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D2.84 Investigation on surface modification of pulp made with new technique to create a high performance linerboard

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PU	Public	X
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D2.84 Investigation on surface modification of pulp made with new technique to create a high performance linerboard

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Summary

A new pulping technique, involving longer impregnation times, has been developed at KTH. It is believed that pulp produced by the new method will result in sheets with less mechano-sorptive creep but also reduced fracture toughness and this is investigated and reported in deliverable D2.83. The objective with the present deliverable is to increase the fracture toughness of the pulp produced in D2.83 by application of starch multilayers. Three layers of starch were adsorbed to the fibres and sheets produced from these. Mechanical testing of the sheets showed that the starch layers increased both the tensile strength and strain at break, at a certain density, significantly. The strength and strain at break of paper specimens with manufactured centre cracks, i.e. the fracture toughness, was however not improved by the starch multilayers. The difference in effect for notched and un-notched test specimens suggests that it is different mechanisms that control the strength in the two cases.

Introduction

The goal of WP2.3 is to reduce the amount of material used in a corrugated box with 30% without sacrificing its performance. The mechano-sorptive creep of a linerboard is very important for the box performance, since it will have a large influence on the stacking lifetime of the 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 from this earlier work was that the isocyclic creep stiffness index is linked to stacking resistance, bottom deflection and bending of sidewalls of corrugated boxes under cyclic humidity.

At KTH a new pulping technique with longer impregnation time has been developed. By using a longer impregnation time a more even delignification can be achieved and the defibration point moved to higher kappa numbers, rendering it possible to avoid in-line refining. In D2.83 it was described how pulp produced with the new technique compared to traditionally produced pulp in terms of mechano-sorptive creep, fracture toughness and other properties. The initial hypothesis was that the pulp produced with new method should have higher isocyclic creep stiffness index than a pulp cooked with conventional technique, but lower fracture toughness, another parameter that is important for box performance. Fracture toughness is the ability for a material to withstand mechanical loading in the presence of defects. In D2.59 it was concluded that the fracture toughness is linked to how well the board can be die-cut without cracking and also to the drop resistance of a box.

The objective with the current work was hence to increase the fracture toughness of the pulp by fibre surface modification. The surface modification was accomplished by forming polyelectrolyte multilayers of cationic and anionic starch onto the fibres. The build-up of multilayers enables more starch to be adsorbed to the fibre surfaces than if only a single layer of cationic starch had been used. Another advantage is that a high adsorbed amount can be

achieved without having high concentration of starch in solution. It has earlier been shown that the paper strength correlates well with the adsorbed amount of polyelectrolyte, thus the multilayer technique makes it possible to increase the paper strength further than if only a single layer of polyelectrolyte is adsorbed to the fibres (Eriksson et al. 2005a). Earlier research has also shown that the build-up of starch multilayers on bleached pulp fibres substantially increases the strength and strainability of the resulting papers sheets (Eriksson et al 2005b). It therefore seems likely that starch multilayers should be able to increase the force and strain a paper with defects can withstand. However, the use of polyelectrolyte multilayers of starch to improve fracture toughness has never been shown before and will be dependent both on the adhesion between polyelectrolyte multilayers and the fibres, and also on the mechanical properties of the polyelectrolyte multilayer films.

Materials and Methods

Fibres

The fibres used were prepared as described in deliverable D2.83 having a kappa number of 75 and there denoted NT 75. The pulp was prepared from a mixture of pine and spruce chips. The impregnation was performed at liquor-to-wood ration of 7:1. The cooking was performed at 135°C and the H-factor of the cook was 165. After defibration the total yield of the cook was determined to 53.2%. See deliverable D2.83 for details. In this study pulp beaten to 1000 and 3000 PFI revolutions were used.

Starch

The cationic potato starch had a degree of substitution of cationic groups of 0.091 and the anionic potato starch had a degree of substitution of anionic groups of 0.065. The cationic starch was gelatinised by heating a 20 g/l starch slurry to 95°C under stirring at 1000 rpm and maintaining this temperature for 25 minutes. The anionic starch was gelatinised by heating a 20 g/l starch slurry to 95°C under stirring at 1000 rpm and maintaining this temperature for 15 minutes. The starches were allowed to cool under ambient conditions before use, but not allowed to be stored more than maximum a day in order to avoid microbial degradation.

Build-up of multilayers

Pulp disintegrated with 30 000 revolutions were diluted to 5 g/L. To three litres of pulp suspension 15 ml of 2 M NaCl solution was added in order to get a background electrolyte concentration of 0.01 M NaCl. The pH of the solution was adjusted to 7. Subsequently 30 ml of cationic starch solution (20 g/l) was added to the suspension and allowed to adsorb for three minutes. The pH was continuously monitored to be approximately 7 throughout the adsorption. After 3 minutes had elapsed the fibre suspension was dewatered on a Büchner funnel fitted with Munktell filter paper no. 3 and subsequently rinsed with two litres of 0.01 M NaCl solution. The fibres were re-dispersed in three litres of 0.01 M NaCl solution. 30 ml of anionic starch solution was added to suspension and adsorbed for three minutes. The dewatering and rinsing step was repeated. Again the fibres were re-dispersed and 30 ml cationic starch solution was added and allowed to adsorb for 3 minutes. Immediately after the final starch layer had been built, sheets were prepared from the fibres.

Sheet preparation

Sheets with a grammage of 120 g/m² 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

Grammage and thickness were determined according to ISO 536:1995 and ISO 534:2005, and subsequently used to calculate apparent sheet density. Dry tensile testing was conducted according to the SCAN P67:93 standard for tensile testing of laboratory-made sheets. Fracture toughness was measured according to SCAN P77:95 with the exception that 6 instead of 20 notched test pieces were tested.

Results and Discussion

The mechanical properties of the produced sheets were evaluated as described above and the result is presented in figures 1 to 5. Before formation of starch multilayers and sheet preparation the pulp had been beaten to 1000 and 3000 PFI revolutions in order to obtain different sheet densities. As seen in the figures the starch multilayers resulted in a moderate densification, for the sheet density increased from 673 kg/m³ to 697 kg/m³ for the fibres beaten to 1000 PFI revolutions and from 731 kg/m³ to 737 kg/m³ for the fibres beaten to 3000 PFI revolutions.

From figure 1 and 2 it can be seen that the starch multilayers increased both the tensile strength and strain at break substantially at a given density. Density is a key property for many paper grades, especially for board qualities, since it has a large influence on the bending stiffness. This means that the use of starch multilayers enables the production of a stronger board with maintained bending stiffness which is advantageous from a box rigidity perspective.

In figure 3 it is seen that the starch multilayers did not have any larger effect on the stiffness of the sheets. This is expected, since for strong sheets with high density (which is the case here) the stiffness is primarily determined by the stiffness of the composing fibres and not by the fibre/fibre joints to any larger extent (Page et al 1979; Page and Seth 1980).

The result from the fracture toughness testing of specimens with manufactured 20 mm centre cracks is shown in figure 4 and 5. The apparent strength index was not considerably increased by the starch multilayers nor was the apparent strain at break. This was somewhat unexpected since the effect of the starch on the tensile strength and strain at break of specimens without manufactured defect were so marked. These findings suggest that it is different mechanisms that control the strength and strain to break of notched and un-notched paper specimens. With available data and knowledge it is, however, difficult to draw any definitive conclusion about what the mechanistic difference between the two cases can be. It is known that the ultimate paper strength is primarily determined by the strength and number of fibre-fibre joints and to a less extent by the strength of the individual fibres (Davison 1972). The presence of a crack will generate a large stress concentration at the crack tip. It can be speculated that the energy dissipation during crack propagation can be markedly influenced by the mechanical properties of the polyelectrolyte multilayer film and that the properties of the film therefore can have different effect depending if there is a notch present or not. Due to the large stress concentration at the crack tip it is also possible that fibres break at the crack tip and the fibre strength has considerable effect on the fracture toughness, something that could explain why the starch multilayers did not improve the fracture toughness. In future investigations it will be important to try to establish the exact mechanisms that determine the strength and strain to break for specimens with and without notches.

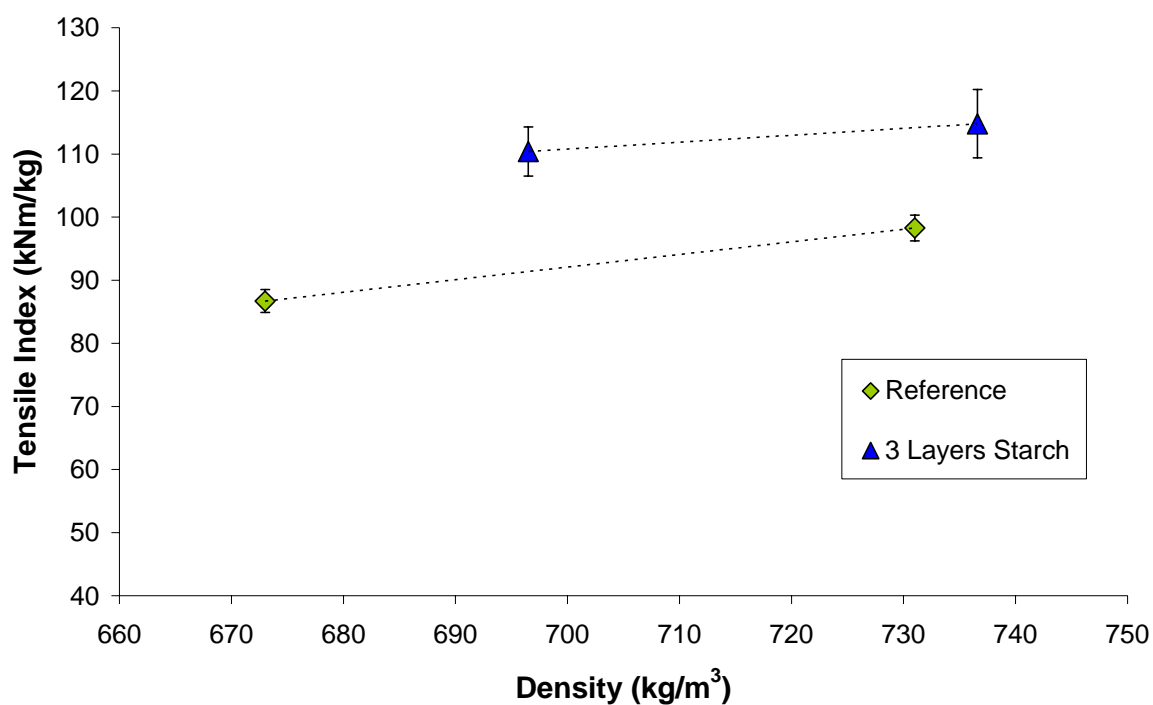


Figure 1. Tensile index as a function of sheet density for reference sheets and sheets made from fibres with three layers of adsorbed starch. The pulp was beaten for 1000 and 3000 revolutions in order to obtain different densities.

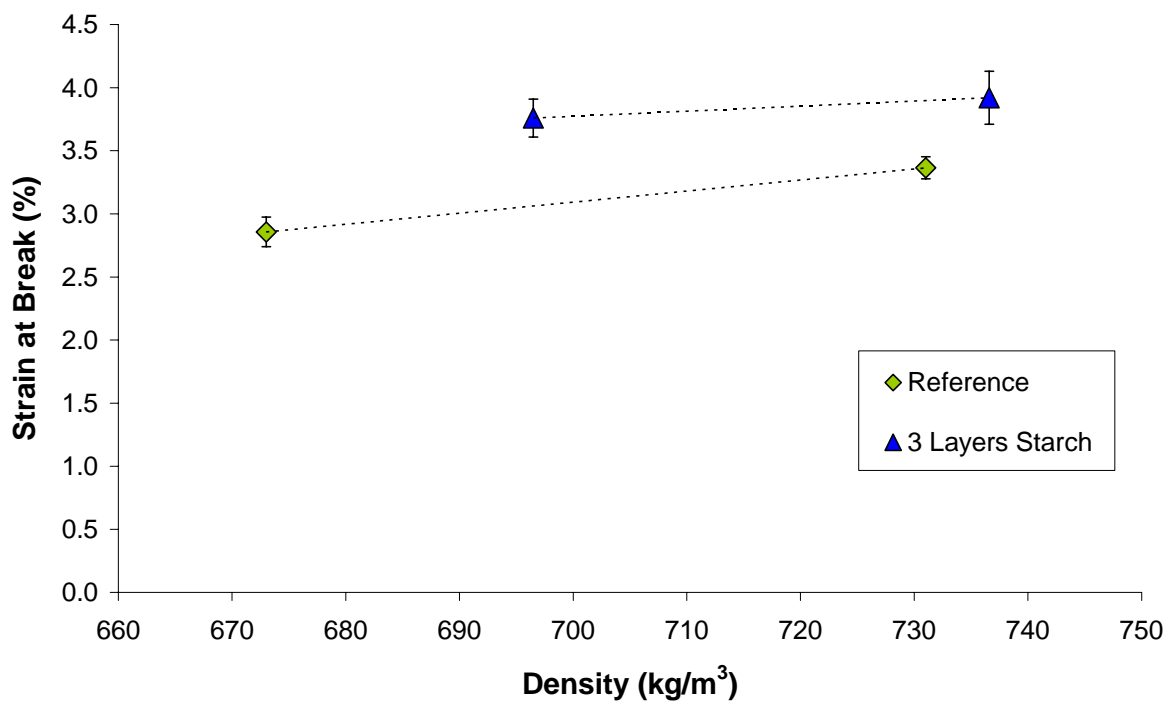


Figure 2. Strain at break as a function of sheet density for reference sheets and sheets made from fibres with three layers of adsorbed starch. The pulp was beaten for 1000 and 3000 revolutions in order to obtain different densities.

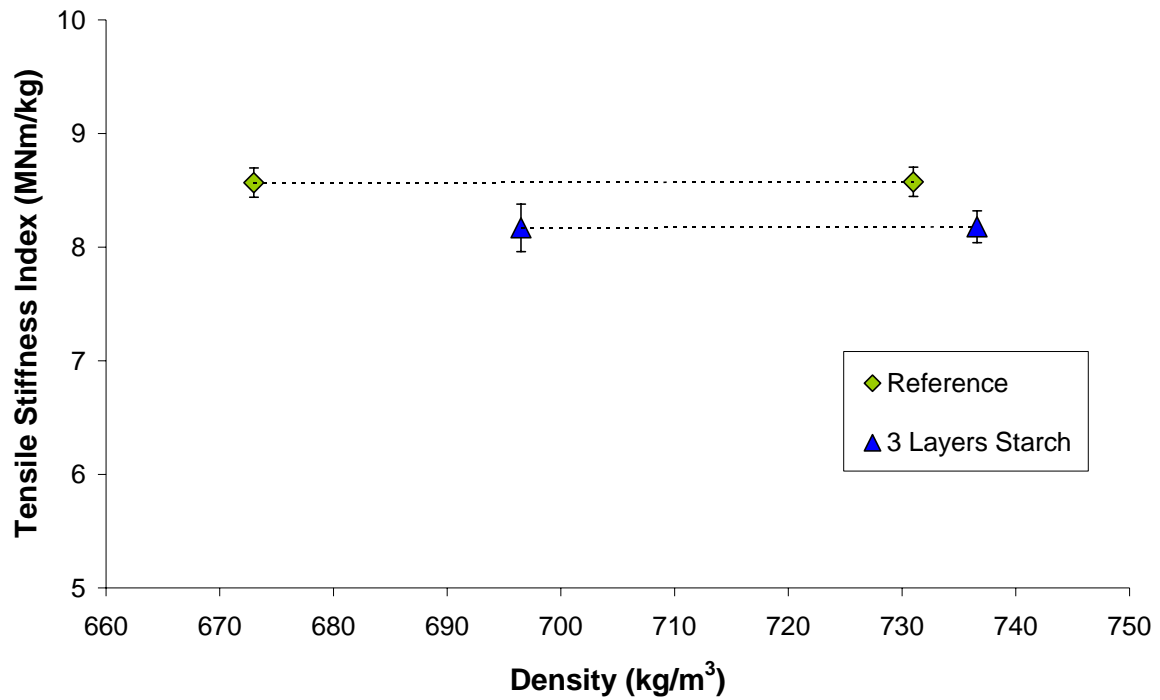


Figure 3. Tensile stiffness index as a function of sheet density for reference sheets and sheets made from fibres with three layers of adsorbed starch. The pulp was beaten for 1000 and 3000 revolutions in order to obtain different densities.

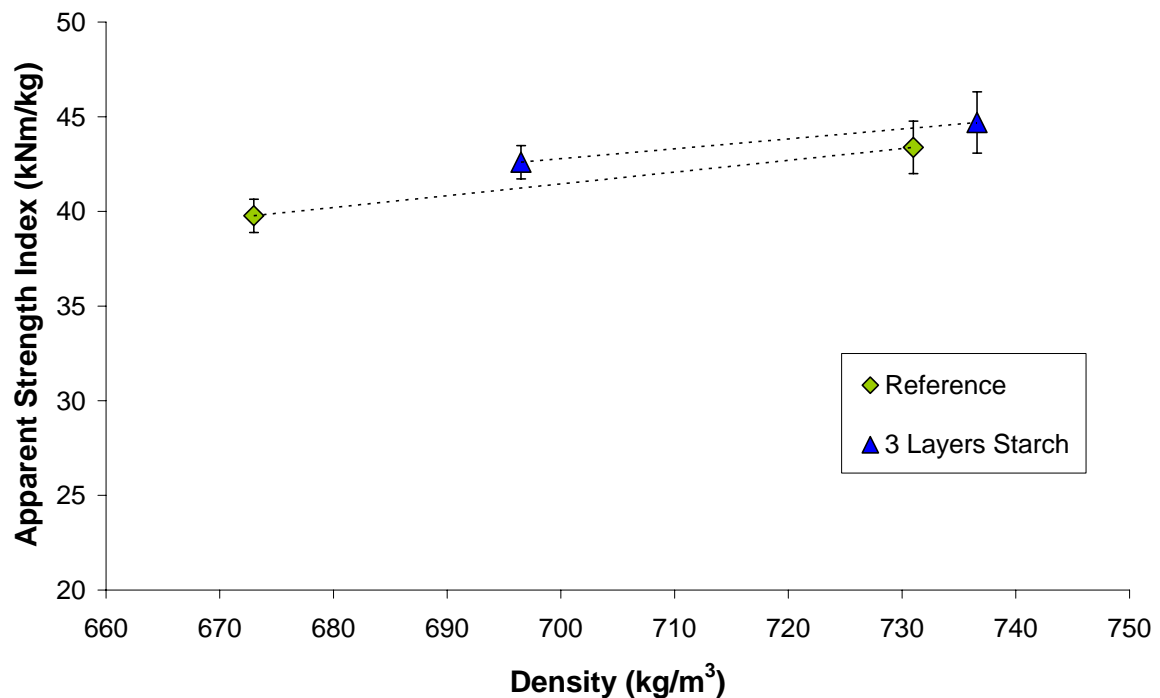


Figure 4. Apparent strength index, i.e. the strength of a specimen with a manufactured 20 mm centre crack, as a function of sheet density for reference sheets and sheets made from fibres with three layers of adsorbed starch. The pulp was beaten for 1000 and 3000 revolutions in order to obtain different densities.

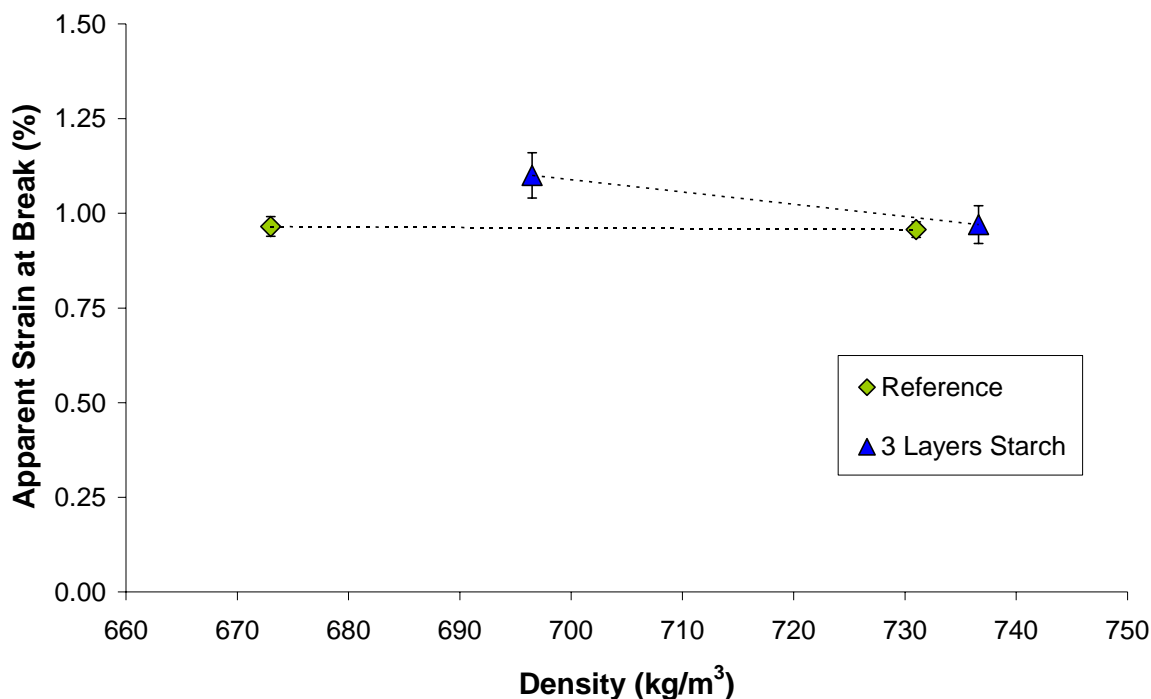


Figure 5. Apparent strain at break, i.e. the strain at break for a specimen with a manufactured 20 mm centre crack, as a function of sheet density for reference sheets and sheets made from fibres with three layers of adsorbed starch. The pulp was beaten for 1000 and 3000 revolutions in order to obtain different densities.

Conclusions

The build-up of starch multilayers significantly increased the tensile strength and strain at break of the produced paper sheets for a given density. The apparent strength and apparent strain at break, i.e. the strength and strain at break for specimens with manufactured centre cracks, was however not significantly affected by the starch multilayers. This suggests that there are different mechanisms controlling the mechanical properties of notched and un-notched specimens. With available data and knowledge it is, however, hard to draw any definitive conclusions about what it is that differs between the two cases.

Literature

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