CHANGE IN THE CAPABILITY OF CELLULOSE FIBRES TO RETAIN WATER DURING THERMALLY ACCELERATED AGEING OF PAPER

ŠTEFAN ŠUTÝ, KATARÍNA PETRILÁKOVÁ, SVETOZÁR KATUŠČÁK, SOŇA KIRSCHNEROVÁ, MICHAL JABLONSKÝ, KATARÍNA VIZÁROVÁ and MILAN VRŠKA

Institute of Polymer Materials, Department of Chemical Technology of Wood, Pulp and Paper, Faculty of Chemical and Food Technology, Slovak University of Technology
Radlinského 9, 831 07 Bratislava, Slovak Republic

Received June 21, 2011

The water retention value (WRV) as a measure of the capability of cellulose fibres to retain water (swelling of fibres) was evaluated during accelerated ageing of acidic wood pulp newspaper containing 20% chemical fibres. It has been found that the WRV considerably decreases with accelerated ageing. Relations between the WRV properties and the mechanical properties of paper have also been evaluated. The characterization of samples by mercury micro-porosimetry has shown that the cumulative column of the pores increases with the period of ageing. On the other hand, the average radius of the pores, as well as their specific surface, decreases. This supports the process of hornification, which occurs during accelerated ageing of paper, as the small pores get smaller and the larger ones get even larger as a result of shrinkage of fibres. When considering accelerated ageing, hornification of fibres as one of the outcomes of fibre brittleness has to be taken into account.

Keywords: hardwood bleached kraft pulp, recycling, swelling kinetics, hornification, thermal treatment

INTRODUCTION

Hornification of cellulose fibres was described already in the year 1944 by G. Jayme.[1] It is a process during which cellulose fibres alter their properties during of repeated morphologic and chemical changes, occurring on drying and wetting. The changes are irreversible, especially as to the water retention value (WRV), which was investigated by G. Jayme.[1] The WRV was originally used to observe the delamination of cell walls. Spin-drying of wet samples, under standard conditions of the spinning force and period, leads to a decrease in moisture content in WRV. Scallan and Charles[2] compared the WRV results with the ones existing at the point of saturation of the fibres and found a good correlation under modest centrifugal forces and time. This event was intensively studied in connection with losses in strength during recycling of cellulose fibres.[3] It has also been proved that hornification is more frequently observed in chemical cellulose than in lignified fibres. The main characteristic of softer hornification in mechanical fibres is that the fibres significantly retain the ability to take up water after drying. The lower yield cellulose fibres do not exhibit this property so obviously.

Lignin is a networking agent in the lamellar micro-fibrilous structure existing in the middle of the fibre.[4] Hemicelluloses are preferably located in the interface of the layers and act as an inter-connecting agent between lignin and cellulose micro-fibrils. The lignin-cellulose gel prevents the hydrogen bonds between the fibrils from being formed during the drying process and secures the space between the lamellas, which is thus accessible to water. The pulping process of lower yield fibres reduces the amount of the lignin hemicellulose gel that makes the irreversible hydrogen bonding between microfibrils possible. In mechanical pulping, this gel primarily remains intact. Experiments on hornification have proved the chemical changes resulting from it. It is quite difficult to indicate probable chemical changes occurring on hornification. The viscosity of some sorts of chemical cellulose, as dissolved in cupri-ethylen-diamine (CED), is related to the measured degradation of cellulose materials and to the indication of their general strength potential.[5] Hornification decreases CED viscosity.[6] Eventually, this fact could be used as a reference factor to measure the degree of hornification. To verify this possibility, Alanko[7] found out the CED viscosity for thermomechanical pulp (TMP) and for sulphate cellulose, recycled with the help of deinking chemicals. The CED viscosity of the beaten, bleached sulphate cellulose went considerably down. On recycling under the same conditions, the TMP viscosity rose rather modestly. CED does not completely dissolve lignin in mechanical cellulose. It may explain why the viscosity behaviour of cellulose was so diversified, thus becoming only partially comparable.

The direction of change points out that changes in cellulose structure of sulphate pulp are not of the same character as those in TMP. In accordance with the prevailing view, hornification occurs in the cellulose matrix of the walls of chemical pulps.[4] The first concept of explanation of this phenomenon was based on the change of amorphous cellulose to a crystalline one. However, this concept was not proved in subsequent works.[8,9] The presently accepted explanation is based on the so-called irreversible hydrogen bonds and has certain drawbacks, for example, the authors[10] argue why some hydrogen bonds can get disintegrated by water and others cannot. Hornification is explained on the basis of covalent lactone bridges. On the contrary, using the FTIR measurements, wide angle dispersion of X-radiation, SEM, Kato and Cameron[11,12] comment that during ageing no evident changes in the crystallinity occur. There is not any evidence of forming covalent networking or other structuring on ageing. The authors primarily assign the influence on the obtained values to the breaking of chains rather than to the increase of inter-fibrous bonds. Thus, there are certain similarities between hornification and thermally accelerated ageing. The conditions, under which both processes run, are similar. The influence on certain properties, e.g. brittleness or WRV, is comparable. However, the mechanisms are explained differently. Hornification occurs as inter-pulp irreversible hydrogen bonds, while thermally accelerated ageing is generally explained by increased disintegration of polymer chains.

This paper contributes to the topic of phenomena occurring during the accelerated ageing of commercially produced paper, obtained from both wood pulp and chemical pulp. The aim of this work has been to find out whether any WRV changes occur during accelerated ageing of paper and how they influence the mechanical properties of paper.

EXPERIMENTAL

The experiment was run on newspaper (wood-based, calendered) produced in Jihočeské papírny Větřní a.s., with a basis mass of 45 g/m^2, with the following composition (55% mechanically bleached ground wood pulp, 20% white sulphate pulp, 15% trapped waste fibres, 10% china clay), pH (surface): 4.5-5.0.

The samples were held under climatic conditions (23 °C, RH = 50%), closed in a three-layer cover, in sacks made of layered polyethylene foil with an aluminium layer, at a temperature t = 98±2 °C, for time periods of 0, 1, 2, 3, 5, 10, 15, 20 and 30 days, according to standard ASTM D 6819-02.[13]

The pore size was measured with a Porosimeter 2000 device at the Department of Chemical and Biochemical Engineering, Faculty of Chemical and Food Technology, STU in Bratislava (FCHPT STU).

In the test of tensile load, a piece of paper with certain length and width was torn off under certain predefined conditions. The tested sample was elongated to break under constant load that was exerted by a tensile strength tester. The test was performed on an INSTRON 1122 universal tensile strength tester, Instron Ltd., High Wycombe, Buckinghamshire, England, pursuant to the specification STN ISO 1924-1 (500340): "Paper and cardboard. Determination of tensile properties".[14]

The tensile test for determining breaking length was performed on an INSTRON 1122 universal tensile strength tester, Instron Ltd., High Wycombe, Buckinghamshire, England, pursuant to the specification STN ISO 1924-1 (500340): "Paper and cardboard. Determination of tensile properties".[14] Folding endurance (load 0.3 kg) was determined according to TAPPI T511 om-96.[15] Changes of folding endurance were studied on modified and aged samples.

The test was carried out by placing a pad of moist fibers in a centrifuge tube, with a fritted glass filter at its base. The centrifuge was accelerated at 900 g_n to remove water from the outside surfaces and lumens of the fiber (a higher force is used according to some European standards). The remaining water is believed to be associated with submicroscopic pores within the cell wall. The centrifuged fiber pad was weighed, dried at 105 °C, and then reweighed. The WRV value equals the ratio of the water mass to the dry mass, as defined by standard ISO 23718:2007.[16]

RESULTS AND DISCUSSION

In the test of accelerated ageing, it was found that the WRV decreased (Fig. 1). The WRV is a measure of the capability of fibres to retain water and it relates to the capability of the fibre structure to interact with water. When the structure becomes impermeable to water, the WRV decreases. Similarly, on fibre recycling the WRV showed a decrease, but at the same time, with a growing number of fibre cycling processes there was an increase in the values of fibre brittleness (repeated defibrillation and drying). This phenomenon is sometimes called hornification, i.e. keratinisation of cellulose fibres by means of humidity and heat. The conditions that favour hornification can occur during accelerated ageing. Hornification is manifested as increased brittleness of paper. Fig. 2 shows the function of changing double-folding endurance as dependent on ageing period. The brittleness of paper increases with the period of ageing. On double-folding endurance test, the paper is folded under a certain strength load. Fig. 3 depicts the dependence of the number of double-folds on WRV.

The tensile length as a measure of fibre strength changes in a linear mode with the period of accelerated ageing (see Fig. 4). Dependence has been found between the tensile length of ageing papers and the WRV (see Fig. 5). With a growing WRV, the tensile length of the paper increased. Similarly, during the tensile tests the relative elongation of the fibres rose with a growing WRV (Fig. 6).

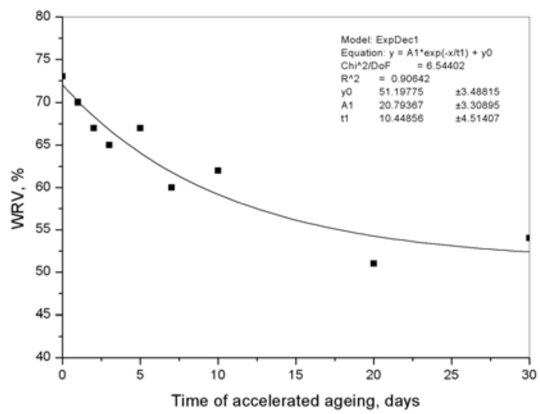

Figure 1: Changes of WRV during accelerated ageing of paper

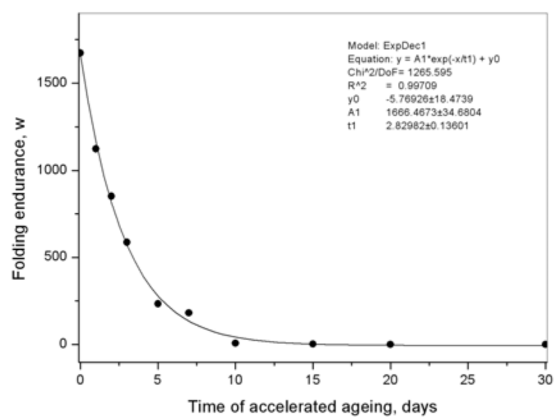

Figure 2: Folding endurance as a function of accelerated ageing time

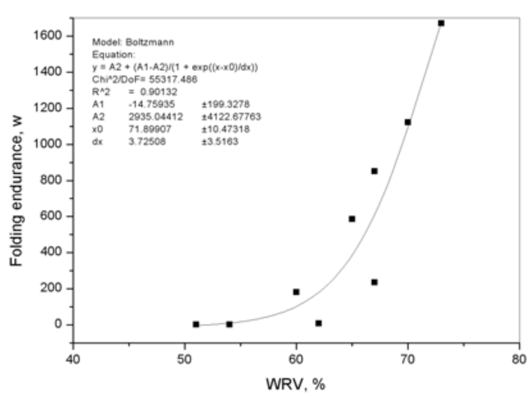

Figure 3: Folding endurance as a function of WRV during accelerated ageing of paper

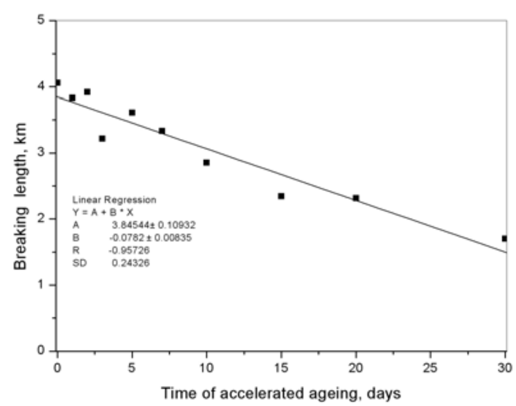

Figure 4: Dependence of breaking length on time of accelerated ageing of paper

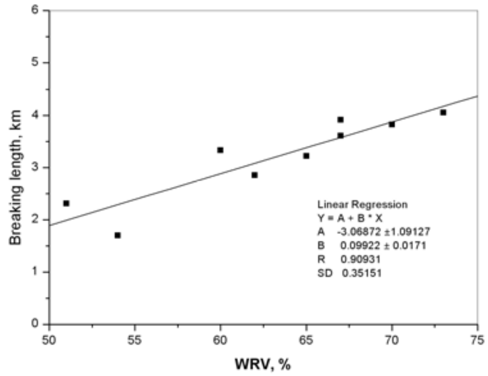

Figure 5: Breaking length as a function of WRV for accelerated aged paper

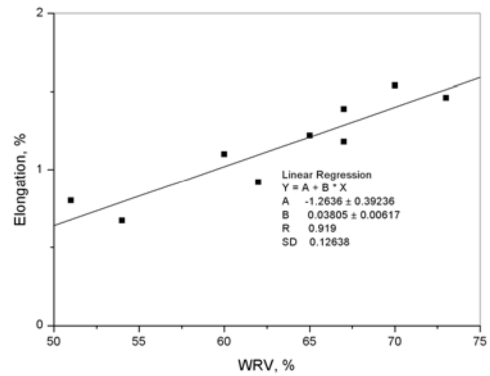

Figure 6: Relative elongation of paper as a function of WRV for accelerated aged paper

Hornification is understood as a process of closing the structure of cellulose fibres to water (impermeability), due to the development of irreversible hydrogen bonds between the micro-fibrils and other structural units of cellulose fibres, which gives them an even denser structure, making them more brittle.

Data from literature[3] state that hornification processes are more common in chemical fibres than in highly lignified ones. For our sort of paper composed mainly of wood pulp, it could be expected that hornification would affect mainly the chemical fibres. Considering that chemical fibres are the ones that give considerable strength properties to paper, hornification can be rather detrimental to the strength of the paper. In case hornification has already started, in the process of accelerated ageing the porous structure of the paper fibres is expected to change as well.

To find out how the size of pores changes as related to the period of ageing, the samples were submitted to analysis by mercury micro-porosimetry. Fig. 7 demonstrates the dependence of overall cumulative pore volume on period of ageing. It is interesting that the values of the overall cumulative pore volume increase with the period of ageing, which could signal that the inter-fibre spaces in paper get larger as a consequence of fibre shrinkage as an impact of hornification, when the tiny pores get closed. This conclusion can also be supported by the fact that the specific surface of the pores, as well as their average radius, decrease during accelerated ageing (see Figs. 8 and 9).

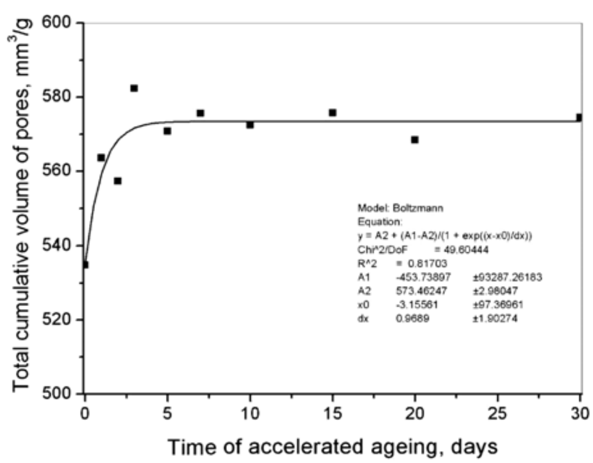

Figure 7: Dependence of total cumulative pore volume on time of accelerated ageing

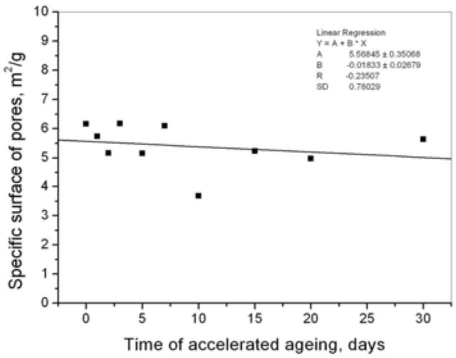

Figure 8: Changes of specific pore surface during accelerated ageing of paper

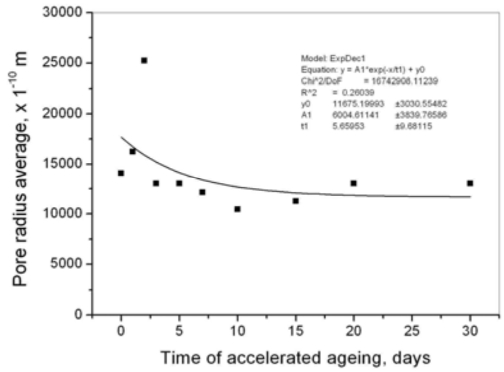

Figure 9: Changes of average pore radius during accelerated ageing of paper

CONCLUSION

The results of this study have proved the mechanism of hornification that starts during the accelerated ageing of wood pulp paper. The results demonstrate that during accelerated ageing of paper the WRV decreases. The relations between the WRV and some strength characteristics were observed, such as the relation between the folding endurance and breaking length. Also, the process of hornification was investigated and evaluated by measuring the porosity of ageing papers. It was found that the cumulative pore volume grows as a consequence of fibre shrinking during the processes of accelerated ageing. Simultaneously, there occurs a decrease of the specific pore surface, as well as a decrease of the average radius of the pores. Thus, it can be presumed that during accelerated ageing, along with chemical changes in fibres, there occurs a morphological change in the structure of cellulose fibres, which is responsible for fibre brittleness.

ACKNOWLEDGEMENTS: We acknowledge the project of the Ministry of Education of Slovak Republic No. 2003 SP200280301 “Preservation, Stabilization and Conservation of Traditional Information Carriers of the Slovak Republic” and VEGA agency for financial support for project No. 1/0770/08.

REFERENCES

[1] G. Jayme, *Papier Fabr*./*Wochbl*. *Papierfabr*., **72**, 187 (1944).
[2] A. M. Scallan, J. E. Charles, *Svensk Papperstid*., **75**, 699 (1972).
[3] C. Ackermann, L. Gottsching, H. Pakarinen, in “Papermaking Science and Technology: Recycled Fiber and Deinking”, edited by L. Göttsching and H. Pakarinen, Fapet Oy, 2000, pp. 357-438.
[4] A. M. Scallan, A. C. Tigerstrom, *Procs*. *1st Research Forum on Recycling*, *CPPA*, Montreal, October 29-31, 1991, pp.149-154.
[5] K. Rutledge-Cropsey, S. M. Abubakr, J. H. Klungness, *Procs*. *The 1995 TAPPI Pulping Conference*, Chicago, October 1-5, 1995, pp. 639-643.
[6] Y. Yamagishi, R. Oye, *Japan Tappi J*., **35**, 33 (1981).
[7] K. Alanko, M.Sc. Thesis, Helsinki, University of Technology, 1993.
[8] T. C. Maloney, A. Todorovic, H. Paulapuro, *Nordic Pulp Pap*. *Res*. *J*., **13**, 285 (1998).
[9] J. Bouchard, M. Douek, *Procs*. *Research Forum on Recycling* (*2nd CPPA*), Montreal, October 5-7, 1993, pp. 23-29.
[10] J. M. B. Fernandez Diniz, M. H. Gil, J. A. A. M. Castro, *Wood Sci*. *Technol*., **37**, 489 (2004).
[11] K. L. Kato, R. E. Cameron, *Cellulose*, **6**, 23 (1999).
[12] K. L. Kato, R. E. Cameron, *J*. *Appl*. *Polym*. *Sci*., **74**, 1465 (1999).
[13] ASTM D 6819-02, Test method for accelerated temperature aging of printing and writing paper by dry oven exposure apparatus.
[14] STN ISO 1924-1 (500340), Paper and cardboard. Determination of tensile properties.
[15] TAPPI T511 om-96, Folding endurance of paper (MIT tester).
[16] ISO 23714:2007, Pulps – Determination of water retention value (WRV).