INFLUENCE OF HEMICELLULOSES PRE-EXTRACTION AND RE-ADSORPTION ON PULP PHYSICAL STRENGTH II. BEATABILITY AND STRENGTH STUDY

WEIPING BAN,[*,**] XIAOWEN CHEN,[**] GRASCON ANDREWS[**] and ADRIAAN VAN HEININGEN[**]

[*]*Guangxi University, Nanning, Guangxi, China 530004*
[**]*Chemical and Biological Engineering Department,*
University of Maine, Orono, ME 04469, USA

Received February 21, 2011

Xylan extracts from southern US hardwood were used for the adsorption of both hardwood and softwood pulp. Pulp beatability and physical strength properties were determined and compared with those of the conventional Kraft pulp and pre-extracted modified Kraft pulp. The results indicated that hemicelluloses adsorption greatly improved pulp beatability. Compared to conventional Kraft pulp, a significant increase in pulp physical strength could be achieved by adsorbing hemicelluloses onto pulp. An increase of up to 20-25% in tensile strength was observed for both hardwood and softwood pulps, as well as an 8-10% increase in tear strength, achieved for comparing pulp tear strength at a certain tensile level. In addition, softwood adsorbed pulp showed a slightly higher bulk property at the same strength level.

Keywords: hemicelluloses adsorption, pulp beatability, pulp strength

INTRODUCTION

Hemicelluloses, the second most abundant biopolymer resource in the world, have attracted much attention in recent years, due to their importance as sugar material, for fuel or for other useful materials conversion. The dominant hemicelluloses are acetyl-galactoglucomannan in softwoods, at about 20 w/w %, and glucoronoxylan in hardwoods (15-30 w/w %). amorphous structure and shorter molecule chain of hemicelluloses make them easier to degrade than cellulose. During the chemical pulping process, substantial amounts of hemicelluloses are removed from wood chips and dissolved in the cooking liquor. The recovery of these dissolved hemicelluloses is of interest for increasing pulp yield and for improving pulp properties.

Studies on hemicelluloses adsorption have been reported in the past decades, as early as in the 1950s, for example, Yllner and Enstrom reported the xylan adsorption on cellulose fiber during pulping.[1] Later on, the increase in pulp yield was reported as the result of xylan retake in Birchwood Kraft pulping.[2] It was revealed that the sorption process was rate-controlled by a diffusion transport of the hemicelluloses molecules from the liquor phase to the fiber surface.[3] Decreases in pH in the liquor phase increased sorption. The alkalinity and temperature of the liquor showed the same influence on hemicelluloses adsorption.[4] Xylan structure also affected adsorption to a considerable extent, while the complete removal of uronic acids accelerated the adsorption rate. The results indicated that high temperature and a low uronic acid content gave maximum adsorption.[5] Hemicelluloses adsorption was considered to have a physical nature and the difference in rates was attributed to the inhibiting effect of the uronic acid carboxyl groups.[6] During adsorption, the xylan molecules were mainly adsorbed on the fiber surface. A large portion (about 50%) was bound to cellulose and was resistant to alkali extraction at high temperatures. The redeposited xylan was located on the outer surface of the cellulose fibers.[7] The location and the charge of xylan had a considerable impact on the formation of inter-fiber bonds.[8]

Most recently, Gatenholm and his work group reported the effects of xylan molecular structure on adsorption. The xylan extracts were agglomerated and adsorption modified fiber surface morphology and surface chemistry.[9] The proposed mechanism suggested that the aggregated form is the major part of the adsorbed xylan. The surface structures are formed by adsorption of the preformed xylan aggregates from the solution rather than by being built up on the cellulose surfaces, in time, by multilayer adsorption of xylan.[10]

It was noticed that the hemicelluloses content in pulp, especially xylan, influenced pulp beatability, as well as the mechanical properties.[11-12] The adsorption of xylan on cotton fiber or Kraft pulp was reported in literature.[13-15] Through xylan adsorption, the strength properties of the fibers were increased.

EXPERIMENTAL

Materials

Wood chips: the hardwood used in the current investigation was mixed hardwood, and the softwood was Southern Loblolly pine. Both series of chips were obtained from International Paper Inc. All barks and knots were removed. The chips were screened using a Weyerhaeuser classifier. The wood fractions passing a 1-inch size screen, but remaining on the 7/8-inch and 5/8-inch round screens were collected, and then classified as to chip thickness to obtain chips less than 10 millimeters thick. The wood chips were air-dried to a constant moisture level (~9%) and stored in plastic bags for subsequent extraction and pulping experiments.

Hemicelluloses extraction

The extraction and pulping operations were performed in an M&K digester, electrically heated, liquor circulated and equipped with a computer-controlled temperature program. For each experiment, 600 g screened wood chips (O.D.) were loaded in the digester. In the current investigation, green liquor (GL) was used as an alkali resource added for hemicelluloses extraction. The GL was made in our laboratory to simulate a representative industrial composition and it contained: 10.15% sodium hydroxide, 29.30% sodium sulfide and 69.36% sodium carbonate (all as Na_2O).

When the extraction was completed, the liquor was cooled down, drained, its volume was measured, it was filtered and then stored in a cold room for further use.

The extracted wood chips were used for continued pulping in the same digester. Extraction conditions are shown in Table 1.

Pulping

The hardwood and softwood were separately cooked in the M&K digester. Four pulps were prepared for the current work, including two conventional Kraft pulps for both hardwood and softwood and two pre-extracted modified Kraft pulps for both hardwood and softwood. The pulping conditions and results are shown in Table 2.

The cooked wood chips were deliberated in a slusher and the pulp was screened to remove rejects, rinsed in the screener and then spin-dried using a laboratory centrifuge. After homogenizing for 30 minutes in a laboratory homogenization mixer, on low speed, the pulps were stored in a refrigerator and the moisture content was determined for each sample.

Pulp Kappa number was determined by TAPPI Standard method T-236.

Hemicelluloses adsorption

Pulp adsorption was carried out in a rocking batch digester, electrically heated and rocked at a frequency between 2 and 6 revolutions per minute through an arc of approximately 135 degrees.

The adsorption process was performed with pre-extracted modified Kraft pulp for both hardwood and softwood pulp. The extraction liquor applied was obtained from hardwood extraction. The chemical composition analysis of the extraction liquor is listed in Table 3. The same adsorption conditions were applied for both hardwood and softwood pulp. The adsorption conditions and adsorbed pulp properties have been summarized in Table 4. After adsorption, the pulps were well-washed, de-watered using a laboratory centrifuge, homogenized using a laboratory mixer and stored in the refrigerator.

Table 1
Wood chips extraction conditions

Wood chips load, g	600
Green liquor charge on wood, %	3.0
Liquor to wood ration	4.0
Ramp time, min	50
Extraction temperature, °C	160
Extraction time, min	110

Table 2
Pulping conditions and results

Pulp ID	Cook EA charge, %	Total EA charge, %	H-Factor	Screened yield, %	Kappa number
Regular Kraft pulp (HW)	15.0	15	1400	47.53	17.70
Pre-extracted Kraft pulp (HW)	12.0	12.67	1400	46.04	17.11
Pre-extracted Kraft pulp (SW)	13.5	14.17	1400	43.69	27.80
Regular Kraft pulp (SW)	15.5	15.5	1400	43.78	30.52

Table 3
Analysis of hemicellulose extracts

Content, %	Uronic acids	Acetates	Lignin	Xylose
on total dry solids	11.1	40.5	5.8	35.75
Content, %	Arabinose	Glucose	Mannose	Galactose
on total dry solids	2.14	1.52	0.75	1.48

Table 4
Adsorption conditions and results

Adsorption conditions		Adsorbed pulp Kappa	
Pulp consistency, %	2.5	Hardwood	Softwood
Extracts ratio to pulp	4.0	22.24	39.83
Temperature, °C	95	Adsorption yield, %	
Time, min	60	Hardwood	Softwood
pH	5.5	9.23	10.17

Pulp refining and testing physical strength

Pulp beating was performed in a PFI mill according to TAPPI Procedure T-248, each sample being refined to the determined number of revolutions. For each softwood pulp, one sample was refined to 2500, 5000, 7500 and 10000 revolutions. For each hardwood pulp, one sample was refined to 2000, 4000, 6000 and 8000 revolutions.

Handsheets were made from the refined pulp samples, using Standard TAPPI Procedure T-220. At least 8 handsheets were prepared for each pulp sample at each beating revolution.

The pulp freeness of the refined pulp was tested using standard TAPPI Method T-227.

The following physical properties were tested using the standard TAPPI Testing Procedure: Sheet Thickness T-220 (T-411), Burst Strength T-220 (T-403), Tear Strength T-220 (T-414), and Tensile Strength T-220 (T-494).

RESULTS AND DISCUSSION

Comparative adsorption of hardwood and softwood pulps

Our previous work[16] has proven that hardwood pulp could adsorb substantially the xylan-rich extracts from hardwood. To determine the adsorption ability of both softwood pulp and softwood extracts, which act as adsorbent and adsorbate, respectively, extractions for both hardwood and softwood were carried out in the digester under the same extraction conditions. Both extraction liquors were separately applied for softwood Kraft pulp adsorption under the same adsorption conditions. The comparison of the adsorption efficiency of the extraction liquors from hardwood and softwood was plotted in Figure 1. Amazingly, a significant difference in the adsorption yield was observed between the two extracts liquor applications, almost 10% of adsorption yield being obtained by applying the extracts from hardwood, *i.e.* three times higher than when using softwood extracts. The reason might be the different dissolving mechanism of glucuronoxylan in hardwood from that of galactoglucomannan in softwood. During the extraction, glucuronoxylan was dissolved mainly in polysaccharide form, while galactoglucomannan underwent degradation before being dissolved, which resulted in smaller molecules and lower polymerization in the galactoglucomannan extracts, compared to the glucuronoxylan ones. The shorter molecule chain usually shows a poor adsorption ability.

To compare the adsorption ability of softwood and hardwood pulps, the same hardwood extraction liquor was used for the adsorption of Kraft Loblolly pine pulp and hardwood Kraft pulp under the same adsorption conditions. The results are presented in Figure 2. Interestingly, softwood pulp exhibited a strong adsorption ability on xylan extracts, in comparison with hardwood pulp, a slightly higher adsorption yield being acquired. The results indicate the same affinity of xylan extracts to both fiber types and the possibility of applying extraction for intercross adsorption to modify the pulping process.

Comparative beatability

The developments of Canadian Freeness (CFS) during the beating process for both the softwood and hardwood pulp groups are shown in Figures 3 and 4. Overall, the adsorbed pulp showed the lowest freeness during the entire beating process, in comparison with other conventional Kraft and pre-extracted modified Kraft pulps. The same results were observed for both softwood and hardwood pulps. The results indicate a tremendous effect of adsorption on pulp beatability, during the beating process. The freeness of hemicelluloses adsorbed pulps developed much faster than that of conventional pulp. For an equivalent freeness, the adsorbed softwood pulp required fewer beating revolutions than the standard Kraft pulp, a 2000-3000 beating revolution reduction for hardwood pulp and an about 1000 revolution reduction for softwood pulp.

To investigate the contribution of beatability to pulp strength, the correlation of different pulps with their strength property was elucidated in Figure 5. It is clear that all groups of pulp freeness are well-correlated with pulp strength, without obvious differences. A lower CFS always corresponds to higher physical strength. Hence, hemicelluloses adsorption generates important benefits for pulp refining. On the one hand, by beating pulp to a specific degree, a lower CFS of the adsorbed pulp leads to higher physical strength. On the other hand, to reach the same CFS, the adsorbed pulp requires less time, which means significant energy saving in the refining process.

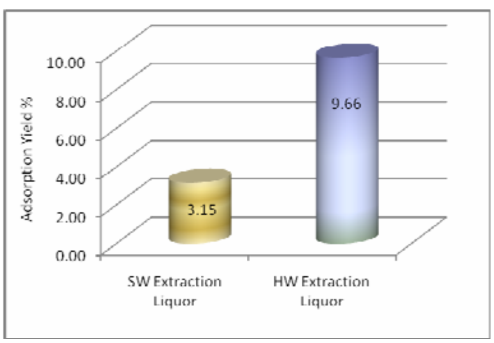

Figure 1: Comparative adsorption efficiency for softwood and hardwood extraction liquors applied to softwood pulp

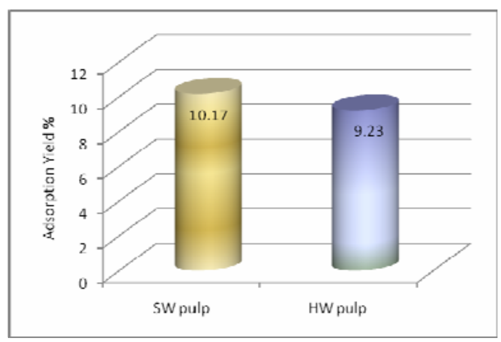

Figure 2: Comparative adsorption yield for hardwood extracts applied to hardwood and softwood pulps

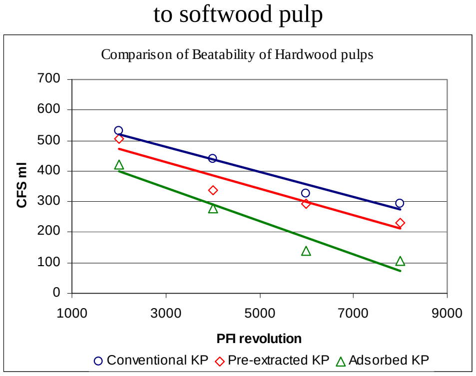

Figure 3: Comparative beatability of hardwood pulps

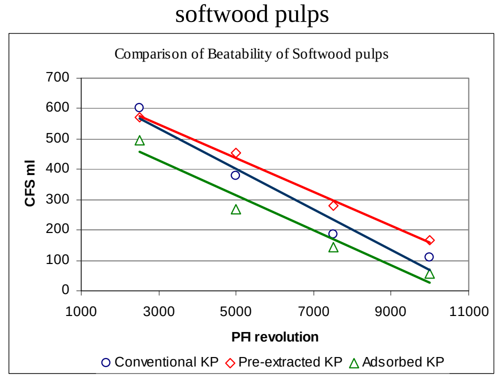

Figure 4: Comparative beatability of softwood pulps

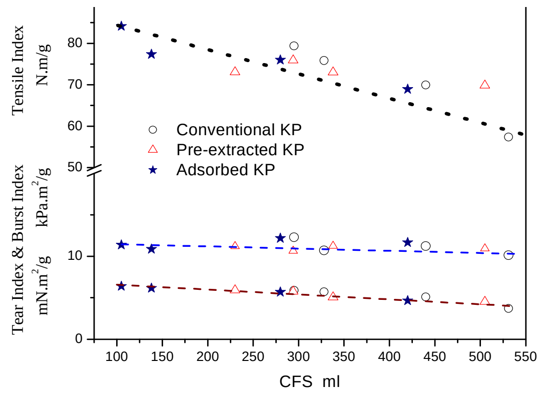

Figure 5: Correlations of pulp strength properties with beating freeness

Moreover, the contributions of adsorption to the beatability of hardwood and softwood pulp were quite different. During the entire beating process, the adsorbed hardwood pulp acquired a 100 to 200 lower CFS, compared to conventional Kraft pulp. However, the adsorbed softwood pulp showed only a 50 to 100 lower CFS, compared to that of conventional Kraft pulp, half of the range of hardwood pulp. The different influence of adsorption on hardwood and softwood pulp will be further discussed.

Finally, pre-extraction also showed an influence on hardwood pulp beatability. Through pre-extraction, pulp exhibited better beatability, which made it easier to acquire a lower CFS, compared to conventional Kraft pulp. Higher strength would be also expected. However, no significant effect on pulp beatability was observed for softwood pulp.

In summary, xylan extracts adsorption effectively improved pulp beatability for both hardwood and softwood pulp. Higher beating efficiency and better pulp strength would be expected.

Comparative physical strength for hardwood pulps

The development of tensile and burst strengths in the beating of three pulp samples – conventional Kraft, pre-extracted Kraft and hemicelluloses adsorbed Kraft pulp – is illustrated in Figure 6. First of all, hemicelluloses adsorption demonstrated a significant effect on both tensile and burst strengths. Compared to conventional Kraft pulp, an increase of up to 20% in tensile strength was achieved through hemicelluloses adsorption, as well as an increase in burst strength of 10-25%. Specifically, the adsorbed pulp and the control Kraft pulp showed the same tendency of strength development during the PFI beating process, but at different levels. The results indicated that adsorbed hemicelluloses normally strengthened fiber bonds, no matter if the fiber was well-refined or not. The contribution of hemicelluloses adsorption to the strength might be attributed to the increase of free hydroxyl groups on the fiber surface from adsorbed hemicelluloses molecules, which would enhance hydrogen bonds between fibers. Moreover, pre-extracted pulp showed a slower development rate for both tensile and burst strengths than the other two pulps. As a result, pre-extracted pulp showed higher strength than the conventional Kraft pulp at a low beating level, however, a slow strength development eventually made pre-extracted pulp strength even lower than that of Kraft pulp at a high fiber refining level. The reason might be the lower amounts of hemicelluloses contained in pre-extracted pulp, which resulted in slower tensile development during beating.

The change in tear strength during pulp refining is plotted in Figure 7. The much higher original tear strength is the most remarkable feature of adsorbed pulp, which indicates that hemicelluloses adsorption would improve the pulp original tear strength. However, the difference of tear strengths between the conventional and adsorbed Kraft pulps became smaller as beating proceeded, and finally both reached a similar level at a high beating level.

In most cases, for evaluating tear strength, it is more meaningful to compare tear strength at a certain tensile level. Figure 8 shows the comparison of three pulps' tear strength at a tensile index of 70 N.m/g. It was clear that an around 8% increase in tear strength at a tensile index of 70 N.m/g would be acquired by hemicelluloses adsorption, compared to conventional Kraft pulp. For pre-extracted Kraft pulp, although higher tear strength was observed in the initial stage of refining, compared to conventional Kraft pulp, no difference was observed when comparing the tear strength of the two at a tensile index of 70 N.m/g.

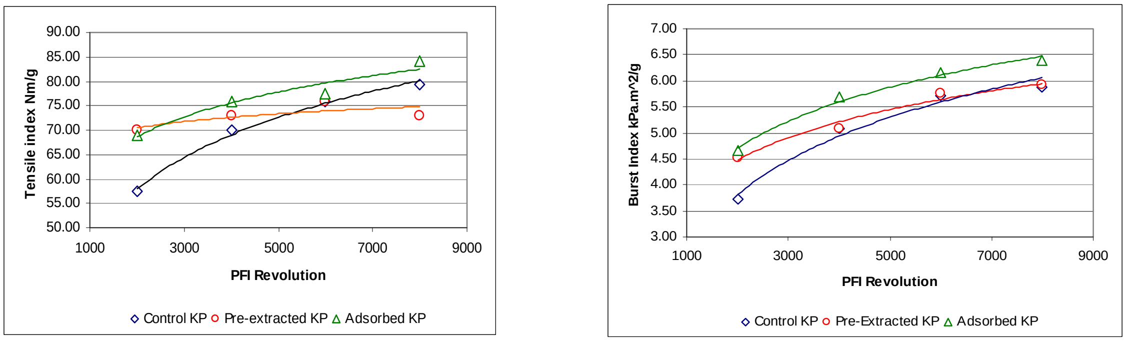

Figure 6: Tensile and burst strength development during PFI beating (hardwood)

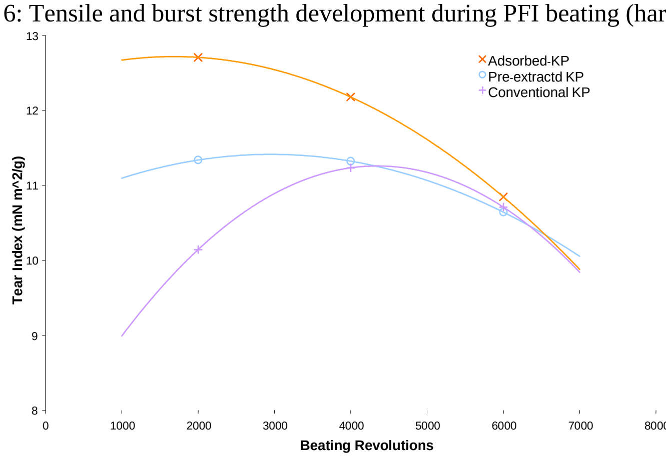

Figure 7: Comparative tear strength development during PFI refining (hardwood)

In summary, the re-deposition of hemicelluloses onto hardwood pulp would significantly improve pulp physical strength, especially bonding, tensile and burst strengths. Pre-extraction showed a certain contribution to physical strength, mostly at lower refining levels.

Comparative physical strength for softwood pulps

Because of the poor adsorption of softwood extracts, the current work used hardwood extracts for softwood pulp adsorption. Similar to hardwood pulp, the adsorption of hardwood hemicelluloses contributed to improving softwood pulp strength properties. Both tensile and burst strengths increased, as shown in Figure 9. Compared to conventional Kraft pulp, a 10-20% increase in tensile strength was achieved, which showed the same extent of tensile improvement as hardwood adsorbed pulp did. However, an increase of only about 5% in burst strength was observed, much lower than that of hardwood adsorbed pulp.

Contrary to tensile and burst strength, adsorbed pulp did not show higher tear strength, as expected, during the beating process, as shown in Figure 10. On the one hand, both conventional Kraft and pre-extracted Kraft pulp showed the same tear strength change in PFI beating, while adsorbed pulp showed lower tear strength than the other two pulps. On the other hand, however, when comparing pulp tear strengths at a certain tensile level, adsorbed pulp still demonstrated higher tear strength (Fig. 11). An increase of 10% in tear strength at a tensile index of 70 N.m/g would be acquired by hemicelluloses adsorbed pulp, compared to conventional Kraft pulp. Although adsorbed softwood pulp showed lower tear strength at a certain beating stage, its greater tensile development during refining resulted in higher tensile strength at earlier beating stages, hence, lower refining requirements would reduce fiber cutting and result in higher tear properties. Pre-extraction showed some benefits for Kraft pulping, such as reduction of pulping chemicals, a slight pulp yield increase, mainly for hardwood. The investigation on pre-extraction will be discussed in the future. The current work indicates the contribution of pre-extraction to improving pulp strength for softwood Kraft pulping. Through extraction, the pulp showed higher tensile strength, in comparison with conventional Kraft pulp.

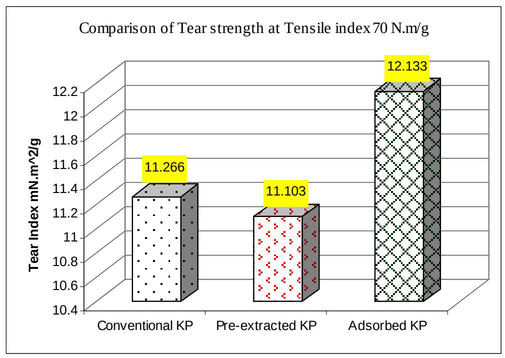

Figure 8: Comparative tear strength at tensile index 70 N.m/g (hardwood)

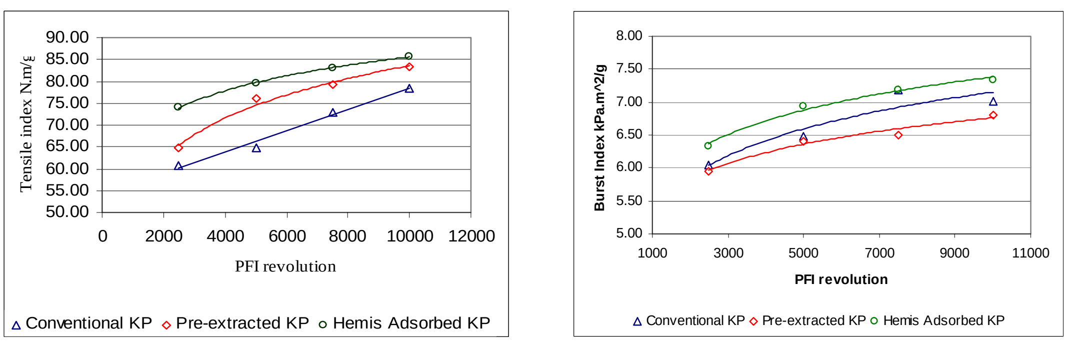

Figure 9: Comparative tensile and burst strength (softwood)

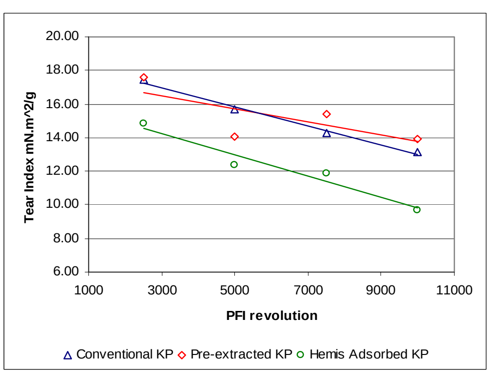

Figure 10: Comparative tear strength development during PFI refining (softwood)

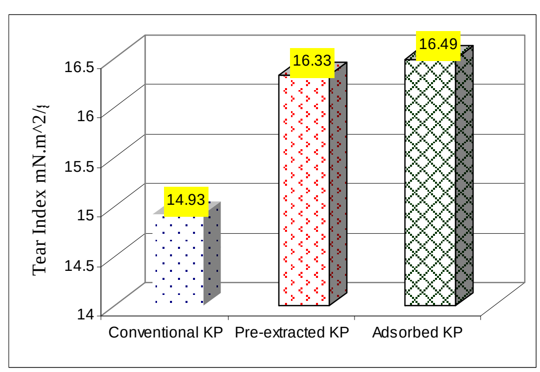

Figure 11: Comparative tear strength at tensile index 70 N.m/g (softwood)

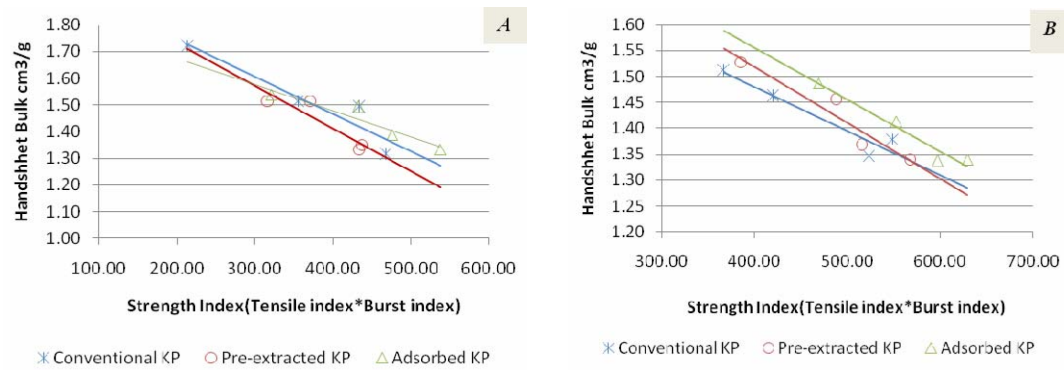

Figure 12: Correlation of pulp strength with bulk property (A: hardwood pulp; B: softwood pulp)

Overall, xylan hemicelluloses adsorption gave softwood fiber higher physical strength; the most significant was tensile strength, compared to hardwood pulp. Tear strength would be also improved to reach a specific tensile level. However, adsorption showed only a slight improvement on the burst strength of softwood pulp.

Influence of hemicelluloses adsorption on pulp bulk properties

In addition to the physical strength properties, hemicelluloses adsorption onto cellulosic fibers also changes some pulp properties, such as absorbability and printability.[17-19] Since hemicelluloses have amorphous structure and diversified chain composition different from that of cellulose, it is interesting to know whether hemicelluloses adsorption also resulted in different bulk properties, besides strength improvement. The correlations of pulp strength and bulk properties are presented in Figure 12 (A, B). A comprehensive strength value, used for the estimation of the pulp bonding strength, was obtained by multiplying tensile index and burst index, which represented pulp strength. The pulp bulk property was plotted against strength.

Hardwood pulps did not show obvious differences in their bulk at a lower strength level. When the pulp reached a higher strength level, the adsorbed pulp showed a slightly higher bulk than the other two pulps at the same strength level, as shown in Figure 12A. Unlike hardwood pulp, the xylan adsorbed softwood pulp exhibited a distinctly higher bulk at a specific strength level, in comparison with the other two pulps, as presented in Figure 12B. A similar conclusion was reported in a previous work,[18] which showed that both tensile and stiffness of softwood pulp were increased by xylan adsorption.

CONCLUSION

In the current work, xylan-rich extracts were extracted from hardwood and applied for both hardwood and softwood pulp adsorption. For both hardwood and softwood, three pulp samples were made and compared as to their beatability and physical strength properties. The main conclusions of this work are summarized below.

Xylan-type hemicelluloses adsorption greatly improved pulp beatability, for both hardwood and softwood pulp. Compared to conventional Kraft and pre-extracted Kraft pulps, adsorbed pulp showed a quick freeness development during pulp refining, which indicated an improvement in pulp beating efficiency with shorter beating time.

Significant physical strength improvements were achieved for hardwood pulp by hemicelluloses adsorption. Compared to conventional Kraft pulp, an increase of 20% in tensile and of 10-25% in burst strength would be acquired through hemicelluloses adsorption. Furthermore, an increase of as much as 8% in tear strength was expected for the adsorbed pulp at a tensile index of 70 N.m/g.

Adsorbing xylan onto softwood pulp also produced an important strength improvement. An increase of 10-20% in tensile strength and of 10% in tear strength was achieved, as in the case of hardwood adsorbed pulp. However, a slighter improvement in burst strength was observed, in comparison with hardwood pulp.

To correlate the pulp strengths with bulk properties, adsorbed softwood pulp showed a slightly higher bulk at the same strength than the control pulps. The adsorbed hardwood pulp did not show differences in the strength–bulk correlation.

ACKNOWLEDGEMENTS: The financial support provided by International Paper Inc. is gratefully acknowledged. We also express our gratitude to Lakshmi Narsimhan, Pooja Ashok, Arvind Lali from the Institute of Chemical Technology in India, who carried out the analysis of extract chemical composition. Dr. Haixuan Zou from the Department of Chemical and Biological Engineering at the University of Maine is appreciated for his assistance in the operation of the equipment.

REFERENCES

[1] S. Yllner, B. Enstrom, *Svensk Papperstidn*., **59**, 229-32 (1956).
[2] Al. Meller, *Holzforschung*, **19**(**4**), 118-24 (1956).
[3] J. A. Hansson, *Svensk Papperstidn*., **73**(**3**), 49-53 (1970).
[4] J. A. Hansson, N. Hartler, *Svensk Papperstidn*., **72**(**17**), 521-30 (1969).
[5] N. Hartler, A. Lund, *Svensk Papperstidn*., **65**, 951-53 (1962).
[6] D. W. Clayton, G. R. Phelps, *J*. *Polym*. *Sci*., *Polym*. *Symp*., **11**, 197-220, (1965).
[7] V. S. Gromov, A. Treimanis, Yu. Yu. Katkevich, *Cellulose Chem*. *Technol*., **6**(**2**), 239-48, (1972).
[8] C. Schonberg, T. Oksanen, A. Suurnakki, H. Kettunen, J. Buchert, *Holzforschung*, **55**(**6**), 639-644 (2001).
[10] P. Westbye, C. Svanberg, P. Gatenholm, *Holzforschung*, **60**, 143-148 (2006).
[11] Å. Linder, R. Bergman, A. Bodin and P. Gatenholm, *Langmuir*, **19**, 5072-5077 (2003).
[12] H. L. Spiegelberg, *Tappi J*., **49**(**9**), 388-396 (1966).
[13] N. Fišerová, E. Opálená and J. Farkaš, *Cellulose Chem*. *Technol*., **21**, 419-430 (1986).
[14] J.-C. Roberts and A. S. El-Karim, *Cellulose Chem*. *Technol*., **17**, 379-386 (1983).
[15] T. Köhnke, *Thesis*, Chalmers University of Technology, 2010, pp. 9-13.
[16] W. Ban and A. Van Heiningen, *Cellulose Chem*. *Technol*., **45**, 57 (2011).
[17] Å. Henriksson and P. Gatenholm, *Cellulose*, **9**, 55-64 (2002).
[18] A.-M. Olsson, L. Salmen, ACS Symposium Series: *Hemicelluloses*, **864**, 184-197 (2004).
[19] S. Danielsson, M. E. Lindstroem, *Nordic Pulp Pap*. *Res*. *J*., **20**(**4**), 436-441 (2005).