Carbohydrate Polymers 88 (2012) 1258–1263

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Influences of configuration and molecular weight of hemicelluloses on their paper-strengthening effects

Likun Bai[a,*], Huiren Hu[a,*], Jianfeng Xu[b]

[a] Tianjin University of Science and Technology, Tianjin Key Laboratory of Pulp and Paper, Tianjin 300457, China
[b] Research Institute of Wood Industry, Chinese Academy of Forestry, Beijing 100091, China

ARTICLE INFO

Article history:
Received 20 October 2011
Received in revised form 1 February 2012
Accepted 2 February 2012
Available online 11 February 2012

Keywords:
Hemicelluloses
Xylan
Galactoglucomannan
Arabinogalactan
Paper strengthening

ABSTRACT

Xylan, galactoglucomannan, arabinogalactan and hemicelluloses with different molecular weights were prepared from wood and then used as wet-end additives and surface sizing agents in papermaking. The results showed that xylan, galactoglucomannan and arabinogalactan all had obvious paper-strengthening effect. As wet-end additives, galactoglucomannan had the best effects, followed by xylan and then arabinogalactan. As surface sizing agents coordinating with starch, xylan showed the best sizing effect (paper-strengthening effect and water resistance), followed by galactoglucomannan. The effects were both greater than that of starch alone. Furthermore, hemicelluloses with higher molecular weights had more significant effects. The results could provide some reference for the use of hemicelluloses in nature and papermaking waste liquor to improve paper physical strength. Although hemicelluloses in APMP (alkaline peroxide mechanical pulp) waste liquor was degraded to a certain degree, it also showed good paper-strengthening effects. Starch as an important papermaking additives comes mainly from food. The hemicelluloses, especially in the high-yield-pulp waste-liquor, can replace starch in papermaking to some extent, which might be beneficial from economic, energy and food standpoints.

1. Introduction

With the development of economic globalization, resource shortages and environmental pollution have become common challenges in the world. One of the important ways to solve this problem is to achieve the transition from fossil-based resources to biomass-based resources (Lv et al., 2006; Paulussen & Wang, 2005; Yukawa, 2002). Hemicelluloses are considered to be one of the most abundant, cheapest renewable resources on the earth.

During the pulping process, hemicelluloses are dissolved out with lignin into waste liquor and become a wood-processing residue. The hemicelluloses in chemical pulping waste liquor is finally burned in the recovery system, while the caloric values of organic compounds in waste liquor are not high and the hemicellulosic caloric value is only about half of that of lignin (Kleen et al., 2011; Yoon & Van Heiningen, 2010). In recent years, high yield pulp (HYP), especially for bleached chemi-thermomechanical pulp (BCTMP) and alkaline peroxide mechanical pulp (APMP), has developed rapidly. Generally, HYP waste liquor is treated through biodegradation or physical and chemical sedimentation to remove the organic compounds, which are expensive and complex processes. It is therefore necessary to find a better way to make use of these hemicelluloses.

Numerous researches have proved that hemicelluloses and modified hemicelluloses can improve some pulp properties when used in papermaking (Bhaduri, Ghosh, & Deb Sarkar, 1995; Denis, Rubens, & Marcos, 2003; Sun, Fang, Rowlands, & Bolton, 1998; Suurnäkki, Oksanen, Kettunen, & Buchert, 2003). In recent years, some studies about the use of hemicelluloses in papermaking waste liquor have been carried out. Hemicelluloses were separated from the waste liquor of commercial soda-bagasse pulp, and then used on surface sizing of waste paper pulp. The paper-strengthening effects were remarkable (Lao, 2004). The APMP waste liquor was used with retention system to improve the physical properties of OCC pulp by using the hemicelluloses in it (Zhang, Hu, & Wu, 2010). Besides, separated hemicelluloses could realize cationization, and the hemicellulose-derived was efficient additives in the paper industry (Zhang & Hu, 2010).

Hemicelluloses can be used as papermaking additives. However, the complicated structure, such as branching, polymerization degree, and different monosaccharide composition, limits its commercial application. (Jacobsen & Wyman, 2000; Sun, Fowler, Rajaratnam, & Zhang, 2010). Hemicelluloses is a group of plant cell wall polysaccharides composed of carbohydrates based on pentose sugars (mainly xylose) as well as hexoses (mainly glucose and

* Corresponding authors. Tel.: +86 22 60601286; fax: +86 22 60601169.
E-mail addresses: baiyueguang1225@126.com (L. Bai), huiren@tust.edu.cn (H. Hu).

0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2012.02.002

mannose). The amount and composition of hemicelluloses vary with the particular plant species. In hardwood, hemicelluloses constitutes about 20–25%, some up to 35% of the dry weight of wood, and xylan is the major constituent (Stuart, 2006); While in softwood, hemicelluloses accounts for 15–20%, mainly galactoglucomannan, with a little xylan; Generally, arabinogalactan takes up a small part of softwood, but more of larch genus, about 5–30% (Yang, 2001). Hemicelluloses are branched polymers of low molecular weight of a degree of polymerization of 80–200 (Cai & Paszner, 1988; Fang, Sun, Tomkinson, & Fowler, 2000). Acidic or alkaline medium can degrade hemicelluloses in various degrees. Therefore, in papermaking, the dissolved types and degradation of hemicelluloses in waste liquor vary with the particular fiber materials and pulping processes. The differences in hemicellulosic structure, even relatively small, can result in changes of chain conformation and intermolecular association, which may have an impact on functionality of these polysaccharides (Cyran & Saulnier, 2007).

This paper, therefore, focuses on the hemicellulosic structure and their paper-strengthening effects. In this work different hemicelluloses were prepared and use as a wet-end additive and surface sizing agent in papermaking. The objective was to investigate the influences of configuration and molecular weight of hemicelluloses on their paper-strengthening effects. Moreover, the paper-strengthening effect of APMP waste-liquor hemicelluloses was also studied. It may contribute to a fundamental understanding of the use of papermaking waste liquor to improve paper physical strength and broaden the application area of hemicelluloses.

2. Material and methods

2.1. Materials

Triploid white poplar was collected from Shandong, China, age of five years. Larch was obtained from Hubei, China. Red spruce was from the northeast of China. The cationic polyacrylamide (CPAM) was from Ciba Corporation, having a molecular weight of 5×10^6. Bleached aspen kraft pulp had a beating degree of 45° SR, mean fiber length of 0.703 mm, fines content of 3.0%.

2.2. Extraction of different raw wood hemicelluloses

Alkaline extraction process was performed to extract xylan from triploid white poplar. The wood powder was treated with acid sodium chlorite at 75 °C for 3 h to get holocellulose. The holocellulose was then extracted with NaOH solution (8%, w/v) (residue: extractant, 1:12, g/ml) at 45 °C for 12 h with constant stirring. After filtration, the filtrate was adjusted to pH 5.0 with hydrochloric acid solution and then mixed with 3 volumes of 95% ethanol (The volume of 95% ethanol was 3 times that of filtrate, the same as below.). The precipitate was filtered, washed with ethanol, and then vacuum-dried at 60 °C for 24 h. The prepared hemicellulose was named as hemicellulose H1.

Arabinogalactan was obtained from larch as the water-soluble fraction. The larch powder (20.0 g) was treated with 400 ml distilled water for 2 h at 60 °C with constant stirring. The slurry was filtered and then concentrated to about 50 ml in a rotary evaporator under reduced pressure at bath temperatures not exceeding 60 °C. The concentrated liquor was treated with the same method as treating the xylan-dissolved filtrate above, and obtained the hemicellulose fraction labeled as hemicellulose H2.

Galactoglucomannan was prepared by stepwise extraction from spruce. The spruce powder was treated firstly with acid sodium chlorite at 75 °C for 4 h to obtain holocellulose. The holocellulose was then extracted with 24% (w/v) KOH solution (residue:extractant, 1:16, g/ml) at 45 °C for 10 h with constant stirring. The filtrate of the slurry was collected and treated with the same method as treating the xylan-dissolved filtrate above. The obtained extractive (xylan and galactoglucomannan) was named as 24% KOH extractive. Afterwards, the 24% KOH extractive was redissolved in 24% KOH solution (residue:extractant, 1:20, g/ml), and then dropped 2 volumes of 5% (w/v) $Ba(OH)_2$ aqueous with stirring. The resulting suspension was centrifuged and the residue was washed with 24% KOH, centrifuged, and dissolved in ice-cold 50% (v/v) HAC by agitation. The solution was then mixed with 3 volumes of 95% ethanol and centrifuged. The final residue was vacuum-dried and considered to be fraction H3.

2.3. Preparation of hemicelluloses with different molecular weights

Xylan was used as a representative here. The extracted xylan (2 g) was added into 1 mol/L HCl solution (100 ml), and stirred at 60 °C. The treat times were 1 h, 2 h, 4 h, and 7 h, respectively. The resulting suspensions were adjusted to pH 5.0 with NaOH solution, and then mixed with 3 volumes of 95% ethanol. The precipitate was filtered, washed with ethanol, and then vacuum-dried.

2.4. Extraction of waste liquor hemicelluloses

The APMP waste liquor was centrifuged to remove the undissolved substance, and then was adjusted to pH 3.0. After 30 min settling at 45 °C, the lignin in waste liquor was precipitated and further separated by filtration. The filtrates was mixed with 3 volumes of 95% ethanol and treated as above. Then the hemicellulosic precipitate H4 was obtained.

2.5. Characterization of the hemicellulosic samples

The FT-IR spectra of hemicellulosic fractions H1, H2, H3, and H4 were obtained on an FT-IR spectrophotometer in the range of 4000–400 cm^{-1} using a KBr disc containing 1% finely ground samples.

The neutral sugars in the hemicellulosic fractions H1, H2, H3 and H4 were liberated by hydrolysis of the polymers with 6% H_2SO_4 for 2.5 h at 105 °C. The analysis of the neutral sugars in the hydrolyzate were carried out by high performance anion exchange chromatography (HPAEC) with a Dionex ICS3000 gradient pump, ED50 electrochemical detector, AS50 autosampler and a Carbopac™ PA1 column (4 mm × 250 mm, Dionex) (Bian, Peng, Xu, Sun, & Kennedy, 2010).

The average molecular weights of hemicelluloses treated with acid were estimated by gel permeation chromatography (GPC) on a PL aquagel-OH 50 column (300 mm × 7.7 mm, Polymer Laboratories Ltd.), calibrated with PL pullulan polysaccharide standards (peak average molecular weights 738, 12,200, 100,000, 1,600,000, Polymer Laboratories Ltd.) (Bian et al., 2010).

2.6. Application of hemicelluloses as wet-end additive and surface sizing agent in papermaking

Wet-end additive: the hemicelluloses and retention aid were introduced into bleached aspen kraft pulp stock with stirring prior to sheet formation. The handsheets (base weight, 60 g/m^2) were formed using laboratory Rapid-Köthen sheet former, followed by pressing and drying. The physical properties of handsheets were determined according to TAPPI standard methods using T402 conditions (50% RH, 23 °C). The retention aid was CPAM with a dosage of 0.05% (w/w, CPAM/oven-dried pulp).

Surface sizing agent: the handsheets (base weight, 60 g/m^2) were made with bleached aspen kraft pulp. The hemicelluloses

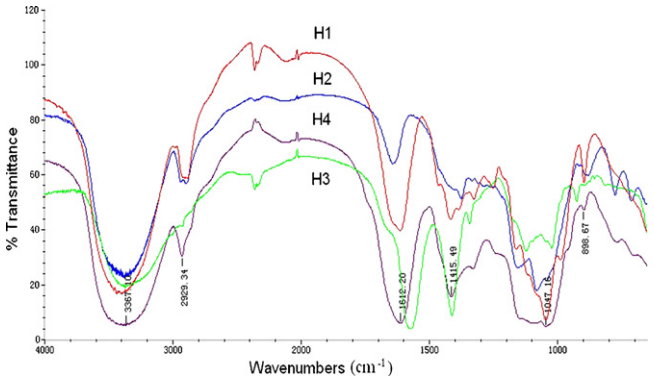

Fig. 1. FT-IR spectra of hemicellulose samples H1, H2, H3 and H4.

were mixed with corn paste starch and $Al_2(SO_4)_3$ aqueous solutions in proportion, and then sized on the surface of handsheets using Laboratory Coater. The sized sheets were dried at 98 °C for 4 min, calendered and then were determined according to TAPPI standard methods.

3. Results and discussion

3.1. Chemical analysis of the isolated hemicelluloses

3.1.1. FT-IR spectra

The FT-IR spectra are illustrated in Fig. 1. Clearly, the absorptions at 3367, 2929, 1415, 1047 and 898 cm^{-1} were indicative of the native hemicelluloses.

The prominent band around 3367 cm^{-1} represented the O–H stretching vibrations. The strong band at 1047 cm^{-1} arose from C–O–C linkages between the sugars units glycosidic linkages. The two bands above indicated the high amount of O–H and C–O–C linkages presented in all the hemicelluloses samples. The C–H stretching vibrations give a signal at 2929 cm^{-1}. In the carbonyl stretching region, the bands between 1659 and 1573 cm^{-1} are due to the absorbed water (Sun, Tomkinson, Ma, & Liang, 2000). The $-CH_2$ stretching vibrations was observed at 1415 cm^{-1}. A small band at 898 cm^{-1}, which was due to the C-1 group frequency or ring frequency, indicated β-glycosidic linkages between the sugar units in the hemicelluloses (Geng, Sun, Sun, & Lu, 2003). Obviously, the disappearance of band at 1510 cm^{-1} relating to the bound lignin demonstrated that the four hemicellulosic samples were free of associated lignin. The absence of band at 1720 cm^{-1} relating to the bound acetyl indicated that acetyl in xylan and galactoglucomannan were removed in alkali solution.

3.1.2. Content of neutral sugars and uronic acids

Table 1 gives the content of neutral sugars (relative% hemicellulosic sample, w/w) and uronic acids (% hemicellulosic sample, w/w) in the hemicellulosic fractions H1, H2, H3 and H4.

Table 1
Content of neutral sugars and uronic acids in the hemicellulose samples.

Sugars (%)	H1	H2	H3	H4
Rhamnose	1.93	ND	ND	2.49
Arabinose	2.46	27.22	2.97	8.46
Galactose	2.54	59.58	7.18	7.81
Glucose	5.32	3.34	13.17	25.73
Xylose	74.13	4.26	10.89	42.84
Mannose	ND	0.18	59.20	ND
Glucuronic acid	9.61	0.07	6.59	11.41
turonic acid	4.01	5.35	ND	1.26

Note. ND, not detectable.

Table 2
Molecular properties of the hemicellulose samples.

Sugars	Mn (g mol^{-1})	M_w (g mol^{-1})	M_w/M_n
X	8664	36,935	4.26
X_{1h}	5570	27,437	4.92
X_{2h}	3776	22,133	5.86
X_{4h}	3158	15,944	5.05
X_{7h}	2289	11,220	4.90
H4	3972	19,661	4.95

Notes. X, Xylan (H1) from triploid white poplar without acid treatment; X_{1h}, X_{2h}, X_{4h} and X_{7h}, Xylan treaded with acid for 1 h, 2 h, 4 h and 7 h. H4, Hemicelluloses from APMP waste liquor (the same as below).

As shown in Table 1, the major monosaccharide in hemicellulose H1 from triploid white poplar was xylose (74.13%). Glucuronic acid appeared as the second major sugar (9.61%). The both comprised 83.74% of the total sugars, which indicated that the hemicellulose H1 could be regarded as the model of xylan for research. In hemicellulose H2 from Larch, the high content of galactose (59.58%) and arabians (27.22%) comprised about 86.8% of the total sugars, which indicated that the hemicellulose H2 could be regarded as the model of arabinogalactan. A high content of Mannose (59.20%), glucose (13.17%) and noticeable amounts of galactose (7.18%) suggested the hemicellulose H3 from spruce could be regarded as model of galactoglucomannan. Besides, the molar ratios of Gal:Glc:Man in H3 was 0.36:0.67:3.00. Xylose was the main constituent sugar (42.84%) in the extracts from aspen-APMP waste liquor, and glucose was the second major sugar (25.73%). Noticeable amounts of gluconicuronic acid (11.41%), arabians (8.46%), and galactose (7.81%) were observed also. Mannose was not found as a free monosaccharide.

3.1.3. Molecular weight

The average molecular weights of hemicelluloses treated with acid were estimated by GPC, and the datas are given in Table 2.

Comparing the results in Table 2, it showed that the number-average molecular weight (M_n) and weight-average molecular weight (M_w) of xylan decreased with acid treatment time prolonged, which revealed that hemicelluloses with different molecular weights were obtained. The decrease of molecular weight owed to the hemicellulosic glucoside bond broken in acidic medium. Hemicelluloses extracted from pulping waste liquor had a low molecular weight, which as hemicelluloses degradation occurred in the pulping process.

3.2. Effects of hemicelluloses as wet-end additive in papermaking

3.2.1. Comparison of effects of different kind hemicelluloses

Hemicelluloses were negatively charged and difficult to retain on the pulp fibers also having negative charge when hemicelluloses as wet-end additive singly. In order to improve the retention of hemicelluloses, retention aid CPAM was used to cooperate with hemicelluloses. CPAM and the extracted xylan (H1), arabinogalactan (H2), galactoglucomannan (H3) were, respectively, added into the stock before sheet formation. The strength properties of the handsheets are shown in Fig. 2.

Fig. 2 showed that all tested hemicelluloses had obvious effects on the strength properties of the paper sheets. In the presence of 1% galactoglucomannan, the tensile index, burst index, tear index and folding endurance of paper increased by 13.5%, 18.2%, 6.43% and 75%, respectively, compared to those of paper sample with only retention aid. The results were attributed to the role of hydroxyl group (OH–) in hemicelluloses molecular which brought about more H-bond formation between cellulose and hemicelluloses and benefited the bonding between the fibers.

Comparing the effects of the three hemicelluloses extracted from different raw wood on paper strength, it was found that

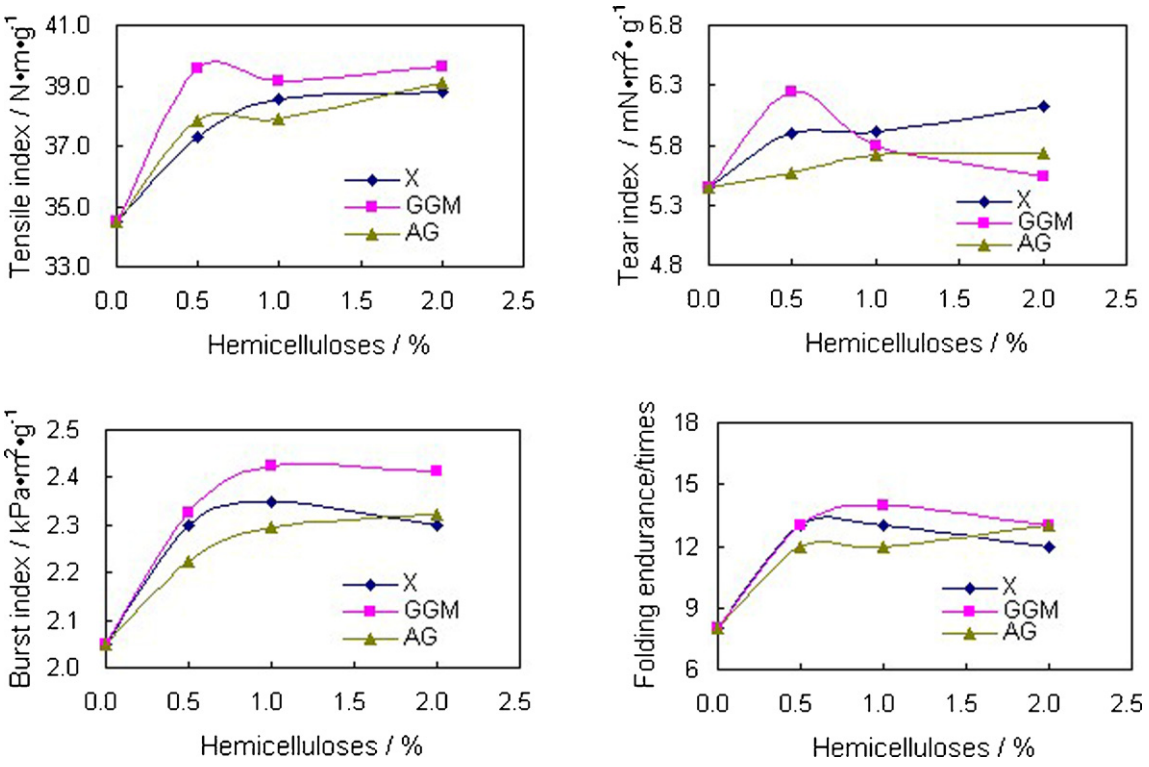

Fig. 2. Effect of xylan, arabinogalactan and galactoglucomannan as wet-end additives on the strength properties of aspen kraft pulp. Notes: AG, Arabinogalactan; GGM, Galactoglucomannan; X, Xylan (the same as below).

galactoglucomannan had the best paper-strengthening effect, followed by xylan. It may because hexasaccharide (mainly mannan), compared with pentosan (mainly xylan), owns an additional hydroxyl group in glycosyl. The additional hydroxyl group is more active than all other hydroxyl groups and can form more hydrogen bonds between hemicelluloses and cellulose to benefit the improvement of paper strength. (Cottrall, 1950; Lao, 1993). Although with mainly hexose group, arabinogalactan owns more branches in the molecules (Yang, 2001; Girio et al., 2010). The highly branched structure seems not easy to be adsorbed by cellulose because it lacks the uniformity and linearity required for close packing. It can explain why the strength properties of handsheets increased more rapidly as using arabinogalactan than galactoglucomannan and xylan at a high hemicellulose dosage (1.0–2.0%). At the dosage, galactoglucomannan and xylan seem to have achieved adsorption saturation.

3.2.2. Comparison of the effects of hemicelluloses with different molecular weights

The paper-strengthening effects of hemicelluloses (xylan) with different molecular weights were investigated, and the results are listed in Table 3. The dosages of hemicelluloses were 1% (w/w, hemicelluloses/oven-dried pulp).

From the Table 3, it was found that all the hemicelluloses could obviously improve handsheets strength. Furthermore, hemicelluloses treated under lower level of acid, which had a higher molecular weight, had more significant strengthening effects. This is in agreement with the opinion of Lao (1993). The molecular chain of hemicelluloses is lengthened with the increase of molecular weight, which gives the pulp more H-bond between fibers, thus contributes to a greater strength of paper.

Hemicelluloses from APMP waste liquor could also raise the strength of handsheets effectively. The tensile index, burst index, tear index and folding endurance of paper sheets increased by 13.8%, 17.3%, 9.59% and 100%, respectively, compared to those of the control, similarly to those of using xylan treated slightly with acid (1–2 h). However, the strengthening effects were lower than that of using original xylan from triploid white poplar. It may due to the lower molecular weight of waste-liquor hemicelluloses. Moreover, waste-liquor hemicelluloses contains more arabinose and galactose which give the hemicelluloses more branches and makes it less effective as a paper-strengthener than xylan and glucomannan.

Many hemicelluloses in nature or produced during pulping process have low molecular weights, which could affect the paper-strengthening effects of hemicelluloses. However, Oinonen, Areskogh, & Henrikss (2011) have developed a simple and cost efficient technique that enables it to polymerize small hemicelluloses into larger and more defined structures by oxidative polymerization. This technique may open up a new approach for the full use of these molecules.

Table 3
Effect of xylan treated with acid as wet-end additive on the strength properties of aspen kraft pulp.

Hemicellulose	Tensile index ($N\,m\,g^{-1}$)	Burst index ($kPa\,m^2\,g^{-1}$)	Tear index ($mN\,m^2\,g^{-1}$)	Folding endurance/times
Control	33.4	1.96	5.32	6
C_R	34.5	2.05	5.44	8
X	38.5	2.35	5.92	13
X_{1h}	37.5	2.31	5.78	13
X_{2h}	36.9	2.21	5.64	12
X_{4h}	36.3	2.19	5.54	12
X_{7h}	36.8	2.14	5.54	10
H4	38.0	2.30	5.73	12

Note. C_R, retention aid only.

Table 4
Effect of xylan, arabinogalactan and galactoglucomannan as surface sizing agent on handsheets physical properties.

Surface sizing agents	Coating weight ($g\,m^{-2}$)	Tensile index ($N\,m\,g^{-1}$)	Tear index ($mN\,m^2\,g^{-1}$)	Folding endurance/times	$Cobb_{15\,s}$ values ($g\,m^{-2}$)
Control	–	33.4	5.32	6	87.1
Only starch	5.29	51.5	5.44	72	59.6
AG	5.33	52.9	5.80	66	63.9
GGM	4.75	49.9	6.09	76	37.2
X	4.78	52.1	6.23	82	52.6

Notes. The sizing agent concentration of only starch sample was 8%. Other sizing agent samples were mixture of starch and hemicelluloses with concentrations both 4%.

Table 5
Effect of xylan treated with acid as surface sizing agent on handsheets physical properties.

Surface sizing agents	Coating weight ($g\,m^{-2}$)	Tensile index ($N\,m\,g^{-1}$)	Tear index ($mN\,m^2\,g^{-1}$)	Folding endurance (times)	$Cobb_{15\,s}$ values ($g\,m^{-2}$)
Control	–	33.4	5.32	6	87.1
Only starch	5.29	51.5	5.44	72	59.6
X	4.78	52.1	6.23	82	52.6
$X_{2\,h}$	5.22	51.7	5.91	71	59.8
$X_{4\,h}$	4.72	51.6	5.83	56	62.7
$X_{7\,h}$	5.25	50.5	5.70	57	62.0
H4	5.07	51.5	5.85	62	62.5

Notes. The sizing agent concentration of only starch sample was 8%. Other sizing agent samples were mixture of starch and hemicelluloses with concentrations both 4%.

3.3. Effects of hemicelluloses as surface sizing agent in papermaking

In the paper industry, the surface sizing agent is usually starch. Hemicelluloses has a nature similar to starch and can be also used as surface sizing agent. In a previous study, it was found that the sizing effects of the mixture of hemicelluloses and starch are better than that of hemicelluloses only.

3.3.1. Comparison of the effects of different kind hemicelluloses

Aqueous solutions of xylan, arabinogalactan and galactoglucomannan were mixed with corn paste starch and $Al_2(SO_4)_3$, then used as surface sizing agent of handsheets of aspen kraft pulp. The sizing conditions were as follows: sizing temperature 70 °C, sizing agent concentration 8%, $Al_2(SO_4)_3$ concentration 0.27%. The physical properties of sized handsheets are summarized in Table 4.

From Table 4, it was demonstrated that the paper-strengthening effects of hemicelluloses combined with starch were obvious, and higher than that of starch alone as a surface sizing agent. Hemicelluloses and starch sized on fiber surface can act as a binder and bond the fibers together, thus increase the handsheets strength. Natural starch is a polysaccharide comprising glucose monomers joined in α-1, 4 or α-1, 6 linkages. The molecular chains tend form helices. However, hemicelluloses has straight, flat β-1,4-linked backbones similar in structure to cellulose. The similarity confers a stronger affinity between hemicelluloses and cellulose. In addition, functional groups in straight molecular chain are easier to approach cellulose, favorable to the combination of molecules (Liu, 2006). All of the above provide good support for the use of hemicelluloses instead of starch in some extent.

Comparing the strength properties of paper sized with different types of hemicelluloses, it could be found that the sizing effect of xylan was best, and greater than that of starch alone. Arabinogalactan had a very obvious effect on paper-tensile-strength improvement, but a relatively smaller effect on tear strength and folding endurance. The water resistance of galactoglucomannan was the best. It increased 57.3% compared with that of the blank sample and 37.6% compared with that using only starch. The water resistance of arabinogalactan was poorer than that of starch. The results may be explained by that arabinogalactan has good water-solubility and low viscosity when blended with starch, which result in excessive penetration of sizing agent into sheet during surface sizing process. Thus, the hydrogen bonding with fibers is strengthened and sheet tensile strength is improved significantly. However, the excessive penetration of sizing agent reduces its film-forming properties on paper surface, further affect the improvement of paper mechanical toughness and moisture barrier properties. At the same time, the good watersolubility of arabinogalactan leads to a poor resistance to liquor. In contrast, the poor watersolubility of galactoglucomannan gives paper better water resistance.

Overall, in combination with starch, the sizing effect of xylan was best, higher than that of galactoglucomannan, and both were greater than that of starch alone.

3.3.2. Comparison of effects of hemicelluloses with different molecular weights

The paper-strengthening effects of hemicelluloses (xylan) with different molecular weights as surface sizing agent were investigated, and the results are listed in Table 5.

These results in Table 5 demonstrated that hemicelluloses (xylan) with larger molecular weight had better surface sizing effect. When original hemicelluloses was degraded to a certain degree ($X_{7\,h}$), the paper strength properties and water resistance were slightly smaller than starch alone, while obviously higher than that of the control. The results illustrated that the molecular chain length affects its ability to bridge connections as surface sizing agent.

Hemicelluloses from APMP waste liquor also had good surface sizing effects. The tensile index, tear index, folding endurance and water resistance of paper increased by 54.2%, 9.96%, 933% and 28.2%, respectively, compared to those of the control, similarly to those of using xylan treated slightly with acid (2–4 h). Hemicelluloses in other HYP waste liquor were degraded similarly to APMP hemicelluloses, thus they might have similar paper-strengthening effects.

We are facing increasing concerns over the security of our food supply. Starch as important papermaking additives comes mainly from food. The hemicelluloses, especially in the HYP waste-liquor, can replace the use of starch in papermaking to some extent, which might be in answer to the economic, energy and food concerns.

4. Conclusions

Xylan, galactoglucomannan and arabinogalactan all showed obvious paper-strengthening effects. As wet-end additives, galactoglucomannan had the best effects, followed by xylan and then arabinogalactan. As surface sizing agents coordinating with starch, xylan showed the best strengthening effect, while

galactoglucomannan gave the best water resistance. Overall, the sizing effect of xylan was best, higher than that of galactoglucomannan, both greater than that of only starch. Furthermore, it was found that hemicelluloses with higher molecular weight had more significant strengthening effects. The results could provide some reference for the use of hemicelluloses in nature and papermaking waste liquor to improve paper strength. Although hemicelluloses in APMP waste liquor changed in a certain degree during pulping process, it also showed good paper-strengthening effect. The hemicelluloses, especially in the HYP waste-liquor, can replace the use of starch in papermaking to some extent, which might be in answer to the economic, energy and food concerns.

Acknowledgements

The authors would like to acknowledge the financial support from the Scientific and Technological Supporting Program of the Ministry of Science and Technology of China (Grant No. 2011BAC11B04), and the Tianjin R&D Innovation System and Facility Development Program (Grant No. 10SYSYJC28000). They also thank Beijing Forestry University, China for technical assistance.

References

Bhaduri, S. K., Ghosh, I. N., & Deb Sarkar, N. L. (1995). Ramie hemicellulose as beater additive in paper making from jute-stick kraft pulp. *Industrial Crops and Products*, *4*, 79–84.

Bian, J., Peng, F., Xu, F., Sun, R. C., & Kennedy, J. F. (2010). Fractional isolation and structural characterization of hemicelluloses from *Caragana korshinskii*. *Carbohydrate Polymers*, *80*, 753–760.

Cai, Z. S., & Paszner, L. (1988). Salt catalyzed wood bonding with hemicelluloses. *Holzforschung*, *42*, 11–20.

Cottrall, L. G. (1950). The influence of hemicelluloses in wood pulp fibers on their papermaking properties. *Tappi*, *33*, 471–480.

Cyran, M. R., & Saulnier, L. (2007). Association and structural diversity of hemicelluloses in the cell walls of rye outer layers: Comparison between two ryes with opposite breadmaking quality. *Journal of Agricultural and Food Chemistry*, *55*, 2329–2341.

Denis, U. L., Rubens, C. O., & Marcos, S. (2003). Seed storage hemicelluloses as wet-end additives in papermaking. *Carbohydrate Polymers*, *52*, 367–373.

Fang, J. M., Sun, R. C., Tomkinson, J., & Fowler, P. (2000). Acetylation of wheat straw hemicellulose B in a new non-aqueous swelling system. *Carbohydrate Polymers*, *41*, 379–387.

Geng, Z. C., Sun, R. C., Sun, X. F., & Lu, Q. (2003). Comparative study of hemicelluloses released during two-stage treatments with acidic organosolv and alkaline peroxide from *Caligonum monogoliacum* and *Tamarix* spp. *Polymer Degradation and Stability*, *80*, 315–325.

Girio, F. M., Fonseca, C., Carvalheiro, F., Duarte, L. C., Marques, S., & Bogel-Łukasik, R. (2010). Hemicelluloses for fuel ethanol: A review. *Bioresource Technology*, *101*, 4775–4800.

Jacobsen, S. E., & Wyman, C. E. (2000). Cellulose and hemicellulose hydrolysis models for application to current and novel pretreatment processes. *Applied Biochemistry and Biotechnology*, *84–86*, 81–96.

Kleen, M. A., Määttänen, M. H., Asikainen, S. A., Liitiä, T. M., & Tehomaa, M. M. (2011). Stepwise hot water and alkali extraction of birch sawdust to produce xylan and cellulose. In *The 16th International Symposium on Wood, Fiber and Pulping Chemistry Proceedings* Tianjin, 8–10 June, (pp. 666–670).

Lao, J. B. (1993). Effect and industrial use of lignin and hemicellulose in papermaking. *South West Pulp and Paper*, *4*, 230–233.

Lao, J. B. (2004). New use of hemicelluloses. *Heilongjiang Pulp and Paper*, *4*, 17–18.

Liu, Y. S. (2006). Application of guar gum and its derivatives in papermaking. *South West Pulp and Paper*, *35*, 48–51.

Lv, W., Wang, C. F., Wang, G. S., Yu, G. S., Zhang, C. H., Zhang, D. H., et al. (2006). Topics of Chinese forest bioenergy development potential report. *China Forestry Industry*, *1*, 6–11.

Oinonen, P., Areskogh, D., & Henrikss, G. (2011). The processing and upgrading of hemicellulose mixtures. In *The 16th International Symposium on Wood, Fiber and Pulping Chemistry Proceedings* Tianjin, 8–10 June, (pp. 1030–1033).

Paulussen, J., & Wang, R. S. (2005). Clean production and ecological industry: A key to eco-city development. *Chinese Journal of Population, Resources and Environment*, *3*, 3–4.

Stuart, P. (2006). The forest biorefinery: Survival strategy for Canada's pulp and paper sector. *Pulp and Paper Canada*, *107*, 13–16.

Sun, R. C., Fang, J. M., Rowlands, P., & Bolton, J. (1998). Physicochemical and thermal characterization of wheat straw hemicelluloses and celluloses. *Journal of Agricultural and Food Chemistry*, *46*, 2804–2809.

Sun, R. C., Tomkinson, J., Ma, P. L., & Liang, S. F. (2000). Comparative study of hemicelluloses from rice straw by alkali and hydrogen peroxide treatment. *Carbohydrate Polymers*, *42*, 111–122.

Sun, X. F., Fowler, P., Rajaratnam, M., & Zhang, G. C. (2010). Extraction and characterization of hemicelluloses from maize stem. *Phytochemical Analysis*, *21*, 406–415.

Suurnäkki, A., Oksanen, T., Kettunen, H., & Buchert, J. (2003). The effect of mannan on physical properties of ECF bleached softwood kraft fiber handsheets. *Nordic Pulp and Paper Research Journal*, *18*, 429–435.

Yang, S. H. (2001). *Plant fiber chemistry* (3rd ed.). Beijing: China Light Industry Press., pp. 227–228.

Yoon, S. H., & Van Heiningen, A. (2010). Green liquor extraction of hemicelluloses from southern pine in an Integrated Forest Biorefinery. *Journal of Industrial and Engineering Chemistry*, *16*, 74–80.

Yukawa, H. (2002). Application of biotechnology in fuel ethanol production from biomass. *Eco-Industry*, *7*, 37–41.

Zhang, J. Y., & Hu, H. R. (2010). Modification and application of hemicellulose separated from APMP spent liquor. *Transactions of China Pulp and Paper*, *25*, 33–35.

Zhang, J. Y., Hu, H. R., & Wu, Y. L. (2010). Improvement of the properties of OCC pulp by using HYP pulping waste liquor. *China Pulp and Paper*, *29*, 25–27.