MONITORING OF KRAFT PULPS SWELLING IN WATER

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The understanding of interaction of pulp fibers with water is of key importance when dealing with paper formation process. The swelling ability and the swelling kinetics of three kraft pulps in the form of sheets were investigated. The swelling ability of pulps was evaluated by determining the WRV (water retention value). The swelling kinetics was determined by a new device measuring the kinetic characteristic of interaction between cellulose fibers and swelling media. The device was provided with a modified monitoring unit; the paper describes the opportunities offered by this measuring unit. We assumed the linear dependence of WRV and the results acquired by kinetic measurements. This assumption was confirmed.

Keywords: swelling, kinetics, pulp, hydration, WRV

INTRODUCTION

Paper is a porous material, composed of natural fibres and other materials, such as fillers and chemical additives, the pore structure in most paper grades being a continuous three-dimensional network of voids. Bristow has described the various modes by which water can be accommodated in the fibre spaces, in the lumens and pits and in the pores of the swollen cell wall substance.[1] He has described the sorption of water into fibres as a complex diffusion process, involving vapour phase diffusion pores, surface diffusion along the fibres, and bulk diffusion through the cellulose material.[2] The degree of swelling of pulp fibres is important both for the mechanical properties of the paper and for the runability and production of paper on paper machines. Water molecules diffuse into the amorphous regions of the cellulose matrix and break inter-molecular hydrogen bonds. This allows an increase in the inter-molecular distance of the cellulose chains, which causes swelling.[3]

Fibers immersed in water get soaked on the surface. Then, penetration continues to the interfiber spaces, capillaries and lumens of cell wall.[4] Water in a process of wetting and penetration gets into interfiber spaces and to the free space of amorphous regions of cell wall. In these regions, water disrupts the hydrogen bonds between cellulose surfaces.[4] Swelling is in progress, which is associated with the rapid increase in volume, while the surface area does not expand.

To measure the interaction of water with pulp fibers, different methods are used. The most common experimentally determined value is the centrifugal WRV (water retention value); samples are frequently measured under the microscope. The principle of WRV method is based on measuring the mass of water retained after centrifugation under specified conditions by a wet pulp sample to the oven-dry mass of the same pulp sample.

WRV provides information on the maximal capacity of cellulose fibers to retain water; however, its measurement cannot be used to monitor the rate (kinetics) of swelling. The swelling kinetics of cellulose fibers is usually observed microscopically. The dimensional changes of cellulose fibers are recorded in certain time intervals, starting from the initial contact of the sample with the water medium.[5] The samples with a certain initial diameter are placed into the swelling medium, and the diameter of the samples is recorded by a digital video camera.

If the actual swelling degree of the fibers differs from its equilibrium value, the network will swell to reach the equilibrium concentration. This volume change can be monitored to follow the changes in size or mass of the fiber in time. To observe these changes, a device enabling

continuous measurement of paper and lignocellulose materials swelling, has been used. The monitoring lies in observing the dimensional changes of pulp sheets immersed in water by dimensional sensors and their conversion into electronic signals. The device for measuring wood swelling is described in detail in a paper of Solar *et al*.[6] In our case, a modified glass monitoring unit was used.

This contribution aims at presenting a new opportunity to measure the kinetics of paper swelling. Another goal is to compare the WRV method with that using the modified device for observing swelling in different types of cellulose fibers.

EXPERIMENTAL

Materials

During measuring, three types of pulp were used. All of them were unbeaten, hardwood or softwood kraft pulps obtained from Mondi SCP a.s. Ruzomberok. Two pulps contained short fibers, of which one was observed after passing through paper machine (marked SF), and the second was never-dried pulp (marked SF_{ND}). The third pulp consisted of long fibers and was observed after passing through the paper machine (marked LF). The basic characterization of each pulp is shown in Table 1.

Each pulp was used to produce three sheets (on sheet former) marked A, B and C according to TAPPI T205 (Technical Association of the Pulp and Paper Industry, 1995). The pulp was soaked for 24 hours in water and disintegrated to 1.2% consistency using a standard disintegrator for 50000 resolutions. The initial thickness of the handsheets was of 0.16 ± 0.02 mm and the basic weight was of 72 ± 2 g/m^2.

Methods

Water retention value

A method to determine WRV is based on measuring the ability of cellulose fibers to retain water. To calculate the WRV, the following relation was used:

$$WRV=100(m_1-m_2)/m_2, \% \quad (1)$$

where m_1 is the mass of centrifuged wet pulp and m_2 is the mass of dry pulp (both in grams).

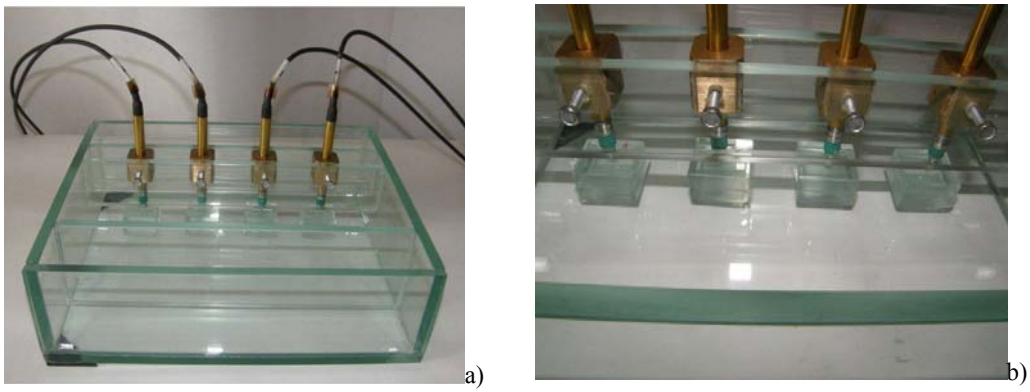
The method proposed by Jayme[7] was used to determine the WRV of samples. Centrifugation was carried out at 3000 min^{-1} for 15 min. After centrifugation, the samples were weighed and subsequently dried in an oven at 105 ± 2 °C to constant mass.

Following the swelling kinetics

To monitor the swelling kinetics of cellulose fibers, the modified monitoring unit measuring the swelling ability of wood was used.[6] The illustration of this unit, with detailed view of the sensors and glass prisms is shown in Figure 1.

Table 1
Characterization of used pulps

	Dry mass, %	Holocelullose content, %	CED viscosity, cm^3/g
SF_{ND}	95.3	95.2	591.2
SF	93.1	99.8	572.3
LF	94.3	99.2	537.6



a) b)

Figure 1: Modified glass monitoring unit (a) and a detailed view of the sensors and glass prisms (b)

During the swelling of the pulp sheets, the dimensional changes were converted to electronic signals. The obtained electronic signals were evaluated in the PC in graphical form, as dependence of swelling on time.[6,8] Swelling was determined as the difference of actual and initial dimensions of the samples and was expressed in percentage. Computation of the sample swelling process in a plane perpendicular to the surface was performed continually applying the formula:[6]

$$S_s = 100(F_{ti}-F_0)/F_0 \quad (2)$$

where S_s is the swelling in a plane perpendicular to the handsheet, F_{ti} is the thickness of the handsheet during monitoring, where t_i is any time within the interval from 0 to 8000 s, F_0 is the initial thickness of the handsheet at the initial moisture content.

The relative rate constant of the first fast phase of swelling was computed as the function of a tangent drawn through the linear part of the kinetic plot.[6] The beginning and end of the linear part in the plot can be determined by a graphical method, first-order numerical derivation or by the regression method. The relative rate constant was calculated as: Δy (swelling, %) / Δx (time, s). Both values are related to the extremes of kinetic curves.

Pulp samples in the form of sheets with an initial diameter of 4 cm^2 were used for the experiment. The measurement was performed to determine the thickness of paper under a total load of 9.92 ± 0.12 g/cm^2. The temperature of swelling media was 30 ± 2 °C. The first 60 seconds were measured with an interval of 0.1 seconds and then the measurement was continued at 1 second intervals for approximately 120 minutes. The final values of swelling represent the average of ten measurements.

RESULTS AND DISCUSSION

The results here reported may be interpreted against the background of a parallelogram, provided that due consideration is given to the limitations of the experimental procedure adopted, particularly to the following factors:

- the weight of the glass prism was of 35.823 ± 0.438 g;
- the load on the pressure foot by means of the sensor was constant at 0.973 ± 0.016 g/cm^2;
- the total load on the pressure foot was constant at 9.92 ± 0.12 g/cm^2;
- swelling was measured on paper thickness of 0.16 mm ± 0.02 mm and weight of 72 ± 2 g/m^2;
- the air entrapped in the pores because of the glass prisms in the apparatus may impede the sorption process;
- the measurement of swelling was a continuous process;
- the measurement of swelling was performed at a constant temperature, of 30 °C ± 2 °C.

The liquid penetration into the sheet was realized through the sheet cross-section from all sides and the penetration of the whole sheet sample lasted for 1.7 ± 0.2 s. After liquid (water) penetrated into the paper surface, further penetration into the entire volume of the paper happened. In Figure 2, there is a schematic description of how the liquid came into contact with the sheet and the penetration of the liquid through the sheet cross-section at the beginning of the measurement happened. Figure 3 shows the process of penetration of the liquid into the paper during the measurement. Here the liquid penetration can be observed at time intervals of 0.3, 0.4, 0.5, 1, 1.5 and 1.7 s. Figures 3a, 3b and 3c document that water initially passes in all four directions and the sample is wholly penetrated after 1.7 s (Figure 3f). Then, water penetration into the sample is performed over the entire surface of the sheet (hence in thickness direction). As shown in Figure 3, during the measurement there is air leakage from the sample. If a higher pressure is used, the air trapped in the fiber pores can fully prevent the liquid transport to the paper.

Continuous measurement of paper swelling kinetics in various media was carried out in an apparatus used for wood sticks swelling measurement. This apparatus made it possible to obtain accurate rate data on paper swelling. This method and equipment was used to measure the swelling of recycled fibres in various works.[8-11] The swelling kinetics of cellulose sheets was affected by several factors, such as initial moisture of the sheets; temperature; pressure and type of used swelling media. This work aimed at monitoring the kinetics of cellulose swelling in water at atmospheric pressure.

The increase in swelling (%) was plotted against time (seconds). The kinetic curves indicate two marked phases: a short and fast initial phase lasting for only a few seconds, with a high swelling gain, where the swelling rate reached a maximum, and a long but slow phase with a poor swelling increment, where the swelling rate approached zero (final swelling). In the latter, fibres were fully saturated.[11]

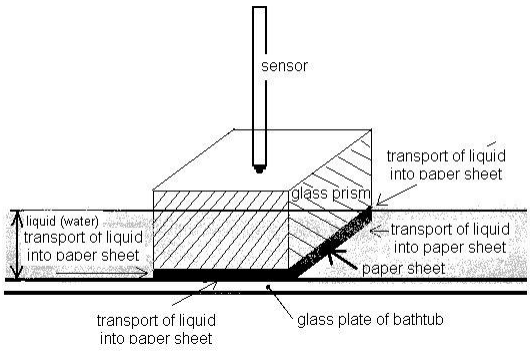


Figure 2: Schematic description of liquid penetration into handsheet through samples cross-section at the beginning of measurement

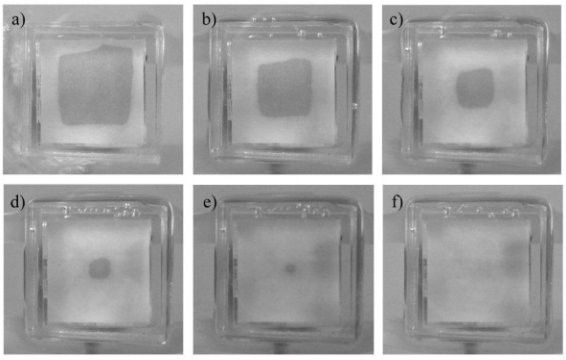


Figure 3: The process of liquid penetration into SF handsheet sample at time intervals of a) 0.3 s, b) 0.4 s, c) 0.5 s, d) 1s, e) 1.5 s and f) 1.7 s

Swelling kinetics was evaluated by the regression analysis of the following equation:

$$y_1 = A(1-e^{-kt}) \quad (3)$$

where y_1 is the swelling (expressed in %), A is the parameter of maximal swelling (%), k is the rate constant determined by achieved velocity of limiting (maximal) value A (s^{-1}), t is the swelling time (s).

The transport of liquids into the paper is a complicated process. The commonly used terms are "liquid transport",[12-14] "sorption",[15,16] "penetration",[17-19] "transudation",[20–24] as well as "wetting" and "diffusion".[1,2,25] Sorption includes adsorption of liquid onto the paper surfaces, the filling of paper pores by liquid and potential absorption of liquid into the fibres. The term "sorption" does not distinguish or describe the wetting mechanisms or where the liquid is located after reaching equilibrium. "Penetration", rather than "sorption", characterizes e.g. the liquid front propagation.[26]

The transport of liquid into the paper can be viewed as a sum of coexisting sub-processes:[26] liquid penetration through capillaries, pores and cavities in the sheet, filling of pores and roughness pits on the paper surface, migration along fibre surfaces, water absorption into fibres and transport within fibres by diffusion and vapour phase diffusion in the pore space and Knudsen diffusion in less than 10 nm pores.[27]

When water penetrates only into fiber pores, then no swelling or network expansion happens. However, if absorption into the fiber walls occurs, the resulting network expansion will cause an increase in the size of the inter-fibre pores and an associated increase in the rate of swelling or penetration. In addition to swelling, water breaks inter-fibre bonds and expands the fibre network.[28]

In the work of Bristow,[1] the Cobb procedure of paper thickness swelling was established. In this work, it was found that when the contact angle between a liquid and paper approaches 90 degrees and there is no capillary penetration, fiber sorption and diffusion become the dominating transport mechanisms.[1,28-31] The increase in the thickness of a paper sheet caused by fibre swelling during sorption is controlled by this intra-fibre diffusion.[1,25] At higher temperatures the diffusion will be faster.

In our case there is a water transport to the sheet sample through paper cross-section and from all directions at the beginning of the measurement. Based on the work and findings of Bristow,[1] we assume that water transport to the sheet is a capillary penetration. After 1.7 s, water reaches the whole sheet sample and then diffusion and sorption occur. This phenomenon could be observed on the swelling curve as the first rapid phase. Consequently, the swelling slowed down, as can be seen on the curve in the second slow phase.

Liquid transport into paper need not be uniform, because paper structure is not homogenous. In our case, the inhomogeneity of sheet samples is due to different arrangement of fibers in single sheets of paper. In addition, differences are due to the morphology of the fibers used. These properties influence the results of swelling and swelling kinetics. It is known that the water uptake differs for different types of fibers, such as hardwood and softwood kraft fibers, etc. This difference can be also partially attributed to fibre swelling. Fiber swells upon rewetting, taking in water and expanding. A wet, swollen fiber has fewer potential bonding sites per unit surface area than it would in its dry collapsed state. This is why the softwood kraft

fibre had a higher swellability than the hardwood kraft fibre.[32]

A paper sheet is a heterogeneous material. During sheet formation, there could be a different fiber arrangement in a sheet, and drying leads to pore closure of cellulose fibers. To determine the influence of paper formation on kinetic of swelling, three sheets (A, B and C) made of the same pulp were investigated.

Figure 4 and Figure 5 show the time evaluation of the size during the swelling of SF and LF sheets. The kinetic curves indicate two distinct phases: a fast and short initial phase lasting only a few seconds, with a high swelling gain, where the swelling rate reaches a maximum, and a slow and long phase with a poor swelling increment with the swelling rate approaching to zero. In this phase, the fibers are fully saturated. The values for the rate constants were obtained by fitting the experimental data. Table 2 summarizes the swelling kinetics parameters, final swelling and WRV for long-fiber and short-fiber handsheets. Based on the results, it is obvious that the swelling process is fast during the first linear phase. The relative rate constant is in the range 20-35 s^{-1} for all monitored samples. In 15 minutes, the swelling ability of sheet samples reaches the maximum value.

Comparing the results of swelling for different fiber types, it could be stated that the long fiber (softwood) has the average value of the rate constant of 23.8 ± 2.4 s^{-1} and maximal swelling of 58.7 ± 3.6%. For short fiber (hardwood) handsheets, maximal swelling of 51.0 ± 16.7% and swelling rate of 28.2 ± 7.4 s^{-1} are achieved. These results agree with the claim that softwood kraft fiber reaches a higher swelling degree than hardwood kraft fiber. In our case, the swelling of long-fiber samples is by 15% higher than that of short-fiber samples.

The maximal swelling variance is higher in the case of the hardwood handsheet (short fiber). The dispersion value of final swelling is of 3.6% for short fiber. The variance is almost five times higher, compared to long-fiber (softwood) handsheet. The reason is the inhomogeneity of the sheets and different arrangement of fibers in the sheet. The arrangement of long fibers is more ordered than that of short ones.

These values are in good agreement with the results of the WRV measurement. On the other hand, the final swelling of SF samples varies from 70 to 40%, which could be caused by fiber arrangement during handsheet formation and by the initial moisture content. The same variation was achieved in the case of WRV.

The main permanent changes of paper can be attributed to drying. As a consequence of drying both reversible and irreversible physical and/or chemical changes of paper take place.[33] Drying is a process accompanied by a partially irreversible closure of pores in the fiber wall, which leads to increased resistance to swelling during rewetting.

It must be taken into account that the change of the swelling ability depends on the temperature and drying method. The influence of drying conditions on the swelling ability of never-dried kraft pulp was observed in a work of Letkova *et al*.[11] They figured out that with increasing drying temperature the relative rate constant decreases, while the final swelling increases. During drying in the sheet former, both temperature (85 °C) and pressure are applied. That is why the handsheet is thinner, denser and less porous. Interfiber distances are shorter, interfiber contacts are more profound and therefore the swelling of the fiber cell walls causes significant increase in the handsheet thickness.[11]

Table 2
Relative rate constants of initial phase, maximal swelling and water retention values of long-fiber and short-fiber sheets

Pulp		Relative rate constant, s^{-1}	Final swelling, %	WRV, %	Initial moisture content, %
Long fibers (LF)	sheet A	23.36	57.23	73.235	6.4
	sheet B	26.46	62.76	73.300	5.7
	sheet C	21.65	56.02	73.245	5.4
Short fibers (SF)	sheet A	35.30	70.16	80.020	7.3
	sheet B	28.94	43.24	64.538	6.0
	sheet C	20.46	39.65	62.188	5.2

As during the WRV measurement a suspension of pulp is used, this irregularity should not occur. However, in the case of the SF sheet in our study (Table 2), irregularities in final swelling occurred in the WRV measurement. The WRV value for single SF sheets varies from 80 to 62%. One can assume that in the case of short-fiber samples, the variation of properties is not caused by handsheet formation, but by the fiber itself and by the higher initial moisture content.

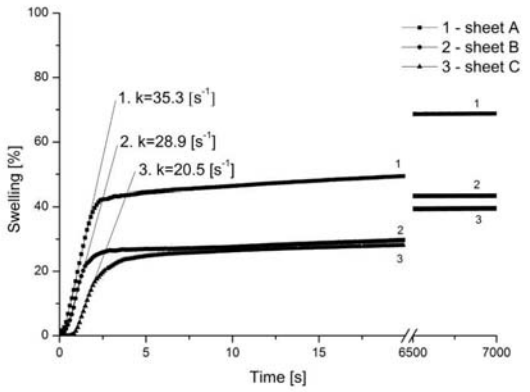


Figure 4: Influence of sheet formation on swelling kinetics of SF sheets (medium: distilled water; t = 30 °C, initial moisture content of paper 7.3% for sample A, 6.0% for sample B and 5.2% for sample C)

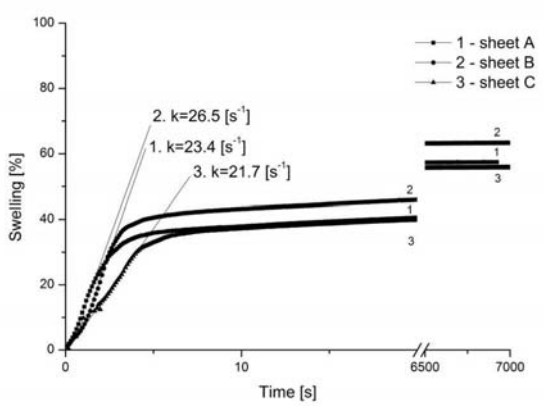


Figure 5: Influence of sheet formation on swelling kinetics of LF sheets (medium: distilled water; t = 30 °C, initial moisture content of paper 6.4% for sample A, 5.7% for sample B and 5.4% for sample C)

Figure 6 represents the swelling kinetics curves of paper sheets obtained from bleached kraft pulp, expressed as a relative change in the thickness of the paper in contact with the medium.

The results lead to the conclusion that the highest swelling ability is achieved for the sheet prepared from never-dried fibers. Its final swelling is of 77.5% at an initial swelling rate of 37.2 s^{-1} and a WRV of 87.1%.

These results agree with the results achieved in the work of Letkova *et al*.[11] The long fibers swell to a high degree and final swelling reaches the value of 58.7% with an initial moisture content of 5.8% and a relative rate constant of initial swelling phase of 28.4 s^{-1}. The short fibers (SF) swell the least. These measurements confirmed the finding that the pulp loses its swelling properties by an additional drying process (first cycle of recycling).[4]

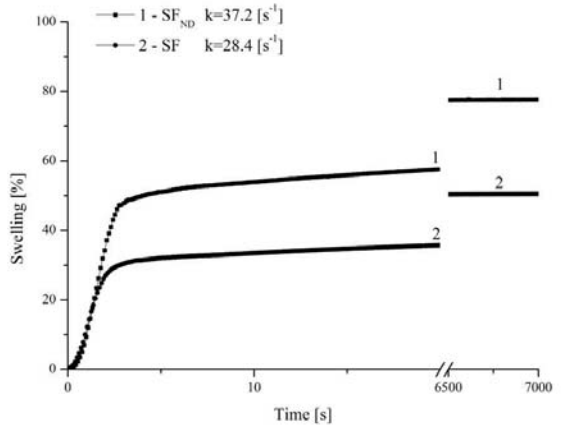


Figure 6: Kinetic curves of sheets prepared from different types of pulp (medium: distilled water; t = 30 °C, initial moisture content of paper 4.7% for sample SF_{ND} and 5.6% for sample SF)

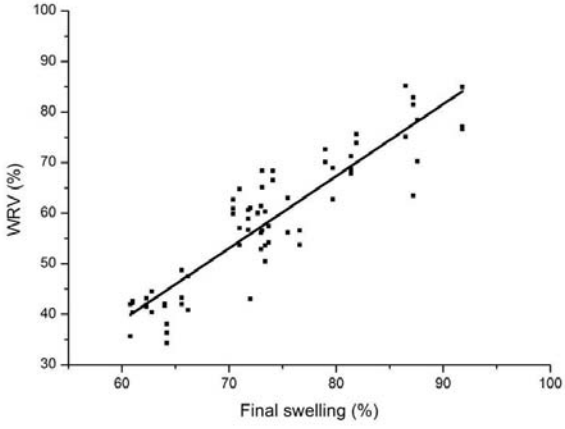


Figure 7: Dependence of water retention values on maximal swelling

We can see that the final swelling of SF, in comparison with never-dried short fiber pulp (SF_{ND}), decreases from 77% to 50%, which represents a 35% loss of the swelling ability.
Fibers do not swell in their width, but swelling causes an increase in the fiber wall thickness in the direction towards the fiber lumen.[34–36] Swelling of the cell wall relates to the WRV.[34,35]

A summary of the relationship between WRV and maximal swelling is shown in Figure 7, which shows that there is a linear correlation between WRV and maximal swelling of the sheet in the measured swelling intervals. In Figure 7, a strong positive correlation is noted and the correlation coefficient is 0.82.

In other publications, the correlation between WRV and other parameters was proven. WRV correlates with fiber saturation point, width of the fibre wall, SR number, sheet properties, such as density and tensile strength.[34–39]

This work suggests the possibility of using continuous measurement of swelling kinetics of heterogeneous materials such as paper. The method can be used to monitor the effects of aging and recycling based on swelling parameters. In addition, it can be used to determine the impact and behaviour of other materials (textiles, leather, parchment, plastic) in the application of various solvent types for the protection and preservation of materials and objects of cultural heritage.

CONCLUSION

To measure the swelling kinetics of cellulose fibers, a new method was applied. The measuring device was used to determine the final swelling of pulps and the obtained data were compared with the WRV of these pulps. A linear dependence of water retention values on final swelling was identified.

The benefits of this device lie in the possibility of easier monitoring of swelling kinetics and maximal swelling. The most important benefit of this method is the possibility of continuous swelling measurement from the very first contact of the liquid (in our case, water) with the sample. The device is capable of measuring the changes in the fast first phase of swelling in short time intervals.

In the case of pulp made of long fibers, the average values of rate constant and maximal swelling were of 23.8 ± 2.4 s^{-1} and 58.7 ± 3.6%, respectively. For short-fiber (hardwood) handsheets, the maximal swelling achieved was of 51.0 ± 16.7% and swelling rate of 28.2 ± 7.4 s^{-1}. Softwood kraft fiber reached a higher swelling degree than hardwood kraft fiber. It has been thus confirmed that the pulp loses its swelling ability by an additional drying process.

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