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# Sustainpack

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### D2.81 On the mechanisms of mechano-sorptive creep reduction by chemical x-linking

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# D2.81 On the mechanisms of mechano-sorptive creep reduction by chemical x-linking

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## Summary

In a previous deliverable D2.57, the effect of chemical cross-linking on properties critical for linerboard materials, especially mechano-sorptive creep, was investigated by oxidising the fibres with sodium metaperiodate. The results showed that the mechano-soprtive creep was substantially reduced by the oxidation. It was, however, not possible elucidate the exact mechanism behind the improvement from the presented data.

The current deliverable aimed at establishing the mechanisms by measuring the hygroexpansion and the moisture sorption of the paper samples during the humidity cycling used for the mechano-sorptive creep testing. Hygroexpansion was calculated from existing data and the moisture sorption was measured by continuously recording the weight of test pieces during the humidity cycling. The data showed that both the hygroexpansion amplitude and the moisture variation decreased with increased oxidation. Hence it was concluded that the basic cause to the reduced creep was reduced moisture variation during the humidity cycling.

## Introduction

The fact that varying humidity accelerates the creep rate of paper, such that the creep during cycling between low and high humidity exceeds the creep found at high constant humidity is well known since the discovery by Byrd in 1972. This phenomenon is usually referred to as mechano-sorptive creep or accelerated creep. Corrugated boxes are often exposed to varying humidity conditions during use, storage and transportation and the mechano-sorptive creep rate will therefore be vital for how long the boxes will be able to withstand compressive loads before failing. As an example, Henriksson et al. (SP2 deliverable D2.59) investigated the relation between mechanical properties of paper and their relation to packaging performance. One conclusion among others was that the isocyclic creep stiffness index is linked to stacking resistance, bottom deflection and bending of sidewalls of corrugated boxes under cyclic humidity.

In a previous deliverable D2.57 it was shown that oxidation of fibres prior to sheet preparation substantially increased the isocyclic creep stiffness index, i.e. the resistance towards mechano-sorptive creep. However, from the result presented in that deliverable, it was not possible to elucidate the exact mechanism behind the observed improvement. Therefore the objective with this deliverable was to collect more data in order to clarify these mechanisms.

Since the discovery of mechano-sorptive creep in the 1970s, it has attracted considerable attention. However, despite all the research efforts, the mechanism behind the phenomenon is not yet fully understood. Today there are two dominant models for describing mechano-sorptive creep in paper. Habeger and Coffin (2000) 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. Alfthan et al. (2002) 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, give rise to an accelerated creep.

Both models have in common that it is the hygroexpansion that give rise to the accelerated creep. Thus the hygroexpansion during the mechano-sorptive creep testing was calculated from the previously recorded data. However, if there is a difference in hygroexpansion, the obvious question then is what this is due to? Since hygroexpansion is closely linked to moisture up-take, the moisture sorption during the humidity cycling used for the testing was also measured in the present investigation.

## Materials and Methods

### Fibres

The fibres used were the SP2 reference softwood kraftliner pulp (kappa number 76) from Kappa Kraftliner Piteå, 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.

### Fibre pre-treatment

It was necessary to remove most of the fines material from the pulp in order to prepare a pulp that is 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 procedure described previously (Wågberg, Hägglund 2001), 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

Pulp was suspended in de-ionised water to a concentration of 7.5 g/l and stirred. The oxidation started with addition of sodium metaperiodate to the fibre suspension. For sample number one, sodium metaperiodate dosage was 1.36 gram per gram fibre and the reaction time two hours. For sample number two, sodium metaperiodate dosage was 2.72 gram per gram fibre and the reaction time 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 μS/cm.

### Determination of carbonyl content

The content of carbonyl groups in the fibres was determined with the hydroxylamine hydrochloride method (Zhao and Heindel 1991; Vicini et al. 2004). Hydroxylamine hydrochloride reacts quantitatively with carbonyls in the fibres to form corresponding oximes, and thus 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 four. 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 four; 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 four 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

Sheets with a grammage of 140 $g/m^2$ were prepared according to the ISO 5269-2:1998 standard using a Rapid-Köthen sheet preparation apparatus from Paper Testing Instruments, Austria. The prepared sheets were dried under restrained conditions at 93°C for 20 minutes.

### 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 (Schultz-Eklund et al. 1992) and used to calculate apparent sheet density.

### Mechano-sorptive creep testing and data evaluation

Mechano-sorptive creep of prepared paper sheets were evaluated using the principles and apparatus described by Panek et al. (2004). This is the same method and apparatus that was used in SustainPack SP2 Deliverable D2.25. The apparatus recorded load, strain, temperature and relative humidity as function of time. A testing climate that changed between 50 to 90%RH with each cycle being seven hours long and having a ramp time of approximately 20 minutes was used. Since paper shrinks permanently when first exposed to humidity cycles, all samples were exposed to six cycles prior to testing, so that a permanent dimensional change no longer could be detected. At least ten paper strips from each sample type was tested, each strip being 25 mm wide and 130 mm long.

The recorded strain is a sum of creep and hygroexpansion (figure 1). 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 is known to change the hygroexpansion. A phenomenon referred to as stress-induced hygroexpansion (Söremark and Fellers 1993).

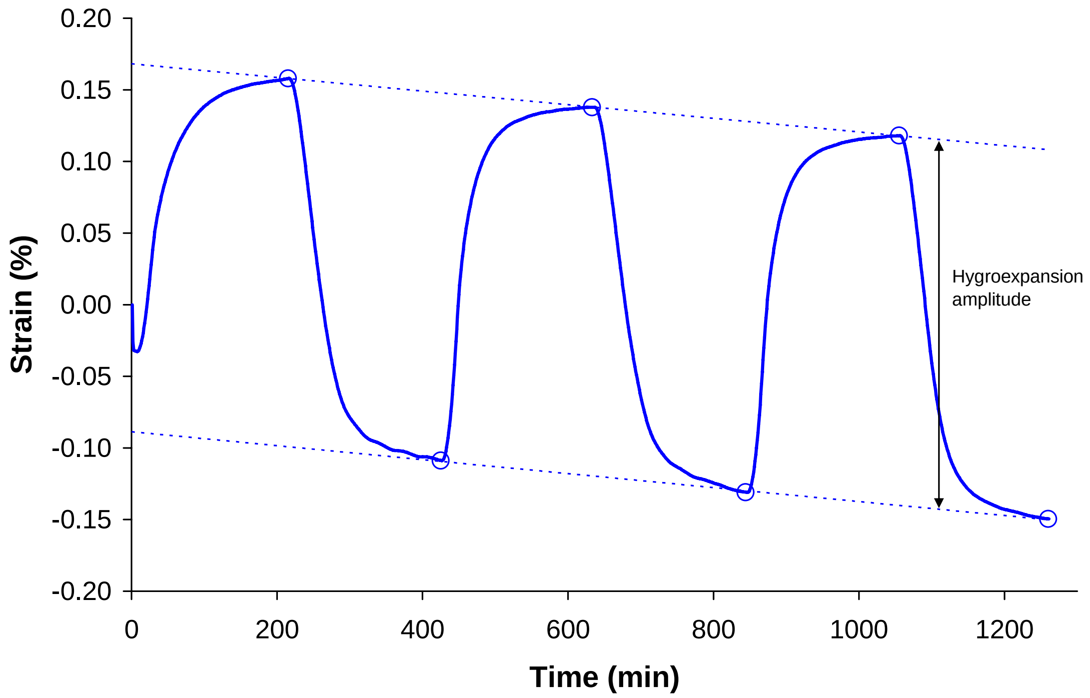


Figure 1. Strain recorded in a typical creep test. By regressing lines to the maximum and minimum points (indicated by circles), the hygroexpansion during the creep test could be estimated.

### Moisture sorption

The moisture up-take during the humidity cycling used for the mechano-soprtive creep testing was continuously recorded by a balance (Sartorius BP 110 S) that had been connected to a PC. After creep testing two samples (with the same degree of oxidation) at a time was placed at the balance and subjected to the moisture cycle shown in figure 3. The procedure was repeated until ten strips of each degree of oxidation had been tested. By then determining the dry mass of the different samples the moisture content during the humidity cycling could be calculated.

## Results and Discussion

Figure 2 shows the result from the mechano-sorptive creep testing using the moisture cycle shown in figure 3. The points are the strains measured after 3 humidity cycles. It is seen that for a certain load the oxidised specimens show a considerably lower creep then the reference, i.e. the oxidised samples had improved resistance towards mechano-sorptive creep. If the isocyclic stiffness indexes, i.e. the slopes of the regressed lines, are calculated it is seen that for the most oxidised sample there was a three fold increase, which has to be considered as a major improvement.

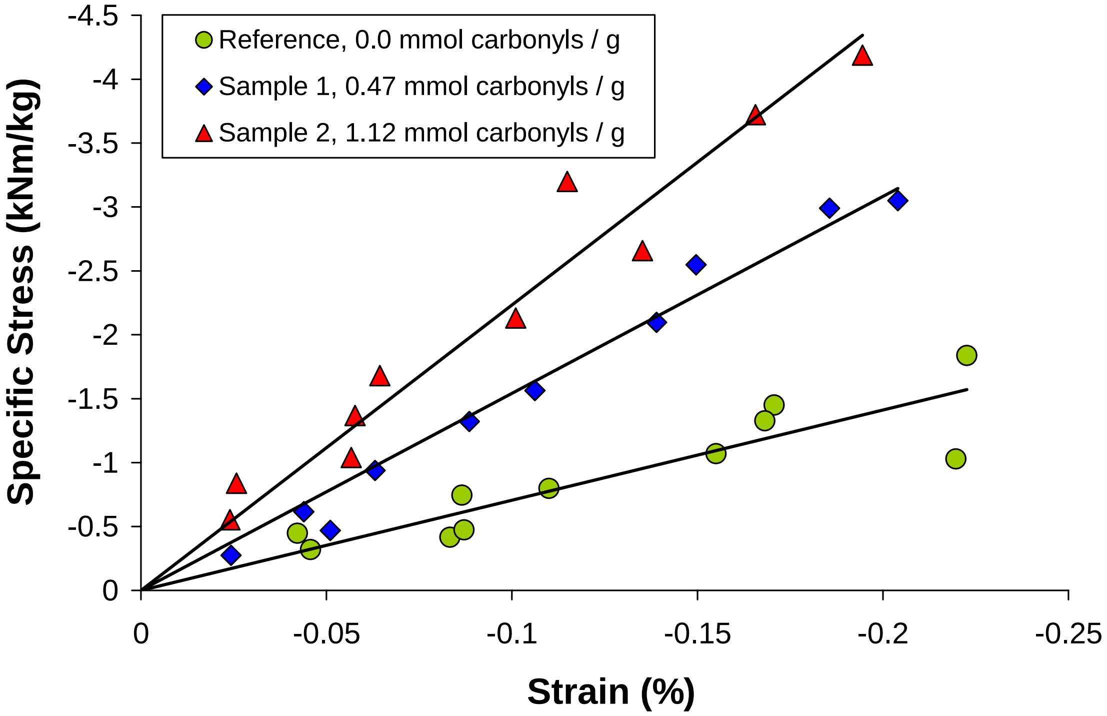


Figure 2. Isocyclic stress-strain data recorded after three 50-90% RH cycles (21 h) for samples with different degree of oxidation (carbonyl content).

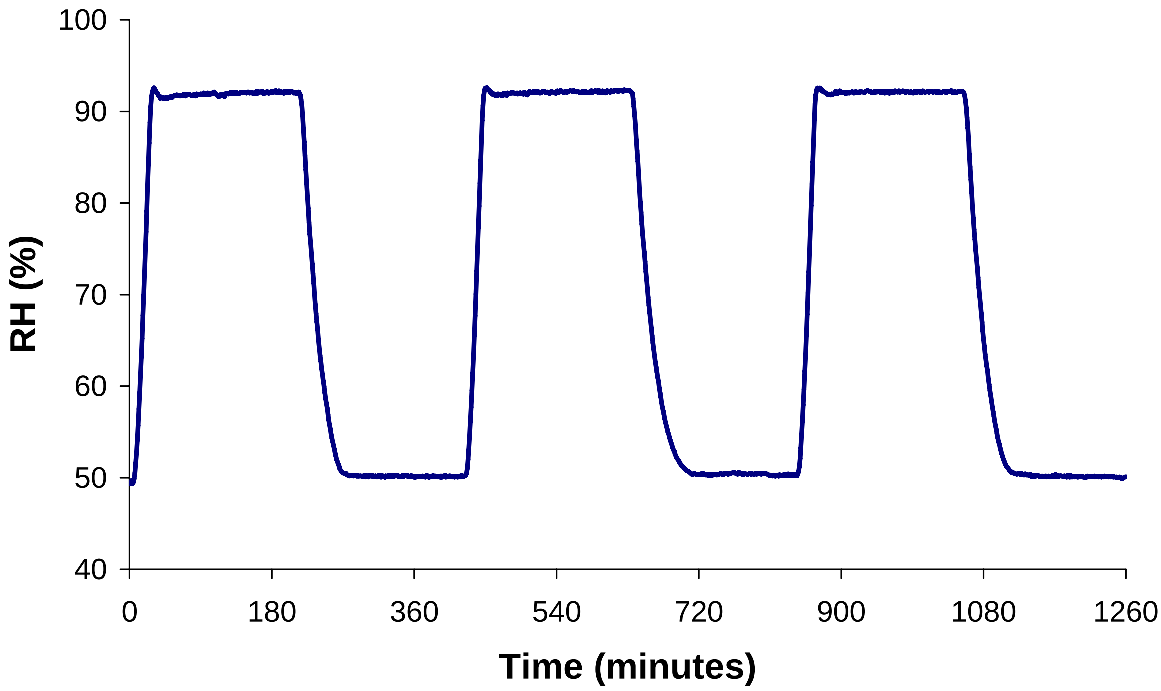


Figure 3. The relative humidity that was recorded in the test chamber during the mechano-sorptive creep testing.

The original strain data for a typical creep test is shown in figure 1. The recorded strain is a sum of creep and hygroexpansional strain. Two lines (shown in the figure) were regressed, using least squares method, to the maximum and minimum strains respectively (depicted by circles in the figure). The hygroexpansion amplitude was calculated as the average difference between these lines and the result, together with the isocyclic creep stiffness indexes, is shown in table 1. As can be seen the hygroexpansion amplitude decreased with increased degree of oxidation. Hence, both mechano-sorptive creep and hygroexpansion decreased with increased oxidation. Considering that the two dominant models for mechano-sorptive creep have hygroexpansion as a common cause for the accelerated creep, it becomes evident that the reduced mechano-sorptive creep must be linked to the decreased hygroexpansivity. To answer the question to why the hygroexpansivity decreased, the moisture content in the samples during the moisture cycling was measured and the result is shown in figure 4. In this figure it is shown that the moisture 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 a reduced moisture sorptivity of the oxidised samples.

The exact reason to why the oxidsised samples sorb less water is not fully understood. A possible explanation is, however, that the introduced cross-links both hinders the fibre wall from swelling and removes sites for water sorption.

Table 1. Carbonyl content, hygroexpansion amplitude and isocyclic creep stiffness index for the three different samples.

| Carbonyl Content (mmol/g fibre) | Hygroexpansion Amplitude | Isocyclic Creep Stiffness Index (MNm/kg) |
|---|---|---|
| 0 | 0.34% | 0.71 ± 0.08 |
| 0.47 ± 0.02 | 0.27% | 1.54 ± 0.06 |
| 1.12 ± 0.02 | 0.22% | 2.23 ± 0.13 |

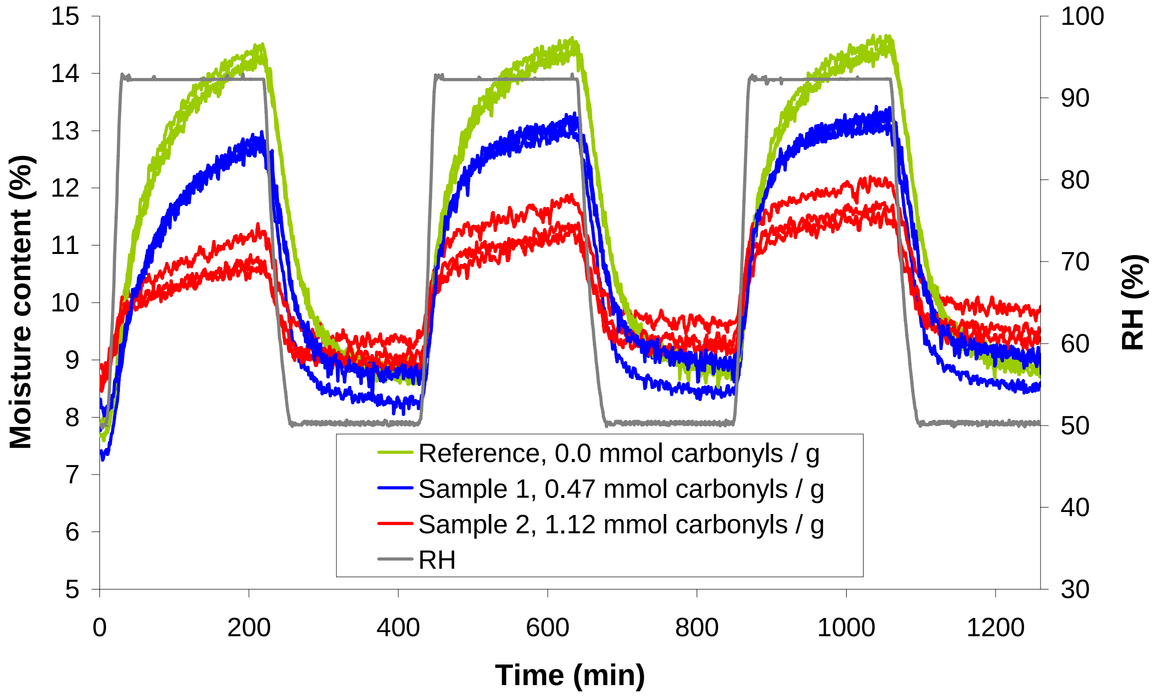


Figure 4. Moisture content during the humidity cycling for the three different samples. The moisture content decreased with increased degree of oxidation.

## Conclusions

The collected data clearly shows that the more oxidised/cross-linked the fibres are the less moisture variation did the paper samples show during the mechano-sorptive creep testing. Hence it is concluded that the basic cause to the reduced mechano-soprtive creep was this reduced moisture variation. The exact 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.

## Literature

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