NMP3 - CT - 2004 - 500311

Sustainpack

Innovation and sustainable Development in the Fibre Based Packaging Value Chain

Instrument: **IP**

D2.49 Report on the effect of chemical treatment of a birch kraft pulp and a reference kraft liner pulp with respect to MSC/SCT/FT

Due date of deliverable: 2007-09-30
Actual submission date: 2007-10-15

Start date of project: **2004-06-01** Duration: **4 years**

Fibre and Polymer Technology
Royal Institute of Technology, KTH

Project co-funded by the European Commission within the Sixth Framework Programme (2002-2006)		
Dissemination Level		
PU	Public	X
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SustainPack WP 2.3
Deliverable D2.49

Report on the effect of chemical treatment of a birch kraft pulp and a reference kraft liner pulp with respect to MSC/SCT/FT

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Abstract

One of the most important parameters for kraftliners is the mechano-sorptive creep stiffness. In a previous study it was found that an unbleached birch pulp had higher mechano-sorptive creep stiffness and tensile stiffness compared to a reference softwood kraftliner pulp but lower tensile strength and fracture toughness. In order to compensate for the lower strength and toughness of the birch pulp, three different strength additives; a polyelectrolyte complex, PEC, consisting of polyallylamine hydrochloride, PAH, and polyacrylicacid, PAA, polyallylamine hydrochloride, PAH, and polyvinylamine, PVAm were added to the birch pulp. Two different addition levels of PEC were used.

The results show that it is possible to increase the strength properties and the fracture properties to, and in some cases above, the kraftliner softwood pulp level, with an exception of the apparent strain-at-break that not fully can be restored by the chemical additives to the same level as for the softwood pulp. The mechano-sorptive creep stiffness was unaffected by the treatments.

Keywords: *kraftliner, birch, polyelectrolyte complex, polyallylamine hydrochloride, polyacrylicacid, polyvinylamine, fracture toughness, SCT index, tensile properties, hygroexpansion, isocyclic creep stiffness.*

Introduction

Corrugated board material is one of the largest areas of use for paper (FAO 1998). Kraftliner, i.e. the top and bottom layer of corrugated board, needs several qualities such as good printability and mechanical properties. One of the most important mechanical properties for kraftliner is mechano-sorptive creep or accelerated creep. Mechano-sorptive creep is a phenomena occurring in any type of paper under load during variations in relative humidity and results in a larger creep than if the same paper was loaded under the same load at constant humidity. This behaviour was discovered in paper by Byrd (Byrd 1972) but, has been known in other materials such as concrete (Pickett 1942) and wool (Mackay 1959) for a longer period of time.

There are also other mechanical properties that are of large importance for kraftliner such as compression strength, tensile stiffness and fracture properties. These parameters as well as mechano-sorptive creep stiffness measured on kraftliner have been shown to correlate well with the mechanical properties of corrugated boxes made from the kraftliner (Henriksson et al 2007). In order to be able to lower the grammage of the corrugated board with preserved box performance it is hence necessary to improve these mechanical properties and especially mechano-sorptive creep stiffness of the paper. In a previous study (Antonsson et al 2007) it was shown that an unbleached birch pulp has higher compression strength, mechano-sorptive creep and tensile stiffness values compared to a kraftliner pulp at equal drainage resistance. However, the tensile energy absorption, strain at break and fracture properties were lower. In order to compensate for these drawbacks of the birch pulp, different strength additives could be added to the pulp before paper formation.

One system that has been proven to give large strength improvements of papers from hardwood pulp is a pre-treatment of the fibres with polyelectrolyte complexes, PEC (Gärdlund 2006). Hence, polyelectrolyte complex consisting of polyallylamine hydrochloride, PAH, and polyacrylicacid, PAA, would be a choice to consider and evaluate together with the birch pulp. Also polyallylamine, PAH, and polyvinylamine, PVAm, could give good effects on the mechanical properties of the birch pulp sheets (Gimåker et al 2007). In the present study the effects of different treatments with these chemicals were evaluated regarding some of the most important mechanical properties of kraftliner products.

Experimental

Materials

Unbleached industrial kraftliner pulp made almost exclusively from Scots Pine, *Pinus sylvestris*, and Norway Spruce, *Picea abies*, as well as unbleached industrial hardwood pulp made mainly from Silver Birch, *Betula verrucosa*, but probably with some traces of Alder, *Alnus glutinosa*, *Alnus incana*, and Aspen, *Populus tremula*, was used in the study. Both pulps were carefully washed with deionised water. The kraftliner pulp had a kappa number of 76 and was Escher-Wyss beaten to 30MºSR (corresponding to 16ºSR) prior to further PFI-beating. The hardwood pulp was "screened" in a water jet NAF disintegrator (Nordiska Armatur Fabriken, Sweden). The pulps were PFI-beaten according to ISO 5264-2:2002 to a drainage resistance of about 25ºSR corresponding to 4000 revolutions for the hardwood pulp and 8000 revolutions for the kraftliner pulp.

Polyallylamine with a molecular weight of 15 000 Da was purchased from Sigma-Aldrich, Stockhom, Sweden, and used without further purification.

Polyvinylamine with a molecular weight of 45 000 Da (Lupamin® 5095) was kindly provided by BASF, Ludwigshafen, Germany. Before use the polyvinylamine was purified by precipitation in ethanol, then dissolved in MilliQ water and freeze dried.

Polyelectrolyte complexes, with a molar mixing ratio (anion/cation) of 0.8, were pre-formed by mixing the two polyelectrolytes polyallylamine hydrochloride (M_w 15 000 Da) and polyacrylic acid (M_w 5 000 Da), dissolved in MilliQ water to concentrations of 4.0 and 3.2 meq/l with respect to charges, respectively. Both solutions contained 10 mmol/l NaCl and were adjusted to pH 7 prior to mixing.

Methods

Polyelectrolyte titration was used to establish adsorption isotherms for the adsorption of polyallylamine and polyvinylamine onto the hardwood kraft pulp fibres. Potassium poly vinyl sulphate was used as the titrant with orthotoluidine blue as the indicator in an equipment setup similar to that described by Horn (1978).

Nitrogen content analysis with an ANTEK 7000, Model 737 elemental analyser, was used to establish adsorption isotherms for the adsorption of polyelectrolyte complexes onto the softwood and hardwood pulp fibres.

Before sheet preparation, polyelectrolytes and polyelectrolyte complexes were adsorbed to the fibres. Polyvinylamine was added at a dosage of 14.8 mg/g. Polyallylamine was added at a dosage of 17 mg/g. For the polyelectrolyte complexes two different dosages were used, 10 and 40 mg/g respectively. All adsorption experiments were performed at pH 8 in tap water and the adsorption time was set to 30 minutes

Rapid Köthen sheets with a grammage of approximately 120 g/m^2 were prepared from the different pulps according to EN ISO 5269-2:1998. The apparent density of the sheets was determined via the grammage of the sheets and the thickness of the sheets determined via a 7 sheet stack according to ISO 536:1995 and ISO 534:2005 (with exception for the number of sheets used), respectively. Short span compression test, SCT, tensile properties and fracture toughness properties were determined according to ISO 9895:1989, SCAN P67:93 and SCAN P77:95 respectively.

The hygroexpansion coefficient was measured between 33%RH and 66%RH according to ISO 8226-1:1994 using a special equipment developed at STFI-Packforsk basically consisting of 30 rigid clamps and 30 freely movable clamps with a gap between the clamps of 100 mm where 30 paper strips were placed independently in a horizontal position. Isocyclic creep measurements were performed on an apparatus described earlier (Haraldsson et al 1994) using pre-cycled paper strips. The strain, after 3 cycles in Relative Humidity (RH) starting and ending at 50%RH and reaching up to 90%RH, with a certain stress applied was used to determine the isocyclic creep stiffness.

Results and Discussion

Adsorption of polyelectrolytes and PEC on unbleached fibres

The adsorption of the PAH on the birch pulp was established and the corresponding adsorption isotherm is shown in figure 1. As seen the maximum adsorption was achieved at approximately 13 mg/g fibre.

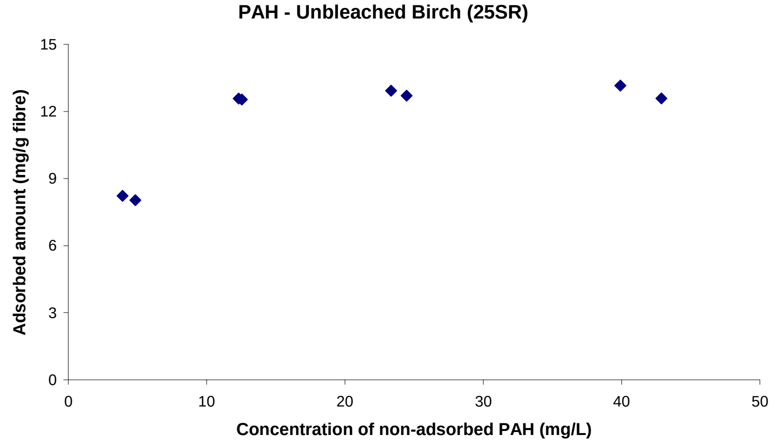

Figure 1: Adsorption isotherm for the adsorption of PAH on the unbleached birch pulp.

Following this, the maximum adsorption of the PVAm on the birch pulp was established to approximately 11 mg/g fibre.

Adsorption isotherms for the adsorption of polyelectrolyte complexes on the softwood and hardwood pulp were established and the results are shown in figure 2. On the basis of the results in Figure 3, the additions of PEC to the birch pulp was chosen to 10 mg/g pulp, PEC LD (low dosage) and 40 mg/g pulp PEC HD (high dosage).

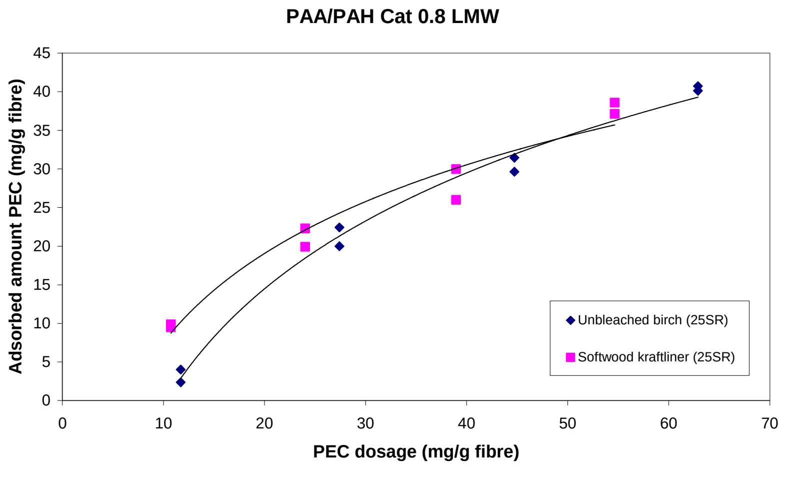

Figure 2: Adsorption isotherms for the adsorption of PEC on hardwood and softwood pulp. The dosage of PEC to the birch pulp was chosen to 10mg/g pulp and 40mg/g pulp due to the adsorbed amount shown in the figure.

Hence, the selected additions of additives were set to 17 mg/g fibre for PAH, 14.8 mg/g for PVAm, 10 mg/g fibre for PEC at low dosage (LD) and 40 mg/g fibre for PEC at high dosage (HD).

Effect on mechanical/physical properties

As can be seen in figure 3 the tensile properties of the birch pulp with addition of PAH, PVAm and PEC respectively reach the same level as the reference kraftliner pulp. In this figure the properties relative to a reference kraftliner pulp is shown. The best results seemed to be achieved with PAH and the high dosage of PEC.

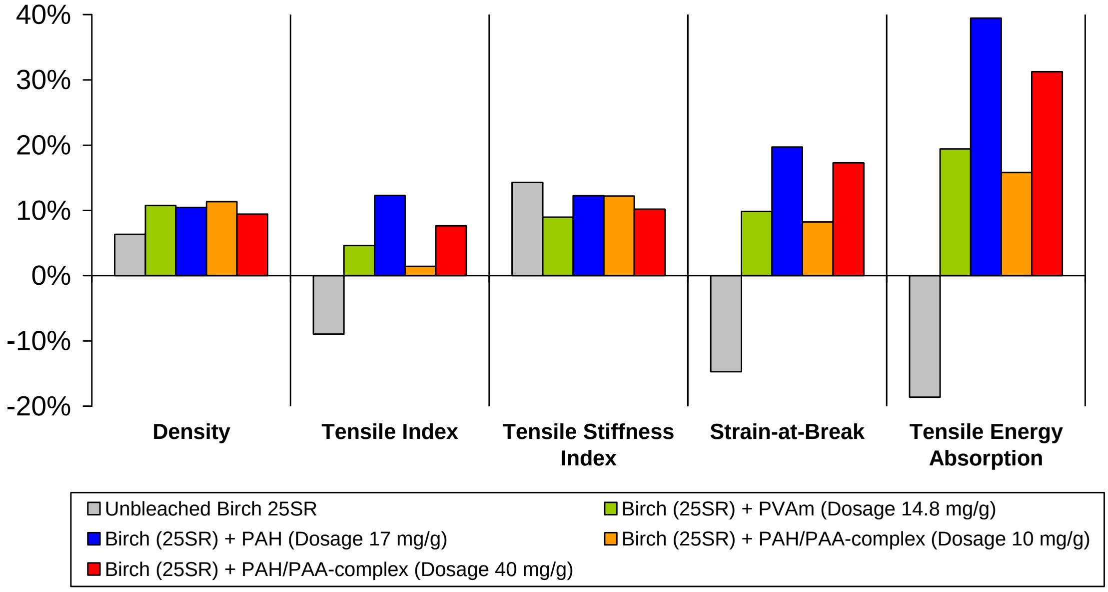

Figure 3: Properties of papers made from a birch pulp with different treatments relative the reference kraftliner pulp beaten to 25°SR. The tensile index, strain at break and tensile energy absorption were all increased by addition of the different chemicals.

With exception from the SCT-index and apparent strength index, it seems as the other tested properties were relatively unaffected by the additions as seen in Figure 4.

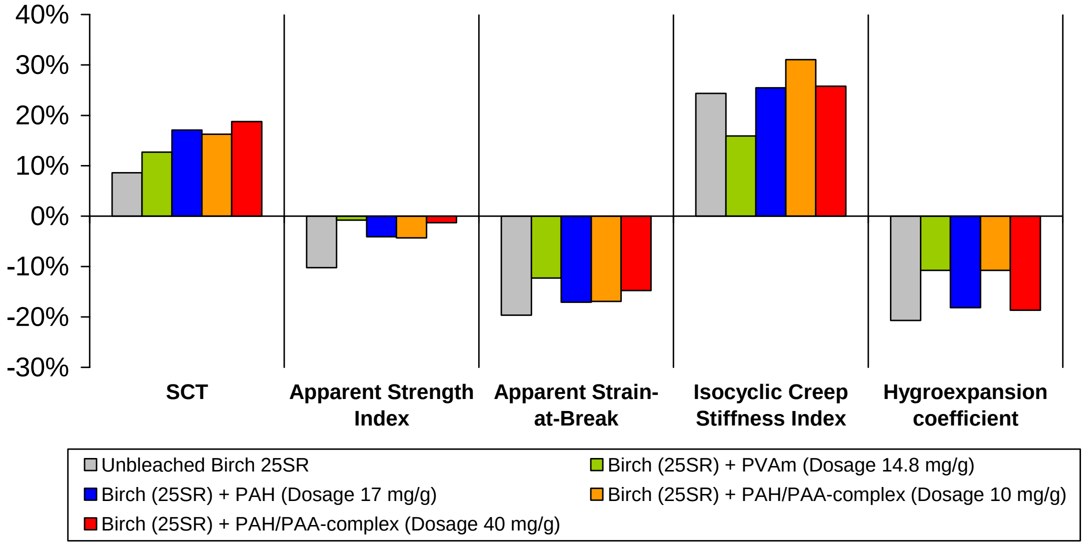

Figure 4 Properties of papers made from a birch pulp with different treatments relative the reference kraftliner pulp beaten to 25°SR. Apparent strength index and SCT index were increased by chemical addition while the other properties were more or less unaffected.

As the tensile properties were plotted as a function of density it seems as the strain at break and tensile energy absorption increased and the tensile stiffness decreased as PAH, PVAm and PEC were added to the birch pulp as seen in Figure 5.

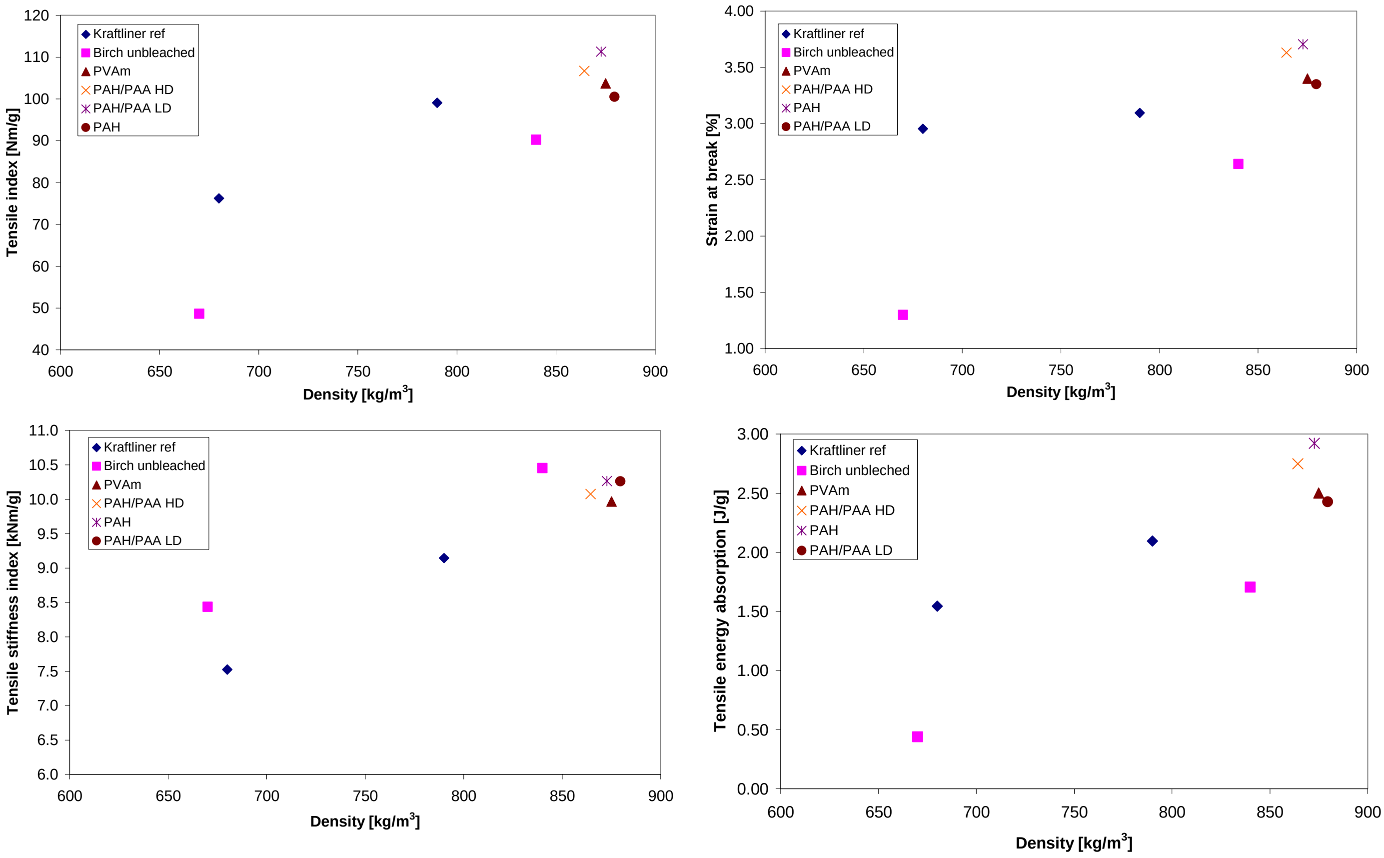

Figure 5: At a given density, the strain at break increased and the tensile stiffness decreased by the addition of chemicals.

A densification from already high numbers of the sheets with addition of chemicals can be noticed. Less beating of the pulp prior to the chemical additions could give sheets with comparable density to the non-treated beaten birch pulp.

The SCT-index at a given density also seemed to be positively affected by addition of the different polymers. Especially the high dosage of PEC seemed to improve the SCT as seen in Figure 6.

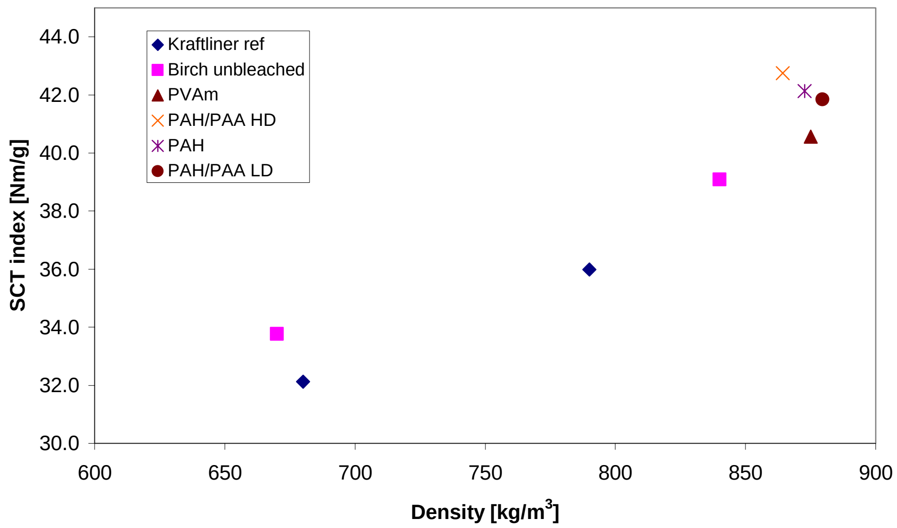

Figure 6: At a given density, the SCT index was increased by the addition of chemicals.

As seen in Figure 7, the mechano-sorptive properties, i.e. the isocyclic creep stiffness is not affected significantly by the density. The addition of polymers seemed not to affect the mechano-sorptive creep to any larger extent.

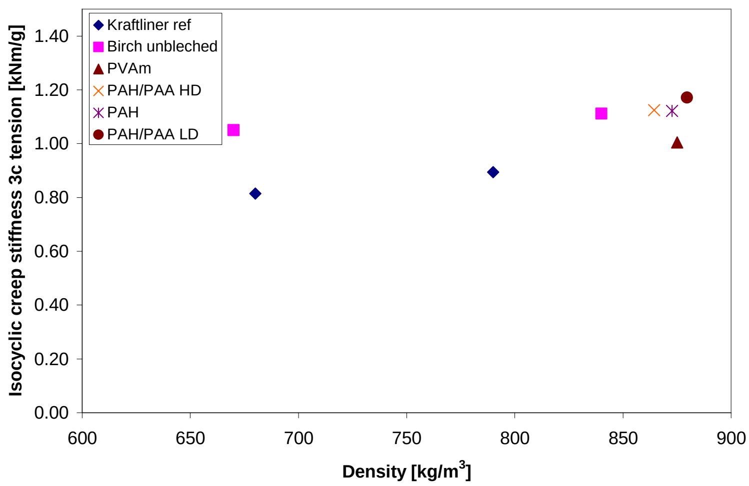

Figure 7: At a given density, the isocyclic creep stiffness index was not affected significantly by the addition of chemicals.

The same result was found for the hygroexpansion coefficient and as shown in figure 8 it was not much affected by the polymer additions.

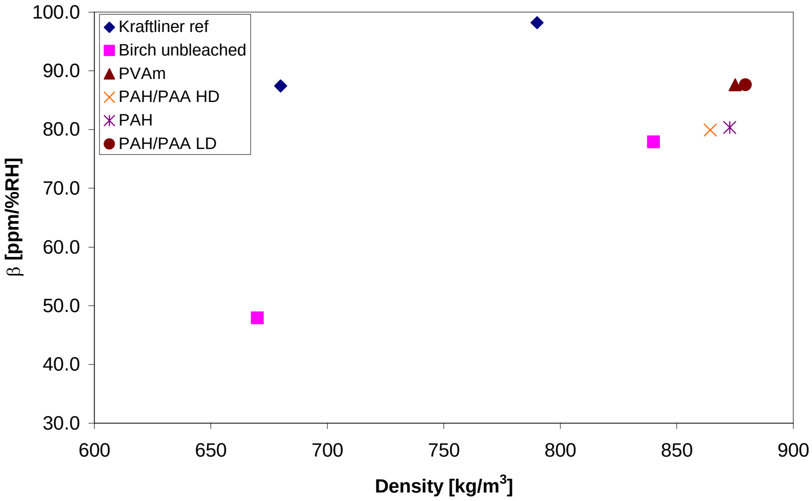

Figure 8: For a given density, the hygroexpansivity was not significantly affected by the addition of chemicals.

Conclusions

It is possible to compensate for the lower tensile strength and fracture toughness properties of the birch pulp, with exception of the apparent strain at break, by addition of PEC, PVAm or PAH. The mechano-sorptive creep was, however, not affected by the polymeric strength additives. Which of the systems that should be used to increase tensile strength and fracture toughness seems to be less important, since they all result in approximately the same effect on mechanical properties of the resulting sheets. In the application of the additives the efficiency has to be matched by production economy.

Acknowledgements

Mona Johansson, KTH, is gratefully acknowledged for performing the PFI-beating of the pulps. Access to the paper physical testing equipment at STFI-Packforsk is also gratefully acknowledged.

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