 L)
Treatment time (min)	6	See Table 6

Table 6. Total Treatment Time (min) in Kilogram-Scale Equipment Calculated from Flow Rate, Number of Passes, and Batch Volume

Dosage of NaClO (mol/kg pulp)*	30 °C	50 °C
2.5	17	-
3.0	24	13
5.0	6	5

* Dosage of primary oxidant and reaction temperature of the samples were according to notations in the table

At the gram scale, an Ultra Turrax high-speed dispersing unit was used, which is shown in Fig. 3. Its dispersing chamber has a 1-ring generator (rotor and stator pair) and a chamber volume of 0.049 L. The design of this unit makes it only suitable for batch-wise operation. Since the viscosity increased during the disintegration treatment, a low pulp consistency was chosen to ensure good mixing in the beaker. The dispersing head was placed in the pulp suspension close to the bottom of the vessel and the disperser was run for a selected amount of time. In operation, the disperser maintained a rapid flow from the inlet holes (above the dispersing chamber), through the narrow gaps between the internal rotor and the stator rings back to the bulk suspension. In the passage through the dispersing chamber, the pulp fibers were subjected to both high shear forces and cutting action.

**Fig. 3.** Gram-scale dispersing unit

The mode of action of the kilogram-scale equipment was similar to that of the gram-scale equipment, *i.e.* use of a dispersing unit that provided both high shear forces and cutting action. Furthermore, this equipment was designed to enable further scale-up, to permit continuous operation, and to make it possible to increase pulp consistency. An Ystral Z 80-3 (Fig. 4) was chosen since it fulfilled the requirements as stated above. It is equipped with a 3-ring generator with a volume of 0.55 L and in operation the pulp suspension was passed through this unit via the inlet and outlet connections. The generator consists of two specially designed metal discs: one rotor disc is shown in Fig. 4 and one stationary disc with a similar design. Two tanks were used to control the number of passes through the dispersing chamber. Therefore, a more even quality could possibly be expected in the kilogram-scale setup.

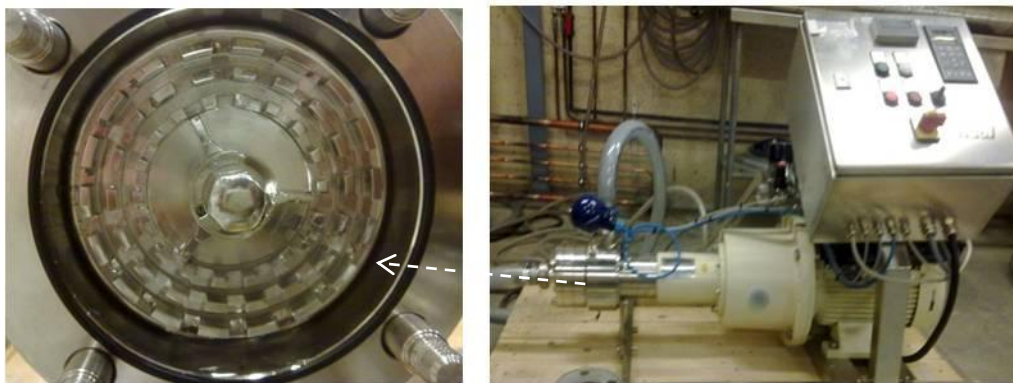


Fig. 4. Kilogram-scale dispersing unit with rotor disc

Drying

Freeze drying was used to obtain dried absorbent materials. Twenty grams of wet sample was put in a Pyrex beaker ($\text{\O} = 47 \text{ mm}$) and thereafter frozen by placing the beaker in liquid nitrogen ($-196 \text{ }^\circ\text{C}$). Frozen samples were put in a Labconco Triad freeze dryer for 48 h (0.37 mbar pressure, $-20 \text{ }^\circ\text{C}$ shelf temperature) to sublimate the water. Dried samples were stored in sealed plastic bags at ambient conditions.

Analysis

The amount of carboxylate groups was characterized based on the principle of sorption of methylene blue (*c.f. e.g. Fardim et al. 2002*). Fifty mg of pulp sample was protonated by ion exchange in 100 mL 0.01 M HCl for 1 h under constant stirring, followed by washing with 50 mL 0.01 M HCl and two 50 mL portions of deionized water. The ion-exchanged pulp was then added to 100 mL phosphate buffer solution (pH 7.8) containing approximately 200% excess of methylene blue in relation to the amount of carboxylic acid groups in the sample. Sorption time was set to 1 h during which the suspension was stirred and protected from light. After the sorption period, pulp and liquid were separated by filtration. The transmittance of light at 664 nm was measured on the filtrate using a Specord 205 UV/Vis-spectrophotometer, and the concentration was determined by comparison with standard solutions. The amount of carboxylate groups on the pulp was calculated based on the dry weight of the pulp sample. Duplicates were made for all samples.

The intrinsic viscosity of the oxidized pulps was measured in a capillary viscosimeter. Samples of oxidized pulp were first freeze-dried and then dissolved in 0.5 M cupriethylene diamine (CED) solution. An average intrinsic viscosity was obtained based on three measurements of the time-to-drain the capillary. Duplicates were made for all samples. The viscosimetric average degree of polymerization (DP_V) was calculated from the intrinsic viscosity of the dissolved pulp solutions at $25 \text{ }^\circ\text{C}$, using standard method SCAN 15:62:

$$\text{DP}_V = \sqrt[0.905]{0.75 \cdot [\eta]} \quad (1)$$

Fiber analysis was performed with a Metso Kajaani FS-300 instrument on samples from the disintegration experiments, to study the progress of the disintegration treatment. Samples were prepared by dilution with tap water, and the material was

carefully dispersed before each measurement. The average fiber length was calculated according to TAPPI T271, including fibers down to a length of about 0.02 mm. Fiber length and content of fines were reported as length-weighted values. The precision of the method was analyzed by making six replicates of one pulp sample, resulting in standard deviations of 0.05 mm for fibre length and 3% for content of fines. The fiber analyzer is designed to characterize paper grade pulps, which implies that the apparatus neglects the smallest objects in a sample with lengths less than about 0.02 mm. Thus, in a sample with a high content of liberated microfibrils, the average fiber length and fines data may represent only a small part of the total solid material.

In order to characterize the smaller objects, particle size was analyzed using laser diffraction in a Malvern Mastersizer 2000 instrument. Samples from the disintegration experiments were diluted and dispersed before measurement. It should also be noted here that the particle analyzer assumes spherical particles when calculating particle size. This implies that the size distributions should be considered as a relative size, since both fibers and fibrils have high aspect ratios (length to width relation) and deviate considerably from spherical geometry.

Scanning Electron Microscopy (SEM) was used to study the freeze-dried materials. Samples were prepared by cutting the dried material with a sharp scalpel. Prior to analysis, the samples were coated with a thin layer (approx. 10 nm) of gold (JEOL JFC-1100E ion sputter). The microscope was a Zeiss EVO HD 15, which was operated in high vacuum mode.

The Centrifuge Retention Capacity (CRC) was measured according to Edana 441.1-99, and Free Swelling Capacity (FSC) standard method Edana 440.1-99 was used. The FSC analysis involved soaking the freeze-dried samples in saline solution (0.9% NaCl) at specified intervals and measuring their liquid uptake (by weight) after 1, 5, and 30 min of absorption time. In the CRC analysis, the amount of liquid retained in a material after centrifugation was measured. The methods deviated from the standard in two ways: the samples were allowed to drip for 2 min before FSC weight measurements, and the sample amount was 25% of a test pad (0.03 to 0.10 g in each sample). The results from these measurements are reported as mean values based on four samples.

RESULTS AND DISCUSSION

Oxidized Pulp

The effects of the oxidation treatments were evaluated by analyzing the amount of carboxylate groups and reduction in DP_v . Figure 5 shows that the amount of carboxylate groups after TEMPO oxidation was similar in the kilogram-scale oxidation experiments as in the gram-scale oxidation experiments at the same reaction conditions. A consequence of using a 2% pulp consistency in the kilogram-scale experiments was that the starting concentration of primary oxidant in the bulk liquid was twice as high as in the gram-scale experiments. It has previously been reported that a higher concentration of primary oxidant decreases the selectivity of carboxylate group formation (Saito *et al.* 2006; Brodin and Theliander 2012). This may explain the decrease in carboxylate group formation in the kilogram-scale experiments, in relation to the gram-scale ones, at the highest dosage of primary oxidant. Furthermore, it was found that a high reaction temperature was, in all cases, unfavorable for achieving a high content of carboxylate groups, which indicates that the selectivity becomes worse with higher temperature.

Analysis of DP_V showed that it decreased from 1250 in the pulps before oxidation to about 120 to 180 in the oxidized pulps. However, in this interval the DP_V decreased at a higher dosage of primary oxidant in the gram-scale pulps, while the opposite trend was found in the kilogram-scale pulps (see Fig. 5). It is likely that these trends, to some extent, can be explained by the differences in total residence time in the alkaline reaction liquid (Table 3): the residence time of the gram-scale samples was increased at a high dosage of primary oxidant, while the residence time of the kilogram-scale samples was longer at a low dosage of primary oxidant. It should also be noted here that the dissolution step in the DP_V determination method has been reported to cause further degradation of the carbohydrate polymers (Kitaoka *et al.* 1999; Isogai *et al.* 2011).

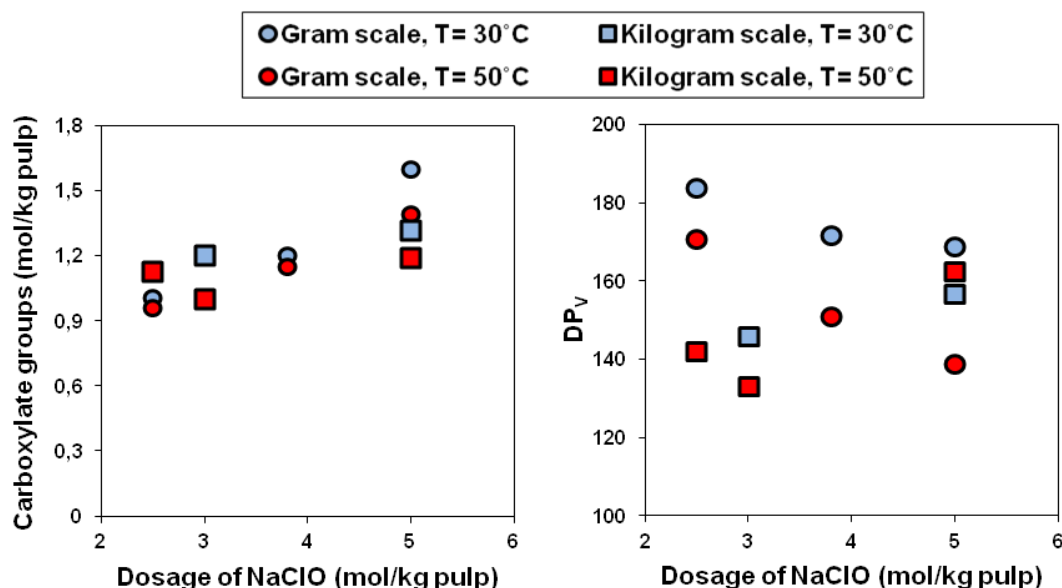


Fig. 5. Carboxylate groups and Degree of Polymerization (DP_V) plotted versus dosage of primary oxidant (NaClO) at different oxidation temperatures and production scales. The pooled standard deviation of the carboxylate group measurements was 0.07 mol/kg pulp and 2.8 units of DP_V measurements.

Fiber Characterization

The disintegration treatment of the samples on both scales was evaluated with fiber analysis, showing that the fibers were gradually converted into smaller sizes; in Fig. 6 the average fiber length is plotted versus residence time. When the fibers become shorter than 0.2 mm long they are considered to be fines; thus, the content of fines provides an approximate yield of fine material in a sample. It was found in the gram-scale experiments that the content of fines increased from about 4% in the original pulp up to 20% at the lowest dosage of primary oxidant, while the pulp treated with the highest amount of primary oxidant reached 95% fines at the end of the experiments (see Fig. 6). This result shows that a higher dosage of primary oxidant was in all cases beneficial to improving the rate of disintegration. The oxidation of the pulp drastically changed the physical and chemical composition of the fiber wall, probably through a combined effect of electrostatic repulsion between carboxylate groups and a decoupling of the carbohydrate network (Brodin and Theliander 2012). The ease of disintegration may possibly be increased by a lower DP_V (Fig. 5) even though the differences between the samples are minor.

Furthermore, it was found that the kilogram-scale equipment disintegrated the fibers more efficiently with respect to residence time in a dispersing chamber, which may be explained by the design of the kilogram-scale equipment with a 3-ring generator (rotor and stator pairs). In the end, the gram-scale samples had a higher average fiber length than the kilogram-scale samples, even though a longer residence time was applied. This may be due to the differences in experimental setups: in the gram-scale experiments the pulp suspension was disintegrated in a beaker with an uncontrolled number of passes through the dispersing chamber, while in the kilogram-scale experiments all material was pumped through the dispersing chamber in each pass. This implies that in the gram-scale experiments some fibers may have had only little disintegration treatment. It should also be noted that sample temperature increased substantially during the gram-scale experiments (from 20 °C to about 80 °C), while in the kilogram-scale experiments the temperature was only increased by a few degrees.

Another observation in Fig. 6 is that the oxidized pulps produced in the kilogram-scale experiments had different fiber lengths after the oxidation treatment (at residence time = 0 s). This shows that the relatively gentle forces the fibers were subjected to during oxidation (mixing) and washing (pumping) were sufficient to cause a major decrease in fiber length for samples treated with a high dosage of primary oxidant.

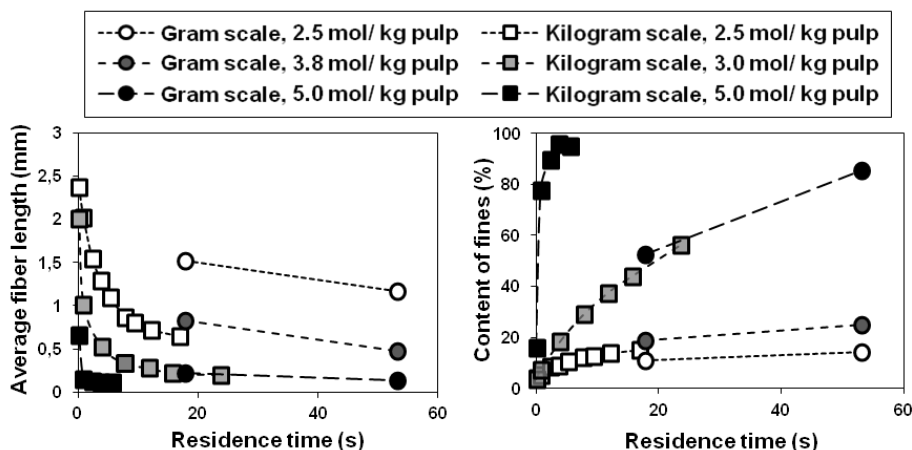


Fig. 6. Average fiber length of pulp fibres (produced at oxidation temperature of 30 °C) plotted versus residence time in dispersing chamber. The standard deviation of the method was 0.05 mm for fiber length and the estimated standard deviation of content of fines was 3%.

Figure 7 shows that the fiber length was reduced to a greater extent if the pulp had been oxidized at a higher oxidation level and at a higher reaction temperature. For example, at 30 °C and a dosage of 2.5 mol NaClO/kg pulp, only 10 to 20% of the pulp is considered to be fines, but at a dosage of 5.0 mol NaClO/kg pulp, more than 80% is considered to be fines at the end of the experiments. Thus, at the highest dosage of primary oxidant, the pulp fibers had been almost completely disintegrated into fines or even smaller objects. It must be noted here that some process conditions may vary between the samples, e.g. total residence time in the reactor vessel and duration of disintegration treatment (Tables 3-6).

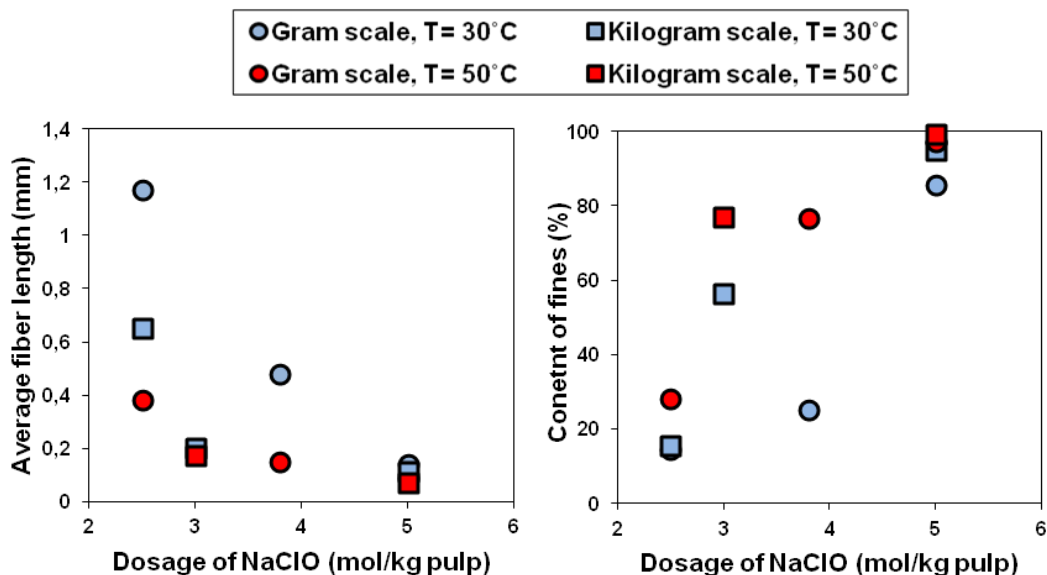


Fig. 7. Average fiber length and content of fines plotted versus dosage of primary oxidant at different temperature and production scales. The standard deviation of the method was 0.05 mm for fiber length and the estimated standard deviation of content of fines was 3%.

To gain a more thorough view of the disintegrated samples including fibers and fines as well as microfibrils, laser diffraction technique was used to obtain a particle size distribution including also the smallest material sizes not detected in fiber analysis. Figure 8 shows, contradictory to the fiber analysis that the kilogram-scale samples consisted of larger objects than the gram-scale samples, given the same dosage of primary oxidant and oxidation temperature. As described in the experimental section, the particle size in Fig. 8 should be recognized as a relative size parameter rather than the actual length or width of the objects. Nevertheless, our results indicate that the treatment provided by the kilogram-scale dispersing unit appears to be more efficient in cutting the pulp fibers but less effective in liberating microfibrils than the gram-scale dispersing unit. Thus, fiber analysis must, in this situation, be combined with other measurement techniques to be able to detect all constituents in the sample including fibers, fines, and microfibrils.

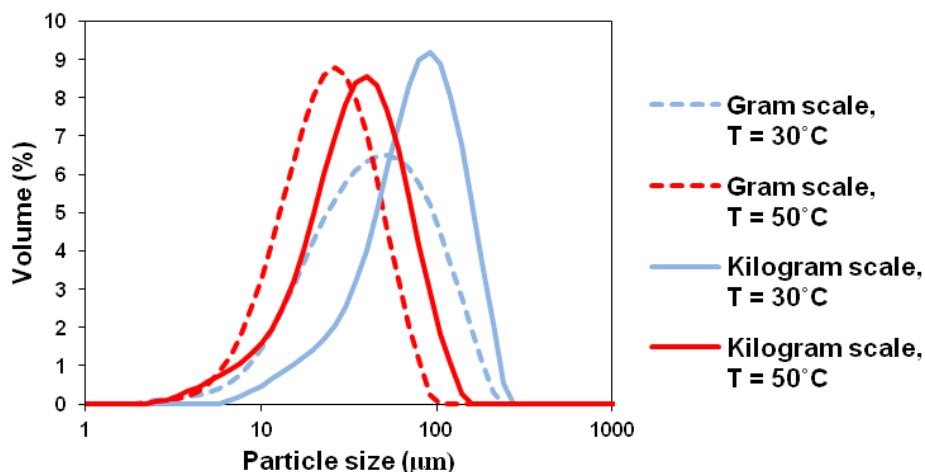


Fig. 8. Volume percentage of particles plotted versus particle size (logarithmic scale) for disintegrated pulp samples from gram and kilogram scales that had been oxidized with 5.0 mol NaClO/kg pulp.

The visual appearance of the disintegrated samples at various passes was also studied (see Fig. 9). At a higher degree of disintegration treatment, the suspensions became more viscous and transparent, as more fibers were disintegrated into smaller sizes.

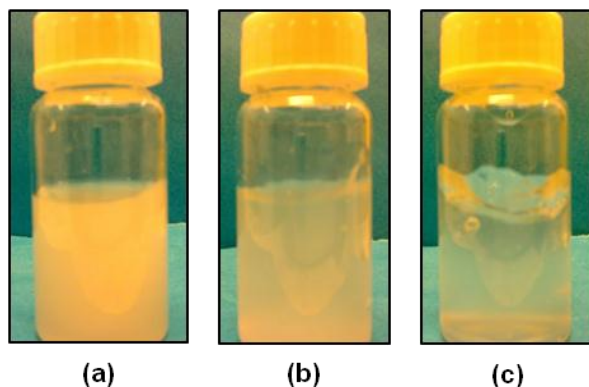


Fig. 9. Disintegrated pulp samples (5.0 mol NaClO/kg pulp at 30 °C) after 5, 10, and 20 passes through the dispersing chamber

Morphology

The morphology of the dried materials will have a major impact on the performance of the materials, since pore size distribution is important for the absorption and retention of liquids. Generally, a smaller pore size is beneficial to entrap liquid inside a material due to larger capillary forces, but also other factors may affect retention capacity; *e.g.* network stability and charge density.

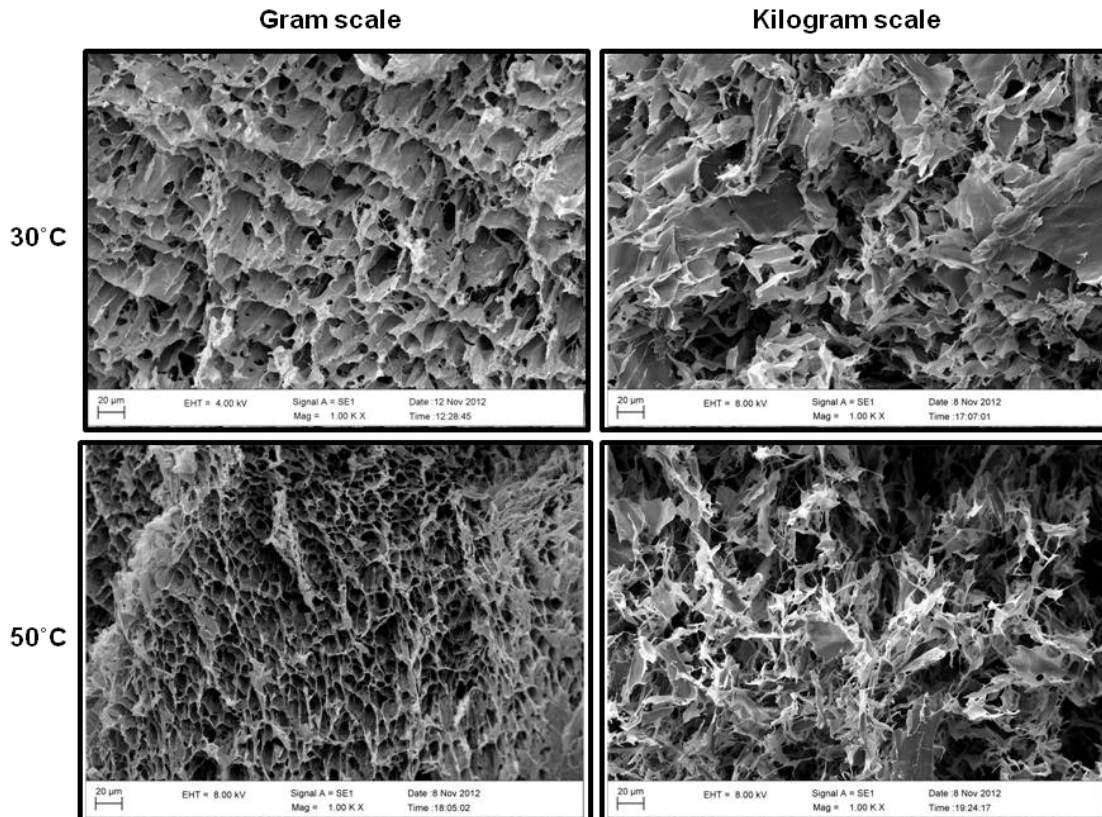


Fig. 10. Scanning electron images of freeze-dried samples all oxidized with 5 mol NaClO/kg pulp. Reaction temperature and production scale are according to notations in the figure.

Evaluation of the materials with SEM showed major differences between gram-scale and kilogram-scale samples (Fig. 10). The material in the kilogram-scale samples appeared to have a random orientation, and it was also found that coarse objects, possibly pieces from the fiber wall, remained even after the disintegration treatment. This finding confirms the results obtained regarding the particle size measured using laser diffraction. At a higher oxidation temperature, the kilogram-scale material was more incoherent, with only thin fibrillar threads to provide strength to the network. A more homogeneous foam-like structure with small oriented pores created during the solidification process was observed in the gram-scale samples. The narrow pores can be seen from the side in the image in the upper left-hand corner, while the pores can be seen in the longitudinal direction in the image in the lower left-hand corner. Such oriented and narrow pores were not detected in the kilogram-scale samples.

The results shown in Fig. 10 indicate that there are important differences in morphology between the materials obtained after freeze drying. It is likely that the changes in morphology originate from differences in material properties after fiber disintegration. In kilogram-scale samples the material may have difficulties in redistributing themselves during the rapid freezing operation due to differences in material properties of the suspensions obtained by the different operation of the gram and kilogram scale.

Absorption and Retention

As mentioned above, the absorption and liquid retention properties in porous materials depend on a large extent upon the size of the pores in the material. In this study, pulp consistency in the disintegration step was increased from 0.6% in the gram-scale samples to 2.0% in the kilogram-scale samples. Thus, it was important to determine if this change in pulp consistency, and thereby the change in porosity in the dried material, would have an impact on the absorption and retention properties of the dried materials. Therefore, a series of disintegration experiments were performed on the kilogram-scale material at different pulp consistencies. It was found that pulp consistency had only minor, if any, influence on the retention capacity of the absorbent material, in the range 0.6 to 2.0%, as seen in Fig. 11. Consequently, the total volume of pores small enough to retain liquid throughout the centrifugation period appears to be independent of pulp consistency before drying, at least in the evaluated consistency range. This result implies that the amount of water in the disintegration step could be reduced by 70% in the kilogram-scale samples without noticeably decreasing the retention capacity. A minor decrease in absorption capacity was seen when increasing the pulp consistency from 0.6 to 2%. This trend can to some extent be explained by less porosity in the material at increased pulp consistencies, *i.e.* fewer mid-sized and large pores.

Absorption properties of the gram- and kilogram-scale samples were also evaluated. Figure 12 shows that both the absorption and retention capacities were 50 to 70% lower in the kilogram-scale samples than in the gram-scale samples. The changes in morphology described above are a probable reason for this difference. Both the retention measurements and the SEM analysis suggest that the kilogram-scale samples consist of fewer small pores, thus having less ability to entrap and immobilize liquid, than the gram-scale samples. As shown in Fig. 11, the increase in pulp consistency can have some negative influence on the absorption capacity.

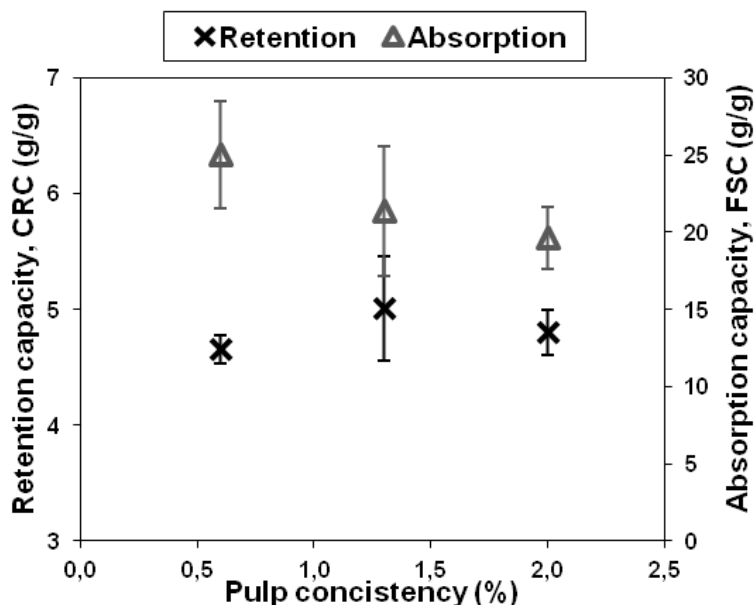


Fig. 11. Absorption capacity (FSC after 30 min of absorption time) and retention capacity (CRC) plotted versus pulp consistency in the disintegration step. The pulp used in these experiments was oxidized in the kilogram-scale experiments (3.0 mol NaClO/kg pulp at 30 °C), and pulp was passed 20 times through the dispersing chamber. The individual error bars represents the standard deviation of the measurements.

The ideal oxidation conditions for high retention capacity were, on both production scales, a high dosage of primary oxidant and a low oxidation temperature. At the same time, absorption capacity was higher in gram-scale samples if less primary oxidant was used, while in kilogram-scale samples absorption capacities were rather constant with no significant change.

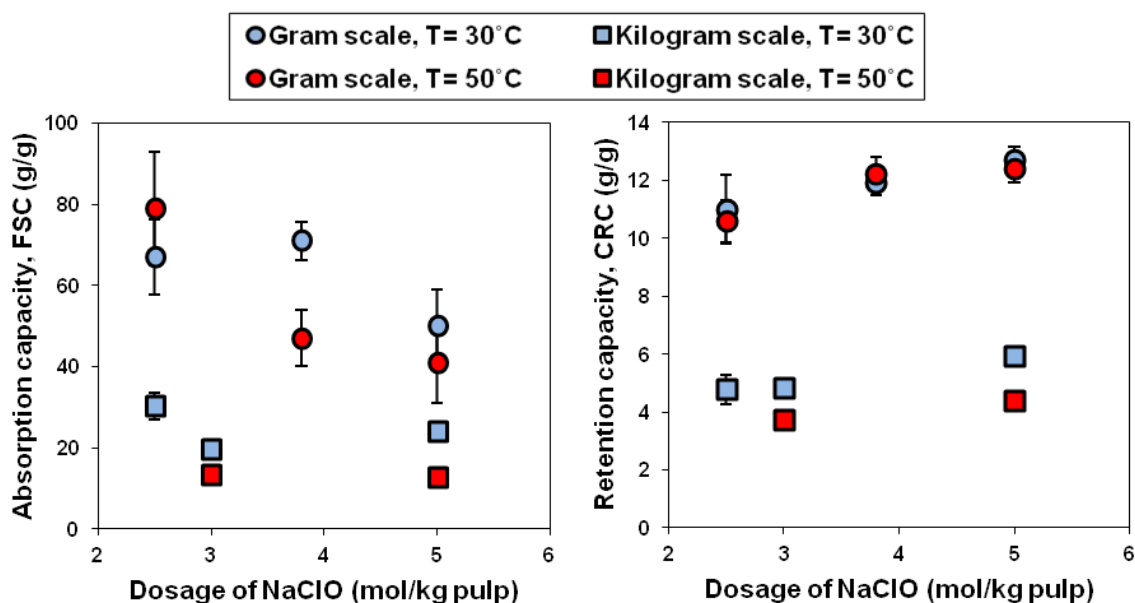


Fig. 12. Absorption capacity (FSC after 30 min of absorption time) and retention capacity (CRC) plotted versus dosage of primary oxidant. The individual error bars represents the standard deviation of the measurements.

An additional finding from the absorption measurements was that the kilogram-scale sample produced with the highest dosage of primary oxidant and the highest temperature had low dry integrity as well as low wet integrity. This sample could very easily be divided by hand and was totally dispersed after a few minutes of wetting in the FSC sample bag. It is likely that the weak network structure observed in Fig. 10 is the reason for this behavior.

Furthermore, the influence of the duration of disintegration treatment on liquid retention was studied in the kilogram-scale experiments. The results in Fig. 13 indicate that the increase in retention capacity was most pronounced in the initial period of disintegration treatment. Thus, the positive effect on liquid retention occurred when relatively intact fibers were broken up into smaller pieces. At some point, the material becomes degraded into a size where additional disintegration treatment only provides a minor additional reduction in material size.

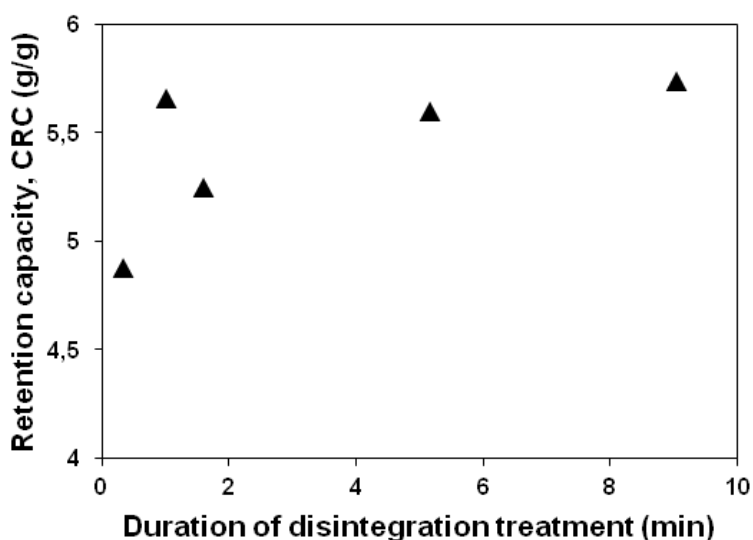


Fig. 13. CRC with respect to time of disintegration treatment for a kilogram-scale pulp oxidized with 5.0 mol/kg pulp at 30 °C. Standard deviation was less than 0.3 g/g for all samples.

DISCUSSION

The results of this study show that the kilogram-scale oxidations produced pulps with similar amounts of carboxylate groups as gram-scale oxidations. However, major differences were observed between the two scales in the performance of the absorbent materials. Measurements of particle size and studies of sample morphology showed significant differences between the materials produced in the gram-scale and kilogram-scale dispersing equipment. The materials produced had different size characteristics, which appear to give major differences in pore size and material orientation during the freezing operation. For example, it appears that kilogram-scale samples were disintegrated into microfibrils to a lesser extent. This may explain why the kilogram-scale samples had such a limited retention capacity as compared to the potential performance demonstrated by the gram-scale samples.

In the kilogram-scale equipment it was found that the reduction in fiber length was rapid down to a certain size, but, after that, the design did not seem to promote further size reduction. The gram-scale dispersing unit, on the other hand, had difficulties breaking down every fiber, but in this equipment a large quantity of liberated microfibrils were obtained. Therefore, it is possible that the two types of equipment used in this study subject the fibers to different combinations of cutting action (that promotes fiber shortening) and shear forces (that promote the liberation of microfibrils). The results from fiber analysis and particle size measurements suggest that the treatment in the kilogram-scale equipment involves more cutting action, while the gram-scale disperser may provide more shear forces. Thus, in order to improve the performance of the kilogram-scale materials, the scale-up of, primarily, the disintegration of oxidized pulp needs to be further studied.

CONCLUSIONS

1. Oxidation treatment in the gram- and kilogram-scale experiments resulted in a similar amount of carboxylate groups and degree of polymerization.
2. Ideal oxidation conditions for obtaining high liquid retention on both the gram and kilogram scales entailed a high dosage of primary oxidant and a low oxidation temperature.
3. Disintegration treatment in the gram-scale equipment produced more liberated microfibrils than in the kilogram-scale equipment. On the other hand there was more fiber cutting in the kilogram-scale equipment.
4. These differences resulted in a large variety in morphology, which was observed in SEM micrographs, where gram-scale samples consisted of small pores with oriented pore channels, while kilogram-scale samples had larger pores and a more random structure.
5. Finally, the observed differences in the morphology are most likely the reason for the 50 to 70% lower absorption and retention capacity of the absorbent foams produced in the kilogram-scale experiments compared to when produced on a gram scale under the same oxidation conditions.

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