Influence of Liquid or Solid Phase Preparation of Cationic Hemicelluloses on Physical Properties of Paper

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Cationizations of galactomannan- and xylan-type hemicelluloses were performed in a solid state, with 2,3-epoxypropyltrimethylammonium chloride (ETA) as the cationic reagent under alkaline conditions. By this method, the reaction efficiency was significantly increased for all hemicellulose types, up to 90% in the case of xylan. The consumption of reagents was reduced by a factor of ten when compared to the reaction in liquid phase, while comparable values of the degree of substitution (DS) were obtained. By reducing the number of purification steps, the consumption of solvents was limited, and high mass yields were preserved. By all aspects, this method constitutes an economical and environmental gain for the cationization reaction of hemicelluloses. Native hemicelluloses and their cationic derivatives were tested as additives to the pulp slurry in order to increase the dry strength of the paper formed. The cationization of hemicelluloses had a beneficial effect on the mechanical properties of paper, with a supplementary gain of properties compared to the unmodified polysaccharides. Cationic derivatives of a DS 0.3 gave the best results for both polysaccharides, with the galactomannan-type being more efficient than the xylan-type with a 90% increase of the burst index.

INTRODUCTION

The papermaking industry uses cationic polysaccharides to enhance some of the physical properties of paper. These modified polysaccharides are positively charged to favor efficient interactions with the negatively charged cellulosic fibers during paper formation. The common procedure for cationization consists of derivatizing the polysaccharide with a cationic reagent by etherification of the hydroxyl groups. For an efficient adsorption of the cationic polysaccharides on the cellulosic fibers, low values of degrees of substitution are preferred (DS <0.1, corresponding to the average number of substituted hydroxyl groups per carbohydrate unit). For this application, cationised starch is currently the most widely used polysaccharide (Hellwig *et al.* 1992; Radosta *et al.* 2004; Roerden and Wessels 1993; Solarek 1986; Tara *et al.* 2004; Xie *et al.* 2006), but it would be interesting to substitute edible starch by a polysaccharide not competitive with the food industry. Hemicelluloses are good candidates because they may become widely available in the future through the implementation of an extraction processes in kraft

pulping processes, for instance, in which the hemicelluloses are not currently valorized except as an energy resource. The use of hemicellulose-related polymers from annual plants (*e.g.* guar gum) for paper-making applications (after cationization) has remained at a low level of usage because of higher production cost compared to starch. However, for hemicelluloses extracted from wood chips, a potential economical advantage has been demonstrated (Huber *et al.* 2012a).

The cationization of hemicelluloses has already been described and proceeds in a similar way as the other polysaccharides (Scheme 1). Reactions are performed in aqueous alcohol or in water in the presence of NaOH and 3-chloro-2-hydroxypropyl-trimethylammonium chloride (CHMAC) or 2,3-epoxypropyltrimethyl-ammonium chloride (ETA) as the etherifying agent, yielding DS values up to 1 to 1.6 depending on the conditions and hemicellulose type (Bigand *et al.* 2011; Cottrell *et al.* 2001; Ebringerova *et al.* 1994; Pal *et al.* 2007; Ren *et al.* 2006, 2007a,b; Schwikal *et al.* 2006). Cationic derivatives of galactomannans from plant seeds (guar or xanthan gums) are now commercially available with DS lower than 0.1 (Dasgupta 1993).
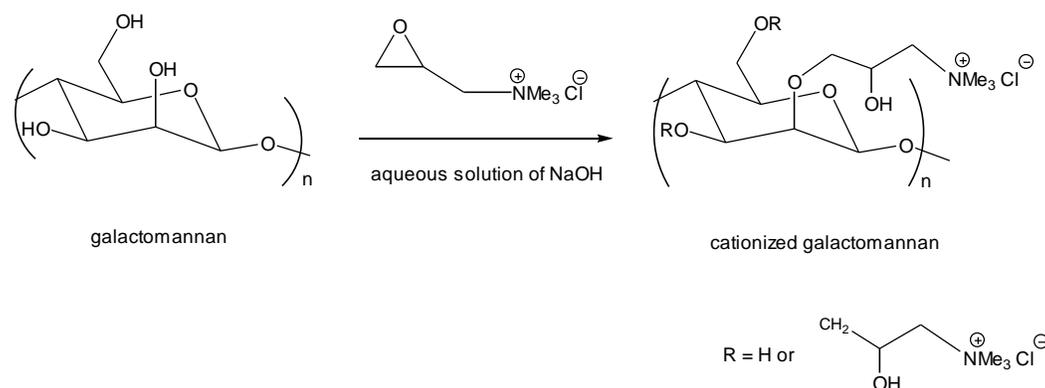
Scheme 1. Cationization of hemicellulose by ETA

In a previous paper the cationization of two commercial model hemicelluloses in an aqueous medium using the cationic reagent 2,3-epoxypropyltrimethylammonium chloride (ETA) was described. Degree of substitution values from 0.1 to 1.3 have been obtained by varying reaction parameters (Bigand *et al.* 2011). The optimization of conditions demonstrated that species concentration is the key parameter in order to improve the reaction efficiency (RE), corresponding to the conversion of the cationic reagent. For example, we showed that by reducing the solvent amount, the RE went up to 50% for the case of birchwood xylan.

In order to increase the reaction efficiency, it was possible to perform the reaction in a solid state, by using a minimum amount of solvent. This kind of process is currently used for the cationization of starch (Fischer *et al.* 1981; Stober *et al.* 1989a) in the presence of solid catalysts, and DS values of 0.02 to 0.04 have been described with reaction efficiencies of 90 to 95%. Concerning hemicelluloses, the method was only reported for cationization of galactomannan, in the presence of a calcium hydroxide catalyst with a maximum DS value of 0.24 (RE 75%) (Stober *et al.* 1989b).

We report here our work on the cationization in solid phase of hemicelluloses. Two hemicellulose types were studied: a galactomannan-type (commercial guar gum) and a xylan-type (commercial and in-house extracted xylan). Reactivity of the two types

of hemicellulose will be compared, along with the data obtained in the liquid phase that we previously reported (Bigand *et al.* 2011). Then, we will report the results on the influence of the cationic hemicelluloses, prepared in both liquid and solid phases, as papermaking additives on the mechanical and optical properties of paper.

EXPERIMENTAL

Materials

Guar gum (Sigma-Aldrich SKU: G4129), birchwood xylan (Sigma-Aldrich SKU: X0502), and 2,3-epoxypropyltrimethylammonium chloride (ETA, Sigma-Aldrich SKU: 50053, >90%) were purchased from Sigma-Aldrich. Absolute ethanol (99%) was purchased from Carlo Erba. A cationic starch provided by Roquette Frères was used as an industrial reference (HI-CAT 142, DS 0.04, 0.37% N) for paper properties studies.

Extraction of Xylan from Birchwood under Alkaline Conditions (ext. xylan)

Xylan hemicellulose was extracted from birchwood under alkaline conditions (NaOH 5%, 160 °C, 20 min) by the method described by Da Silva Perez *et al.* (2011). After the extraction, the pH of spent liquors was adjusted to 6 and concentrated to *ca*. 1/3 of their initial volumes at 60 °C; the resulting hemicelluloses were then precipitated with the addition of 95% ethanol (1 part liquor (vol.) to 3 parts ethanol (vol.)). After the separation of the supernatant, the purification of the hemicelluloses-rich fractions consisted of 4 cycles of dispersion of the precipitate in 70% ethanol and centrifugation, followed by drying at 45 °C.

The extraction yield on wood was 12% and the purification yield was 20%, so that 2.4% of the initial wood dry mass was recovered as a hemicelluloses-rich fraction. Note that up to 12% of lignin were still present in the final material.

Cationization of Hemicelluloses in Liquid Phase

The cationization procedure for the two types of hemicelluloses was identical to what was reported previously (Bigand *et al.* 2011) without the addition of a catalyst other than NaOH. In a typical procedure, 0.36 g (2 mmol or 6 mmol hydroxyl functional groups) was dispersed in a 13 mL of distilled water, and the suspension was heated at 60 °C for 20 min. Then 2 mL of a selected aqueous solution of NaOH was added to activate the substrate for 20 min at 60 °C. Then a selected amount of ETA was added, and the mixture was stirred for 5 h at 60 °C. The cationized product was then precipitated by dropwise addition of 20 mL of ethanol. After filtration and washing with ethanol, the purified product was collected and dried in a vacuum oven for 16 h at 80 °C. The dry product was characterized by ^{1}H NMR spectroscopy to determine the degree of substitution (DS), and the yield was calculated from the recovered mass.

Cationization of Hemicelluloses in Solid Phase

For a better understanding, NaOH and ETA amounts are expressed in equivalent number per hydroxyl function of hemicellulose (equiv./OH).

Etherification of guar gum

In a typical procedure, 1 g (6.17 mmol or 18 mmol hydroxyl functional groups) of guar gum was successively impregnated with 0.15 mL of an aqueous solution of sodium

hydroxide (25%, 0.925 mmol, 0.05 equiv./OH) and 0.4 mL of a commercial solution of ETA (80%, 2.23 mmol, 0.12 equiv./OH). The solutions were added dropwise to the solid, which was regularly homogenized with a spatula in order to be uniformly impregnated. The reaction proceeded in a flask in thermostated bath at 60 °C, at atmospheric pressure, with mixing set at 150 rpm. The reaction time was varied from 5 min to 5 h. After completion, the solid was dispersed in 10 mL of water, and the resulting gel was acidified to pH 5 upon HCl (10%) addition. Isolation of characterisation of the cationized product were performed as described above.

Etherification of birchwood xylan (model and extracted)

The same procedure used for guar gum was followed with 1 g (7.6 mmol or 15.2 mmol hydroxyl functional groups) of xylan, 0.4 mL of an aqueous solution of sodium hydroxide (15%, 1.5 mmol, 0.1 equiv./OH), and 0.3 mL of the commercial solution of ETA (80%, 1.8 mmol, 0.12 equiv./OH).

Characterization of Cationic Hemicelluloses Obtained in Solid Phase

The liquid-state ^{1}H NMR spectra was obtained on a 250 MHz Bruker spectrometer at 25 °C. The ^{1}H NMR spectra of both hemicelluloses were recorded after the hydrolysis of 10 mg of the hemicellulose dissolved in a DCl/ D$_2$O mixture (32 scans). The hydrolysis procedure was as follows: a solution of 10 mg of product in 0.2 mL of 35% DCl/D$_2$O was heated at 100 °C for 1 min. The yellow solution was then diluted with 0.7 mL of 99% deuterium oxide and the spectrum was recorded directly.

Substitution degree (DS) was determined directly by the ratio of the integration of the signal due to the ammonium group of the substituent (singlet, 2.5 ppm) and the sum of the integration (normalized to 1) of the signals due to the anomeric proton (multiplets, 3.8 to 4.6 ppm).

The average molecular weights (M_w) of native hemicelluloses were determined by gel permeation chromatography (GPC) on a Dionex system using Polysep GFC columns (P3000, P4000, NaOH pH 11.7, 0.5 mL/min, 23 °C). Detection was performed with a Shimadzu RID-10A refractometer along with a UV-Vis PDA100 spectrophotometer. Calibration was performed with dextran standards (M_W: 5000; 12,000; 25,000; 50,000; 80,000; 150,000; 270,000; and 410,000).

Reaction efficiency (RE) was determined by the ratio of the amount of grafted reagent compared to the amount of reagent initially introduced in the medium

Handsheet Preparation and Study of Physical Properties

Preparation of additive solutions

The commercial cationic starch was added into a pulp slurry as a gel solution obtained after cooking in water at 90 °C for 1 h. Hemicellulose derivatives were added as aqueous solutions at 3 g/L prepared by solubilisation at 80 °C for 1 h.

Paper pulp slurry and handsheet making

The base stock slurry consisted of a hardwood bleached kraft pulp refined at 34°SR (mixture of birch, beech and eucalyptus in equal proportions). The fibers were re-slushed in water at a concentration of 3 g/L (0.3% consistency) before making handsheets.

Handsheets were made firstly on the FRET device (Handsheet Retention Tester, Techpap), which can form handsheets at near headbox consistency and allows recovering

of filtrates after the sheet formation. The hemicellulose derivatives were added directly to the pulp slurry contained in the FRET bowl and mixed at 1000 rpm for a contact period of 1 min before handsheet formation. Handsheets were made by draining the mixed slurry through a metallic wire cloth (Martel Catala, Tricot 25/cm (40 mesh), newsprint grade) under a 400 mbar vacuum pressure). Each formed handsheet was then dried on a Rapid Köthen Drying device (Sms-Labo) for 7 min at 93 °C. The targeted handsheet grammage was 75 g/m². The FRET handsheet former also makes it possible to assess possible improvement of sheet formation with added hemicelluloses (otherwise difficult to detect on a standard laboratory handsheet former).

Physical properties

The physical tests were performed on handsheets according to the following standard methods: pre-conditioning (NF EN 20 187, 1993), burst index (NF EN ISO 2758, 2004, using a RegMed MTA-1000P burst tester), tensile index (NF EN ISO 1924.2, 1995, using a RegMed-DI500 tensile tester), tear index (NF EN 21974, 1994, using a Twin-Albert Protear® tester), and brightness (ISO/CD 2470-2, 2006, using a Technidyne Color Touch brightness meter). Homogeneity of the sheet formation was measured on an Epair 2D device (Techpap); the transmitted light image of the sheet was characterized by spectral analysis, which calculates an index related to floc size distribution.

RESULTS AND DISCUSSION

Solid State Synthesis of Cationic Hemicelluloses

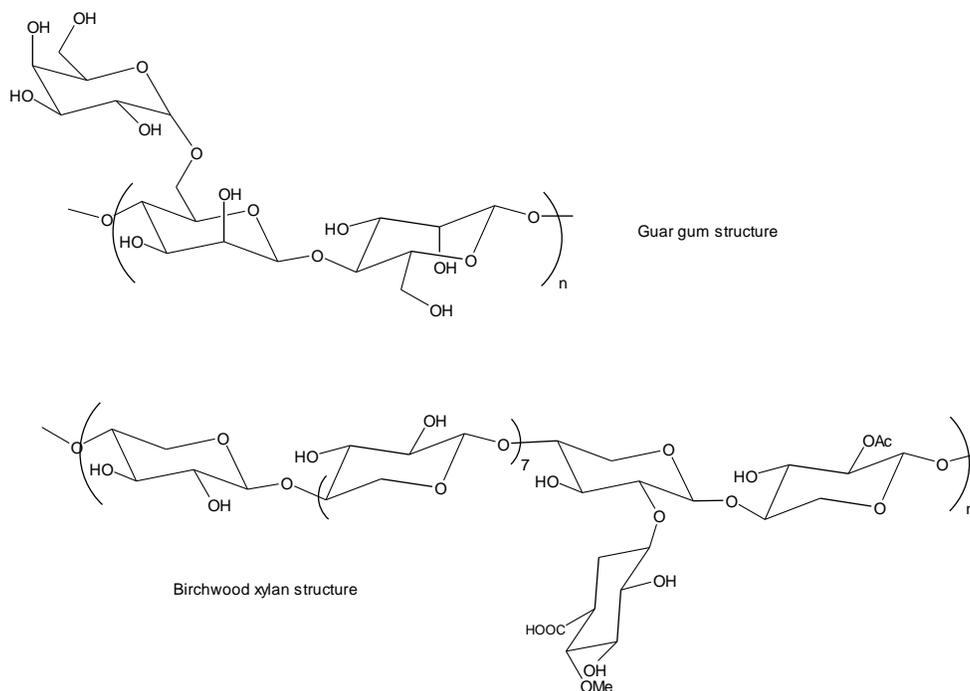The solid phase cationization synthesis was evaluated with two types of hemicelluloses (Fig. 1).

Fig. 1. Guar gum and birchwood xylan structures

The first one was a galactomannan-type (guar gum) composed of a backbone of β-1,4-D-mannopyranosyl units, branched with α-1,6-D-galactopyranosyl unit every two units, yielding a mannose/galactose ratio of 2:1. This hemicellulose is characterized by a degree of polymerization (DP) of about 6000 and a high level of branching (Cheng *et al.* 2002). The average number of OH functional groups per sugar unit (hexose) is 3. The dry galactomannan formed a gel when placed into water, even at low concentrations. The propensity of guar gum to form gels requires that highly diluted solutions must be used, which leads to low productivity. Initially, the free volume saturation of guar gum determined with water reached 4 mL/g. However, when sodium hydroxide solution was used (25 wt.%), the volume was considerably reduced to *ca.* 1 mL/g. Typically, the maximum volume of solution (caustic soda solution and epoxide) introduced on the guar gum is 1 mL/g.

The second type of hemicellulose was a birchwood xylan, which is a more linear polymer consisting of β-1,4-D-xylopyranosyl units as the backbone with 10% substitution of the C-2 hydroxyl groups with 4-*O*-methyl-D-glucuronic acid (Fig. 1b). Its degree of polymerization is relatively low at about 200. The average number of OH functions per sugar unit (pentose) is 2. Two different birchwood xylan samples were compared in this study, commercial and in-house extracted samples (com. and ext., respectively). With this polysaccharide, only 0.7 mL/g of solution can be used to maintain solid state.

The measured average molecular weights, as determined by gel permeation chromatography, are reported in Table 1. The DP obtained for the galactomannan was in accordance with the theoretical value of about 6000. Concerning the xylan hemicellulose, DP values of about 500 to 600 were obtained, which appears to have been slightly overestimated when compared to the expected values (200 to 400). These values show that the molecular weight of the ext. xylan is scarcely lower than the com. xylan one, which could influence their reactivity.

Table 1. Molecular Weights (M_w) and Corresponding Degrees of Polymerisation (DP) for the Three Hemicelluloses

Hemicellulose	M_w (g•mol^{-1})	*DP*
Model galactomannan	1,080,790	6059
Com. xylan	98,066	586
Ext. xylan	81,319	466

The aim of this study was to maximize the species concentration to improve the reaction efficiency. Therefore the cationization of the hemicelluloses was carried out in a solid phase. Following this objective, the solid was impregnated with a minimal amount of concentrated aqueous solutions of sodium hydroxide and cationic reagent, in order to prevent the dissolution and to minimize the swelling of the hemicelluloses.

The results of the cationization in dry phase and in aqueous medium were compared in terms of:
- DS value: number of grafted cationic functions per sugar unit. DS_{max} is the highest DS that could be obtained under the reaction conditions.
- Reaction Efficiency (RE).

As a preliminary parameter, the effect of the reaction time on the DS was studied for the different hemicellulose types at 60 °C. It was observed that the DS value reached a plateau level after a 60-min reaction period with all the polysaccharides, but the initial reaction rate was higher for the galactomannan when compared to the xylans (Fig. 2). This could be attributed to the higher reactivity of the primary hydroxyl groups of galactomannan. However, in all cases, the reaction was completed after one hour as compared to several hours for the reaction in liquid phase (Bigand *et al.* 2011).
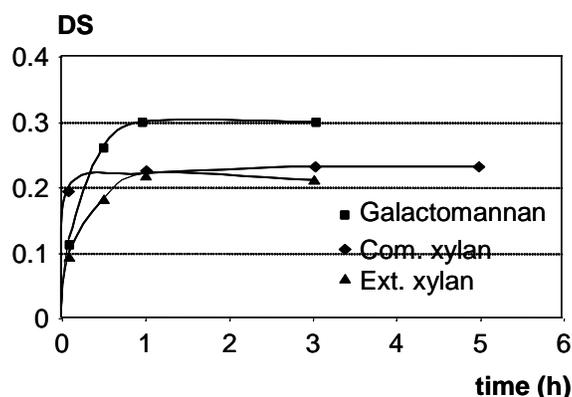

Fig. 2. Evolution of DS as a function of time of the galactomannan and of the commercial (com.) and extracted (ext.) xylans. Conditions: 60°C, 0.12 equiv./OH of ETA

Optimal NaOH Amount

We first studied the influence of the sodium hydroxide amount on the DS. The NaOH equivalents were modulated from 0.05 to 0.3 equiv./OH (Fig. 3), by varying the concentration of the NaOH solution while preserving a constant volume of hemicelluloses impregnation. The amount of ETA was kept constant at 0.12 equiv./OH using the highly concentrated commercially available ETA solution (80 wt.%). The results are presented in Fig. 3.
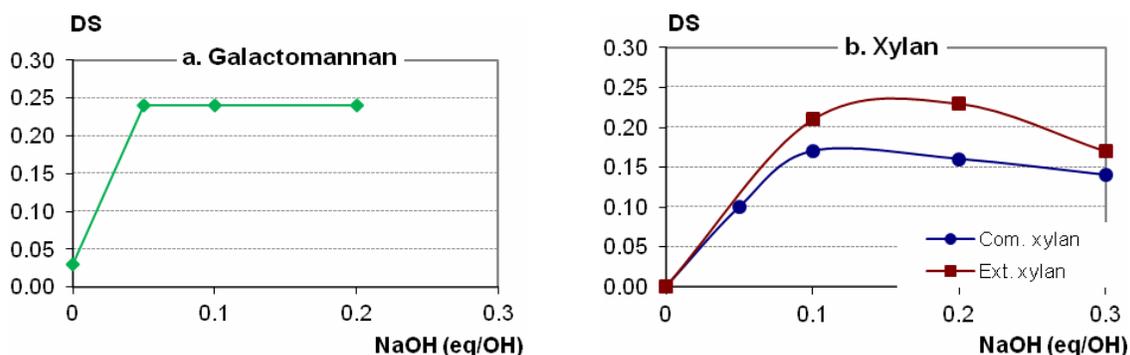

Fig. 3. Evolution of DS as a function of sodium hydroxide amount in the case of (a) the galactomannan and (b) the commercial (com.) and extracted (ext.) xylans. Conditions: 60 °C, 5 h, 0.12 equiv./OH of ETA

By varying the sodium hydroxide level, the DS values went up to *ca.* 0.24 for the three polysaccharides. Note that the presence of the alkali was essential while performing

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this reaction in dry phase, since the DS values obtained without alkaline medium was close to zero.

Here, we found the optimal amounts of NaOH to be 0.05 equiv./OH for the galactomannan (versus 0.25 equiv. in aqueous media) (Bigand *et al.* 2011) and 0.1-0.15 equiv./OH for the two xylans (versus 0.4 equiv. in aqueous media) to obtain a DS of 0.18 to 0.25. Therefore, the required amounts of caustic soda are considerably reduced when compared to the case where the reactions are performed in aqueous medium. Here, the catalytic activity of the base was enhanced with the reaction conducted in dry state, since the number of substituted hydroxyl groups were well above the equivalents of base used to obtain a DS value ≥0.2.

The DS evolution profiles were close to those obtained in aqueous medium (Bigand *et al.* 2011). In the case of the galactomannan, the DS value remained constant after increasing the NaOH amount beyond 0.05 equiv./OH, while it started to decrease at > 0.2 equiv./OH in the case of xylans. Com. and Ext. xylans had the same DS evolution profile, with DS values slightly higher for the in-house extracted xylan. One explanation is that the latter had a lower molecular weight, which could facilitate contact with the cationic reagent. Moreover, due to the presence of lignin (up to 12%), a slight excess of ETA was used in that case.

The optimal amount of NaOH was lower for the galactomannan than for xylans (0.05 vs 0.1 equiv./OH). This can be clearly attributed to the presence of more reactive primary OH function groups in galactomannan, while only secondary hydroxyl groups are present in xylan.

The reaction efficiencies (RE), calculated from the degree of substitution, as well as the mass yields are reported in Table 2.

Table 2. RE and Mass Yield Obtained for the Three Cationic Hemicellulose Types Prepared in Dry State or in Solution (Bigand *et al.* 2011)

	Hemicellulose	ETA / OH	DS_{max}	DS_{obs} (±0.01)	RE (%)	Mass yield (%)
Dry State	Galactomannan	0.12	0.36	0.24	67	80
	Com. Xylan	0.12	0.24	0.17	71	85
	Ext. Xylan	0.12	0.24	0.22	92	70
Solution	Galactomannan	1	3	0.21	7	80
	Com. Xylan	1.5	3	0.4	14	80

The reproducibility of the reaction was evaluated in some cases, and it was established that the standard deviation of the DS determined by NMR analysis was ±0.01. The DS deviation should be due to the cationisation experiment itself rather than the NMR determination. For comparison, RE's and mass yields achieved for solution reactions for similar DS are reported in Table 2.

It is clear that RE's of the cationization were considerably higher when the reaction proceeded in a dry phase. In the case of the galactomannan, the DS_{obs} obtained in the presence of 0.12 equiv./OH of ETA was 0.24, corresponding to a RE of 67%. This

value is ten times higher than the RE obtained for the reaction in aqueous medium (maximum 7% due to the gel viscosity). In other words, a similar DS value was obtained by using ten times less of cationic reagent than in aqueous medium (1 equiv./OH). The reactivity of the two xylans was slightly different with a DS_{obs} of 0.17 for the commercial one and 0.24 for the in-house extracted one, corresponding to RE's of 71% and 92%, respectively. When prepared in solution, RE reached 14% for the cationization of the commercial model xylan corresponding to DS = 0.4.

In all cases, reaction efficiencies were improved in a dry phase compared to the synthesis in a liquid phase, while considerably reducing the amounts of the expensive cationizing reagent used. It is now possible to achieve the same RE for the two commercial hemicelluloses by excluding the solubilisation limits in water, and this shows clearly the advantage of this method. The mass yields were similar to those obtained after the reaction in aqueous solution with values of about 80 to 90%. Moreover, a significant improvement concerns the work-up of the reaction since only one purification step (solubilisation-precipitation) is necessary with this method, while two purification steps are required after the cationization in water. This allows decreasing the amount of solvent and reagents, thereby participating in a greener process.

Influence of the Cationic Reagent Amount on DS and RE

In order to prepare cationized hemicelluloses with higher DS, the amount of cationization agent (ETA) introduced in the system was increased (see Fig. 4).
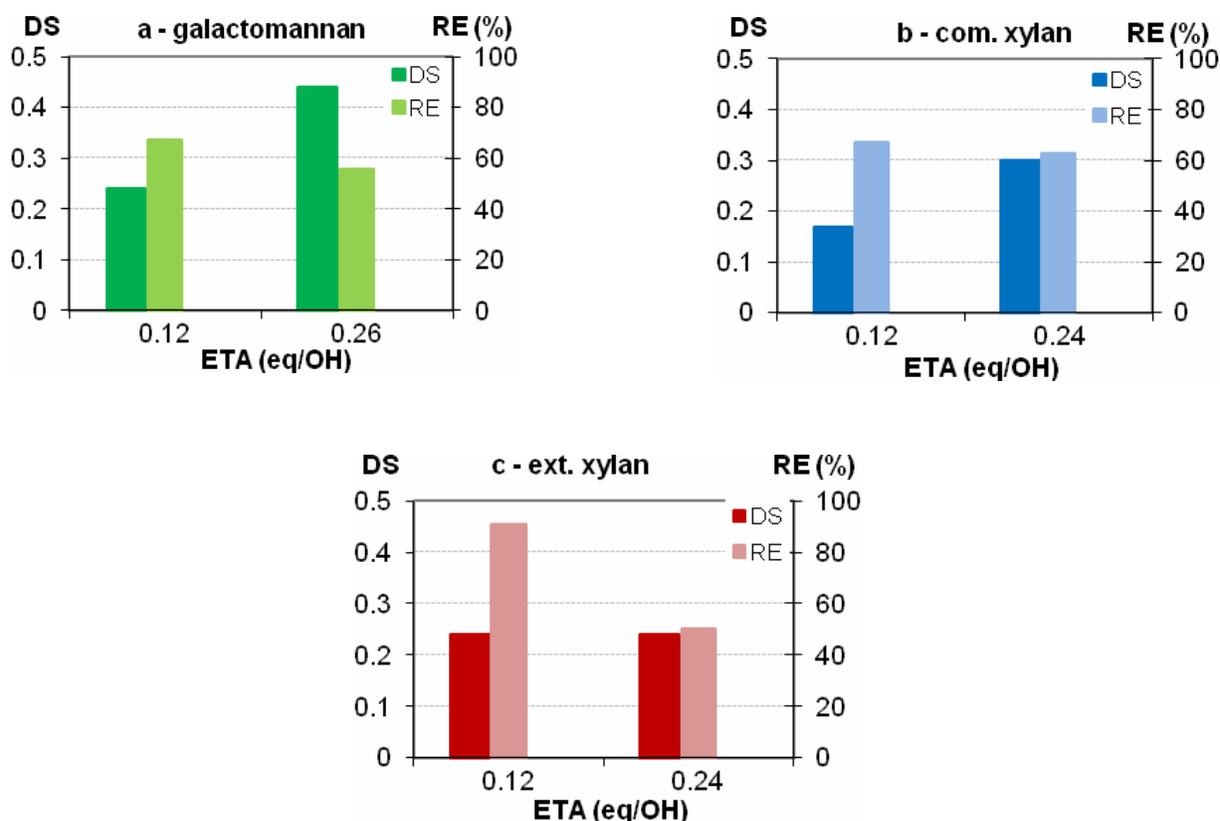

Fig. 4. Evolution of DS and RE as a function of the epoxide amount in the case of (a) the galactomannan, (b) the commercial xylan, and (c) the extracted xylan. Conditions: 60 °C, 5 h, 0.2 equiv./OH of NaOH, dry state preparation.

It was observed that the three hemicelluloses did not behave identically upon the addition of the cationization agent. To maintain the reaction in the solid state, the maximum operating amount of ETA was determined for each polysaccharide, which slightly differs from one to the other. This should be due to different absorption capacities of the polymers. Indeed, the galactomannan type is able to absorb more liquid in its structure than the xylan type which is due to its network structure where molecules can be easily inserted. Figure 4 shows the influence of the ETA amount for each of the hemicellulose, as well as the resulting DS and RE values.

In the case of the galactomannan, the ETA amount could be increased up to 0.26 equiv./OH, resulting in a DS value of 0.44. Since the epoxide amount increased, the reaction efficiency decreased slightly to 56%. The com. xylan could be impregnated with a maximum of 0.24 equiv./OH of epoxide, leading to a DS value of 0.30, while maintaining a high RE of 63%. On the other hand, when the extracted xylan was impregnated with 0.24 equiv./OH ETA, a small part of the solution was not absorbed by the solid and did not react, thus resulting in an unchanged DS value of 0.24, which corresponding to a RE of 50%. The absorption capacity of the polysaccharides is mainly related to their structure and molecular weight. Galactomannan is more suitable for this kind of reaction due to network structure and a high molecular weight. In the case of xylan, the solid surface is easily saturated, resulting in a DS of 0.30. Nevertheless, this value is sufficient for most of the applications considered for cationic xylans (biologic, cosmetic, *etc*.). We evaluated their properties as a paper additive in comparison with commercially available cationized starch.

Influence of the Presence of Cationic Hemicelluloses on Paper Mechanical and Optical Properties

Cationic derivatives prepared in aqueous solution and in dry state were evaluated as wet-end additives for improving paper mechanical strength. For handsheet preparation, a refined bleached kraft pulp obtained from hardwoods was used with the FRET unit. Hemicelluloses were added in aqueous solution at 3 g/L, with an amount corresponding to 1% or 3% of the mass of the dry matter. Note that no difference in the dissolution behavior was observed when comparing the preparation mode for a given DS. In order to evaluate the ability of the additives to improve paper strength, three mechanical properties were measured: the burst index, the tensile index, and the tear index. In addition, the influence of hemicelluloses on the optical properties of paper was evaluated by measuring the brightness and the homogeneity of sheet formation.

Mechanical properties

The mechanical properties of paper made with the cationic derivatives prepared in the aqueous phase from the two model hemicelluloses (guar gum and xylan) were measured and compared with the native hemicelluloses and the reference cationic starch. Figure 5 shows the variation of the burst index for the different additives, for a level of 1 and 3% (% w/w, dry basis).

The reference cationic starch (HI-CAT 142, DS 0.04), which is currently used as dry-strength additive in papermaking, significantly increased the burst index from 70 to 130% for a level of 1 and 3% dosage, respectively. When native hemicelluloses were added as a strength agent, the burst index gain was limited. Native guar gum was considerably more efficient than native xylan, with a 50 to 60% increase of burst index (Fig. 5a), while the native xylan achieved a slight increase of 9% (Fig. 5b). That was

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attributed to a lower retention of the native xylan on fibers, due to electrostatic repulsion between the ionized glucuronic acid groups on both the added xylan and the hemicelluloses of the pulp fibers (Hannuksela and Holmbom 2004; Kabel *et al.* 2007).
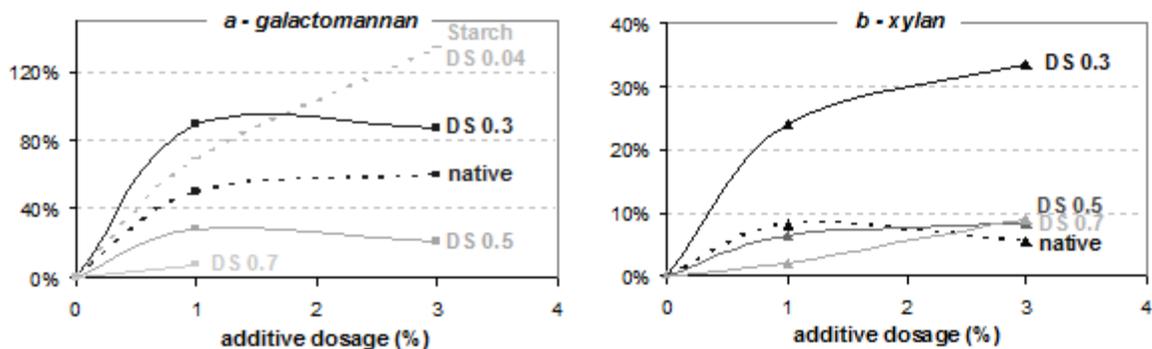

Fig. 5. Burst index variation with cationic derivatives of (a) galactomannan and (b) xylan prepared in liquid phase (increase of burst index over handsheet without additive: reference 0.62 kPa.m²/g)

As shown in Fig. 5, the cationization of the two hemicelluloses before their addition into the pulp slurry reinforced their beneficial effect. For both hemicelluloses, the best effect was obtained with a DS of 0.3; a burst index increase of 90% was observed in the case of the galactomannan, which was higher than the cationic starch at the 1% dosage. In the case of the xylan, a 25% increase in the burst index was observed at 1% dosage, and a 35% increase at 3% dosage. The increase of the DS value to 0.5 and 0.7 did not further improve the burst index, with a gain of burst index comparable to that obtained with the unmodified polysaccharide, in the case of galactomannan and as for xylan.

These tendencies are confirmed with the tear and tensile indexes, with the best gain of properties for derivatives with a low degree of substitution.

Figure 6 shows the strength improvements obtained with the cationic derivatives of DS 0.3 compared to the unmodified hemicellulose. Here the reference is the handsheet to which native hemicellulose had been added, in order to highlight the effect of the cationic groups.
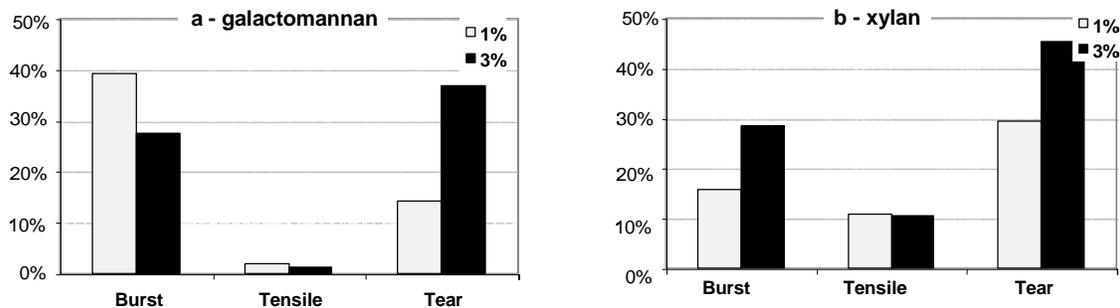

Fig. 6. Gains of mechanical properties obtained with a cationic derivative of DS 0.3 compared to the unmodified hemicellulose in the case of (a) the galactomannan and (b) the xylan (handsheet containing unmodified hemicelluloses additive is the reference).

The introduction of cationic functional groups onto the hemicellulose backbone of these additives greatly improved the tear index, which increased by 38% in the case of

the galactomannan and by 45% for the xylan, for a dosage of 3%. A lower effect was observed on the tensile index, with a moderate increase of 10% in the case of xylan and a negligible change for the galactomannan.

So, an optimal DS value of 0.3 was identified for both hemicellulose types, and the best results were obtained with the galactomannan (Fig. 5). Indeed, polysaccharide derivatives with the higher molecular weight are the most efficient since their capacity to promote inter-fiber bonds is greater (Hubbe 2006). Moreover, derivatives with a DS value too high are generally less efficient because their high charge density prevents them from creating effective links between fibers since they tend to adsorb in a relatively flat conformation due to interaction with their numerous charged positions (Hubbe 2006). In terms of these considerations, the behaviour of positively charged hemicelluloses is similar to that of cationic starch.

Cationic guar can greatly promote inter-fiber bonding through bridging flocculation, due to their high molecular weight, therefore maximizing the physical strength improvements. That is not possible with short chain xylans, which can favor fiber-fiber interaction through a patch flocculation mechanism. Using higher DS hemicelluloses may over-cationize the pulp and re-disperse it. Also, a higher DS decreases the amount of available OH groups to develop inter-fiber hydrogen bonding. So a minimum level of DS is required to favor adsorption, while a DS value too high will impair fiber-fiber bonding. Both of these phenomena explain why an optimum DS (~0.3) was observed for the development of paper mechanical properties.

The retention of the various cationic derivatives onto the fibers was measured by analyzing the sugar content of the filtrates recovered after sheet formation with the FRET device. In the case of xylan, 80% of the added hemicelluloses were retained on the fibers, regardless of the DS value. The same behaviour was observed for the galactomannan with 70% retention for the DS 0.3 and 0.5 derivatives. These observed differences could be related to the derivatives intrinsic properties, and not to their retention values.

Optical properties

The influence of the cationic derivatives on the optical properties of paper was studied by measuring the Epair 2D formation index, which represents the homogeneity of the sheet formation, as well as the Color Touch brightness.

For the homogeneity of sheet formation (Fig. 7a), a decreasing Epair index indicates a better homogeneity of the paper sheet. We observed that the addition of the hemicellulose additives into the pulp slurry favoured a homogeneous distribution of the fiber network during the sheet formation, and avoided the formation of flocs. This effect was more pronounced with the galactomannan since its action was facilitated by its higher molecular weight (Hannuksela *et al.* 2004). Interestingly, the cationized hemicelluloses did not cause over-flocculation of the fiber network, and thus, contribute to pulp de-flocculation in the same way as the unmodified hemicelluloses (Huber *et al.* 2012b). This improved sheet formation also contributes to the development of the mechanical properties.

The brightness of paper somewhat decreased with the utilization of the cationic hemicelluloses (Fig. 7b), which are slightly colored. A higher decrease in brightness was obtained by using xylan derivatives because of their beige to brown colour. In all cases, it will be necessary to bleach such hemicelluloses before using them in white paper grades (on the other hand, their brownish colour would be an advantage in brown board grades).
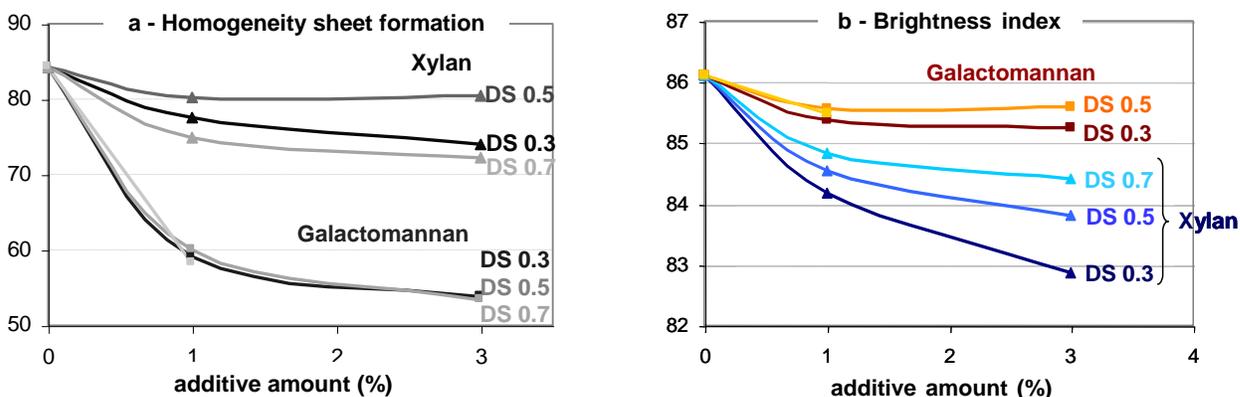
Fig. 7. Influence of hemicellulose derivatives on the optical properties of paper: (a) homogeneity of the sheet formation (%) and (b) paper brightness (% ISO).

Comparison of two xylan samples and influence of low DS value derivatives

In a second part of this study, the properties of the hemicellulose derivatives with DS values lower than 0.3 were examined, and two xylan types were compared. Besides the commercial batch xylan, an in-house extracted xylan was also used. Figure 8 shows the burst index variation for the cationic derivatives of xylan with DS values from 0.1 to 0.3, for the commercial and extracted xylans.
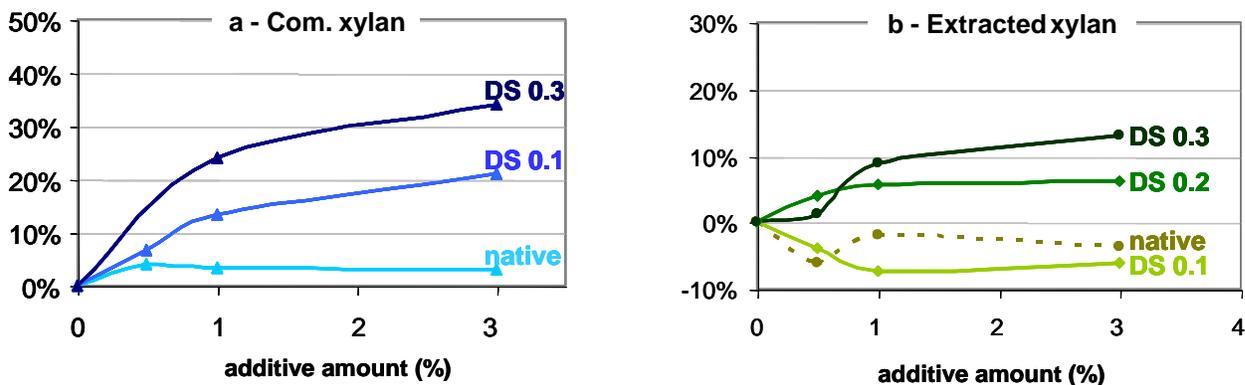

Fig. 8. Burst index variation for (a) commercial and (b) extracted xylan with DS values of 0.1 to 0.3 (prepared in aqueous phase); (increase of burst index over handsheet without additive, reference : 1.12 kPa.m²/g)

It was observed that DS values lower than 0.3 for both xylans did not substantially improve the mechanical properties. In the case of the commercial xylan, a 20% increase of the burst index was obtained with a DS of 0.1, at a dosage of 3% (30 mg/g). A DS value of 0.2 was required by extracted xylan to obtain a nominal gain in burst index at the addition levels examined. Then, from the range of DS studied (from 0.1 to 0.7), an optimal DS value of 0.3 has been highlighted. In the literature, the majority of studies for either cationized xylan or galactomannan indicate that the optimal DS for such applications falls in the range of 0.1 to 0.2 (Köhnke *et al.* 2009; Rojas and Neuman 1999; Schwikal *et al.* 2011). On the other hand, a report showed that for cationised xylan, an optimal DS of 0.37 was obtained (Ren *et al.* 2009). Therefore it seems that comparison to

earlier results is not straightforward, and many parameters other than DS can influence the final properties.

The performances of the extracted xylan were lower than the commercial xylan with a maximum burst index increase of 13%. These tendencies were also confirmed with the tear and tensile indices, with a 15% point gap between performances of the commercial and extracted xylans with a DS of 0.3. This could be due to the lower molecular weight of the extracted xylan or to the presence of lignin and other sugars in the sample.

Influence of the preparation method of the cationic derivatives

Finally, the influence of the method of preparation of the cationic derivatives was studied. For this purpose, the properties of cationic derivatives with the same DS value prepared by the two methods were compared. Concerning the galactomannan, the derivatives prepared in dry state showed the same efficiency as the derivatives prepared in aqueous solution (not shown). In the case of xylan, the influence of the preparation method was observed for the burst index variation. It appeared that the samples prepared by the dry state method were less effective than samples prepared in aqueous solutions, with a loss of 10% points in burst index increase for both xylans (Fig. 9).
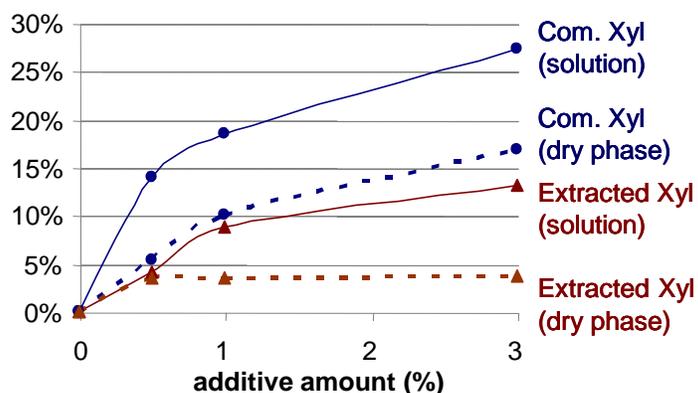

Fig. 9. Burst index variation of xylans with DS 0.3 prepared in aqueous solution and in dry state (increase of burst index over handsheet without additive, reference without additive: 1.14 kPa.m²/g)

These tendencies were not so obvious for the tear and tensile indices, since no differences of tensile index were observed between samples prepared by one or the other method. Concerning the tear index, a better efficiency of the sample prepared by the solid state method was obtained with the extracted xylan, while the inverse was observed for the commercial xylan. Globally, a minor loss of properties was observed for derivatives prepared by the dry state method.

The difference between the two syntheses is that in the solid phase reaction, the highly concentrated sodium hydroxide solution is directly in contact with the hemicellulose backbone due to the very low amount of solvent. Then the alkaline hydrolysis of the hemicellulose chains could be more important in the dry phase than in aqueous solution, resulting in lower properties for the corresponding derivatives. Unfortunately, we could not determine the polymerisation degrees of the derivatives to confirm this hypothesis.

CONCLUSIONS

1. The cationization of different hemicellulose types in the solid phase has been studied. This method has some advantages compared to the case where the reaction is performed in liquid medium.

2. The solid-phase process minimized the reagent amounts and reaction time needed to obtain the maximum DS, globally yielding better reaction efficiencies. The purification procedure was simplified, contributing to better efficiency by preventing the loss of final product and limiting waste solvents. This method was more appropriate for galactomannan-type hemicellulose, but can also be applicable to xylan-type hemicelluloses. DS values of 0.10 to 0.30 were obtained for the xylan-type, and up to 0.44 for the galactomannan-type. These values were in agreement with the ones typically used in most applications targeted for these cationic polysaccharides.

3. The use of cationic derivatives of hemicelluloses as wet-end paper strength additives was demonstrated.

4. The introduction of cationic functional groups along the polymer backbone resulted in a gain of efficiency compared to the native polysaccharides. From all the tested derivatives, it appeared that the galactomannan derivatives were more efficient than the xylan derivatives, due to their difference in structure and their molecular weights. A range of cationic derivatives with DS values from 0.1 to 0.7 was evaluated, and an optimal DS value of 0.3 was observed. If low DS values are generally employed for the cationic starch (0.02 to 0.04), higher DS values are required in the case of the hemicelluloses in order to be efficient. The gain of mechanical properties obtained with the cationic hemicelluloses is at the moment insufficient to completely replace the cationic starch. The importance of the molecular weight of the polysaccharides involved in the inter-fiber bonding has been pointed out; therefore other chemical modifications like crosslinking of the xylan chains should be investigated in order to increase their molecular weight.

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