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Seed storage hemicelluloses as wet-end additives in papermaking☆

Denis U. Lima[a], Rubens C. Oliveira[b], Marcos S. Buckeridge[a,*]

[a]*Seção de Fisiologia e Bioquímica de Plantas—Instituto de Botânica, Caixa Postal 4005, CEP 01061-970, São Paulo, SP, Brazil*
[b]*Departamento de Engenharia Florestal, Universidade Federal de Viçosa, Campus Universitário s/n, 36571-000- Viçosa, MG, Brazil*

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Abstract

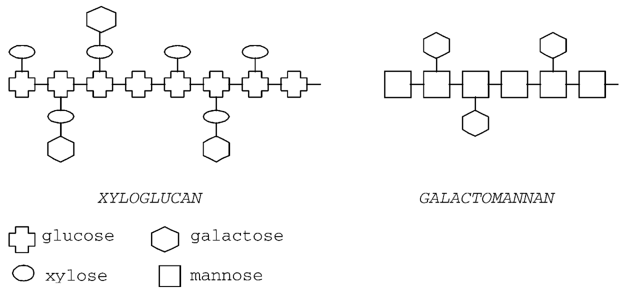
Xyloglucans and galactomannans are examples of hemicelluloses that can be accumulated in seeds of many plants, being extensively studied and used for industrial applications. Guar gum and starch are polysaccharides currently used as wet-end additives in papermaking, whereas xyloglucans have never been reported to improve paper quality. In this work we show that different types of xyloglucans improved the mechanical properties of paper sheets without affecting the optical ones. Addition of 1% (w/w) of hemicelluloses to cellulosic pulp was able to increase by about 30% the mechanical properties such as burst and tear indexes. Seeds of several species could be used as source for the production of wet-end additives, since the results did not vary with the source of polysaccharides. Even if the utilisation of these hemicelluloses will not cost less than starch or guar gum, it might represent an important strategy for sustainable use of rainforest species.

Keywords: Hemicellulose; Xyloglucan; Galactomannan; Papermaking; Wet-end additives; Industrial application; Seed

1. Introduction

Hemicelluloses are plant cell wall polysaccharides closely associated to cellulose. Unlike the former, the cellulose is formed only by β-(1,4) glucosyl linkages in a linear backbone whereas hemicelluloses are branched polymers composed of several monosaccharides, which confer to this class of cell wall polysaccharides a higher level of complexity. Xyloglucans and galactomannans are the principal hemicelluloses found in the primary cell wall of dicotyledonous plants, where their interaction with cellulose plays a key role in the properties of the wall. In secondary walls of seeds from several species these hemicelluloses serve as storage polysaccharides. (Buckeridge, Dietrich, & Lima, 2000a).

Xyloglucan has a cellulose-like glucan backbone to which units of xylose and xylosyl-galactose disaccharides are attached to the main chain as seen below.



Xyloglucans with different structural features are known to interact specifically with cellulose (Lima & Buckeridge, 2001; Vincken, Keizer, Beldman, & Voragen, 1995). The basis for such interaction is thought to be the similarity of the backbone of xyloglucans to cellulose (both β-1,4 linked glucans). This binding capacity seems to be altered by the degree of galactosylation and/or by the distribution of galactosyl residues along the main chain (Lima & Buckeridge, 2001).

Galactomannans (schematically shown above) are composed of a linear backbone of β-(1 → 4) linked mannose, branched with single units of galactosyl residues. This polysaccharide is widely found as a storage compound in seeds of leguminous species (Buckeridge, Santos, & Tiné, 2000b; Dea & Morrison, 1975).

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* Corresponding author. Address: Instituto de Botanica, Secao de Fisiologia e Bioquimica, Avenida Miguel Stefano 3678 Agua Funda, Sao Paulo 04301-902, Brazil. Fax: +55-11-577-3678.
E-mail address: msbuck@usp.br (M.S. Buckeridge).

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The accumulation of hemicellulose in seeds can reach ca. 40% of seed dry mass (xyloglucan in cotyledons of *Hymenaea courbaril* and galactomannan in endosperms of *Dimorphandra mollis*, for example) (Buckeridge et al., 2000a). These hemicelluloses differ strongly from polysaccharides extracted from wood pulps. In softwood glucomannans and galactoglucomannans are present in large proportions, whereas glucuronoxylans dominate in the hardwood hemicelluloses (El-Ashmawy, Mobarak, & Fahmy, 1973; Sjostrom, 1981).

It has been demonstrated that the presence of soft or hardwood hemicelluloses in the cellulosic pulp can improve some features of papermaking. The time and energy utilised to achieve a required fibrillation level can be diminished during the refining process in the presence of hemicellulose. The plasticity and the high superficial area conferred by hemicelluloses result in an increased binding among the fibres and a higher tensile strength in the paper sheet. However, high amounts of hemicelluloses seem to be deleterious to the mechanical properties of the paper due to a decrease in the individual fibre resistance and to the optical properties due to the low opacity in the paper sheet (Senai/IPT, 1998).

The information cited above were obtained from studies that analysed only wood hemicelluloses based on xylan and mannan groups. Other wet-end additives, such as guar gum (galactomannan) and starch, are often used on account of their adsorption behaviour. These additives improve the mechanical properties of paper by regulating the state of flocculation in the cellulosic fibre suspension during the sheet-forming process.

The effects of guar gum, glucomannan and starch derivatives on paper properties are well documented (Abson & Brooks, 1985; Blumenthal & Paul, 1994; Sundberg, Holmbom, Willfor, & Pranovich, 2000). However, the utilisation of xyloglucans as wet-end additives is firstly shown in this work. The data obtained here showed that the use of storage hemicelluloses (such as xyloglucan and galactomannan) might improve some of the mechanical properties of the paper sheet without altering the optical ones.

2. Material and methods

2.1. Plant material

Hemicelluloses: Storage xyloglucans were obtained from seeds of *H. courbaril* L. (jatoba), *Copaifera langsdorffii* Desf.(copaiba), *Tamarindus indica* L. (tamarind) and *Tropaeolum majus* L. (nasturtium). Galactomannan was obtained from seeds of *Dimorphandra mollis*. The polysaccharides were extracted from cotyledon powders (or endosperm for galactomannan) with water (1% w/v) at 80 °C for 8 h with constant stirring. After filtration, 3 volumes of ethanol were added to the aqueous extracts, kept overnight at 5 °C and centrifuged (12,000 g for 15 min at 5 °C). The pellet was partially dried at room temperature and, after resuspension in water, freeze-dried.

2.2. Methods

Sheet formation: Five sheets were formed for each treatment according to ABTCP norms (Brazilian Technical Association of Pulp and Paper). These sheets were made to have a grammage (weight per unit area) of ~ 60 g/m^2 and a thickness of 0.110 mm. The pulp was obtained from wood of *Eucalyptus* sp by the kraft process being subsequently delignified and bleached. The refining process was performed to achieve ~ 30°SR (Schopper–Riegler degree). This unit (°SR) is related to the degree of refining process of the cellulosic pulp. The higher the SR degree the higher the refining (from 0 to 100°SR). The mechanical properties are improved with the higher °SR, however, it leads to a higher expenditure of energy.

Aqueous solutions of hemicelluloses (xyloglucans and galactomannan) were added to the pulp fibre during homogenisation before sheet formation.

Properties analysed: Burst Index—BI (ABTCP P8/1994), Tear Index—TI (ABTCP P9/1994), Porosity (ABTCP P11/1994), Capillarity (SCAN-P 13:64) and Water Retention Value—WRV (LCP 01 pp-96), Brightness (ABTCP P16/1994) and Opacity (ABTCP P18/1994). Tensile Index, Tensile Energy Absorption—TEA and Specific Elastic Modulus—SEM (given as Mega Newton meter per kg of paper or MPa per kg m^{-3}), were performed automatically using an Instron tester (Instron Corporation-Series IX system 1.09).

The samples were kept and analysed under controlled environment (temperature of 23 ± 1 °C and RH of 50 ± 1%) according to ABTCP (P4/1994).

In order to determine the optimal concentration and time of homogenisation for testing all the hemicelluloses used in this work, xyloglucan from seeds of *T. indica* was used for preliminary assays.

Variations tested: (1) the amount of hemicellulose added (0–10% w/w—hemicellulose/pulp fibre); (2) the time of homogenisation; (3) refining or non-refining of pulp fibres; (4) the addition of hemicellulose before and after the refining process and (5) the effects of different hemicelluloses added.

3. Results and discussion

3.1. Optimisation of assays

Aqueous solutions of xyloglucan were added to the cellulosic pulp at 0, 0.25, 0.50, 1.0, 2.5, 5.0 and 10% (w/w–xyloglucan/pulp fibre) (Fig. 1). The additions were performed during the homogenisation process of the pulp just before sheet formation. Excluding the tensile (Fig. 1B)

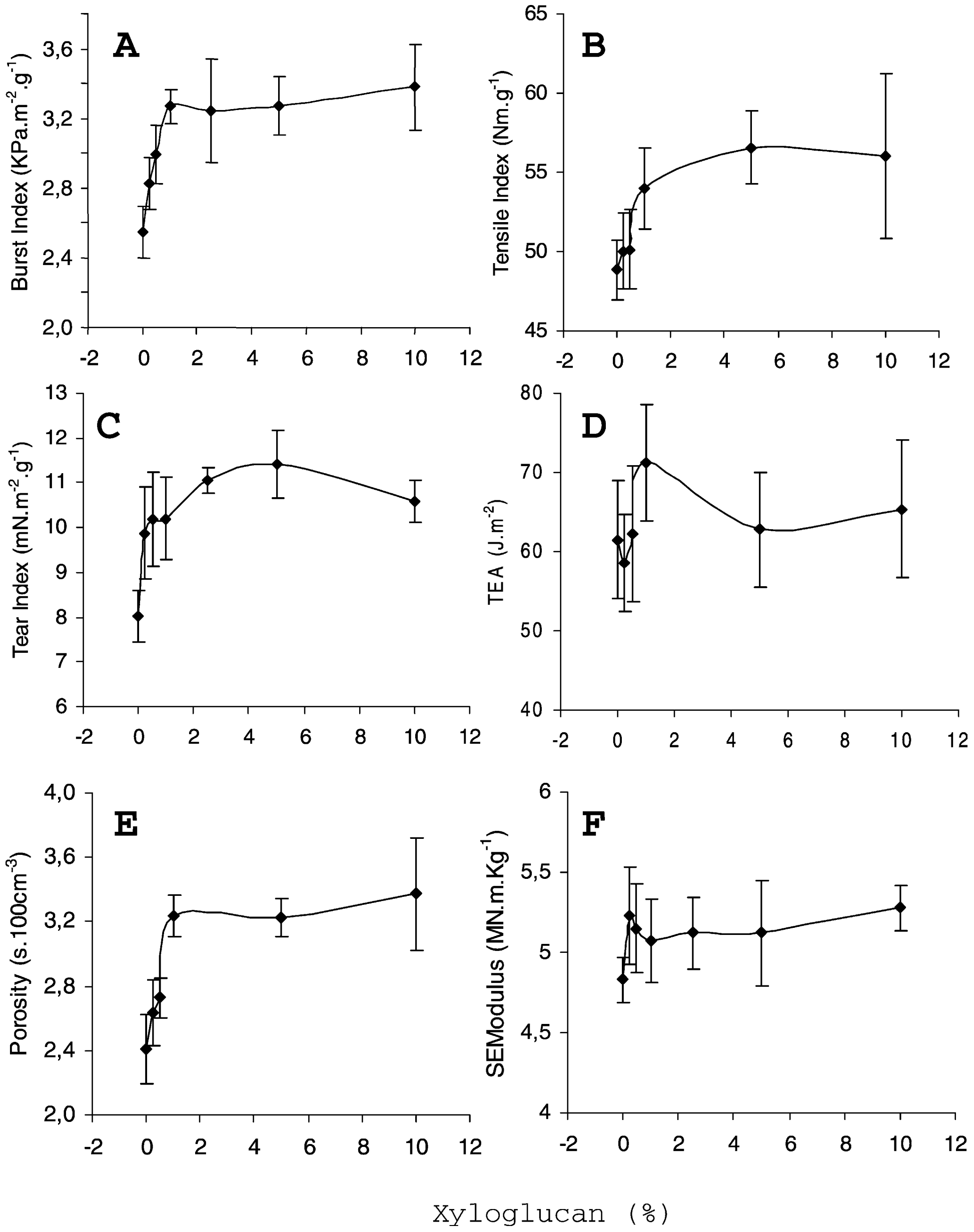

Fig. 1. Optimisation of the concentration of hemicellulose added to cellulosic pulp. The assays were performed with *T. indica* xyloglucan at 0, 0.25, 0.50, 1.0, 5.0 and 10% (w/w) final concentrations. Methods and analysis were performed according to ABTCP norms. TEA—Tensile Energy Absorption; SEModulus—Specific Elastic Modulus (given as Mega Newton meter per kg of paper or MPa per kg m^{-3}, but it is an unusual unit in paper application).

and tear (Fig. 1C) indexes analyses, the further mechanical parameters reached the maximum improvement at 1% of added xyloglucan. The tensile and tear indexes were maximal at 5% of added xyloglucan (Fig. 1B and C).

The time necessary for complete homogenisation of hemicelluloses and pulp fibres was also tested. There was no significant difference in the mechanical properties when the solutions were kept under homogenisation either for 1 or for 18 h (data not shown). This suggests that the hydrogen bonding seems to occur immediately after the mixture of polysaccharides, as already shown by Lima and Buckeridge (2001) and Rojas and Neuman (1999).

The optical properties analysed (brightness and opacity) were not affected by the presence of xyloglucan or galactomannan, even when the mixtures were made with high hemicellulose concentrations (10%, data not shown).

Hence, the subsequent analyses were performed at a final hemicellulose concentration of 1% (w/w) with 20 min of homogenisation.

3.2. Effects of hemicelluloses in non-refined pulp

The addition of xyloglucan or galactomannan to the non-refined pulp fibres did not affect the mechanical

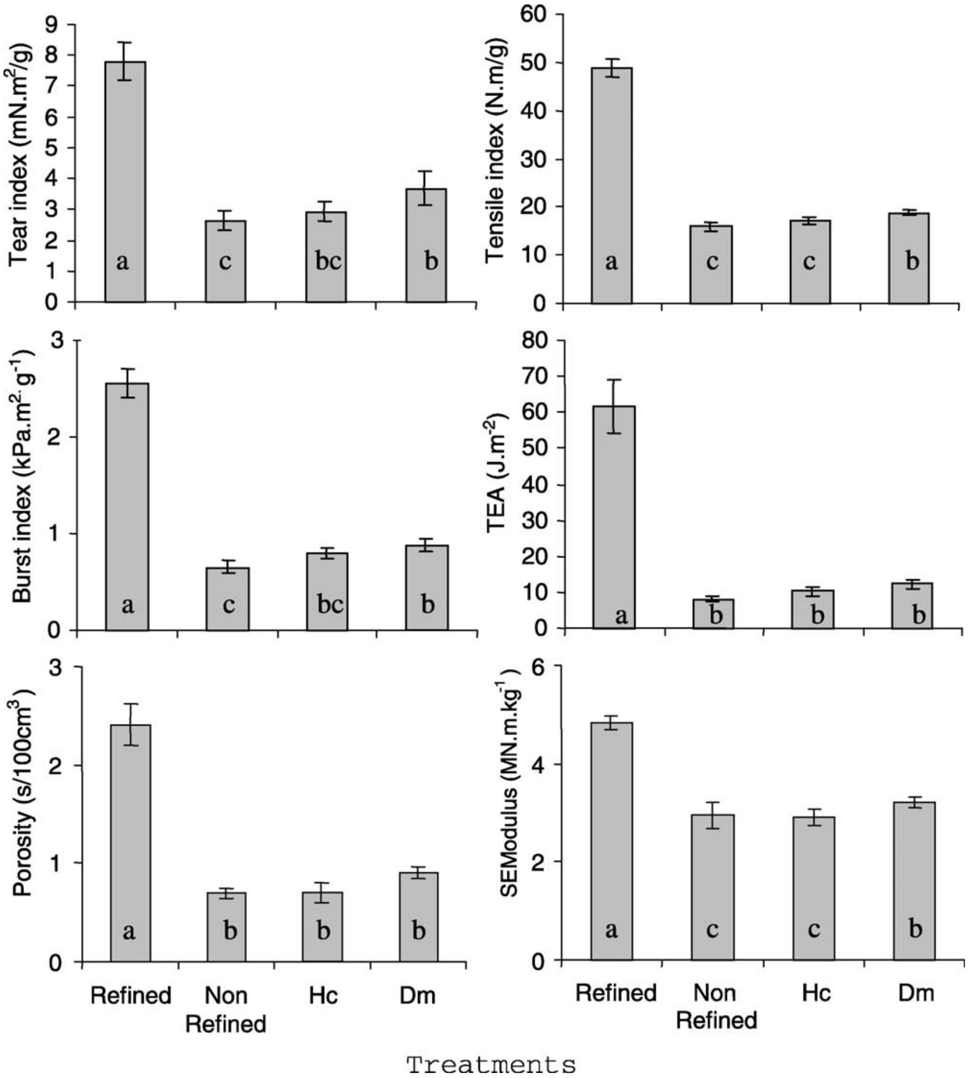

Fig. 2. Effects of hemicelluloses on non-refined pulp. Refined pulp without hemicelluloses was the control sample. Hc—non-refined pulp with *H. courbaril* xyloglucan; Dm—non-refined pulp with *D. mollis* galactomannan. The assays were performed with hemicelluloses at a final concentration of 1% (w/w). Methods and analyses were performed according to ABTCP norms. TEA—Tensile Energy Absorption; SEModulus—Specific Elastic Modulus (given as Mega Newton meter per kg of paper). The data were averaged from 5 sheets and the bars represent the standard deviation. Different letters represent statistical differences according to Tukey test ($P < 0.05$).

properties (Fig. 2) in comparison to refined pulp without wet-end additives. The addition of galactomannan from *D. mollis* promoted a slight improvement but was irrelevant compared to the control of refined pulp. The values obtained by the treatments of non-refined pulp were about 80% lower than the refined one, even when the hemicelluloses were added during the sheet formation. The refining of pulp fibres is a mechanical process (beating) that increases the number of bond-forming sites on the fibre surface as well as the number of interfibre bonds due to the higher superficial area produced. The absence of effect of hemicelluloses on non-refined pulp could be explained by the lower capacity of binding to those cellulose fibres, resulting in paper sheets with lower values of mechanical properties.

Fig. 3 shows the effect on the mechanical properties of the addition of xyloglucan before and after the refining process. It was observed that the addition of hemicellulose after beating, specifically during the homogenisation of the pulp, had better effect on the properties analysed, excepted for TEA and SEModulus. The data obtained from the pulp refined in the presence of xyloglucan showed an intermediate level (Fig. 3). It has already been observed that the presence of xylan-based hemicellulose (from wood) during beating could also improve some properties of the resulting pulp (Senai/IPT, 1998).

The results showed that the addition of wet-end additives, such as xyloglucans or galactomannans, achieve a better response when they are added after refining, possibly due to a higher H-bond formation between cellulose and hemicellulose.

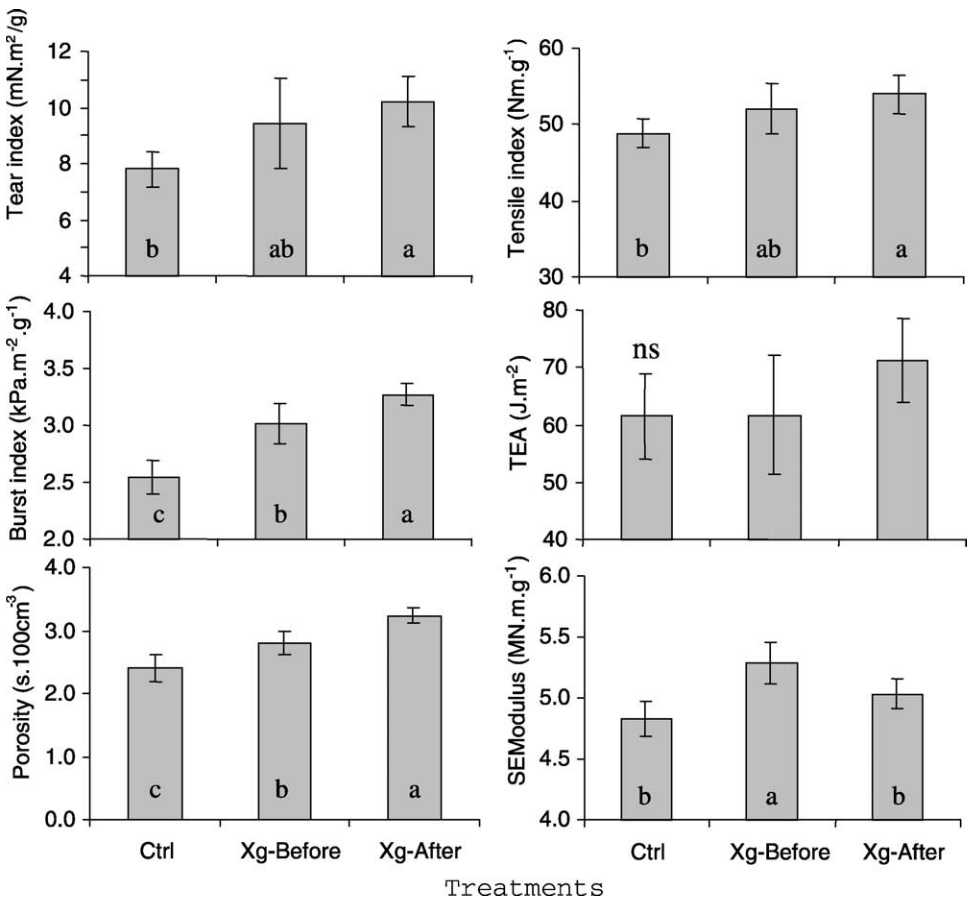

Fig. 3. Effect of the addition of *T. indica* xyloglucan on the mechanical properties before and after the refining process. Control samples were performed without hemicelluloses. The assays were performed with hemicelluloses at final concentration of 1% (w/w). TEA—Tensile Energy Absorption; SEModulus—Specific Elastic Modulus (given as Mega Newton meter per kg of paper). The data were averaged from 5 sheets and the bars represent the standard deviation. Different letters represent statistical differences according to Tukey test ($P < 0.05$). ns—not significant.

3.3. Comparison of effects of different hemicelluloses

Xyloglucans from seeds of *H. courbaril*, *T. majus*, *T. indica* and *C. langsdorffii*, and galactomannan from *D. mollis* were added to the cellulosic pulp during paper sheet formation. Their mechanical and optical properties were analysed and compared. Xyloglucans from different sources have different fine structural features such as degree of galactosylation and galactose distribution along the polymer main chain (Buckeridge et al. 2000a). The galactomannan from seeds of *D. mollis* presents a mannose:galactose ratio of 2.1 (Panegassi, Serra, & Buckeridge, 2000), similar to guar gum (*Cyamopsis tetragonolobus* galactomannan), which is commonly used as wet-end additive to papermaking.

Veluraja, Ayyalnarayanasubbaraj, and Paulraj (1998) showed that tamarind xyloglucan could be used as a good adhesive in a composite with cellulosic rich sisal fibres. These authors used a high concentration of xyloglucan (2 g of fibre per 200 ml of 3% xyloglucan), therefore, their data could neither be compared to the ones obtained in this work nor to be used at industrial level.

Fig. 4 shows that all hemicelluloses tested had some effect on the mechanical properties of the paper sheets, whereas the optical features were not affected by the presence of the wet-end additives studied (data not shown). Indeed, the specific elastic modulus (Fig. 4F) was slightly improved only by the addition of *T. indica* xyloglucan. However, in general, the hemicelluloses seem not to be very effective in changing this mechanical property probably due to the type of strength related to it, i.e. elasticity is affected by the individual fibres more than the binding among them.

With the exception of porosity (Fig. 4E), capillarity (Fig. 5A) and water retention value (WRV) (Fig. 5B) the other properties analysed increased as a consequence of the addition of hemicelluloses. For example, it can be highlighted that the burst and tear indexes are probably related to the bonding strength among the fibres. In spite of the fact that hemicelluloses have a high capacity to retain water due to their hydrodynamic properties (Buckeridge et al., 2000a, b) the amount of hemicelluloses added to the paper sheet was not enough to change the WRV (Fig. 5B).

On the basis of the results described above, the role of hemicelluloses as wet-end additives might be the improvement of mechanical properties rather than increasing the water adsorption capacity. Similar data were obtained in an

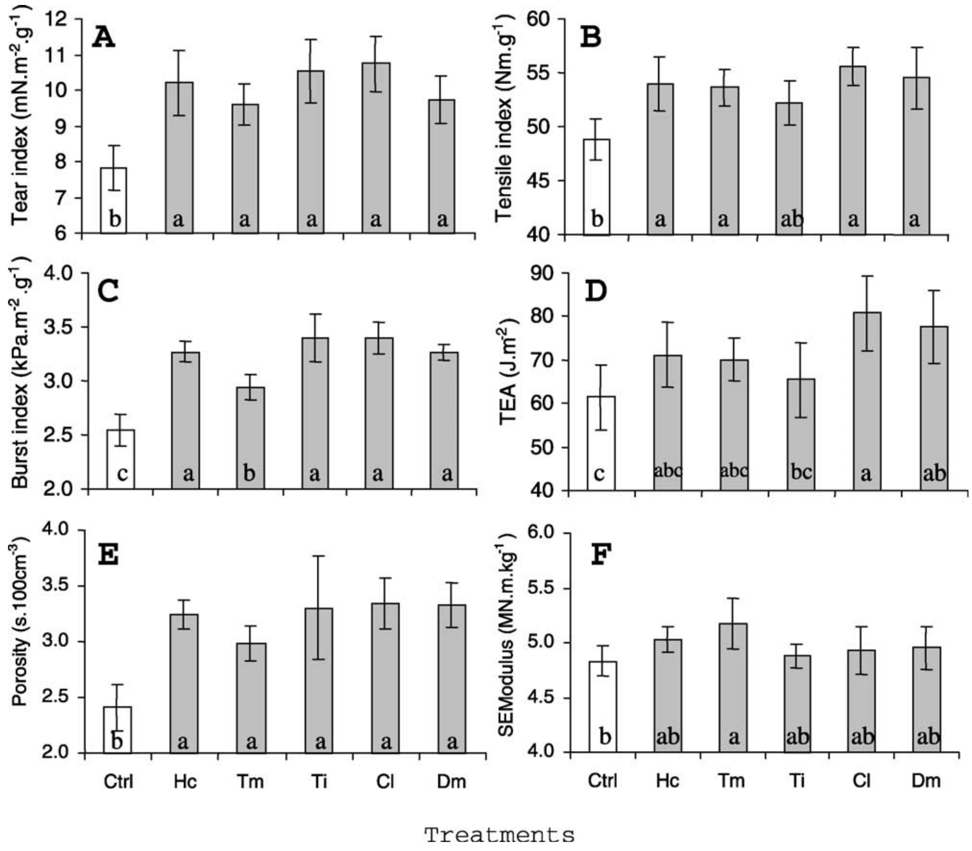

Fig. 4. Comparison among different hemicelluloses added to the cellulosic pulp. The assays were performed with xyloglucans from Hc (*H. courbaril*), Tm (*T. majus*), Ti (*T. indica*), Cl (*C. langsdorffii*) and galactomannan from Dm (*D. mollis*) at a final concentration of 1%. TEA—Tensile Energy Absorption; SEModulus—Specific Elastic Modulus (given as Mega Newton meter per kg of paper). The data were averaged from 5 sheets and the bars represent the standard deviation. Different letters represent statistical differences according to Tukey test ($P < 0.05$).

experiment where deacetylated glucomannan was added to fibre suspension, resulting in an increasing of the strength properties of the paper sheets (Sundberg et al., 2000).

Among the hemicelluloses tested, *T. majus* xyloglucan seems to have the lowest effect on burst and tear indexes and porosity, (Figs. 4A, C and E) and galactomannan effects were similar to other xyloglucan.

Table 1 summarises the main results obtained in this work. The burst and tear indexes had the highest improvement after addition of hemicelluloses (28 and 30%, respectively). As these properties are highly affected by the bonding strength among the fibres, our observations indicate that bonding strength was strongly affected by xyloglucans and galactomannan. Besides

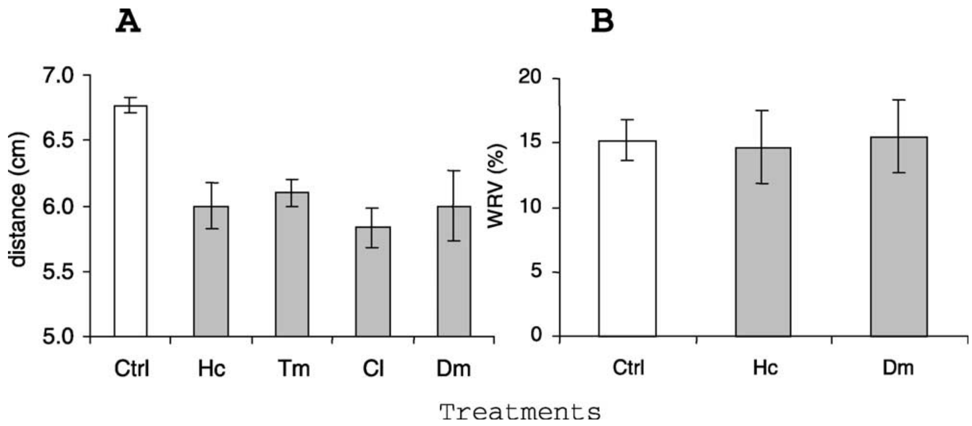

Fig. 5. Capillarity (given by distance moved by water in cm) and Water Retention Value (WRV) of sheets produced with different hemicelluloses, Hc (H. courbaril), Tm (T. majus), Cl (C. langsdorffii) and galactomannan from Dm (D. mollis) at 1% final concentration.

Table 1
Improvement (%) on properties due to the addition of hemicelluloses to paper sheets. the assays were performed with xyloglucans from Hc (*H. courbaril*),Tm (*T. majus*), Ti (*T. indica*), Cl (*C. langsdorffii*) and galactomannan from Dm (*D. mollis*) at 1% final concentration. The analysis were Ti (Tear index), Bi (Burst index), TEA (Tensile Energy Absorption), SEM (Specific Elastic Modulus), ASW (Apparent Specific Weight), Porosity and Capillarity. Negative values means a percentual decreased in those properties due to the presence of hemicelluloses in comparison to the control samples

Hemi cellulose	Ti	Bi	Porosity	Tensile index	TEA	SEM	ASW	Capi llarity
Hc	28	31	−34	10	16	4	4	−12
Tm	15	23	−24	10	14	7	3	−10
Ti	33	35	−37	7	6	1	2	–
Cl	33	38	−39	14	31	2	4	−14
Dm	28	25	−38	12	26	2	3	−12
Average	28	30	−34	11	19	3	3	−12

higher adhesion among the fibres, the presence of hemicelluloses also helps in the retention of fines as observed by the increase (3%) in the Apparent Specific Weight (ASW—kg/m^3).

Analysis related to tensile strength (Table 1) as tensile index, tensile energy absorption and specific elastic modulus showed lower improvement (11, 19 and 3%, respectively) compared to the control samples.

In general, the improvement observed on the mechanical properties of paper sheets shows that the gums analysed in this work have some promise as wet-end additives and might be used in papermaking. This includes the xyloglucans that have not been previously reported as wet-end additive in the literature. Different types of hemicellulose (from rice straw pulp and hardwood pulp) were tested by Mobarak, El-Ashmawy, and Fahmy (1973). These authors showed that hemicelluloses added as an additive were more effective than hemicelluloses in situ (in the pulp) as a strength promoter. Moreover, it has been demonstrated that raising the hemicellulose content by addition was more effective on paper strength promotion than raising the hemicellulose content in the pulp through adjusting pulping conditions (Mobarak et al., 1973).

As the effects among the different hemicelluloses used in this work did not vary greatly, neither affected the optical properties, these polymers could be extracted from various sources and used as a pooled sample, improving the yielding of the hemicellulose production for industrial use.

Seeds of several species from tropical rainforest as those studied here could be used as source for production of wet-end additives. Even if the utilisation of these products will not cost less than starch or guar gum, it might represent an important strategy for sustainable use of Brazilian rainforest species.

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References

Abson, D., & Brooks, D. F. (1985). Wet-end behavior of dry strength additives. *Tappi Journal*, *68*(1), 76–78.

Blumenthal, M., & Paul, C. W. (1994). Starch-based hot melts for adhesive applications. *Tappi Journal*, *77*(9), 193–195.

Buckeridge, M. S., Dietrich, S. M. C., & Lima, D. U. (2000a). Galactomannan as the reserve carbohydrate in legume seeds. In A. K. Gupta, & N. Kaur (Eds.), *Carbohydrate reserves in plants—synthesis and regulation* (p. 372) Amsterdam: Elsevier.

Buckeridge, M. S., Santos, H. P., & Tiné, M. A. (2000b). Mobilisation of storage cell wall polysaccharides in seeds. *Plant Physiology and Biochemistry*, *38*, 141–156.

Dea, I. C. M., & Morrison, A. (1975). Chemistry and interactions of seed galactomannans. *Advances in Carbohydrate Chemistry and Biochemistry*, *31*, 241–312.

El-Ashmawy, A. E., Mobarak, F., & Fahmy, Y. (1973). Hemicelluloses as additive in papermaking. Part I. Isolation and characterization of hemicelluloses from straw and wood pulps. *Cellulose Chemistry and Technololgy*, *7*, 315–323.

Lima, D. U. de, & Buckeridge, M. S. (2001). Interaction between cellulose and storage xyloglucans: The influence of the degree of galactosylation. *Carbohydrate Polymers*, *46*, 157–163.

Mobarak, F., El-Ashmawy, A. E., & Fahmy, Y. (1973). Hemicelluloses as additive in papermaking. Part II. The role of added hemicellulose, and hemicellulose in situ on paper properties. *Cellulose Chemistry and Technololgy*, *7*, 325–335.

Panegassi, V. R., Serra, G. E., & Buckeridge, M. S. (2000). Potencial tecnológico do galactomanano de sementes de faveiro (*D. mollis*) para uso na indústria de alimentos. *Revista Brasileira de Ciência e Tecnologia de Alimentos*, *20*(3), 406–415 (www.scielo.br).

Rojas, O. J., & Neuman, R. D. (1999). Adsorption of polysaccharide wet-end additives in papermaking systems. *Colloids and Surfaces*, *155*, 419–432.

Senai/IPT (1998). *Celulose e Papel—Tecnologia de fabricação de pasta celulósica*, Vol. 1, p. 180.

Sjostrom, E. (1981). *Wood chemistry. Fundamentals and applications*. London: Academic Press, p. 223.

Sundberg, A., Holmbom, B., Willfor, S., & Pranovich, A. (2000). Effects of retained wood resin and polysaccharides on paper properties. In J. F. Kennedy, G. O. Phillips, & P. A. Williams (Eds.), *Cellulosic pulps, fibres and materials*. Woodhead publishing Ltd.

Veluraja, K., Ayyalnarayanasubburaj, S., & Paulraj, A. J. (1998). Preparation of gum from tamarind seed—and its application in the preparation of composite material with sisal fibre. *Carbohydrate Polymers*, *34*, 377–379.

Vincken, J. P., Keizer, A., Beldman, G., & Voragen, A. G. J. (1995). Fractionation of xyloglucan fragments and their interaction with cellulose. *Plant Physiology*, *108*, 1579–1585.