Swelling of Cellulosic Porous Materials - Mathematical Description and Verification

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The swelling of natural porous materials, including bleached pulp, as represented by mathematical descriptions, is influenced by a variety of different operating factors. The formerly used Generalised Hygroscopicity Model leads to either a disproportion between a model and a limit value of the sorption capacity or to noticeable deviation in the early swelling phase. Alternatively, the so-called Simple Bounded Growth model solely depends on the maximum sorption capacity, ignoring the physical properties that affect the fibre swelling rate. This research shows that the combination of the two models best describes the swelling process of bleached pulp – a rapid swelling phase and a slower swelling phase. The combined model was found to be useful in characterizing the well-known hornification process.

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INTRODUCTION

The phenomenon of swelling of cellulosic porous materials was studied and described for the first time in the 19th century. This phenomenon is the characteristic feature of all elastic colloidal materials, but it differs depending on the types of materials (Stamm 1935). According to Nägeli (1858) a solid swells when it takes up a liquid and at the same time the following three conditions are fulfilled: an increase in the material's dimensions is supported by a thermal change as a result of the sorption of another phase, homogeneity is maintained at the microscopic level, and cohesion is reduced but not eliminated, *i.e.* the substances become soft and flexible instead of hard and brittle (Nägeli 1858).

Wood is well coincident with the ideas that have been developed for elastic porous materials. Due to its chemical composition and specific surface area that is caused by macrostructure (lumen) and microstructure (capillaries), wood readily binds and releases water. Due to adsorption or desorption, the mass and dimensions change, while the structure remains basically the same, yet softer and more flexible. The sorption behavior of wood is caused by its hygroscopicity, whereby the water is retained in the cell walls in the molecular form by the physical forces of attraction. Residing in the cell wall, the bound water affects volume of wood. This in turn affects the mass and dimensions of the wood in proportion to the volume of water gained or lost (Fan *et al.* 2010).

Swelling, as one of the physical characteristics of wood and wood-based materials, is of great practical importance, whether in wood technology and products or in the production of pulp and paper. There is a significant difference between the swelling of wood and the swelling of pulp fibres.

Swelling of wood is explained by the fact that the bound water gets into the non-oriented regions of the cellulosic fibrils and enlarges the cell walls of particular elements and the whole wood. The wood swells, sorbing water and water vapour until reaching the fibre saturation point (FSP). An additional increase of water content does not cause further swelling because the water fills only lumens or eventually inter-cell cavities (Požgaj *et al.* 1997).

Later research has been dedicated to understanding the inhomogeneity of the swelling of cellulose fibres, which is accompanied by the so-called balloon phenomenon, when the swelling of the secondary wall causes the extension and bursting of the primary wall in one or more places. This phenomenon of cotton fibres has been described in detail by different authors (Nägeli 1864; Pennetier 1883; Flemming and Thaysen 1919; Marsh 1941; Hock 1950; Rollins and Tripp 1954). The inhomogeneity is related to the type of the fibre and the properties of the solvent.

Dobbins (1970) writes that swelling of pulp is caused by polar molecules of water, not by the presence of soluble substances. Stone and Scallan (1968) describe the swelling mechanism of the delignified cell wall based on the idea of pushing with cellulose layers.

Calvini and Gorassini (2006) describe the sorption of water into the fibres as a complex diffusion process, involving diffusion into the pores, surface diffusion along the surface, and volume diffusion through the cellulosic material. Water molecules diffuse into the non-oriented regions of the cellulosic matrix and tear intermolecular hydrogen bonds. This allows for the increase of the intermolecular distances of cellulosic chains, causing swelling (Burchard and Husemann 1961; Blažej and Krkoška 1989).

The swelling of cellulose is often associated with the charge creation of cellulose, primarily by dissociation of cellulose carboxyl groups. However, there were observed reductions in the dissociation of carboxyl groups in the cellulose matrix and on its external surface. It is believed that the increased charge density (local accumulation of the acidic carboxyl groups) and eventually the ordered structure of water cause significant differences in the behavior of the carboxyl groups of the cellulose layer within and on the surface (Freudenberg *et al.* 2007).

In the papermaking process, especially in recycling, the pulp fibres pass through various changes due to repeated refining and drying. The original structure of the pulp fibre wall is deprived of the outer layers P and S1 *via* beating. Simultaneously, the fibres are fibrillated and swell in aqueous media. The subsequent drying causes the collapse of fibres, which results in decreased swelling ability (Geffert *et al.* 2015).

The supermolecular and hypermolecular structure of cellulosic materials as paper is changed upon drying. The pores and lumens collapse and the hydrogel structures are transformed into xerogels (*e.g.* hydrogel in dry state). The opposite process, swelling, is not fully reversible, and its characteristic feature is that water flows into the porous cellulosic matter and this process is followed by swelling. Proper swelling at equilibrium is given by the concentration of ionactive and nonionactive hydrophilic soluble and nonsoluble substances embedding cellulosic interfaces and by the participation of osmotic pressure in equilibrium with the inner stress of the stretched swollen cellulosic matter (Milichovský 2013). However, the materials are unable to subsequently swell to their initial state. The whole process is well known as the hornification phenomenon.

Recycling of pulp fibres causes a reduction of the fibre wall thickness and a reduction in tensile strength, while the ratio of lumen diameter/width of the fibre is increased, and there is a direct correlation between the tensile strength and fibre wall thickness (Okayama 2001).

Hornification is known as the irreversible loss of a swelling ability of the pulp fibres, when most of the macropores and micropores irreversibly collapse if the fibres are dried and re-wetted. This indicates that hornification is caused by the formation of the water resisting hydrogen bonds between adjacent lamellae. This formation also involves the displacement of hydration water. The process of beating tends to open up submicroscopic spaces within the lamellar structure of the fibre cell walls. The regeneration of macropores, which have collapsed in hornification, is an important function of beating of previously dried pulp (Maloney and Paulapuro 1999; Letková *et al.* 2011).

Swelling is usually closely related to the dissolution of wood cellulose fibres in a NaOH solution. Some of the cellulose chains dissolve and the others do not dissolve, although they have the same molecular weight. This fact indicates that the poorly soluble chains are less accessible and embedded in the lignocellulosic matrix. Le Moigne and Navard (2010) have shown that the dissolution capacity of the cellulose chains is strongly dependent on their location in the cell wall structure and on the cellulose-hemicellulose complex. The presence of a small amount of hemicellulose can prevent or reduce the solubility of the cellulose, but it should be noted that the so-called "cellulose solution" is not the molecular solution in the thermodynamic sense, and there are mainly cellulose aggregates present. The most important fact is that there are hemicelluloses that link elementary fibrils in the non-oriented parts of the microfibrils.

As explained above, from a theoretical point of view, the swelling of the fibres upon cellulose basis as a manifestation of the interaction of water-cellulose fibre has been described in sufficient detail. However, it is much more difficult to describe it mathematically, as swelling depends on many factors, such as the nature of the fibre, solvent properties, and specific process conditions.

Due to a number of factors influencing the water transport and the associated swelling, the use of physical relationships, such as Darcy's law, Poiseuille's law, Fick's law, Lucas-Washburn equation, Flory and Rehner's equilibrium theory of swelling, and others, is significantly inaccurate and inadequate without proper treatment. As usual, the swelling stresses in wood and wood materials are described by use of the well-known pressure equations of Katz and Porter (Barkas 1949), originally derived for the swelling of elastic gels.

The complexity of the process led to the attempts to derive some empirical equations, for example the so-called power law $Y(t) = a.t^n, 0 < t < 1$ and its modifications used by Siepmann and Peppas (2001). The cited authors dealt with other issues related to cellulose, but not paper. Moreover, the power law suggests that the swelling process is not bounded and that the proportions of the examined material swell to infinity.

One of the goals of this paper is to show that the kinetics of water sorption or other liquid organic substances in the porous material can be fairly well described by a mathematical model that takes into account the hypermolecular properties and the microstructure of the examined material. Such a model should be consistent with the fact that there is some maximum value of percentage increase that should not contradict the measured data.

The present work is analogous to water vapour transport (diffusion) into a paper strip (indicated as weight increment of condensed water vapour in appropriate centres of porous paper sample). The case to be considered involves liquid water penetration into the appropriate swelling centres of porous paper sample, indicated as a dimensional change (*e.g.* an increase in thickness of the paper strip).

The model was created and built on the basis of the well-known GHM model (Generalised Hygroscopicity model), which was successively used to describe the kinetics of vapour absorption (condensation) in paper as shown by Eq. 1,

$$Y_1 = \frac{d.t^b}{(c + t^b)}$$

(1)

where Y_1 (%) is the increase in liquid content (*i.e.* humidity concentration) at a given time, d (%) is the maximum value of percentage increase, which is explained by the GHM model, t(s) is the time of swelling, c (s^b) is proportional to the reciprocal value of the vapour diffusivity, and b is the parameter that describes the uniform increase of sample humidity in connection with the homogeneity of the material.

The GHM model was employed by solving differential equations described by Češek *et al.* (2011). It was shown that if $b \leq 1$, a humidification kinetic curve has a monotonic ascending character. If $b > 1$, a humidification kinetic curve has a typical S character with an inflexion point being moved to higher time values with increased b values (Večeřa *et al.* 2016).

The aim of the present work was to refine the initial GHM model, because the authors' first works devoted to the swelling of recycled low yield pulp fibres had not achieved satisfactory results (Geffert *et al.* 2013).

EXPERIMENTAL

Materials and Methods

The faculty of Wood Science and Technology at Technical University in Zvolen, Slovakia developed a simple method for determining the wood swelling kinetics in the first seconds of contact with water or other polar solvent (Solár *et al.* 2006).

The monitoring principle of fiber swelling (as well as in the original method) consists of recording the dimensional changes in the water-swollen experimental sheet. These changes are examined by sensors and transformed into electric signals. These sensors are in vertical contact with the pulp sheet (min. size 25 x 25 mm) through distance glass inlet. The measured electric signals are processed by PC and evaluated by graphic dependence of swelling on time. The disadvantage of this method has been that the data could not be considered absolute. Swelling is defined as the difference between the immediate and initial inlet distance (in %). This method was successfully used also for the monitoring of dimensional changes of the swelling of pulp and paper (Botková *et al.* 2013; Jablonský *et al.* 2014).

Paper swelling kinetics was investigated on the handsheets made from bleached sulphate pulp composed of a blend of hardwood species (original pulp once industrial dried), subjected to an 8-fold recycling model at two temperatures of drying: 80°C and 120 °C. The first treatment of fibres (0th recycling) represented a hand laceration of the pulp, defibering, beating to 29 SR (dewatering capacity of pulp stock according to the Schopper Riegler method), paper hand-sheet preparation, and drying. During the process of the 8-fold recycling model, pulp was returned repeatedly to the process of pulping, additional beating to 29 SR, and drying (Geffertová and Geffert 2012).

RESULTS AND DISCUSSION

It seems that the problem of swelling dynamics has not been adequately examined until now. For example, the *Handbook of Physical Testing of Paper, Vol. 2* (Borch *et al.* 2001) offered only references to Hawkes and Bedford (1963) and Bristow (1971), mentioning estimation of liquid transfer to the paper of the form, $Y(t) = a + b.\sqrt{t}$.

A more general empirical equation was derived, $Y(t) = a.t^n, t < 1$, which Siepmann and Peppas (2001) used in considering the swelling of cellulose fibres. Such a mathematical relationship might roughly estimate the process in the initial phase, but the conclusion of boundless growth was in contradiction with the mechanism of the swelling, and hence the later swelling phase could not be estimated correctly. The function (Geffert *et al.* 2013),

$$Y(t) = a(1 - e^{-kt}) + \frac{2b}{\pi}\arctan(q.t^n) \tag{2}$$

describes the process from the statistical viewpoint quite well, but the second part of the function was suspiciously artificial, and it was hard to explain which part of the swelling phenomenon should be responsible for such behaviour.

The refinement of the original GHM model was done by supplementing it with the so-called simple bounded growth model (Brody 1945), which was suggested for the description of the kinetics of the swelling process by Milichovsky (2013) and described by the following differential Eq. 3,

$$\frac{dY_2(t)}{dt} = k(a - Y_2(t)); Y_2(0) = 0 \tag{3}$$

that has a solution of the form,

$$Y_2(t) = a(1 - e^{-kt}) \tag{4}$$

where Y_2 is the increase of the fluid content at a given time (%), a is the equilibrium of the fluid content at t $\to \infty$ (%), t is the time of swelling (s), and k is the parameter describing the dynamics of water sorption of the material (s^{-1}).

Providing that the moisture content in pulp mass is proportional to thickness of water-swellable fibres and that the kinetics describing this process has a subsequent character, then combining both models (*i.e.* from Eqs. 1 and 3) results in Eq. 5,

$$Y(t) = Y_1(t) + Y_2(t) \tag{5}$$

where Y_1 is dependent upon the rapid penetration of water through cellulosic material and the term Y_2 describes the slower binding of water molecules into swelling centers of the cellulosic material (Fig. 9). The sum of $d + a$ gives the total sorption capacity of the material, and it was statistically derived based on empirical measurements.

It was crucial to examine the swelling process in the initial seconds. Therefore, in the process of construction of the desired function, only a part of the data up to the 25th second was considered. In the case of statistical analysis of the whole set (600 s), the relative influence of the initial phase of the process was suppressed into the background.

Figure 1 discloses the percentage increase in the paper sample thickness connected with water-swellable centers of the paper made from original pulp, after the 0th and 8th recycling, with drying at 120 °C within each cycle. The swelling capacity of the pulp after

the 8th recycling was reduced to the level of the original (non-beaten) pulp, and that after a certain period exhibited no noticeable change in the saturation of samples of pulp.
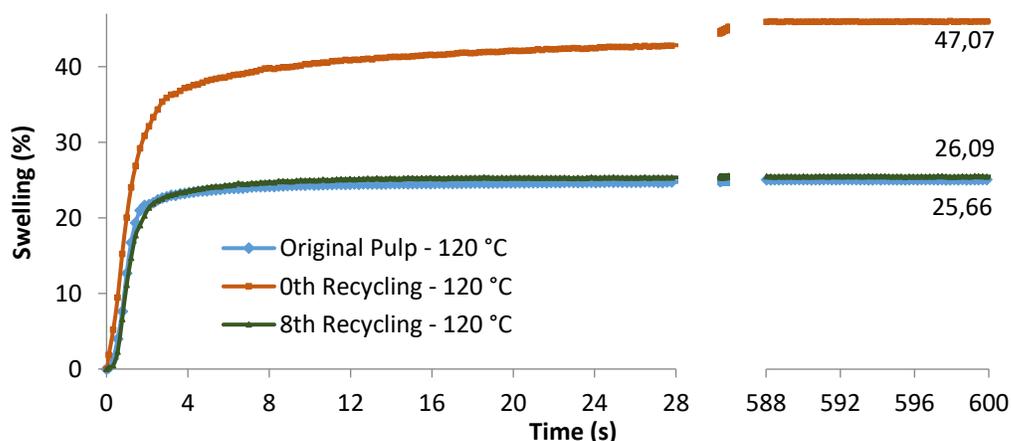

Fig. 1. The progress of swelling of studied pulp samples beaten to a fixed value of 29 SR

The values of swelling measured at the last second (after 600 s) were used for a statistical estimate (arithmetic mean) of the sorption capacity limit value in all models of the last 101 measurements. In this case, the received limit values are shown in Table 1.

Table 1. Statistical Estimate of the Sorption Capacity Limit Value in All Treatments

| Variable | Valid N | Descriptive Statistics (120 °C) | | | | | |
		Mean (%) (Est. sorption capacity)	Confidence (-95.00%)	Confidence (95.00%)	Min.	Max.	Standard Deviation
Original Pulp	101	25.66	25.659	25.666	25.615	25.700	0.017
0th Recycling	101	47.07	47.066	47.077	47.009	47.155	0.030
8th Recycling	101	26.09	26.084	26.094	26.026	26.145	0.025

In the case of the swelling of paper it was desirable to supplement the GHM model by the function Y_2, and the accuracy with which the different models explained the studied phenomenon were compared. The following functions were created by a means of an approximation *via* the method of least squares. The analyzed data belonged to 120 °C after 0th recycling. The initial 25 s were evaluated, during which there was a crucial stage of swelling and the increase in the material thickness was greatest.

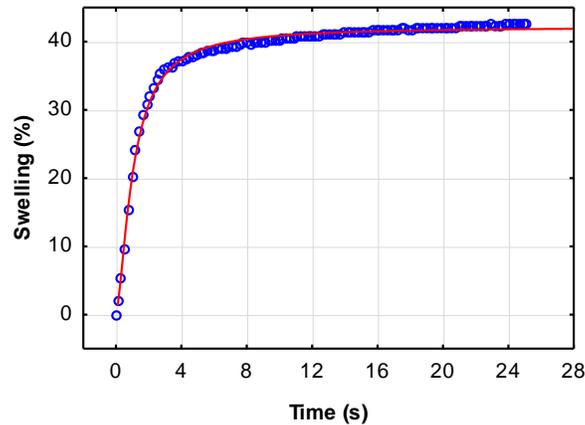Figure 2 shows the previously used model GHM (function Y_1).

Fig. 2. Swelling described by GHM model $(Y_1 = 42.15 \frac{t^{1.54}}{1.073 + t^{1.54}})$

The use of function Y_1 alone leads to a huge disproportion of the model and the estimated limit value of the sorption capacity (42.15% *vs.* 47.07%).

The attempt to improve a model by option of parameter $d = 47.07$ (to achieve the desired limit value) would cause further deviation of the GHM model from its actual course in the initial swelling phase (0 s to 8 s) (Fig. 3).
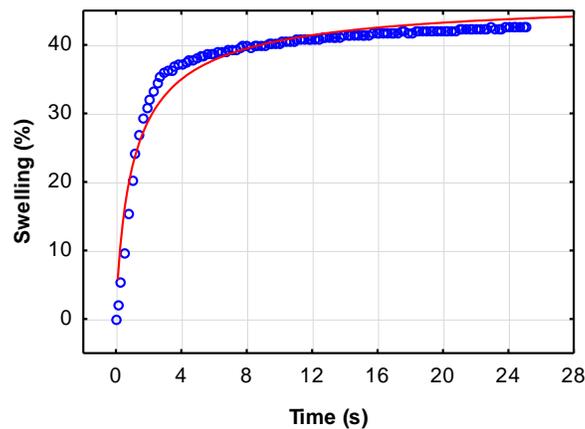

Fig. 3. Swelling described by adjusted GHM model $(Y_1 = 47.07 \frac{t^{0.85}}{1.122 + t^{0.85}})$

The use of function Y_2 alone, as expected, also did not lead to the acceptable solution. The model constructed in this way would only depend on the maximum sorption capacity, but it would ignore the physical properties of fibres that affect the swelling rate (Fig. 4).
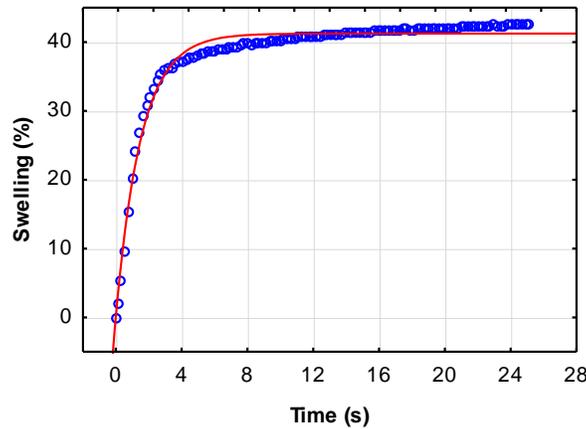
Fig. 4. Swelling described only by function $\quad Y_2 = 41.24(1 - \mathrm{e}^{-0.651t})$

The authors obtained the best prediction by combining both models. The initial phase of swelling was exactly described (Fig. 5) and also $\lim_{t \to \infty}(Y_1 + Y_2) = 47.07.$ The share of variance explained by the model was $R^2 = 0.9993$, *i.e.* R = 0.9996.

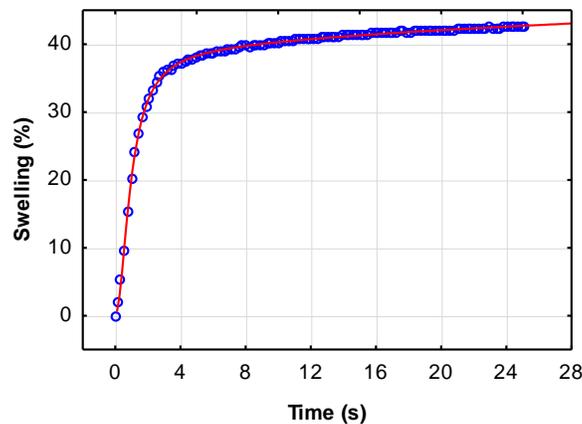**Fig. 5.** Swelling described by combination of both models:

$$Y = Y_1 + Y_2 = 8.26(1 - \mathrm{e}^{-0.026t}) + (47.07 - 8.26)\frac{t^{1.93}}{0.924 + t^{1.93}}$$

Table 2. Statistical Parameters of the Model $Y_1 + Y_2$

Variable	Model: $Y(t) = a(1 - \mathrm{e}^{-kt}) + *(47.07 - 4)\dfrac{t^b}{(c + t^b)}$ Level of Confidence: 95.0 %					
	Estimate	Standard (Error)	t-value (df = 112)	p-value	Lower Confidence (Limit)	Upper Confidence (Limit)
a	8.26	0.108	76.47	0.000	8.05	8.48
k	-0.026	0.001	-34.91	0.000	-0.028	-0.025
b	1.93	0.020	97.53	0.000	1.89	1.97
c	0.924	0.010	97.69	0.000	0.905	0.942

All model parameters were statistically significant with 99.9% confidence (p<0.001). The model depicted in Fig. 9, drawn in this way, made it possible to estimate

the impact of individual factors on the overall change in the samples. Note the rapid progress of the function Y_1 (dotted line) and a slower function of Y_2 (dashed line) (Fig. 6).
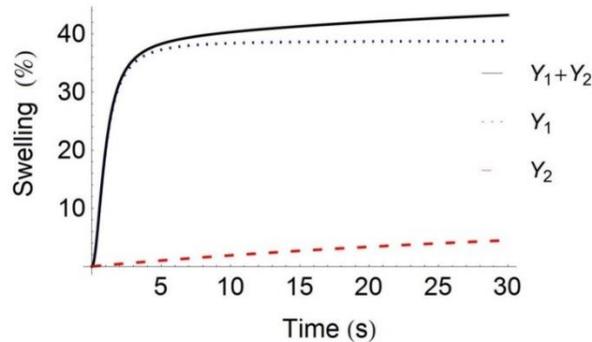

Fig. 6. Estimated impact of the various factors on overall change of swelling

The estimates of the individual parameters for various temperatures and recycling numbers are listed in Table 3.

Table 3. Individual Parameters for Various Temperatures and Recycling Cycles

Temp.	Recycling No.	*a*	*k*	*b*	*c*
80 °C	Original Pulp	3.41	-0.027	2.46	0.470
80 °C	0th	9.46	-0.026	1.70	0.635
80 °C	8th	6.73	-0.027	1.95	0.522
120 °C	Original Pulp	2.28	-0.043	3.25	0.795
120 °C	0th	8.26	-0.026	1.93	0.924
120 °C	8th	2.41	-0.063	3.05	1.165

The received results indicated that the swelling process of paper material took place during two time phases. The first one was the quick phase being controlled by transport of water into pores of the paper matter. The second delayed phase was the slow swelling, and was only a proper swelling process (Fig. 9).

A summary description of the effects of individual functions Y_1 and Y_2 is shown in Tables 4 and 5.

Table 4. The Effects of Individual Functions Y_1 and Y_2 at t = 120 °C

120 °C	Y	Y_1	Y_1/Y (%)	Y_2	Y_2/Y (%)
Original Pulp	25.66	23.38	91.11	2.28	8.89
0th Recycling	47.07	38.81	82.45	8.26	17.55
8th Recycling	26.09	23.68	90.76	2.41	9.24

Table 5. The Effects of Individual Functions Y_1 and Y_2 at 80 °C

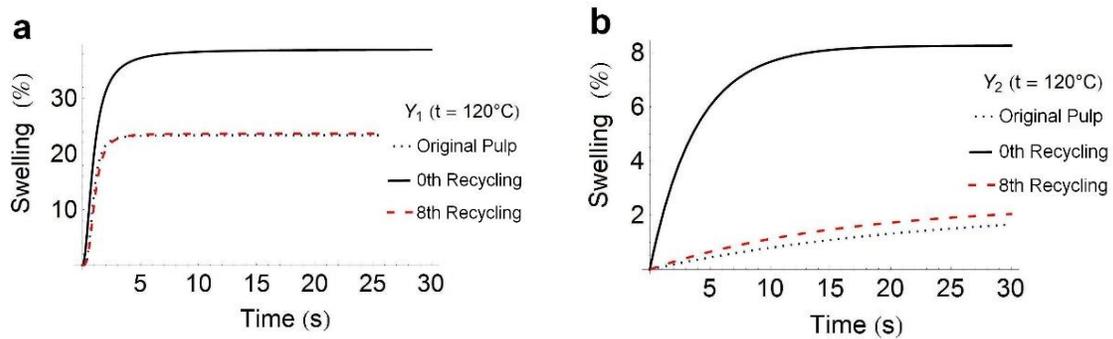| 80 °C	Y	Y_1	Y_1/Y (%)	Y_2	Y_2/Y (%)
Original Pulp	27.97	24.56	87.81	3.41	12.19
0th Recycling	48.92	39.45	80.65	9.46	19.35
8th Recycling	36.56	29.83	81.59	6.73	18.41

Fig. 7. The influence of the function Y_1 (a) and Y_2 (b), depending on the number of recycling
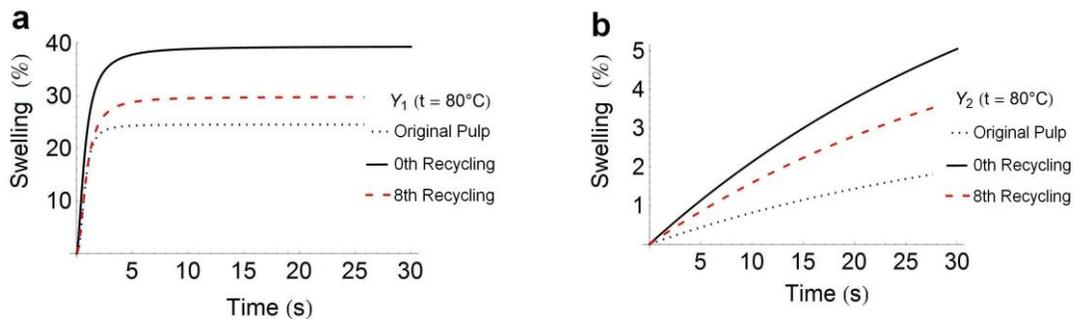

Fig. 8. The influence of the function Y_1 (a) Y_2 (b) depending on the number of recycling

At 80 °C, as expected, there was a slower reduction of the sorption capacity with increasing number of recycling cycles, even at each function separately (Figs. 7 and 8). A decrease in the change rate of the function Y_2 was also observed, which could be explained by the more gradual closing of the pores and lumens, *e.g.* by hornification of cellulose fibres.

However, more information about an influence of the recycling process upon the hypermolecular properties of porous matter was received by rectification of parameter *b*. As documented in Table 3, this parameter was strongly influenced by beating (compare original unbeaten sample and 0th beaten sample) and recycling. The beating decreased *b*, while the recycling increased it. These changes were larger in the case of higher temperature drying.

At compared conditions, an increase of *b*, *i.e.* shifting of the inflection point to higher values of time, was accompanied by the delaying of a proper swelling process, because it can be assumed that the amount of appropriate micro- and nano-centres of the porous cellulosic matter to swell was decreased.

As the results in Table 3 indicated, the prolonged recycling noticeable increased the value of *b*, which revealed a decrease in the amount of these appropriate potentially swelling centres. This fact was reflected in a higher rigidity of individual fibres accompanied by a depression of water sorption ability, WRV (water retention volume), *i.e.* the process led to hornification. Beating approximately reversibly eliminated this unpleasant behaviour of cellulosic matter.
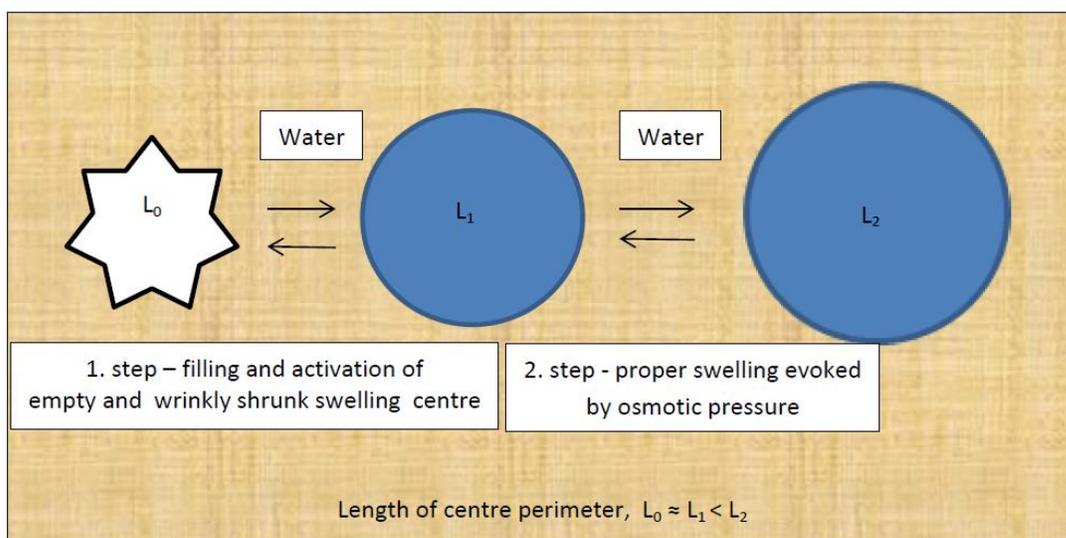
Fig. 9. Schematic description of swelling process

CONCLUSION

It was shown that the swelling process of cellulosic porous materials such as paper strips can be indicated as dimensional changes, which can be regarded as taking place in two steps. The first step of swelling involves the filling and activation of empty and wrinkly shrunk swelling centres with water. This is followed by a second step, *i.e.* a proper swelling, accompanied by further volume increase. The proper swelling process is governed by osmotic pressure, which arises due to the presence of – active hydrophilic soluble and insoluble substances and fragments embedding cellulosic interfaces in the wall surface of the swelling centre.

1. The model proposed by this paper seems to be a considerable improvement compared to the previous models. Its components are explainable by either physical or chemical properties of a paper strip, and it is satisfactorily justified by measured data.

2. The use of this study's model revealed a mechanism of the well-known hornification process, which takes place during the recycling of cellulose fibres. Clearly, as the results indicate, transport of water in the porous cellulosic material is controlled by penetration (according to GSM model) while there is a slow transport process (diffusion) into cellulose fibres.

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