Effect of the Free Swelling of Refined Cellulose Fibres on the Mechanical Properties of Paper

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Abstract
The purpose of this work was to determine the optimal duration of free swelling for refined unbleached kraft pine pulp. Free swelling is the effect of water sorption by cellulose fibres without their simultaneous mechanical treatment (e.g. refining). The second purpose was to determine the possibility of improving the mechanical properties of paper by testing various combinations of refining and free swelling processes. The pulp SR value and water retention value (WRV) of the fibres were tested. As regards paper properties, the tensile index and tear index were tested. Based on the results obtained, it was found that for the pulp tested, refined to 35 °SR, the optimal time of free swelling was 70 min. It was also proved that the free swelling had a significant impact on both the WRV of fibres and the mechanical parameters of paper tested. For the scheme in which refining was followed by free swelling, a 7% increase in the tear index was obtained. However, an 11% increase in the tear index was attained for the scheme with three refining stages, followed by free swelling after each refining.

Key words: *pulp, free swelling, WRV, refining, paper strength.*

Introduction

It is well known that the unrefined plant-based cellulose fibres used in paper production have low papermaking potential (the ability to create a desired paper structure of desired paper properties). Paper made from this type of fibre is characterised by high porosity and low strength. Such characteristics result from the fact that the strength properties of a paper product depend on the surface of fibre bonding. Unrefined cellulose fibres are relatively stiff, therefore the surface of their mutual contact in a paper product will be marginal. Paper made from such fibres will have a loose structure and low strength (F***igure 1.a***). Basic efforts - aimed at improving papermaking ability - have to be focused on the maximal development of the bound surface in paper. This effect is obtained by increasing fibre flexibility [7, 8].

In the forming and pressing stage, sufficiently flexible and softened fibres build a paper web of compact structure, where the area of fibre mutual contact is large [7, 8]. In the drying process, in the places of fibre contact, the bonds influencing the high strength of the final product are fixed (***Figure 1.b***).

To increase the flexibility of cellulose fibres, it is necessary to weaken the bonds connecting their structural elements. In practice, this is done in the pulp refining process. It should be noted that the desired effect of this operation is possible only in the presence of polar liquid (on an industrial scale – only in a water medium). Mechanical interactions between knives in refining equipment damage the external, impermeable layers of cellulose fibres and make internal layers available for water [7]. Water molecules are strongly attracted by free, polar carboxyl, hydroxyl or sulfo groups [11 - 13], which are present in chemical compounds (e.g. cellulose, hemicellulose, lignin), constituting the building material of the plant fibre cell wall or are brought into the fibre structure by their treatment (pulping, bleaching) [1, 11 - 13]. The effect of this attraction results in the replacement of hydrogen bonds with hydrous bridges that loosen, as a consequence, each layer of the cell wall. In paper technology this phenomenon is called internal fibrillation. The swelling of cellulose fibres is the result of internal fibrillation. One of the factors that allows to determine the progress of internal fibrillation is the water retention value (WRV), developed by Jayme [2, 3]. The tests [7, 10] showed that an increase in the WRV of fibres is clearly connected with an increase in the mechanical properties of the paper. It is important to remember that water penetration and swelling are processes of specific kinetics [6, 9]. A certain period of time is required for water to penetrate into all available spaces. Therefore fibre swelling occurs not only during the refining operation but also (in a limited

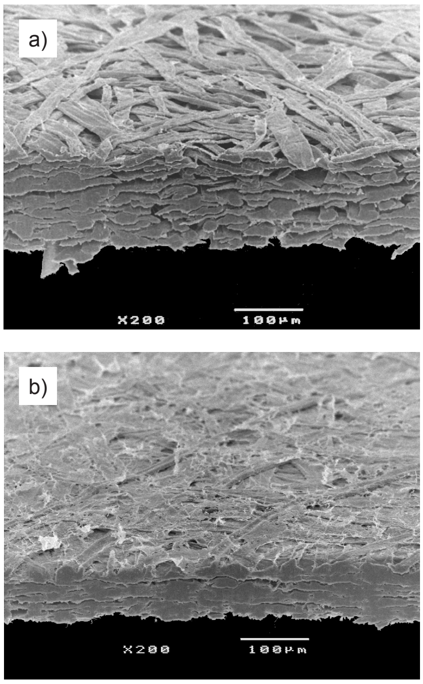

Figure 1. *a) Structure of a paper sample made from unrefined pulp (stiff fibres), b) Structure of paper made from refined pulp (flexible fibres).*

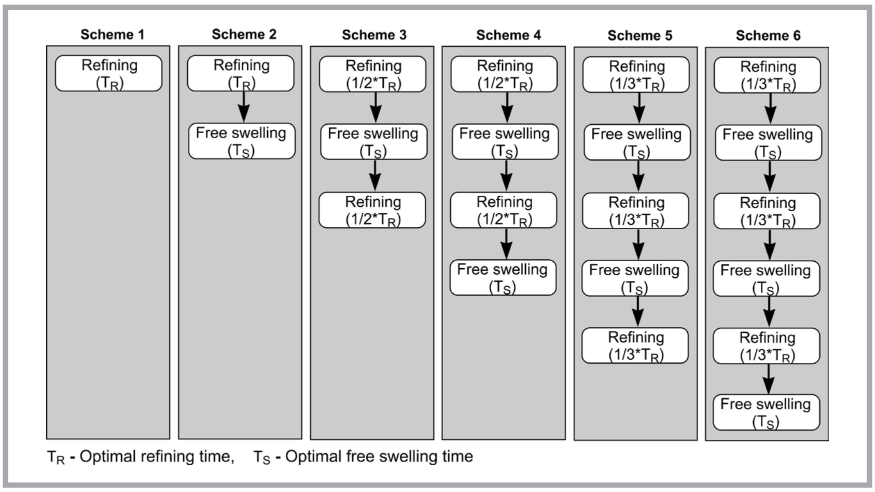

***Figure 2**. Schemes of refining and swelling sequences tested.*

***Table 1.** Typical accuracy of all laboratory measurements accomplished (Student-Fischer method, confidence level = 95%)*

Measurement	Mean Square Error	Standard Deviation
SR value, °SR	0.239	0.76
WRV, %	0.0732	0.17
Tensile index, N×m/g	0.853	2.71
Tear index, mN×m^2/g	0.0645	0.21

range) during free contact with water (free swelling). The most comprehensive research works in this field were carried out by Wultsch and Weissmann [15] in the 1950s, in which they found that the time after which the pulp reaches maximum hydration depends on several factors, including the pulp grade and refining rate. They also discovered that after four hours of free swelling it was possible to obtain an increase in paper strength of 15%. Using limited refining combined with free swelling, they obtained the same strength with better pulp drainability, which had a good result as it helped to dewater the paper web on the paper machine's wire. The swelling of papermaking cellulose fibres was the subject of Maloney and Paulapuro's research work. The researchers, however, mainly focused on measurements of the fundamental relationships between the fibre structure and water. They determined the size of capillaries in the fibre cell walls and water distribution in the fibre structure [4, 5]. There are also available test results for free swelling itself, but only regarding fibres dedicated to textile purposes [14, 16]. The tests used solutions of various compounds, e.g. NaOH, KOH, LiOH or different alcohols. For this reason they are not that important for paper technology. Literature analyses show that few authors have concentrated their work on the possible improvement of papermaking ability by combining refining with free swelling.

At present, thorough knowledge of the kinetics in the swelling process of papermaking from cellulose fibres is becoming particularly important. The growing capacities of technological lines connected with higher paper machine capacities are making the time of specific unit operations shorter. Batch refining systems, where papermaking pulp had enough time to swell, have been replaced by continuous systems, meaning that refined pulp flows through all the refiners within a relatively short period of time, after which - it is immediately used in the production cycle. Such a system does not usually ensure the minimal time needed for appropriate fibre swelling, the effect of which may involve the non-optimal development of the papermaking properties of a given pulp. As a result, lower paper quality could be obtained.

The lack of new research results regarding free swelling encouraged the author to undertake a research project in this field. The aim of the project was to determine the optimal time of free swelling of a selected cellulose pulp, with the other aim being to determine possible improvements in the strength properties of paper by testing various combinations of refining and free swelling processes.

One must remember that the refining process in industrial conditions is always a result of a compromise between decreasing (along with refining) the drainability and increasing the papermaking potential (defined by certain product quality indices). It was decided that the basic limitation of the refining process would be the ability to drain the pulp tested (measured by SR value). The SR value was used as the most popular (especially in industrial practice) and was the simplest to accomplish, being the indicator of drainage. Free swelling was characterised by the fibers' WRV. As regards paper properties, the tensile index and tear index were tested.

Materials and methods

Unbleached kraft pine pulp was used in the experiments. All refinings were done in a PFI mill according to standard method TAPPI T 248. The water retention value (WRV) of fibres was tested according to SCAN-C 102 XE (8 measurements per sample were made). It was assumed that, after centrifuging of the pulp sample tested, free swelling was finished. The refined pulp was examined, and laboratory sheets of 70 g/m^2 were formed in Rapid-Köthen apparatus according to Standard ISO 5259-2:2001. Paper samples were conditioned according to the ISO 187:1990 standard. The mechanical properties of paper were tested in accordance with adequate ISO standards: tensile index - ISO 1924-2:2008 (10 measurements per sample were made), and tear index - ISO 1974:1990 (4 measurements per sample were made). The schemes of refining and subsequent swelling tested are shown in ***Figure 2***. T_R stands for the optimal refining time and T_S stands for the optimal free swelling time (both values were experimentally determined). Information about the typical accuracy of all measurements is given in ***Table 1***.

Results

On the basis of an analysis of the SR value for similar pulp grades processed in industrial conditions, it was assumed that upon refining, the SR value of the test pulp could not exceed 35 °SR. For the limit defined in this way, it was assumed that optimal pulp and paper properties were obtained for that refining degree. ***Figure 3*** shows the relationship between the refining time and SR values obtained. The SR value assumed was achieved after time T_R = 6 min. Therefore, further tests of free swelling were conducted for pulp refined for determined time T_R.

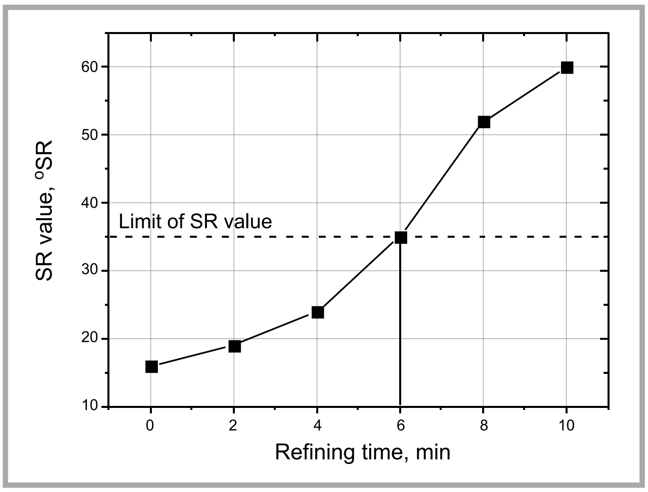

Figure 3. *Changes in dewatering ability (measured in SR degrees) of unbleached kraft pine pulp refined in a laboratory PFI mill.*

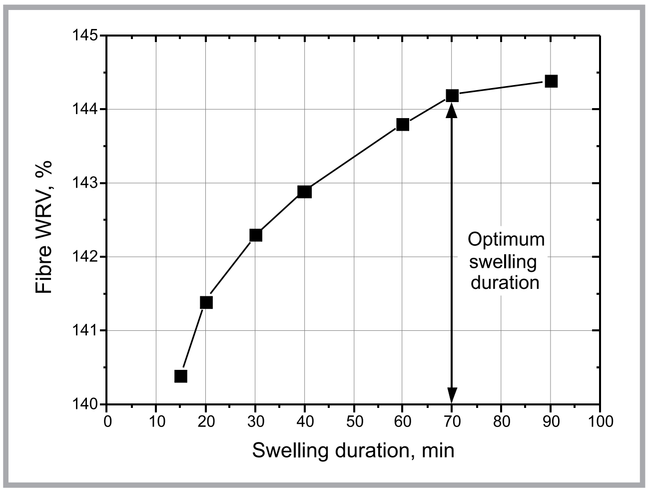

Figure 4. *Determination of the optimum duration of free swelling for test pulp refined to 35 °SR.*

From a practical point of view, the time of the pulp staying (and swelling) in the technological line is a function of the total capacity of the stock system and paper machine. If the pulp has to stay longer there, the capacity of the technological line has to be increased (e.g. by construction of an additional chest). To reduce costs, it is necessary to determine an optimal and possibly short swelling time. In these tests, the boundary time of the free swelling was defined as that after which the increases in swelling degrees were less than 5% of the total WRV increase (obtained in given conditions for a given pulp). ***Figure 4*** shows changes in this value determined for different times of free swelling. On the basis of the previously given definition of the swelling time limit, it was found that the time required for the test pulp was T_S = 70 min. Therefore in all further experiments, free swelling was carried out for time TS. ***Figure 4*** also shows that free swelling is not a linear process. Free swelling is fastest within the initial minutes, then the dynamics of water sorption start to drop, reaching a defined maximum boundary value in the end. It can be suspected that this effect can be a result of the fact that water absorption creates pressure on the fibre cell wall structure, and there is pressure induced creep during the loosening of the cell wall structure. The whole process of free swelling is relatively slow, lasting several minutes. In the case presented, the WRV of fibres after T_S = 70 minutes of free swelling additionally increased by around 4%.

On the basis of the refining and free swelling time determined, 6 different schemes combining refining and free swelling operations in different sequences were developed. The sequence of the operations was marked in the following way: R – refining, and S – free swelling. In the schemes, where several refinings were used, the total refining time had to be the same as the T_R time. In such cases, each of the refinings lasted for a shorter time, proportional to the number of the refinings (e.g. with two refinings, each of which lasted $0.5{\times}T_R$). Nevertheless, in each case, free swelling was conducted for a time T_S.

Figure 5 shows the final WRV values obtained for each refining-free swelling scheme. The results indicate that, depending on the sequence used and the number of these two unit operations, the WRV may have values differing even by 11%. The highest WRV of 146.6% was obtained for the R-S sequence, whereas the lowest was for the R-S-R (135.1%). Generally, it can be observed that higher WRVs were obtained for the sequences that were finished with free swelling. Therefore, it can be concluded that during the refining process, the impact of forces in the refining zone forces some water to be drained from fibres once again, resulting in a repeated decrease in the swelling rate. It is also worth mentioning that using several shorter refinings instead of one long one did not improve the WRV. Therefore, in order to obtain the optimal effect, the best solution is to use free swelling after refining.

The analysis of the tensile index of laboratory paper samples made of pulps from the different schemes of refining and free swelling (***Figure 6,*** see page 116) shows that t free swelling considerably improves the strength properties of paper. Wherever free swelling was used, higher values of the tensile indices were obtained for scheme 1, which only involved refining. On the basis of these results it can be concluded that the best effects (the highest tensile index) were achieved for scheme 2, where one refining was used, followed by free swelling. In this instance, almost

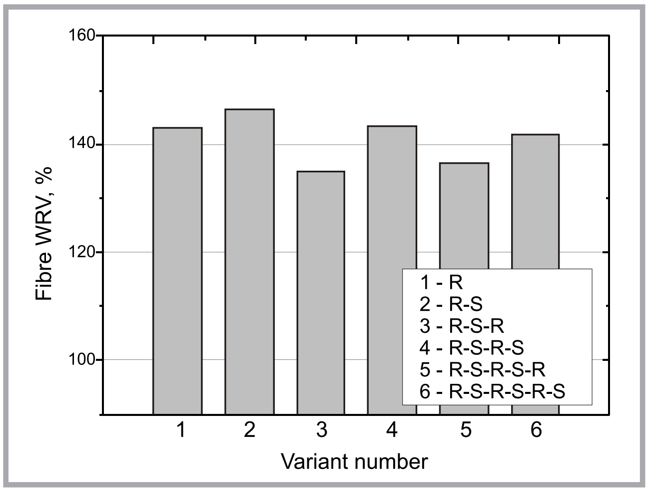

Figure 5. *Fibre WRV for different refining and free swelling schemes.*

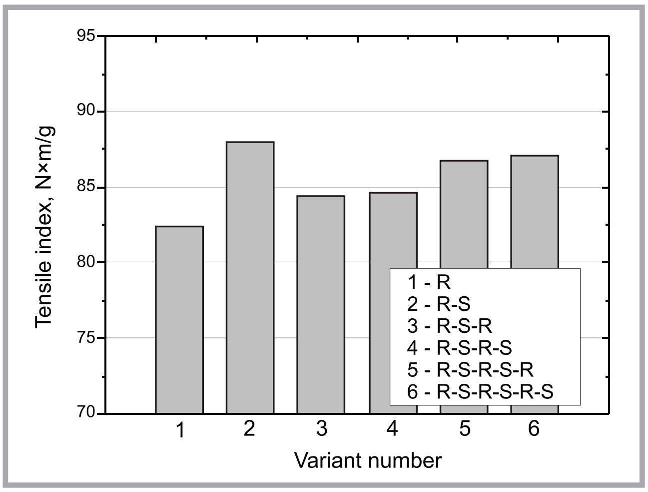

Figure 6. *Values of the tensile index of laboratory paper samples made from the test pulp for different schemes of fibre refining and free swelling.*

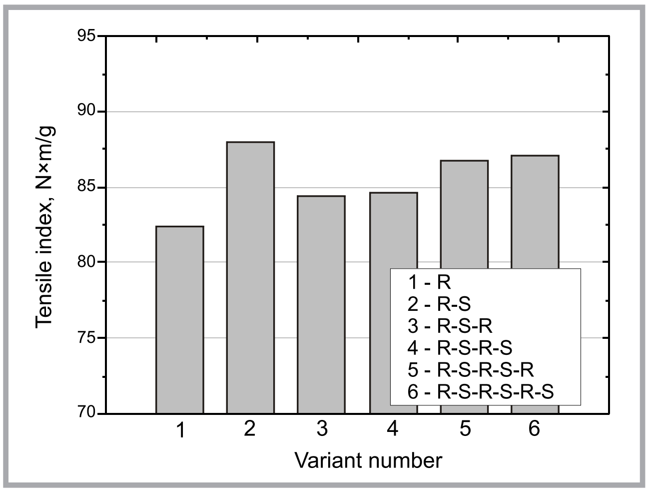

Figure 7. *Values of the tear index of laboratory paper samples made from the test pulp for various refining and free swelling schemes.*

a 7% increase in the tensile index was achieved. A not much lower increase was obtained for scheme 6 (three refinings followed by free swelling after each). The relatively lowest increase was obtained for schemes 3 and 4. Therefore, it can be concluded that,when the tensile index is the parameter determining paper quality, the best solution would be to use one free swelling after refining (scheme 2).

The situation looks different for the tear index. This is a parameter reflecting the dynamic strength properies of paper. These properties usually decrease after refining. ***Figure 7*** shows values of the tear index obtained for all the schemes tested. It turned out that free swelling also has a positive impact on this index. In the case discussed, the best results were obtained for scheme 6, where the pulp was refined three times (always for a time of $1/3 \times T_R$), and after each refining the pulp underwent free swelling for a time T_S, resulting in an 11% increase in the tear index for scheme 1 (refining only). On the basis of the results obtained, a general rule can be formulated that for the tear index, short repeated refinings with necessary interruptions for free swelling are advantageous.

Summary

On the basis of the test results, it can be concluded that free swelling is a long-lasting process. For the pulp tested, refined to a value of 35 °SR, the optimal time of free swelling was 70 minutes. The test results show that free swelling definitely has a positive effect on both the WRV of fibres and the strength properties of paper tested. The best results were achieved when free swelling was used at the very end, after the final refining. In the experiment with one final free swelling after a single refining stage, a 7% increase in the tensile index was obtained. The highest increase in the tear index (11%) was obtained in the experiment where 3 refining stages and 3 stages of free swelling were applied alternately.

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References

1. Carlsson, G.; Kolseth, P.; Lindström, T. Polyelectrolyte swelling behaviour of chlorite delignified spruce wood fibers, *Wood Sci. Technol.*, **1983**, *17*, 69-73.
2. Jayme, G. Mikro–quellungsmessungen an zellstoffen, *Wochenbl. Papierfabr.*, **1944**, *6*, 187-194.
3. Jayme, G.; Bfittel, H. Ober die Bestimmung und Bedeutung des Wasserrfickbaltevermgens (des WRV-Wertes) verschiedener gebleichter und ungebleichter Zellstoffe, *Das Papier,* **1966**, *20*, 7, 357-366.
4. Maloney, C. T.; Paulapuro, H.; Stenius, P. Hydratation and swelling of pulp fibres measured with differential scanning calorimetry, *Nord. Pulp Pap. Res. J.*, **1998**, *13* (1), 31-36.
5. Maloney, T.C.; Laine, J. E.; Paulapuro, H. Comments on the measurement of cell wall water, *Tappi J.* **1999**, 82(9), 125-127.
6. Mantanis, I. G.; Young, A. R.; Rowell, M. R. Swelling of compressed cellulose fiber webs in organic liquids, *Cellulose,* **1995**, *2*, 1-22.
7. Przybysz, K. Badania przebiegu fibrylacji włókien w procesie mielenia, *Przegląd Papierniczy,* **1975**, *32 (5)*, 197-201.
8. Przybysz, K. Wiązania między włóknami w papierze cz. I. Istota, mechanizm powstawania oraz czynniki kształtujące wytrzymałość wiązań między włóknami w papierze, *Przegląd Papierniczy*, **1977**, *33(6)*, 342-348.
9. *Pulp and* Paper Chemistry. ed. by Monica Ek, Göran Gellerstedt, Gunnar Henriksson, Berlin. De Gruyter, **2009**,*3*
10. Scallan, A.M.; Grignon, J. The effect of cations on pulp and paper properties, *Svensk Papperstidning*, **1979**, *82(2)*, 40-47.
11. Scallan, A. M. The effect of acidic groups on the swelling of pulps: A review, *Tappi J.* **1983**, *66*, 73-75.
12. Sjöström, E. Wood Chemistry fundamentals and applications. Academic Press Inc. London, UK., **1981**.
13. Sjöström, E. The origin of charge on cellulosic fibers. *Nord. Pulp Pap. Res. J.* **1989**, *2*, 90-93.
14. Wangsun Zhang, W.; Okubayashi S.; Bechtold T. Fibrillation tendency of cellulosic fibers. Part 1: Effects of swelling, *Cellulose*, **2005**, *12*, 267-273.
15. Wultsch, F.; Weissmann, L. Mahlungseigenschaften von gequollenen Zellstoffen, Akademische Druck - U. Verlagsanstalt, Graz, **1959**.
16. Xie, Y.; Hill, A. S. C.; Jalaludin, Z.; Curling, F. S.; Anandjiwala, D. R.; Norton, J. A.; Newman, G. The dynamic water vapour sorption behaviour of natural fibres and kinetic analysis using the parallel exponential kinetics model, *J. Mater. Sci.,* **2011**, *46*, 479-489.

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