

ON THE MECHANISMS OF MECHANO-SORPTIVE CREEP REDUCTION BY CHEMICAL CROSS-LINKING

*Magnus Gimåker¹, Anne-Mari Olsson²,
Lennart Salmén² and Lars Wågberg¹*

¹Department of Fibre and Polymer Technology, Royal Institute of
Technology, KTH, SE-100 44 Stockholm, Sweden

²INNVENTIA AB, Box 5604, SE-114 86 Stockholm, Sweden

ABSTRACT

Despite the technical importance of mechano-sorptive creep in paper, the exact mechanism behind this phenomenon is still not fully understood. In this study it was shown that the mechano-sorptive creep of paper sheets can be significantly reduced by chemical cross-linking through periodate oxidation. The mechanism behind this reduction has been examined through creep measurements of both sheets and individual fibres. For sheets the creep acceleration due to varying humidity was significantly reduced by the chemical cross-linking. For single fibres, however, the creep acceleration was not affected by the chemical cross-linking. In fact the absolute creep rate for the periodate oxidised fibres were higher than that of the reference fibres. This clearly showed that the improvement in mechano-sorptive creep found on a sheet level does not originate from an improved creep resistance for individual fibres but rather from mechanisms operating at the fibre network level. Hygroexpansion and moisture sorption of the sheets during the humidity cycling used for creep testing have also been measured, and the results showed that both was

reduced by the periodate oxidation. Reduced moisture sorptivity and hygroexpansion probably minimises stress concentrations at the fibre network level and thereby also the creep acceleration.

BACKGROUND

Creep, the time-dependent deformation of a specimen held under a constant load, affects paper and many other materials. Humidity affects the creep of paper materials, with faster creep at higher moisture conditions (i.e. at higher amounts of adsorbed water). Varying humidity accelerates the creep rate, such that the creep during cycling between low and high humidity exceeds the creep found at high constant humidity [1, 2]. This phenomenon is usually referred to as mechano-sorptive creep or accelerated creep.

The mechano-sorptive creep of a linerboard is very important since it will have a large influence on the stacking lifetime of a corrugated box [3]. To ensure an adequate stacking life for boxes of corrugated board a large safety factor is used when designing the container. If it would be possible to produce a linerboard with less mechano-sorptive creep, the safety factor and material use could be significantly reduced, with both economical and environmental benefits.

Despite its technical importance, the exact mechanism behind this acceleration of the creep rate is still not fully understood. There are two dominant models for mechano-sorptive creep in paper. Habeger and Coffin [4] suggest that humidity variations give rise to moisture gradients within the sheet and hence stress gradients due to hygroexpansion, and that these in combination with the non-linear creep of paper give rise to an accelerated creep. Alftan *et al.* [5] suggest that the anisotropic hygroexpansion of the fibres upon exposure to moisture leads to a mismatch of hygroexpansive strains at the fibre/fibre joints, causing large stresses at the bond sites, and that these, together with the non-linear creep of paper, give rise to an accelerated creep. Common for these two models is that it is the hygroexpansion of the fibres that accelerates the creep rate.

One of the few methods that have shown to substantially decrease the mechano-sorptive creep is cross-linking by chemical means [6, 7]. Caulfield [6] used multifunctional carboxylic acids to cross-link the fibres, which substantially reduced the mechano-sorptive creep. It was suggested that the mechanism for the creep reduction was that the covalent cross-links stabilises arrays of moisture sensitive hydrogen bonds and reduce their tendency to creep into a stress-relaxed configuration. No direct experimental support for

the validity of this molecular mechanism was however presented. The present study uses periodate oxidation to achieve cross-linking. Sodium metaperiodate specifically cleaves the C2–C3 bond of 1,4-glucans such that the cellulose is partly converted into dialdehyde cellulose. The formed aldehydes are reactive and can during drying form hemiacetal and acetal links to hydroxyl groups present in/on the fibres, thereby cross-linking the fibres and paper sheets [8–10]. The objective with this paper was to identify the mechanism behind the reduction in mechano-sorptive creep by chemical cross-linking and by that shed light upon the mechanism behind the mechano-sorptive creep as such.

Earlier studies have claimed that single wood fibres do not show mechano-sorptive creep [11, 12]. It has however later been argued that the lack of mechano-sorptive creep in these studies is only an effect of improper humidity changing rates, i.e. very short time with moisture gradients present in the material compared to the total loading time and hence little creep acceleration [13]. More recent measurements of creep on single wood fibres during cyclic humidity have in fact shown that wood fibres do exhibit mechano-sorptive creep [14]. In this study the later methodology has been adopted and the fibres measured clearly shows accelerated creep.

By testing both paper sheets and individual fibres for their creep at constant and varying humidity it is possible to distinguish if the reduction in accelerated creep is caused by mechanisms at fibre or fibre network level. As already mentioned moisture gradients are believed to be a probable mechanism behind accelerated creep. Since periodate oxidation is known to influence the moisture sorption of fibres [10] both thick and very thin sheets were prepared and tested to eliminate the risk that the effects seen for the thicker sheets was not only due to changed moisture sorption kinetics and moisture gradients.

EXPERIMENTAL

Materials

Fibres

The fibres used were from a softwood kraftliner pulp (kappa number 76) from Kappa Kraftliner Piteå, Sweden, which had been beaten in an Escher-Wyss laboratory refiner to about 30 MSR.

Chemicals

Sodium metaperiodate used for fibre oxidation and hydroxylamine hydrochloride used for carbonyl content determination was purchased from

Sigma-Aldrich, Sweden. Sodium hydroxide solution used for titration was of analytical grade.

Methods

Fibre pre-treatment

It was necessary to remove most of the fines material from the pulp in order to prepare a pulp that was suitable for evaluating the influence of fibre properties on sheet properties. Successive spraying through a spray disk filter fitted with a plastic wire with 75 μm openings removed the fines. Washing of the long fibre fraction at both low and high pH, using a previously described procedure [15], removed most of the remaining adsorbed metal ions and dissolved and colloidal material, and converted the carboxyl groups of the fibres to their sodium form.

Fibre oxidation

The fibres were suspended in de-ionised water to a concentration of 7.5 g/l and stirred. The oxidation was initiated with an addition of sodium metaperiodate to the fibre suspension. A low degree of oxidation was prepared by a sodium metaperiodate dosage of 1.36 gram per gram fibre and a reaction time of two hours. A high degree of oxidation was prepared by a sodium metaperiodate dosage of 2.72 gram per gram fibre and a reaction time of 4 hours. The oxidation reaction was stopped by dewatering the fibres in a Büchner funnel fitted with filter paper (Munktell no. 3). Subsequently the fibres were repeatedly washed with de-ionised water until the conductivity of the filtrate was below 5 $\mu\text{S/cm}$.

Determination of carbonyl content

The content of carbonyl groups in the fibres was determined with the hydroxylamine hydrochloride method [16, 17]. Hydroxylamine hydrochloride reacts quantitatively with carbonyls in the fibres to form corresponding oximes, releasing an equivalent amount of hydrochloric acid. The released amount hydrochloric acid and hence the carbonyl content, can easily be determined by a simple potentiometric neutralisation titration.

Approximately 0.1 g fibres were suspended in 40 ml deionised water and the pH of the suspension was adjusted to pH = 4. Subsequently, 10 ml of 2.5 M hydroxylamine hydrochloride solution (previously adjusted to pH = 4) was added to the suspension. Reaction was allowed to take place for two hours

under stirring. The reaction was stopped by dewatering the fibres on a Büchner funnel fitted with filter paper (Munktell no. 3). The fibres were collected, dried and weighed to determine the exact mass of dry fibres. The filtrate was diluted with deionised water to a total volume of 100 ml. The pH of a blank determination was 4; therefore the filtrate was titrated back to pH 4 with 0.01 M sodium hydroxide solution. The amount of sodium hydroxide needed to reach pH 4 thus equals the amount of carbonyls present in the sample. For un-oxidised fibres the pH of the filtrate was approximately 4 after two hours of reaction indicating that there were no carbonyls in these fibres. However, ordinary pulp fibres do contain small amounts of carbonyl, in the range of few micromoles per gram fibre, but this low amount is too small to be detected by the current method.

Sheet preparation

Isotropic sheets with a grammage of 140 g/m² were prepared using a Rapid-Köthen sheet preparation apparatus. The prepared sheets were dried under restrained conditions at 93°C for 15 minutes. Thin anisotropic sheets with a grammage of 20 g/m² were prepared on a dynamic sheet former (Formette Dynamique), role pressed, restrained dried at ambient conditions and then post-dried at 93°C for 15 minutes. Elevated temperature is probably important for the formation of hemiacetal and acetal cross-links and it is therefore important that the thin sheets was exposed to elevated temperature for the same duration of time as the thick sheets.

Paper testing

Dry tensile testing was conducted according to the SCAN P:67 standard for tensile testing of laboratory-made sheets. The thickness of the prepared sheets was measured as structural thickness [18] and used to calculate the apparent sheet density.

Mechano-sorptive creep testing of sheets and fibres

The mechano-sorptive creep of the sheets with a grammage of 140 g/m² were tested in compression using the principles and apparatus described in [19]. The apparatus enables measurement of creep in compression since the paper specimen is prevented from buckling by supporting columns. The test employed three 50 to 90% RH cycles with each cycle being seven hours long and having a ramp time of approximately 20 minutes. After a specimen (25 × 130 mm) had been mounted in the apparatus the humidity cycling was

started and the load, strain, temperature and relative humidity were recorded by the apparatus. The result was subsequently analysed using so called isocyclic stress-strain curves as proposed in [19]. An isocyclic stress-strain curve gives the relation between total strain, stress and number of humidity cycles.

Since hygroexpansion is closely linked to the accelerated creep phenomenon [4, 5], it is of interest to estimate the hygroexpansional movements during the humidity cycling used for the creep testing. The recorded strain is a sum of creep and hygroexpansion (figure 1) and the hygroexpansional strain variation can be estimated by the difference between the maximum and minimum strain at each half and full moisture cycle. In detail, this was done by regressing straight lines (using least-squares method) between the maximum and minimum points respectively and then calculating the mean difference between these lines (see figure 1). It should, however, be emphasised that the hygroexpansion measured in this way is not exactly the same as if it would have been measured on un-loaded specimens, since applied stress increases the adsorbed moisture content [20] and hence the hygroexpansion. A phenomenon referred to as stress-induced hygroexpansion [21].

The mechano-sorptive creep behaviour of single fibres and thin sheets (20 g/m^2) was examined using the method developed by Olsson *et al.* [14, 22].

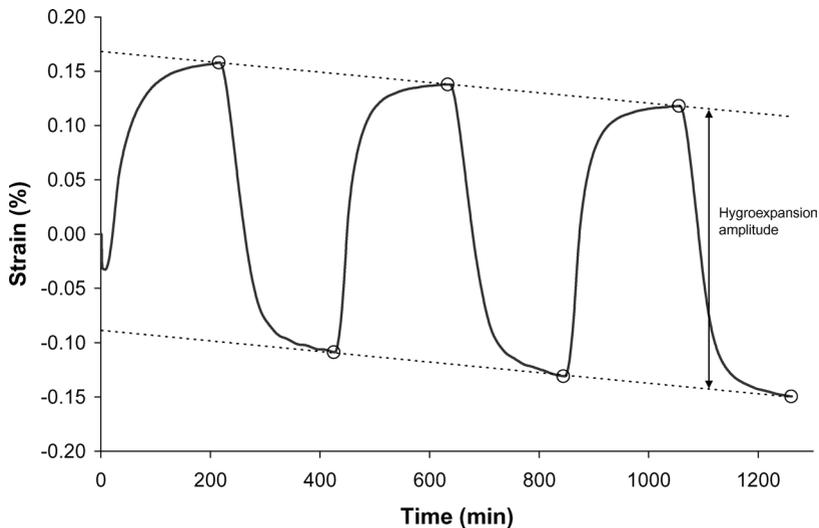


Figure 1. Strain recorded in a typical creep test. By regression lines to the maximum and minimum points (indicated by circles), the hygroexpansion during the creep test could be estimated.

Prior to testing all individual fibres were heated in an oven at 93°C for 15 minutes, such that they had received the same heat treatment as the fibres in the produced sheets. Dried single fibres were then glued onto metal clamps in a Perkin Elmer dynamic mechanical analyser (DMA), with a distance between the clamps of 2.1 mm. Paper samples (approximately 10 mm wide) were clamped in the same equipment with a clamp gap of 11 mm. For fibres, loads from 40 to 70 mN and for papers loads from 1 to 3 N were used. The samples were first loaded under constant humidity (80%RH) for 3 hours to establish the creep rate at constant humidity. Thereafter the humidity was cycled 10 times between 80 and 30%RH, with each cycle being 1 hour long, to establish the creep rate at varying humidity. By normalising the creep rate at cyclic humidity with the creep rate at constant humidity it was possible to eliminate the experimental scatter due to the large difference between individual fibres. This ratio gives an excellent measure on how much the creep is accelerated by varying humidity as compared to the constant humidity condition.

Moisture sorption

The moisture up-take during the humidity cycling, used for the mechano-sorptive creep testing of thick sheet, was continuously recorded by a balance (Sartorius BP 110 S) that had been connected to a PC. After creep testing, two samples at a time (with the same degree of oxidation) was placed on the balance and subjected to the moisture cycling. The procedure was repeated until ten strips of each degree of oxidation had been tested. By determining the dry mass of the different samples the moisture content during the humidity cycling could be calculated.

Cross-sectional area

In order to calculate the stress the single fibres were subjected to during the creep testing their cross-sectional area must be known. This was determined from thin optical crosssections recorded with confocal laser scanning microscopy, using the auto-fluorescence from the lignin. A Bio-Rad Radiance 2000 confocal system mounted on a Nikon Eclipse 800 microscope was used to image four cross-sections along each fibre. A Krypton Argon laser was used for excitation at 488 and 568 nm and the images of the fibres were taken using a 100x N.A. 1.4 oil-immersion lens. The obtained images were manually converted into binary images by tracking the fibre contours (see figure 4) and the cross-sectional area subsequently determined by counting the pixels belonging to the fibre.

RESULTS AND DISCUSSION

Thick sheets

The results from the paper testing of thick (140 g/m^2) sheets are shown in table 1. Cross-linking had no major influence on the apparent density, tensile strength or tensile stiffness. This fact indicates that the oxidation did not influence the interaction between fibres in the dry state or the consolidation process. The strain at break, however, was severely impaired. These results are similar to those found by Caulfield who used multifunctional carboxylic acids for crosslinking the fibre wall [6]. The embrittlement could be due to that the cross-links prevent relative movement of adjacent cellulose chains [6] or that the oxidation depolymerises the cellulose [23]. The fact that the wet tensile strength for the most oxidised sample was 40% of the dry tensile strength is a clear indication of the existence of covalent links, since covalent linkages are assumed to be a prerequisite for achieving a relative wet strength above 30% [24].

Mechano-sorptive creep of the thick 140 g/m^2 sheets was evaluated as described above. By combining the strain measured after 3 humidity cycles with the applied loads the result shown in figure 2 was achieved. It is seen that for a certain stress, the creep strain after 3 cycles was considerably lower for the oxidised samples, i.e. the sheets made from oxidised fibres had improved resistance towards mechano-sorptive creep. If the nomenclature proposed in [19] is adopted, the slope of the linear part of a isocyclic stress-strain curve is denominated the isocyclic creep stiffness index. The calculated isocyclic creep stiffness indexes and corresponding carbonyl contents can be found in table 2. For the most oxidised sample more than a three-fold increase compared to the reference could be detected and has to be considered a major improvement.

Table 1. Results from the paper testing: mean values and 95%-confidence limits.

<i>Carbonyl content (mmoll g fibre)</i>	<i>Density (kg/m^3)</i>	<i>Tensile index (kNm/kg)</i>	<i>Tensile stiffness index (MNm/kg)</i>	<i>Strain-at-Break (%)</i>	<i>Wet Tensile index (kNm/kg)</i>
0	682	75 ± 1	7.5 ± 0.1	2.9 ± 0.1	3.0 ± 0.1
0.47 ± 0.02	666	83 ± 3	7.8 ± 0.2	2.2 ± 0.1	29 ± 1
1.12 ± 0.02	695	76 ± 2	7.6 ± 0.1	1.6 ± 0.1	30 ± 1

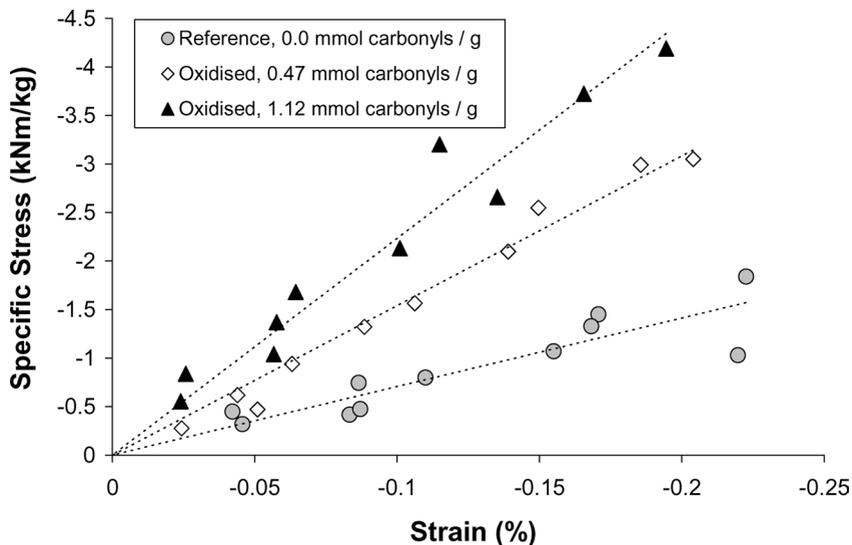


Figure 2. Isocyclic stress-strain data for paper sheets (140 g/m^2) made from unbleached chemical fibres recorded after 3 humidity cycles (21 h) for three different levels of fibre cross-linking.

Single fibres

In order to understand if this improvement in mechano-sorptive creep resistance stems from a fibre or fibre network level, single fibres were also tested for their creep behaviour. In figure 3 the creep rate in cyclic humidity is plotted as function of the creep rate in constant humidity. In this way the scatter in data due to large invariance's between different fibres is avoided. The ratio between creep at cyclic and constant humidity gives an excellent measure on how much the creep is accelerated by varying humidity. As seen in figure 3 the increase in creep rate due to varying humidity is the same for reference and cross-linked fibres, suggesting that the fibres themselves were not improved from a accelerated creep perspective even though the sheets showed significant improvements. The acceleration ratio was 2.4 in this case which is in fairly good agreement with previous results where the ratio for single fibres have been found to be around three [22].

Cross-section of fibres were imaged in the confocal laser scanning microscope (see figure 4) and used to calculate the stress in the fibres during the creep tests. With this information the creep rate in constant and cyclic humidity could be calculated as function of applied stress and the results are

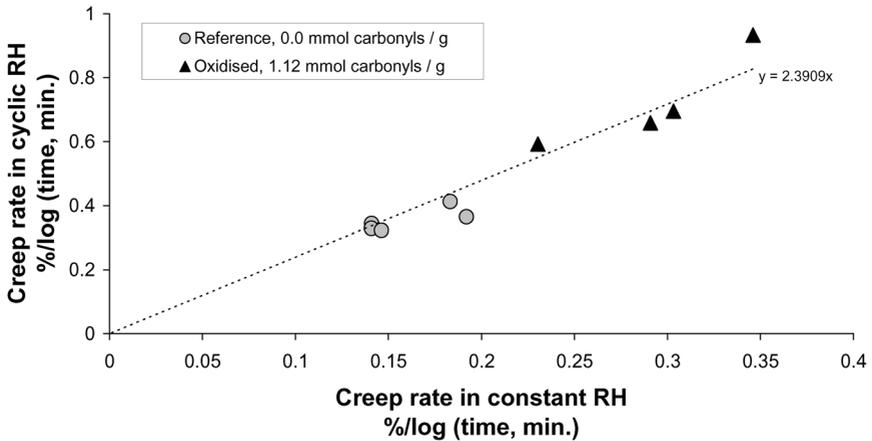


Figure 3. Creep strain rate at cyclic humidity versus creep strain rate at constant climate (logarithmic time) for reference and cross-linked single fibres.

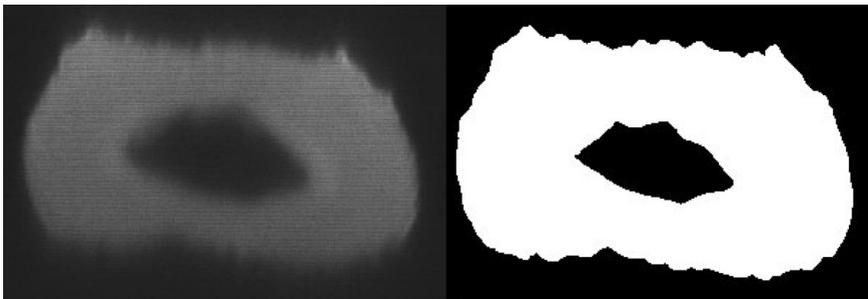


Figure 4. Example of fibre cross-section obtained with the CLSM (left) and a binary equivalent of this image (right). Cross-section images were subsequently used to calculate cross-sectional areas and stress in the fibres during the creep tests.

presented in figure 5 and 6 respectively. As seen the creep rate for a certain stress was higher for the cross-linked fibres in both constant and cyclic humidity. Thus the cross-linking actually worsened the mechano-sorptive creep properties of the fibres themselves, despite the fact that the accelerated creep was decreased on a fibre network level. Hence it is clear that the reduction in mechano-sorptive creep for sheets made from oxidised fibres does not originate from an improved creep resistance of the individual fibres but rather from mechanisms acting at the fibre network level.

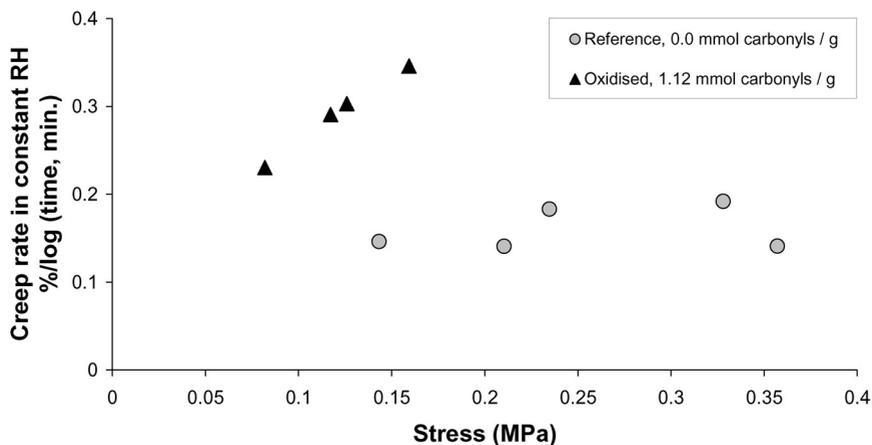


Figure 5. Creep rate in constant humidity for single fibres from an unbleached chemical pulp. For a certain stress the oxidised fibres showed a notably higher creep rate.

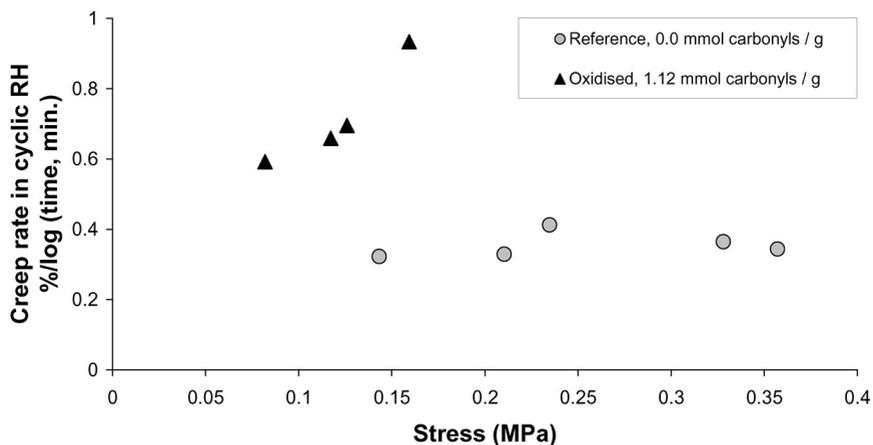


Figure 6. Creep rate in cyclic humidity (1 hour 80–30% RH cycles) for single fibres from an unbleached chemical pulp. For a certain stress the oxidised fibres showed a notably higher creep rate.

Since it is clear that the creep of the fibres themselves was not reduced by the chemical cross-linking it can be concluded that the hypothesis that the introduced cross-links stabilises arrays of moisture sensitive hydrogen bonds and hinder them to creep into a stress-relaxed configuration [6] can not hold true at the fibre level. It can still be so that hydrogen bonds between adjacent fibres are stabilised by the covalent bonds. It has however previously been shown that total fibre/fibre joint breakage does not occur in any major extent until close to sheet failure and that total joint breakage is not sufficiently common to produce significant permanent strain [25]. It is thus not likely that stabilisation of hydrogen bonds between fibres by covalent cross-links is the explanation for the reduced mechano-sorptive creep detected for the sheets made from periodate oxidised fibres.

Hygroexpansion and moisture sorption

If the reduction in accelerated creep by chemical cross-linking is not explained by the creep of the fibres, the explanation should be found at the fibre network level. The two dominant theories for accelerated creep [4, 5] both have hygroexpansion as a common factor. The hygroexpansional strain during the creep testing of the thick sheets (140 g/m^2) was therefore estimated as described above and the results are presented in table 2 together with the corresponding isocyclic creep stiffness indexes. As seen the hygroexpansion amplitude decreased with increased degree of oxidation. Hence, both mechano-sorptive creep and hygroexpansion decreased with increased oxidation. Therefore it becomes evident that the reduction in hygroexpansion induced by the cross-linking is one of the major mechanisms behind the reduced mechano-sorptive creep found for the prepared sheets. The mechanism behind the mechano-sorptive creep reduction is probably that the reduced hygroexpansion minimises stress concentrations within the sheet. A previous study has in more detail studied the influence of periodate oxidation on the hygroexpansion of paper [10]. Here it was found that the equilibrium

Table 2. Carbonyl content, hygroexpansion amplitude and isocyclic creep stiffness index for thick sheets made from fibres with different degree of oxidation.

	<i>Carbonyl Content (mmollg fibre)</i>	<i>Isocyclic Creep Stiffness Index (MNmlkg)</i>	<i>Hygroexpansion Amplitude (%)</i>
Reference	0	0.71 ± 0.08	0.34
Low oxidised	0.47 ± 0.02	1.54 ± 0.06	0.27
High oxidised	1.12 ± 0.02	2.23 ± 0.13	0.22

hygroexpansion when cycling between 20 and 85% RH decreased with increasing degree of oxidation. The cross-linking hence decreased the total hygroexpansion potential. Nevertheless, the hygroexpansion coefficients (hygroexpansion normalised with moisture content change) were not decreased by the cross-linking, due to that the cross-linking simultaneously decreased the moisture content change.

To collect information to get an answer to the question why the hygroexpansivity decreased, the moisture content in the samples during the humidity cycling was measured and the result is shown in figure 7. It is seen that the moisture content variation amplitude, just as the hygroexpansion amplitude, decreased with increased oxidation. Hence it can be concluded that the basic cause to the mechano-sorptive creep reduction is reduced moisture content changes in the oxidised samples. This is in accordance with previous studies that have shown a relationship between creep acceleration and moisture content changes. Alftan found that the creep strain after a certain number of moisture cycles increased with increasing moisture content variation amplitude [26]. A similar behaviour was also observed by Fellers and Panek who found that the creep acceleration due to varying humidity, measured as mechano-sorptive creep factor (creep stiffness at varying humidity divided by

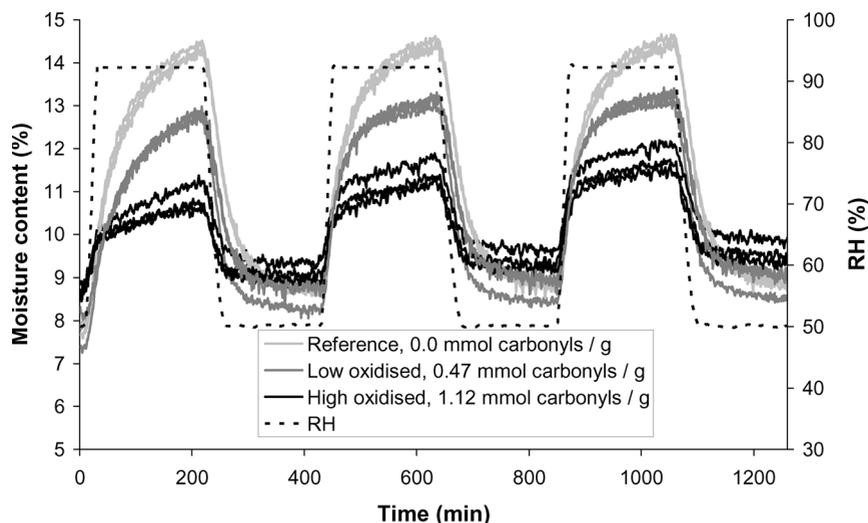


Figure 7. Moisture-sorption for thick sheets during the three 50–90% RH cycles used for the creep testing of the thick 140 g/m² sheets made from unbleached chemical fibres. The moisture variation amplitude decreased with increased oxidation.

creep stiffness at constant humidity), increased with increasing difference in moisture ratio at low and high humidity [27].

It has also previously been shown that periodate oxidation influences both the kinetics of and the equilibrium moisture sorption [10]. More information regarding the moisture sorption behaviour of periodate oxidised fibres can be found in this paper. The exact reason to why the oxidised samples adsorb less water is, however, not fully understood but a possible explanation is that the introduced cross-links both hinders the fibre wall from swelling and removes sites for water sorption.

Thin sheets

The fact that the moisture sorption behaviour was altered by the oxidation could suggest that the only reason to the decreased mechano-sorptive creep in the thick sheets was that they did not reach moisture equilibrium during the moisture cycling. Therefore the creep properties of sheets with a thickness of only 45 μm (20 g/m^2), i.e. only a few fibres thick, were determined. Since these sheets are very thin they should adsorb moisture very quickly, almost at the same rate as for single fibres, thereby reaching moisture equilibrium well within the cycle time and minimise the time for which moisture gradients through the thickness direction of the sheet exists. As seen in figure 8, the

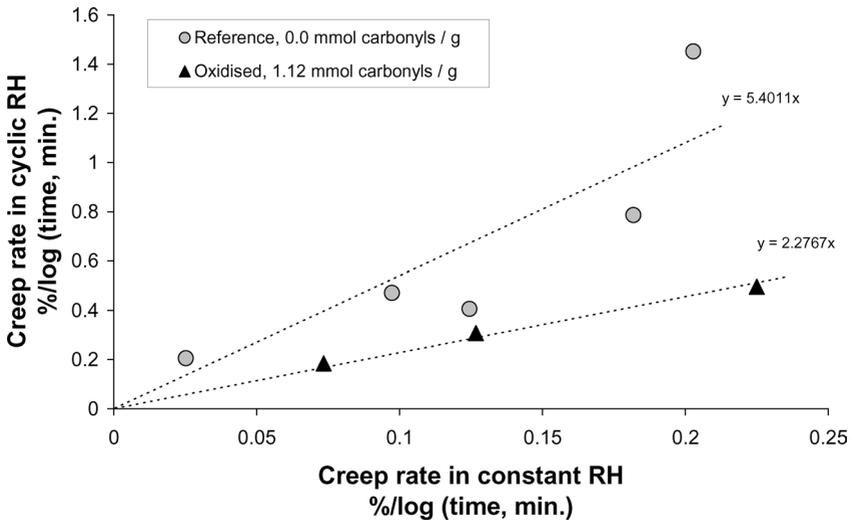


Figure 8. Creep strain rate at cyclic humidity versus creep strain rate at constant climate (logarithmic time) for thin (20 g/m^2) reference and cross-linked sheets.

creep rate is accelerated significantly more for the reference sheets than for the sheets from oxidised fibres, 5.4 times as compared to 2.3 times. This fact shows that the decreased creep acceleration during moisture cycling was not due only to altered moisture-sorption kinetics or moisture gradients, but rather from decreased absolute moisture sorptivity and hygroexpansion of the sheets.

CONCLUSIONS

It has been shown that the resistance towards mechano-sorptive creep can be significantly improved by chemical cross-linking of the fibre wall through periodate oxidation. The creep in both constant and cyclic humidity of individually tested fibres was, however, not reduced by the chemical cross-linking of the fibre wall but instead increased with oxidation. This clearly shows that the improvement found on the sheet level does not originate from that the individual fibres had improved creep resistance but instead from mechanisms at the fibre network level. Furthermore, since the creep of the fibres themselves was not improved by the chemical cross-linking it can be concluded that the hypothesis proposed by Caulfield [6], that the introduced cross-links stabilises arrays of moisture sensitive hydrogen bonds and hinder them to creep into a stress-relaxed configuration can not hold true at the fibre level.

Measurements of the moisture sorption during the humidity cycling clearly showed reduced moisture content variation amplitude for sheets made from oxidised fibres. Considering previous results [26, 27] showing that moisture content variation is linked to the degree of creep acceleration, this implies that the basic mechanism behind the mechano-sorptive creep reduction by chemical cross-linking is reduced moisture content variations. The reduced moisture variations leads to less hygroexpansion during humidity cycling which probably in turn reduces stress concentrations at the fibre network level and thereby the creep acceleration. The mechanism behind the reduced moisture sorptivity is not fully understood, but is suggested to be linked to that the introduced cross-links both hinder the fibre walls from swelling and removes adsorption sites for water molecules.

REFERENCES

1. V.L. Byrd, Effect of Relative Humidity Changes During Creep on Handsheet Paper Properties. *Tappi*, **55**(2):247–252, 1972.
2. V.L. Byrd, Effect of Relative Humidity Changes on Compressive Creep Response of Paper. *Tappi*, **55**(11):1612–1613, 1972.

3. L. Henriksson, R. Bredemo, C. Fellers, and G. Stubbfält. Mechanical Properties of Paper and Their Relation to Packaging Performance. In proc. *61st Appita Annual Conference and Exhibition*. pp305–312, Gold Coast, Australia, 2007.
4. C.C. Habeger and D.W. Coffin, The role of stress concentrations in accelerated creep and sorption-induced physical aging. *Journal of Pulp and Paper Science*, **26**(4):145–157, 2000.
5. J. Alftan, P. Gudmundson, and S. Östlund, A micromechanical model for mechano-sorptive creep in paper. *Journal of Pulp and Paper Science*, **28**(3):98–104, 2002.
6. D.F. Caulfield, Ester crosslinking to improve wet performance of paper using multifunctional carboxylic acids, butanetetracarboxylic and citric acid. *Tappi Journal*, **77**(3):205–12, 1994.
7. P. Larsson, M. Gimåker, and L. Wågberg. The influence of periodate oxidation on the moisture sorptivity, dimensional stability and mechano-sorptive creep of paper. In proc. *Progress in Paper Physics Seminar 2008*. pp101–104, Espoo, Finland, 2008.
8. S.H. Zeronian, F.L. Hudson, and R.H. Peters, The mechanical properties of paper made from periodate oxycellulose pulp and from the same pulp after reduction with borohydride. *Tappi*, **47**(9):557–64, 1964.
9. P. Ghosh and J.C. Dalal, Studies on crosslinking of dialdehyde cellulose and dialdehyde starch using poly(vinyl alcohol). *Journal of Polymer Materials*, **5**(4):241–7, 1988.
10. P.A. Larsson, M. Gimåker, and L. Wågberg, The influence of periodate oxidation on the moisture sorptivity and dimensional stability of paper. *Cellulose*, **15**(6):837–847, 2008.
11. K. Sedlachek and R. Ellis. The effect of cyclic humidity on the creep of single fibers of southern pine. In proc. *Moisture-induced Creep Behaviour of Paper and Board*. pp29–49, Stockholm, Sweden, 1994.
12. D.W. Coffin and S. Boese. Tensile creep behaviour of single fibres and paper in a cyclic humidity environment. In proc. *Moisture and creep effects on Paper, Board and Containers*. Rotorua, New Zealand, 1997.
13. C.C. Habeger, D.W. Coffin, and B. Hojjatie, Influence of humidity cycling parameters on the moisture-accelerated creep of polymeric fibers. *Journal of Polymer Science, Part B: Polymer Physics*, **39**(17):2048–2062, 2001.
14. A.-M. Olsson, L. Salmén, M. Eder, and I. Burgert, Mechano-sorptive creep in wood fibres. *Wood Science and Technology*, **41**(1):59–67, 2007.
15. L. Wågberg and R. Häggglund, Kinetics of polyelectrolyte adsorption on cellulosic fibers. *Langmuir*, **17**(4):1096–1103, 2001.
16. H. Zhao and N.D. Heindel, Determination of degree of substitution of formyl groups in polyaldehyde dextran by the hydroxylamine hydrochloride method. *Pharmaceutical Research*, **8**(3):400–2, 1991.
17. S. Vicini, E. Princi, G. Luciano, E. Franceschi, E. Pedemonte, D. Oldak, H. Kaczmarek, and A. Sionkowska, Thermal analysis and characterisation of cellulose oxidised with sodium methaperiodate. *Thermochemica Acta*, **418**(1–2):123–130, 2004.

18. O. Schultz-Eklund, C. Fellers, and P.Å. Johansson, Method for the local determination of the thickness and density of paper. *Nordic Pulp & Paper Research Journal*, **7**(3):133–9, 154, 1992.
19. J. Panek, C. Fellers, and T. Haraldsson, Principles of evaluation for the creep of paperboard in constant and cyclic humidity. *Nordic Pulp & Paper Research Journal*, **19**(2):155–163, 2004.
20. A.-M. Olsson and L. Salmen, Molecular mechanisms involved in creep phenomena of paper. *Journal of Applied Polymer Science*, **79**(9):1590–1595, 2000.
21. C. Söremark and C. Fellers, Mechano-sorptive creep and hygroexpansion of corrugated board in bending. *Journal of Pulp and Paper Science*, **19**(1):19–26, 1993.
22. A.-M. Olsson and L. Salmen. Mechanosorptive creep a fibre property, comparison between the behaviour of fibres and paper. In proc. *Progress in Paper Physics Seminar*. pp49–51, Espoo, Finland, 2008.
23. Q.X. Hou, W. Liu, Z.H. Liu, and L.L. Bai, Characteristics of wood cellulose fibers treated with periodate and bisulfite. *Industrial & Engineering Chemistry Research*, **46**(23):7830–7837, 2007.
24. H.H. Espy, The mechanism of wet-strength development in paper: a review. *Tappi Journal*, **78**(4):90–9, 1995.
25. D.H. Page and P.A. Tydeman, A new theory of the shrinkage, structure and properties of paper. *Formation and Structure of Paper, Transactions of the Fundamental Research Symposium, 2nd, Oxford, UK, Sept. 1961*:397–413, 1961.
26. J. Alfthan, The Effect of Humidity Cycle Amplitude on Accelerated Tensile Creep of Paper. *Mechanics of Time-Dependent Materials*, **8**(4):586–597, 2004.
27. C. Fellers and J. Panek. Effect of relative humidity cycle start point and amplitude on the mechano-sorptive creep of containerboard. In proc. *International Paper Physics Conference*. Gold Coast, Australia, 2007.

Transcription of Discussion

ON THE MECHANISMS OF MECHANO-SORPTIVE CREEP REDUCTION BY CHEMICAL CROSS-LINKING

*Magnus Gimåker,¹ Anne-Mari Olsson,² Lennart
Salmén² and Lars Wågberg¹*

¹Department of Fibre and Polymer Technology, Royal Institute of
Technology, KTH, SE-100 44 Stockholm, Sweden

²INNVENTIA AB, Box 5604, SE-114 86 Stockholm, Sweden

Ian Parker Australian Pulp and Paper Institute

As you change the moisture content, don't you also change the stiffness of the material and therefore change the dimensions?

Magnus Gimåker

Yes, I guess so.

Ian Parker

So, therefore you cannot just calculate hygro-expansion from a change in the dimensions.

Magnus Gimåker

That is probably true. I have not actually considered that, but I still believe that the mechanism is the reduced hygro-expansion.

Discussion

Ian Parker

Well, if you are going to compare the hygro-expansions of the treated and untreated sheets, you will have to make an allowance for that.

Magnus Gimåker

Yes, true.

Gary Baum PaperFuture Technologies (from the chair)

How big do you think that effect would be, Ian?

Ian Parker

I have no idea what the stiffness will be, and how that will effect the measurement of over-expansion.

Ramin Farnood University of Toronto

Thank you for a very interesting talk. Can you tell me in your opinion if the reduction in hygro-expansion is due to lower moisture uptake, or is it because fibres are better locked; therefore, they cannot expand as much due to the covalent bonding? What do you think about the mechanism behind that?

Magnus Gimåker

I am not certain, but I would propose two mechanisms. The first involves a restriction of the fibre swelling. Between crystalline regions of cellulose you have amorphous cellulose. For moisture to enter these regions you would have to separate the crystallites and I think the covalent bonds can hinder this separation and thereby the moisture from adsorbing. We also have a fairly high-degree of oxidation and thus many cross-links. I think also here, when making these cross-links, you take away adsorption sites for water, which could be an effect.

Ramin Farnood

So if I understood correctly, you think the main mechanism is the intra-fibre covalent bonding as opposed to fibre-fibre bonding. Is it correct? Because if you enhance fibre-fibre bonding you may also potentially decrease the degree to which fibres and the sheet can expand.

Magnus Gimåker

Yes, possibly, but I think the main mechanism is related to the intra-fibre covalent bonds; that is my guess.

Bob Pelton McMaster University

Interesting talk, thank you. I was just curious, what about conventional PAE wet-strength resins. How do they affect this creep?

Magnus Gimåker

To my knowledge, I do not think you get very much of an effect, and I think that it might be due to the fact that the actual cross-links you get with PAE are not so very efficient. At KTH, we have tried a concept similar to PAE; Andrew Horvath and I did some trials with modified dextran where we introduced reactive groups, but that did not have an effect. I would suggest that that is due to the cross-link density that you get. You have this polymeric substance, this reactive dextran or PAE, which covalently attaches to the cellulose chains, then you have a number of monomers and then you have another attachment – and so I do not think you get enough cross-linking. The polymer is too flexible, so it does not hinder fibre swelling and you do not get any effect on the moisture sorption. That is why they do not work very well.

Bob Pelton

So what degree of reaction do you think you are getting on your cellulose surfaces? Is it every other group that is reacting, or one per chain? What is your mental picture of this?

Magnus Gimåker

We did a calculation, but I cannot remember exactly. I think it falls in the region of 0.3 or something. About every third glucose unit is reacted.

Bob Pelton

So that is quite high.

Magnus Gimåker

It is very high, yes.

Discussion

Tetsu Uesaka FPIInnovations

Could you please explain why you did not see the change in the accelerated creep on the fibre level?

Magnus Gimåker

I think it can be coupled to the model proposed by Johan Alfthan. That it is the stress concentrations at the fibre bonds that drives a big part of the creep acceleration, and that you need fibre-fibre bonds to see a change in creep acceleration with cross-linking. For the single fibres you do not have these fibre-fibre bonds.

Tetsu Uesaka

But according to the first mechanism proposed a long time ago, as long as you have some moisture gradient, and if this moisture gradient is large enough to create nonlinear creep, you are supposed to see accelerated creep – even on the fibre level. Regardless of whether it is the moisture diffusion or structural non-uniformity, as long as there is a moisture gradient, coupled with non-linear creep, you should see accelerated creep, right?

Magnus Gimåker

But you have accelerated creep for the single fibres.

Tetsu Uesaka

Yes, but why couldn't you change this by cross-linking? The cross-linking will clearly affect the driving force through hygro-expansion. Therefore, you should see the same thing in single fibres. So why didn't you see this?

Magnus Gimåker

I am not certain, but by cross-linking you may not influence the moisture gradients or structural non-uniformities within the fibres. Cross-linking influences creep acceleration at the sheet level by reducing stress concentrations at the fibre bonds.

Doug Coffin Miami University

The treated fibres at much lower creep rates than untreated fibres here and so

you are not in a same region. How do you know that at different levels you might have seen differences? You are not creeping them at the same rates here, so how do you know that there might not be differences at the same rate? Why are the samples at two different rates?

Magnus Gimåker

That we do not know. The intention was to get the same creep rate using the same load. But apparently we did get a different creep rate. That might be because the oxidation depolymerised the cellulose, thereby increasing the creep rate of the cross-linked fibres. But, of course, the intention was to have the data points at the same creep rate, but we did not succeed in that. So there could be a difference if the fibres were compared at the same creep rate.

Gary Baum PaperFuture Technologies (from the chair)

I have one comment and that is, I have seen all these pictures of crushed corrugated containers and I was just wondering, why you do not stack the cement below the boxes of sweaters?