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#### **D2.57 Report on the evaluation of the effects of chemical x-linking on critical properties of linerboard materials**

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## **D2.57 Report on the evaluation of the effects of chemical x-linking on critical properties of linerboard materials**

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### **Summary**

The effect of chemical cross-linking on properties critical for linerboard materials, especially mechano-sorptive creep, has been investigated by oxidising the fibres with sodium metaperiodate. This was done prior to sheet preparation and the oxidation introduced reactive aldehyde groups into the fibres. These groups could then react during sheet drying to form intra- and inter-fibre cross-links.

The results showed that  $1.12 \cdot 10^{-3}$  moles of aldehyde groups per gram fibre were introduced for the highest degree of periodate oxidation. However, the increased carbonyl content had no major impact on sheet density, tensile strength or tensile stiffness. Contrary, the effect on mechano-sorptive creep and toughness were significant. The highest level of oxidation increased the isocyclic creep stiffness three fold. The effect on toughness was detrimental, for both strain-at-break and tensile energy absorption index were approximately halved at the highest degree of oxidation. However, considering the target increase in isocyclic creep stiffness index, set to 30% in WP2.3, the decrease in strain-at-break and tensile energy absorption index would only be approximately 7% and 8% respectively, which has to be considered as minor.

Periodate oxidation and the introduction of cross-links within the fibre wall hence gives a new opportunity to control and optimize a linerboard quality with respect towards mechano-sorptive creep, something that has been shown to be very difficult to achieve by changing standard papermaking variables.

### **Introduction**

Creep, the time-dependent deformation of a sample held under a constant load, affects paper and many other materials. Humidity affects the creep of paper materials, with faster creep occurring 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 (Byrd 1972a; Byrd 1972b). 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. 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. Another conclusion from the study was that fracture toughness is linked to die-cutting in the converting process as well as drop resistance of a box.

In the present study the effect of chemical cross-linking on properties critical for linerboard materials, especially mechano-soprtive creep, evaluated as isocyclic creep stiffness index, was investigated. Fracture toughness was not evaluated in this study. But, the tensile energy absorption index and strain-at-break as measured by standard tensile testing should give an indication on convertibility and drop resistance.

The strategy for chemically cross-linking fibres and sheets in the present study was to introduce reactive groups into the fibres prior to sheet preparation. The introduced reactive groups can then react during sheet drying to form intra- and inter-fibre cross-links. More specifically, fibres were oxidised by sodium metaperiodate, which specifically cleaves the C2-C3 bond of 1,4-glucans (cellulose and hemicellulose). The formed aldehydes are reactive and can during drying form hemiacetal and acetal links to other hydroxyl groups present in/on the fibres (Fig 1).

Caulfield (1994) also investigated the effect of cross-linking sheets with multifunctional carboxylic acids and found that it significantly decreased the mechano-soprtive creep. Sheets were immersed in a solution containing a multifunctional carboxylic acid and a catalyst, then re-dried and cured at 180°C. If this strategy is to be put into industrial application, a size-press application seems reasonable. However, it seems that the corrosive nature of the carboxylic acid solution might give rise to corrosion related problems etc, and to the knowledge of the authors, this process have not reached industrial application. Furthermore, the low pH of the solution will undoubtedly lead to a very fast ageing of the paper.

Oxidation of fibres can take place prior to the paper machine, for example in the bleaching plant, which is already adapted to corrosive reaction conditions. Hence, the strategy presented here is more feasible for an industrial application. By using other chemicals for oxidation, for example TEMPO or some of its analogues (Bragd et al. 2004), similar effects can most probably be achieved.

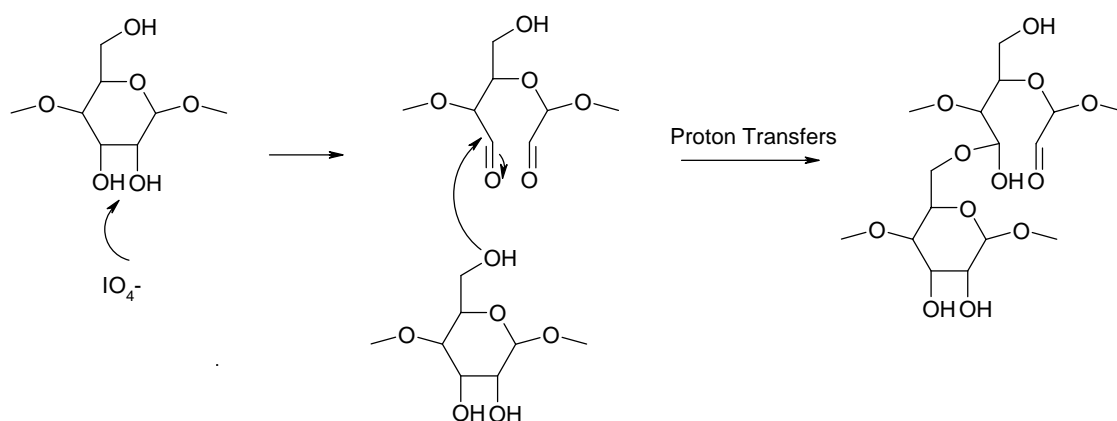


Figure 1. The mechanism for cross-linking. Step one. The periodate ion cleaves the C2-C3 bond, forming two aldehydes. Step two. The aldehydes can react with neighbouring hydroxyl groups to form a hemiacetal link.

## **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.

### **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 2 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), and then repeatedly wash the fibres 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 will react 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 de-ionised 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 2 hours under stirring. The reaction was stopped by dewatering the fibres on a Büchner funnel fitted with filter paper. The fibres were collected, dried and weighed to determine the exact mass of dry fibres. The filtrate was diluted with de-ionised water to a total volume of 100 ml. The filtrate was then titrated back to pH 4 with 0.01 M sodium hydroxide solution. The amount of sodium hydroxide needed to reach pH 4 equals the amount of carbonyls present in the sample.

## Sheet preparation

Sheets with a grammage of 140 g/m<sup>2</sup> 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 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. We used a testing climate that varied from 50 to 90%RH with each cycle being seven hours long and having a ramp time of approximately 20 minutes (Figure 7). Since, paper shrinks permanently when first exposed to humidity cycles, all samples were exposed to six cycles prior to testing, so that permanent 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.

## Results

The carbonyl content (Table 1) of the oxidised and reference fibres, was determined using the presented method. The pH of the reference fibre suspension was 4 after 2 hours of reaction, same as for a blank sample. Hence, the reaction of hydroxylamine hydrochloride with the reference fibres released such a small amount of hydrochloric acid, that it could not be detected with a pH-meter. Consequently, the carbonyl content of the reference fibres was too small to be analysed by this method. Contrary, the oxidised samples contained a considerable amount of carbonyls, well above the detection limit of the method.

It is important that papers made from fibres subjected to different treatments can be compared at a constant density. Consequently, the density of the different sheets was determined. Apparent sheet density remained fairly constant at approximately 680 kg/m<sup>3</sup>, independent of carbonyl content. This finding was important for it indicated that any improvement obtained by the periodate oxidation was not related to possible changes in sheet density.

Tensile properties were evaluated in accordance with the SCAN P:67 standard. The measured properties as a function of carbonyl content in the fibres are presented in Figures 5 through 7. Unless otherwise indicated, the confidence intervals (95%) for the measured mean values were approximately as the size of the markers used.

As can be seen in Fig 5, the oxidation had no large influence on tensile strength, even if there was a moderate increase for the intermediate carbonyl content. The oxidation did not have any effect on the tensile stiffness at 50%RH either. It is well accepted that the stiffness of efficiently loaded paper sheets is primarily determined by the stiffness of the individual fibres (Page et al 1979; Page and Seth 1980). Since the prepared sheets had high density and relatively high strength, they should correspond to efficiently loaded structures, suggesting that the cross-linking had no major effect on the stiffness of the individual fibres at 50%RH.

Contrary to the effect on strength and stiffness, oxidation had a detrimental effect on toughness of the prepared sheets. As can be seen from Figs 5 and 6 both strain-at-break and tensile energy absorption index at 50%RH decreased significantly with increasing carbonyl content.

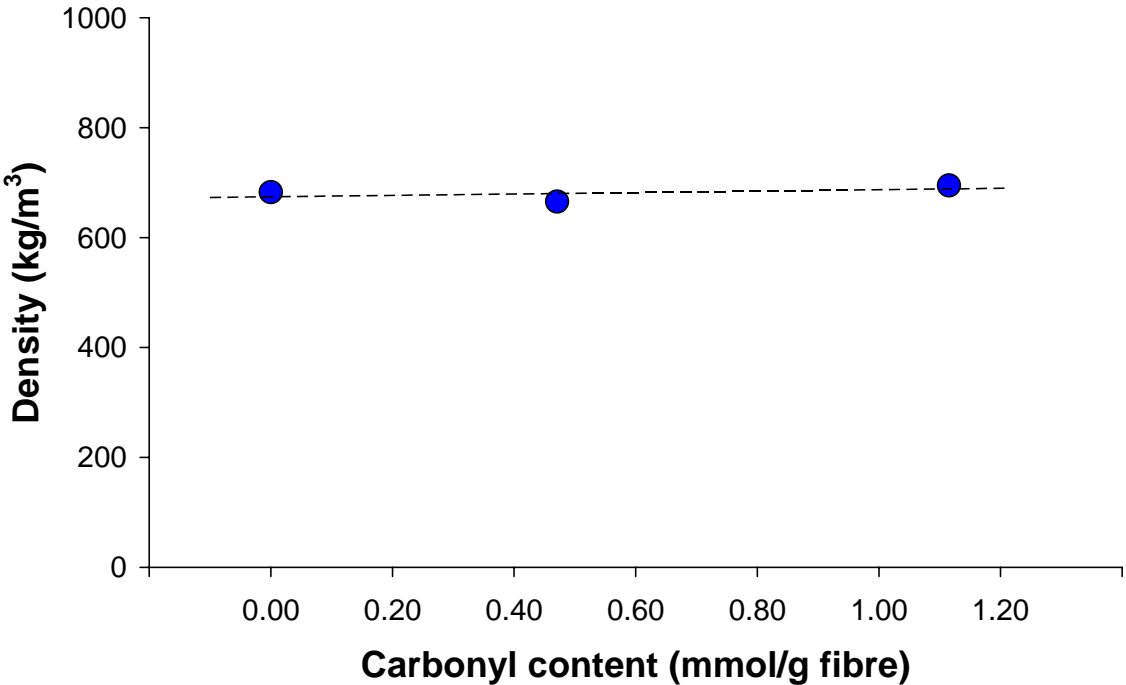


Figure 2. Apparent sheet density as function of carbonyl content in the fibres.

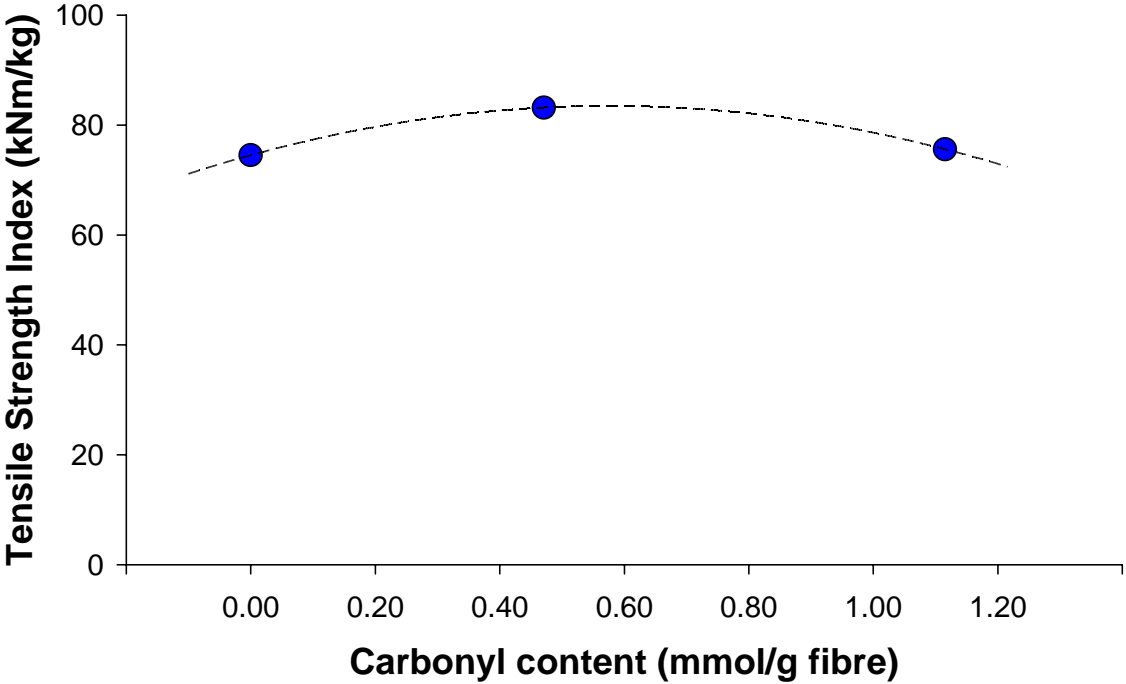


Figure 3. Tensile strength index as function of carbonyl content in the fibres.

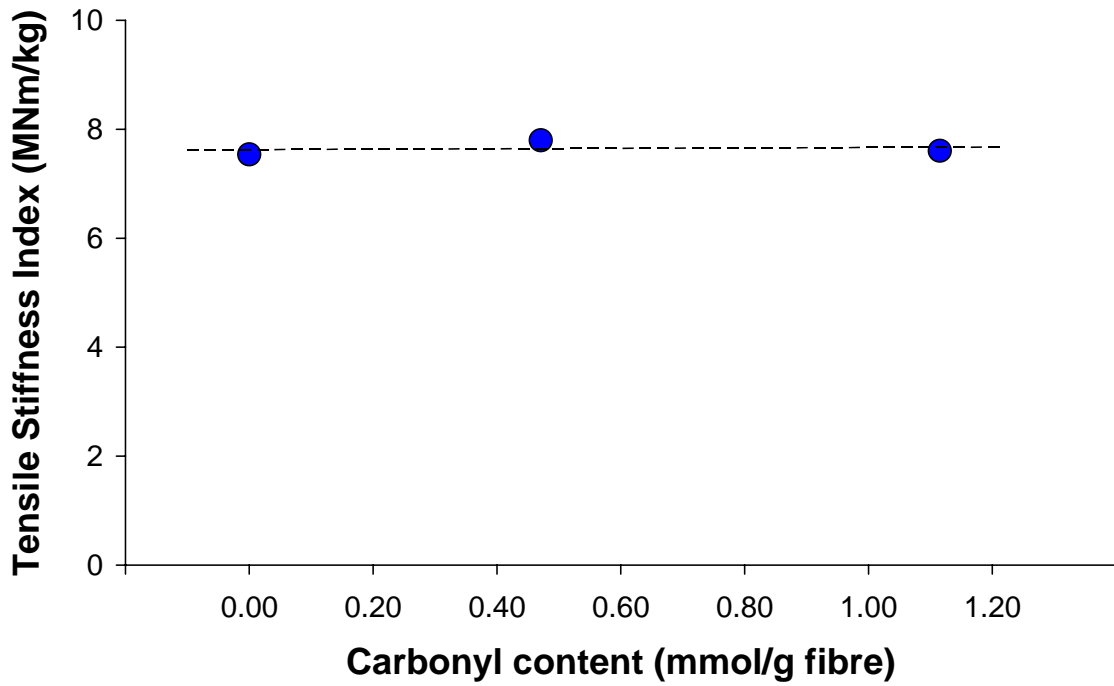


Figure 4. Tensile stiffness index as function of carbonyl content in the fibres.

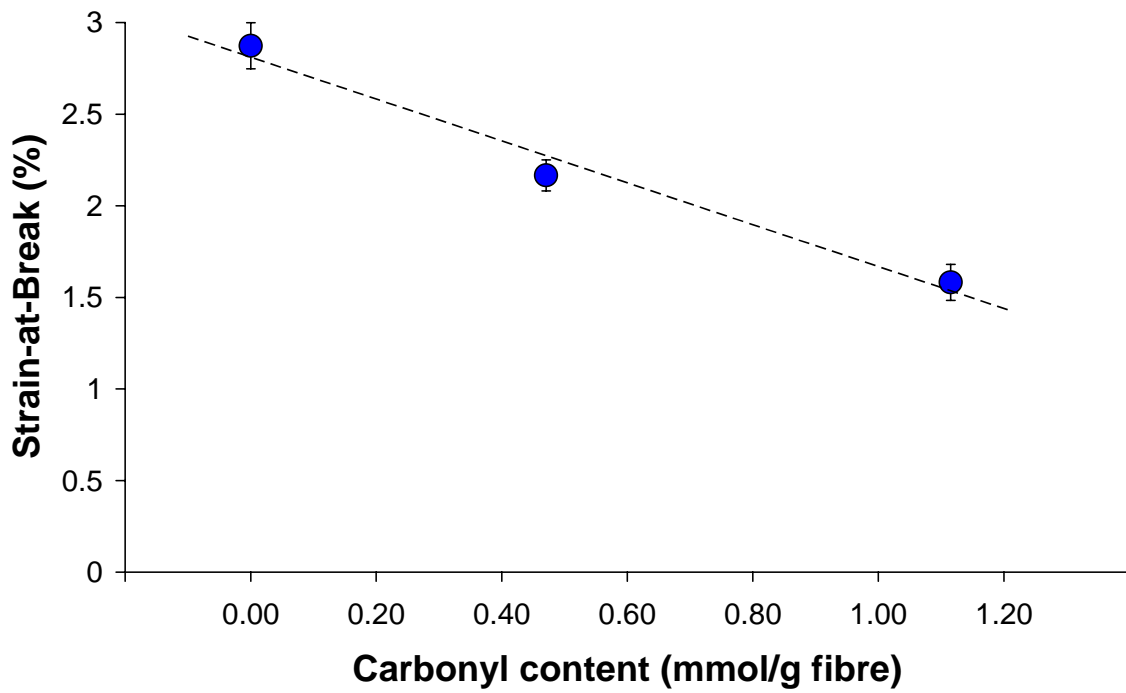


Figure 5. Strain-at-break as function of carbonyl content in the fibres.

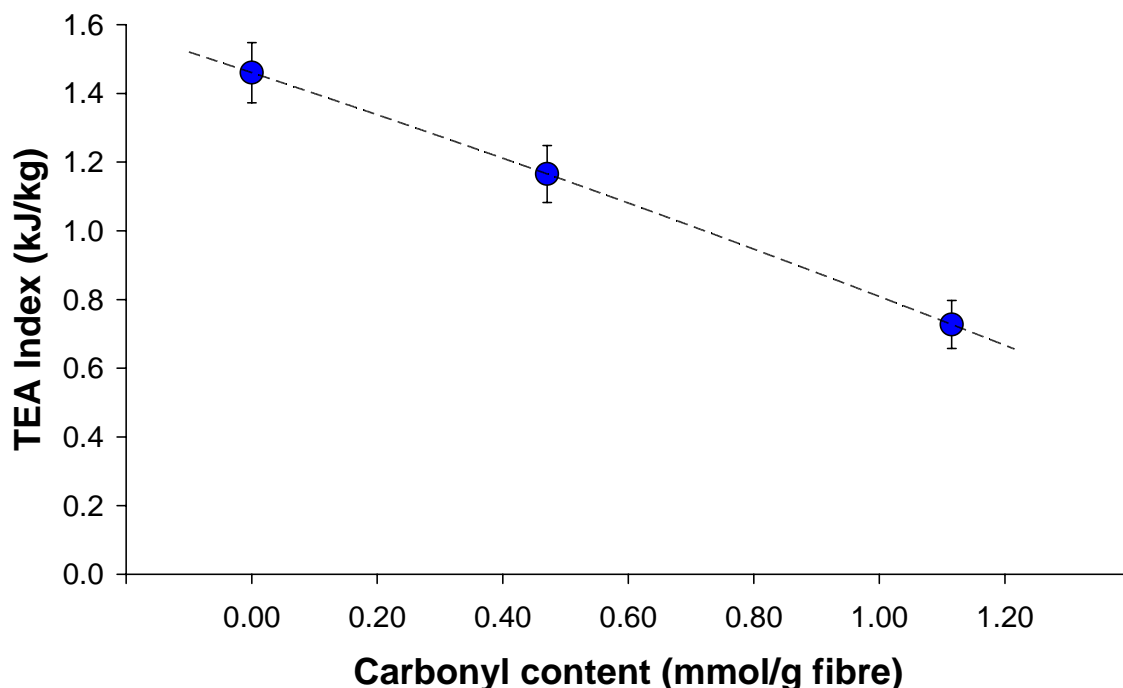


Figure 6. Tensile energy absorption index as function of carbonyl content in the fibres.

Mechano-sorptive creep was evaluated as presented above. Figure 7 shows the relative humidity measured in the test chamber during a test. By taking the strain measured after 3 humidity cycles for each sample and combining it with the load applied to each sample, the result shown in figure 8 could be calculated. Figure 8 shows isocyclic stress-strain curves, which relate the applied stress and resulting strain for a specific number of humidity cycles. For a certain load, it is seen that the oxidised samples showed much lower creep during the three humidity cycles, i.e. they had improved resistance towards mechano-sorptive creep.

The slopes of the lines regressed to the data sets in Figure 8 were calculated. If the nomenclature proposed by Panek et al (2004) is adopted, the slope of the linear part of a isocyclic stress-strain curve is denominated the isocyclic creep stiffness index. Table 1 shows the calculated isocyclic creep stiffness indexes and the corresponding carbonyl contents. For sample 2, slightly more than a three-fold increase compared to the reference could be detected, which has to be considered as a major improvement. Considering the confidence intervals for the calculated isocyclic creep stiffness indexes, it is seen that the improvements were much larger than the statistical variations.

Figure 9 shows isocyclic creep stiffness index and strain-at-break as function of carbonyl content in the fibres. It can be seen that the isocyclic creep stiffness increased almost linearly with increasing carbonyl content, whereas the strain-at-break showed a similar decrease.

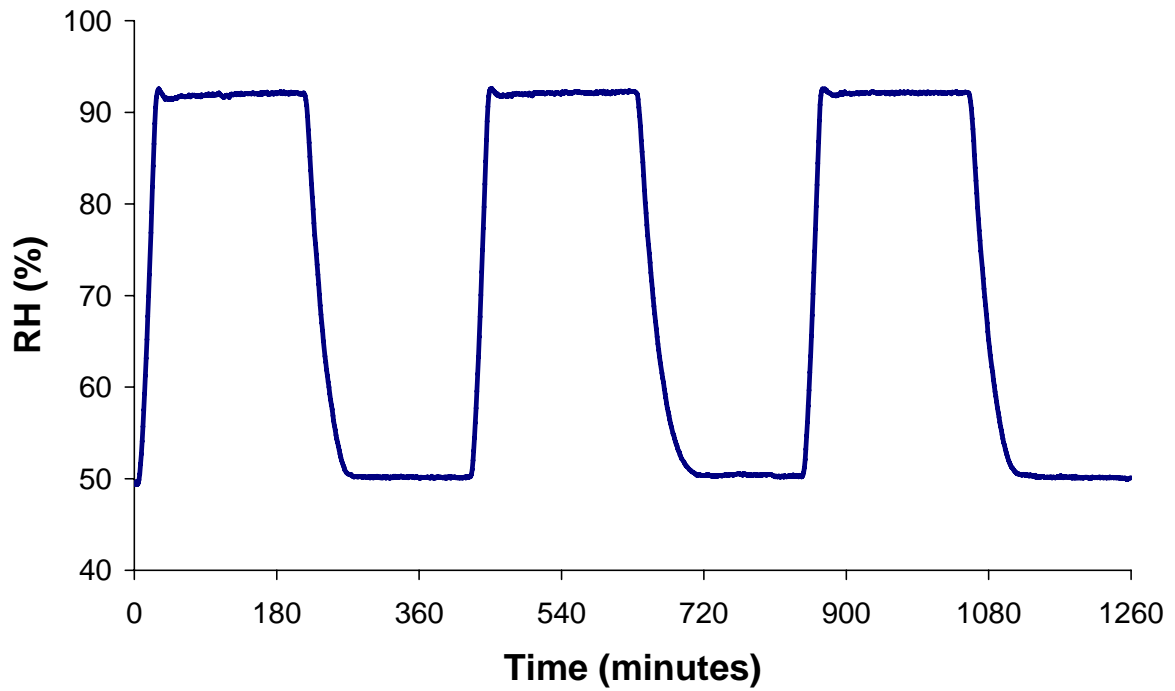


Figure 7. The relative humidity that was recorded in the test chamber during the mechano-sorptive creep testing.

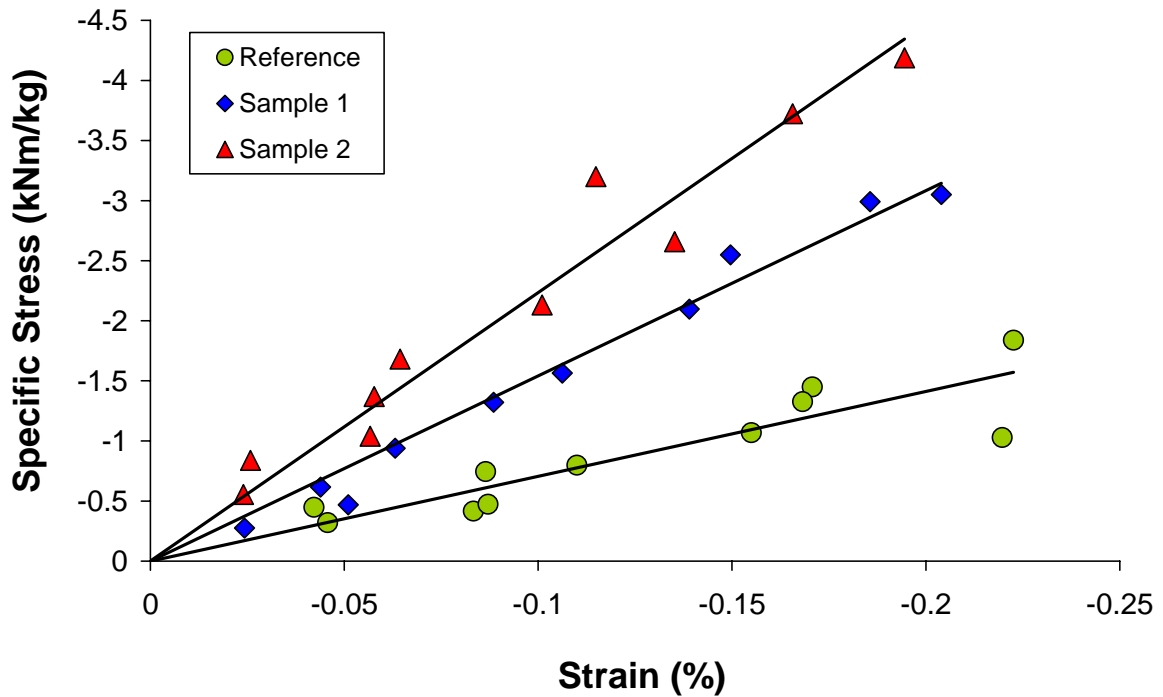


Figure 8. Isocyclic stress-strain data recorded after 3 cycles (21 h).

| Carbonyl content (mmol/g fibre) | Isocyclic creep stiffness index after 3 cycles (MNm/kg) |
|---------------------------------|---|
| 0                               | $0.71 \pm 0.08$   |
| $0.47 \pm 0.02$                 | $1.54 \pm 0.06$   |
| $1.12 \pm 0.02$                 | $2.23 \pm 0.13$   |

Table 1. Carbonyl content and isocyclic creep stiffness index, with 95%-confidence intervals, for the three different samples.

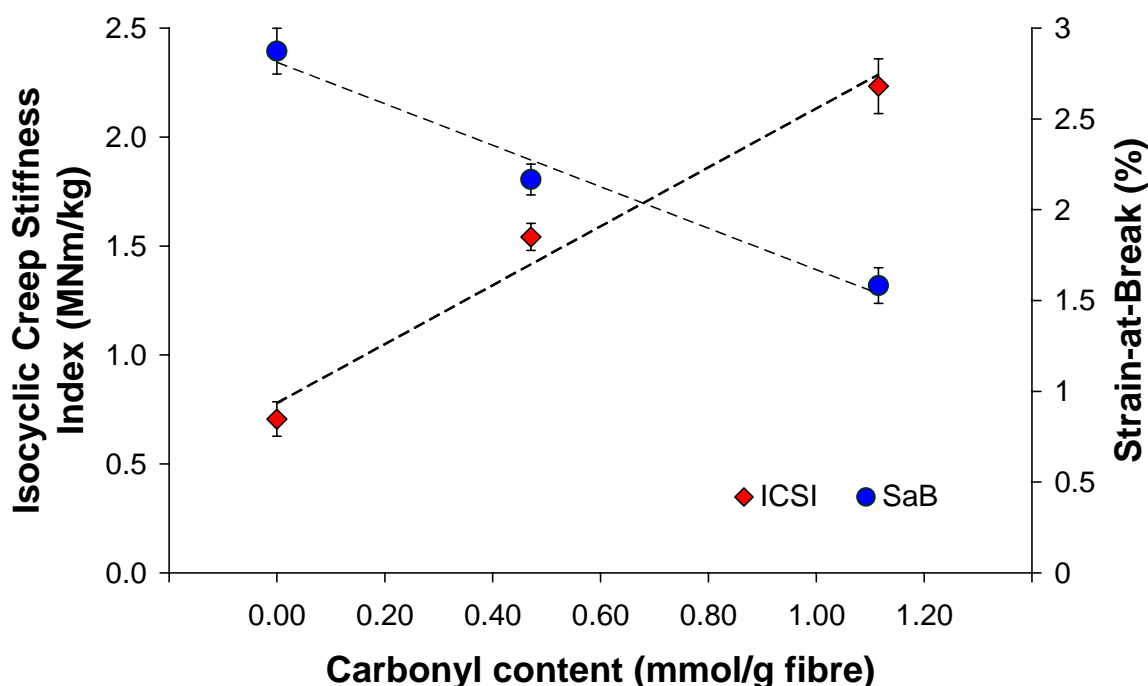


Figure 9. Isocyclic Creep Stiffness Index (3 cycles) and Strain-at-Break as function of carbonyl content in the fibres.

## Discussion

The goal of WP2.3 is to produce a corrugated box that uses 30% less material, with preserved converting and end-use performance. In order to reach this goal, it is necessary to reduce the mechano-sorptive creep of the linerboard with approximately 30%, without impairing other important linerboard properties, for example fracture toughness.

The chemical cross-linking did indeed decrease the toughness severely. But if the target increase in isocyclic creep stiffness index of 30% is considered and it is assumed that there is an approximately linear relationship between isocyclic creep stiffness index, strain-at-break, tensile energy absorption and carbonyl content (as indicated by the results), the decrease in strain-at-break and tensile energy absorption index would only be 7% and 8% respectively, which have to be considered as minor decreases.

As concluded by SP2 deliverable D2.59, the stacking life-time of corrugated boxes in varying humidity is primarily determined by the mechano-sorptive creep of the components, and not by strength or toughness of these components. However, fracture toughness is important for convertibility (die-cutting) and drop resistance of boxes. However, for certain linerboard qualities, the toughness is larger than what is needed for convertibility, and then cross-linking through oxidation could be used to increase mechano-sorptive creep resistance until the toughness reaches the critical level.

Another issue that needs to be addressed in the future is whether the cross-linking has a negative impact on repulpability and recyclability or not. It can be anticipated that this could be the case, since a high degree of cross-linking probably results in a high wet strength. However, this probably depends on the degree of oxidation and needs further investigation.

## Conclusions

It has been demonstrated that use of chemical cross-linking through fibre oxidation with periodate could increase the resistance towards mechano-sorptive creep significantly. In fact, much more than the target level of 30% set in WP2.3.

The isocyclic creep stiffness index of the tested samples increased approximately linear with increasing carbonyl content. However, there was a simultaneous undesired decrease of strain-at-break and tensile energy absorption index with increasing carbonyl content.

Even though the periodate oxidation results in a toughness loss, it gives a new opportunity to control and optimize a linerboard quality with respect towards mechano-sorptive creep. This is something that has been shown to be very difficult to achieve by changing standard papermaking variables.

## Literature

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