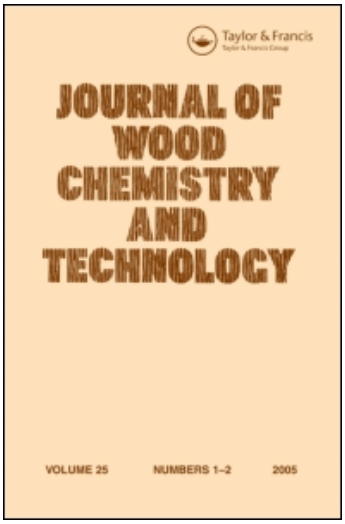

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Hemicellulose Distribution in Pulp Fibers Anti Alkaline Extraction Rates

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HEMICELLULOSE DISTRIBUTION IN PULP FIBERS AND ALKALINE EXTRACTION RATES

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ABSTRACT

Hemicellulose molecules available for fiber-fiber bonding should also be among those most readily extracted by alkali. With this premise in mind the extraction rates of hemicellulose from chemical pulps were examined and interpreted as being dependent on hemicellulose distribution. Measurements of the rates of extraction of glucuronoxylan and glucomannan from primarily southern pine oxygen pulps showed that the bulk of hemicellulose was not immediately available to extraction. After a few seconds of initial rapid extraction by 6% NaOH, removal rates quickly decreased but extraction continued indefinitely. Adsorbed hemicellulose by comparison was initially more rapidly extracted. About half of the hemicellulose most rapidly extracted from high-yield oxygen pulps was associated with lumens and large pores. The remaining half (perhaps 5% of the xylan and 2-3% of the glucomannan) was estimated to be the maximum amount potentially, but not necessarily, available for fiber-fiber bonding.

INTRODUCTION

Many people have investigated the distribution of hemicellulose within pulp fibers because of its possible relationship to pulp and paper strength. Various proposals for the composition of

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primary through S3 cell wall layers of pulped fibers resulted.[2-7] There is some, but not complete, agreement that in kraft softwood fibers the xylan concentration is higher in outer layers, and glucomannan more concentrated in S2.

Interest has increased in the distribution of hemicelluloses at a lower scale of magnitude than the major cell wall layers. Parameswaran and Liese[8] have reviewed some of the pertinent literature, and Scallan[9] summarized the evidence for a multi-lamellar arrangement of cellulose within the major cell wall layers of pulp fibers. Kerr and Goring[10] proposed a cellulose fibril unit (transverse section about 3.5 nm by 7-14 nm) which might be embedded in a hemicellulose-lignin matrix with one-third of the hemicellulose associated directly with the cellulose. Ruel and Barnoud[11] have observed 7-8 nm wide fibrils within a lignin-containing matrix.

Hemicelluloses in the external surface layers of pulped fibers are likely to be important in fiber-to-fiber bonding. For any particular fiber the question is what hemicellulose is surface-exposed for possible interfiber hydrogen bonding, and what is within the cell wall engaged in intrafiber bonding, perhaps between cellulose fibrils? Kibblewhite and Brookes[5] found 83% cellulose in the carbohydrate fraction of the primary-S1 layer of kraft-pulped pine fibers. Consequently, even the primary and S1 wall layers of pulped fibers may contain sufficient cellulose to embed all of their hemicellulose within a cellulose framework.

An estimation of surface-exposed hemicelluloses was attempted by means of brief alkaline extractions of hemicellulose from pulp fibers. It would be expected that hemicellulose molecules lying on fiber surfaces would be immediately removed by aqueous alkali capable of swelling cellulose. The removal rates of other soluble molecules within the pulp should be controlled by diffusion.

Extraction techniques were designed to measure the quantities of very accessible 4-O-methylglucuronoxylan and galactoglucomannan. The 4-O-methylglucuronoxylan will be referred to as xylan and the

galactoglucomannan as glucomannan. Analysis of total xylose and total mannose in an extract is the basis for calculating the percentage removal of the two polysaccharides. Most measurements were with slash and shortleaf pine pulps and primarily with oxygen pulps rich in hemicellulose.

EXPERIMENTAL

Preparation of Pulps and Holocellulose

Shortleaf pine, oxygen pulps, which had been prepared in a previous study[12], were suitable to demonstrate the important variables in alkaline extractions. These pulps of about 60% yield contained about 14% mannose anhydride, 8-9% xylose anhydride, and 3-6% lignin. Ratios of mannose to galactose were 8 and 12 in the only two oxygen pulps analyzed for galactose. Analyses of two shortleaf pine kraft pulps and a hemlock sulfite pulp are included in the notes with Table 1. The loblolly pine holocellulose, a mixture of springwood and summerwood tangential slices, was prepared in 77% yield by low-temperature chlorite oxidation[13]. It contained 60% glucose anhydride, 17% mannose anhydride, and 10% xylose anhydride.

Samples having adsorbed glucomannan were prepared by adding 20 mL of hemicellulose solution in water to 0.5 g of cotton or alpha pulp in 10 mL of water. The alpha pulp (bleached, Sitka spruce, sulfite) was extracted with 6% NaOH, washed, and air-dried before the adsorption step. The hemicellulose, extracted by NaOH from an oxygen pulp, was isolated by acidification and alcohol precipitation and included both xylan and glucomannan. Only the glucomannan was measurably adsorbed in a 10-min soak and then retained after two 15-s washes with water; the mannose, as anhydride, was then about 2% of the pulp. The pulp samples with adsorbed glucomannan were not dried before being extracted with alkali.

Extraction Techniques

Air-dry pulp samples (0.5 g ovendry) were stirred with a glass rod into two successive 15-mL amounts of extraction solution ("double-extraction procedure"). The dispersal of fibers assured their washing by solvent during each extraction. The extracts were drawn through a coarse ground-glass filter and followed by a final 5-mL rinse with solution while still applying suction. Moderate tamping of the mat aided removal of solvent. As closely as possible the recorded extraction time included only the time of contact between fibers and alkaline solution (except for the very brief 5-mL rinse). It was possible to shorten the total extraction time to two successive 15-s extractions by stirring the pulp in the filter funnel. Longer double extractions were in a small beaker with transfer to the funnel. The first of the double extractions was about half of the total time, up to totals of 5 min. Beyond totals of 5 min it made no difference whether the first extraction was a few minutes or a much larger part of the total extraction time.

The following additional methods were used for a single extraction step to obtain still shorter extraction times. The first method was extraction of a moist pulp bed on a 3-cm-diameter filter funnel by washing with an alkaline solution, using suction to obtain short contact times. For the second method an 8.8-cm-diameter Büchner funnel was fitted with a 100-mesh screen upon which 0.5 g of beaten pulp was poured to give a uniform layer. A second screen was placed above the wet pulp to prevent disruption of the layer when alkaline solution was added. Extract was collected without suction for contact times as low as 2-3 s. Lastly, a method which furnished several extract samples for each pulp sample consisted of 100 mL of mechanically stirred 6% NaOH into which the moist pulp sample was quickly added and dispersed. One-mL samples of solution were taken at intervals and the few fibers removed by centrifugation. The 30-s extract by this method was equal to that from the double-extraction procedure,

probably because the mechanical stirring caused a rapid exchange of lumen and external solutions.

Six grams of NaOH in 100 g H_2O (with the approximate designation, 6% NaOH, in the text) was chosen for most extractions because it accomplished adequate swelling without mercerization at room temperature (at which temperature all extractions were made).

Chemical Analyses

Pulps and extracts contained the glycosidically combined forms of glucose, mannose, xylose, and uronic acid. The combined neutral glycoses were determined directly by a spectrophotometric method[14] and uronic anhydride was determined by a colorimetric method.[15] The ease with which these methods supplied analyses was important because of the large number of extractions. The percentages of the polymers, xylan and glucomannan, removed from pulp were equated with respective percentages of total xylose and mannose removed and found in extracts. This assumes that the polymers have a uniform composition. Uniformity of the xylan will be discussed in the next section. Accurate analyses for xylose by the method[14] used would require corrections for uronic anhydride and arabinose, but were not applied here because they would have little effect on the reported percentage of xylan extracted and would require much more extensive analyses. Chemical stability of the polymeric glycoses in alkaline extracts was demonstrated by successive analyses which did not decrease during several days at room temperature.

RESULTS AND DISCUSSION

Measurements of Extraction Rates

The first result from several extractions of a single pulp type was that the time of contact between pulp and solution was the important variable. That is, the amounts of xylan and glucomannan removed depended primarily on the contact time and not

on the amount of solution (above a minimum), nor on the number of successive extractions (over two) within a time period. With a single pulp and uniform extraction procedure, such as the double extraction described in the experimental section, equal time periods produced equal extracts. Consequently, rates of removal of xylan and glucomannan could be measured by analyses for xylose and mannose in separate, but uniformly obtained, extracts with increasing durations.

The amounts and rates of removal of xylan and glucomannan from an oxygen pulp are illustrated in Fig. 1. The results of seven separate pulp extractions are combined to form the rate curves in Fig. 1A. Approximately 9% of the pulp mass was extracted within 5 min. This amount is a substantial part of the hemicelluloses. It is apparent that the initial rate must be much greater than rates after the first half minute. Within 30 s the extract contained 40% of the xylan and 14% of the glucomannan of the pulp. After 6 days, 73% of the xylan and 41% of the glucomannan were extracted, and extraction continued at a slow rate. These results are similar to those of Ohlsson[16], who stressed the importance of time in measurements of beta and gamma cellulose in pulps, and produced graphs such as Fig. 1A, but for generally longer extraction times.

A change of extraction procedure can give different, but informative, results. For example, the effect of suction on the removal of hemicelluloses is shown in Fig. 1, B and C. In these tests the volumes of solution were several times the minimum used for the 30-s double extraction of Fig. 1A. Yet, with the procedure used for Fig. 1B results, the amounts extracted in 30 s were lower than those in Fig. 1A. The difference was due to one less suction step for removal of solution from lumens and from the larger pore spaces within cell walls. The decreased extraction is still more apparent in Fig. 1C because there was no suction. A comparison of the 30-s data in Fig. 1, A and C, indicates that about half of the 30-s extract with two suction steps (Fig. 1A) came from lumens and large pores.

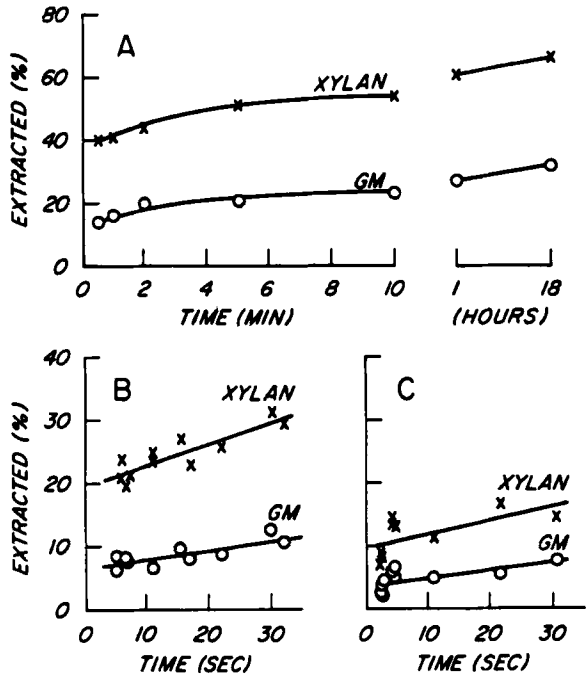

FIGURE 1. Extraction of xylan and glucomannan (GM) from shortleaf pine oxygen pulp with 6 g NaOH in 100 g of water (A, with two suction steps; B, with one suction step; and C, with no suction). Percentages of the initial pulp xylan and glucomannan are plotted.

It should be noted that the uniform extraction procedures, with or without suction, do not contain a water-wash step. The reason for this omission is not only that extraction rates would be interrupted by a solvent change, but also that the change in ionic strength would introduce a new, interfering factor. This was apparent from significant amounts of hemicellulose in water washes. Most likely there was an expulsion of solubilized molecules from many small pores as the hydroxide was diluted. It can be demonstrated that this material is in addition to material removed by suction and designated as contents of lumens and large pores. Two pulp samples were double-extracted with 6% NaOH for a total of

TABLE 1

Rates of Extraction of Xylan and Glucomannan From Oxygen, Kraft, and Sulfite Pulps[a]

Pulp[b]	Percentage of xylan extracted			Percentage of glucomannan extracted		
	30 sec	1 h	18 h	30 sec	1 h	18 h
Shortleaf pine, oxygen (SD-51)	40	61	67	14	27	32
Shortleaf pine, kraft (6140)	28	51	61	4	8	8
Shortleaf pine, kraft (5671)	21	37	47	3	8	7
Hemlock, sulfite	50	68	77	28	42	50

[a]Double extractions by 6 g NaOH in 100 g H_2O.

[b]Pulp SD-51: screened yield 40% (total yield, 63%), kappa No. 38, xylose 9.1%, mannose 13.9%, galactose 1.7%. Pulp 6140: kappa No. 46, xylose 8.9%, mannose 6.8%. Pulp 5671: kappa No. 31, xylose 7.5%, mannose 7.5%. Sulfite pulp: 2.5% xylose, 6.6% mannose, 1.7% lignin. Sugars as anhydrides.

10 min to remove the most extractable hemicelluloses, which were then discarded. One of the samples was then extracted successively seven times with 6% NaOH for a total of 23 min. The second sample was extracted in the same manner except for four 1-min water washes in series with three alkaline extractions, which totaled 20 min. The extracts were combined, and the water washes were included with the second sample's extracts. The water-washed sample lost 20% more glucomannan and 60% more xylan than did the unwashed sample.

Pulps can be compared on the basis of hemicellulose extractability. Extractions of all three pulp types listed in Table 1 were much more effective in removing xylan than glucomannan. However, the pulps differed greatly in the extractability of the two hemicelluloses. The differences may have been partly due to variable degradation of hemicellulose during pulping, partly to

differences in the openness of pore structure,[17] and partly to locations altered during pulping. Crystallinity of xylan adsorbed during a sulfate cook has been suggested as a reason for its slow extraction from sulfate pulps[18], but the removal of lignin and sodium ion during washing is also slower for sulfate than for sulfite pulp.[19]

Significance of Extraction Rates

Intrinsic factors which were possibly influencing the rates of removal of hemicelluloses were their chemical constitution, their molecular weights, and their locations within the fibers. Chemical uniformity in the xylan was indicated by a test with oxygen pulp having about 0.5% uronic anhydride; the xylose:uronic acid mole ratio in extracts did not change in the first 3 days of extraction. Lindberg and Meier[20] found differences in extractability of glucommanans with $\overline{DP}_n$ values varying from 70 to 140. However, their spruce holocellulose might have had a greater range of DP than these pulps, which would have lost some hemicellulose in preparation. Variations in the molecular weights of extracted polymers as extraction progressed appeared to be small because there were only minor changes in alcohol precipitability of hemicelluloses during a 3-day extraction. For example, when 30-s, 5-h, and 3-day successive extracts were diluted with water and ethanol to about 2-3% NaOH and 28% ethanol by weight, the amounts precipitated were 12, 13, and 17% of the extracted xylan and 72, 78, and 85% of the extracted glucomannan. Although there is indication of molecular weight differences (i.e. in partial precipitation), the differences between extracts are not large. It was concluded that the hemicellulose location within a fiber was the most important factor determining its extraction rate, particularly within the first hour. That amount of each polymer eluted within 30 s clearly had a simpler diffusion path than that remaining in the fibers.

Extracts were a result of three successive mass transfers: entrance of alkali with resultant swelling, dissolution of soluble

material, and egress of soluble material with solvent. Hoyland[21] considered surface wetting time as negligible and water swelling of unsized sheets as accomplished within 2-3 s. Removal of completely exposed alkali-soluble molecules should proceed at the rate of water swelling. The slowest step, removal of dissolved hemicellulose from within fibers, was greatly influenced by the extraction procedure, as Fig. 1 and the results of water washing showed. Many small voids within the fibers contained dissolved hemicellulose, but their smallness limited the rates at which polymer molecules could diffuse into pores large enough for emptying by suction filtration. Thompson et al.[22] pointed out that the dependence of diffusion on local porosity would cause some outer-layer hemicellulose to be inaccessible while some inner-layer hemicellulose could be accessible in a particular extraction.

Holocellulose Extraction. Lumen Contribution.

The effect of suction and the contribution of lumen and large pore contents to the total pulp extract was also shown by extractions of chlorite holocellulose wafers. These were 5-cm square, tangential slices of loblolly pine about 0.6 mm (12 cells) in thickness. Their extracts were compared before and after brief fiberization that partially separated fiber bundles (Table 2). Extractability of hemicellulose from the holocellulose wafers in 30 s was very low but greatly increased by the fiberization. When extractions were continued for a few hours, fiberized and unfiberized holocellulose wafers gave identical extracts, showing that only the rate of extraction was affected by fiberization. To explain the large difference during brief extractions, holocellulose wafers were transversely cut into about 0.8-mm lengths, thereby exposing the lumens as the primary alteration of the fibers. Such exposure resulted in the greatly increased 30-s extracts shown in Table 2.

Amounts extracted from fiberized wafers and from oxygen pulp were similar (Table 2). The larger amount of xylose extracted from

TABLE 2

Percentage of Original Xylan and Glucomannan in 30-Second, 6% NaOH Extracts of Loblolly Pine Holocellulose Wafers[a] and of Southern Pine Oxygen Pulp

	Xylan	Glucomannan
Wafers, uncut	7	2
Wafers, fiberized	52	11
Wafers, cut to 0.8 mm	22	6
Pulp	40	14

[a]Wafers were a mixture of springwood and summerwood, tangential, 5-cm squares about 12 cells thick. The 0.8 mm after cutting was in the fiber direction.

the fiberized loblolly holocellulose came from its additional xylan, a relatively accessible amount possibly lost during oxygen pulping.

A further demonstration of the effect of transversely cutting holocellulose fibers is shown in Fig. 2. In this case a graded series of transverse sections was cut from separated springwood, tangential slices of the same holocellulose. The sections to be extracted differed dimensionally only in the fiber direction. The graphs show that once the lengths of cut sections reached the cell length (about 3 mm), the amount of hemicellulose extracted in 30 s rose sharply. The abrupt increase indicates that exposure of lumens was very important to the increased extraction rate. The high values from the two shortest lengths in Fig. 2 show that the springwood hemicellulose was more extractable than that of the mixed springwood-summerwood of Table 2. It is evident that in 30 s the extraction of lumen contents from the unfiberized or uncut wafers was limited to those few pit pores leading to the external solution. Suction steps applied to intact tangential wafers could not be as efficient in withdrawing lumen contents as suction applied to the fiberized holocellulose or to pulp mats. Also, fiberization greatly increased the fiber surface exposed to solvent.

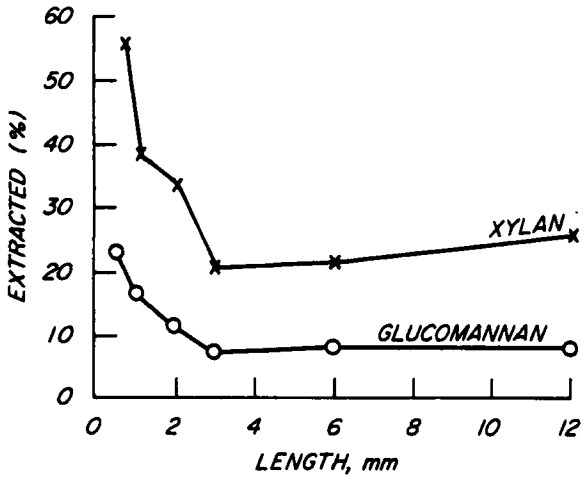

FIGURE 2. Dependence of percentage xylan and glucomannan extracted in 30 s upon length of segments transversely cut from tangential springwood wafers of loblolly pine holocellulose. Solvent: 6 g NaOH in 100 g of water.

Surface Area and Extraction Rate

Evidence of the influence of surface area upon hemicellulose extraction came from ground pulp. Oxygen pulp was ground to 40 mesh or was vibratory ball-milled for 30 min as described by Pew.[23] Water extraction of the ball-milled fibers removed 68% of the xylan in 30 s (all of which passed through a 0.45-μm cellulose acetate filter). The extraction by water of more xylan than extracted by 6% NaOH from the same pulp before grinding (Table 1) can be attributed to increased surface area.

One-hour extracts of whole and milled fiber are listed in Table 3. Some contribution to solubility due to loss of DP in ball-milling may be indicated by the 16% solubility of glucose polymers in 2% NaOH, but the primary cause of the large differences in extraction rates appears to be increased surface area. The water solubility of the xylan is notable because it indicates that complete surface exposure of xylan would cause it to be

TABLE 3

Effect of Milling on 1-Hour Extracts of Oxygen Pulp

Solvent	Pulp	Percentage extracted[a]		
		Xylose	Mannose	Glucose
Water	Whole fiber	7	0.4	0.1
	40 mesh	24	2	0.3
	Ball-milled	80	22	3
2% NaOH	Whole fiber	32	6	0.5
	40 mesh	61	12	1
	Ball-milled	97	55	16
6% NaOH	Whole fiber	79	22	2
	40 mesh	100	40	5

[a]Data are percentages of each pulp constituent. The pulp analysis was 6% xylose, 14.6% mannose, and 73.5% glucose (amounts as anhydrides).

removed in a water wash. From these measurements and the finding that soluble xylan was not adsorbed by the oxygen pulp fibers (experimental section, pulp preparation), it is concluded that the fibers had no completely exposed xylan.

Extraction of Adsorbed Glucomannan

To provide a guide for detection of surface-adsorbed hemicellulose, the removal rates of adsorbed glucomannan from cotton and alpha pulp were measured. Although 90% of adsorbed glucomannan was removed from cotton in the usual 30-s double extraction with suction, only 65% was removed in 30 s by the method of Fig. 1C, which did not empty the lumens.

In order to include the lumen contents in the extracts and to obtain a series of samples over a brief period, alpha pulp samples with adsorbed glucomannan were rapidly stirred with alkali, the last extraction procedure described in the experi-

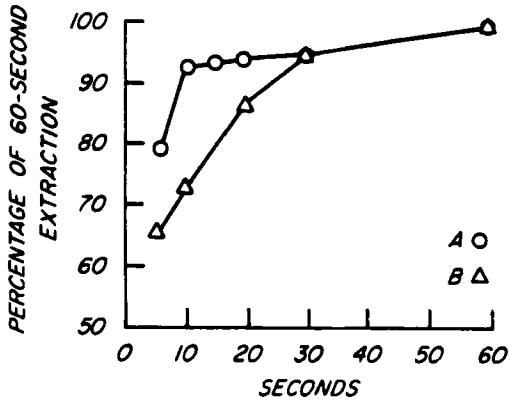

FIGURE 3. Relative rates of removal of glucomannan: (A) adsorbed on alpha pulp and (B) as an oxygen pulp constituent. Solvent: 6 g NaOH in 100 g of water.

mental section. The amounts of mannose found were corrected for the small amounts of mannose extracted from alpha pulp having no adsorbed glucomannan. In Fig. 3 (an average of three runs) the rate of removal of adsorbed glucomannan from alpha pulp is compared to the rate of removal of constituent glucomannan from an oxygen pulp. The more rapid removal of adsorbed glucomannan is apparent in curve A of Fig. 3. The shape of the curve is an indication that most of the adsorbed glucomannan was removed in 10 s. However, the amount extracted from the oxygen pulp in 10 s (about 10% of the glucomannan in this case) cannot be considered as only adsorbed glucomannan because the 10-s extraction could not distinguish adsorbed hemicellulose from that which may have been enclosed in surface pores.

Comparative Distribution of Xylan and Glucomannan

Leopold and McIntosh[24] discussed possible xylan and glucomannan distributions after observing that single fiber strength loss was proportional to the alkaline extraction of xylan rather than of glucomannan. They reasoned that if glucuronoxylan were

in spaces between fibrils, its loss would affect fibril to fibril attachment, whereas loss of less accessible glucomannan, if contained within fibrils, would have less effect on fibril to fibril bonds. They assumed that single fiber strength was directly related to such bonding.

The relatively slow and less complete removal of glucomannan compared to the xylan removal in all cases reported here does indicate a lower accessibility of much of the glucomannan. The much greater effect of pulp subdivision on xylan removal than on glucomannan removal (Table 2) is also an indication of a closer association of at least part of the glucomannan with cellulose. However, in a comparison of extraction rates between different polymers, their molecular weights, conformations, and chemical structures may be as important as their locations. Consequently, more information than extraction rate data is necessary to indicate relative microdistributions of the hemicelluloses.

Fiber Bonding

For a hemicellulose molecule to serve as a direct partner in a fiber-fiber bond it must be exposed on the outer fiber surface at the time such a bond is formed and in a position capable of intimate, about 0.2 nm, contact with an adjacent fiber. This, in turn, requires that some mechanism must be postulated to hold hemicellulose on the external cellulose surface during the last stage of pulping and during draining for sheet formation. The extractions of ball-milled pulp demonstrated the water solubility of xylan and of glucomannan. However, the preferential adsorption of glucomannan onto alpha pulp was also shown. These results do not support the notion that significant amounts of adsorbed xylan will remain on the pulp surface after washing.

There have been many reports showing the sorption of hemicellulose by cellulose and showing the well-known increase of pulp xylan during kraft pulping. Much of the experimental work was done under alkaline conditions at temperatures over 100°C, often at 170°C. Examples are the reports of Yllner and Enström,[18,25]

Hartler and Lund,[26] Hansson and Hartler,[27] Hansson,[28] and Clayton and Stone,[29] which demonstrated uptake of xylan and glucomannan by cellulose. It may be that the high temperatures and the 1-10% concentrations of hemicellulose applied in experiments by these authors resulted in the intermixing of cellulose and hemicellulose by diffusion.[27,28] Alkali consumption during cooking then decreased the swelling of cellulose, thereby preventing removal of some hemicellulose. Furthermore, loss of uronic acid during cooking altered xylan properties. Part of the hemicellulose taken up by the pulp or cotton was shown to be resistant to removal by 10-20% NaOH.[25,27,29] This could not be surface-adsorbed material.

Many of the sorption results and the few desorption data reported by the above authors were similar to those in Fig. 1A; that is, initial rapid uptake or loss followed by slow change. Hansson[28] concluded that the rate control of sorption was a "diffusional process." The resulting fibers were probably like those of the pulps used here in that most of the hemicellulose was within cell walls. Some of this hemicellulose is difficult to extract because of its initial location or its location as a result of pulping. Lindberg and Meier[20] found that glucomannan which was resistant to alkaline extraction became extractable after the holocellulose was dissolved in "cuen" and then regenerated. They concluded that microarrangement and localization of glucomannan within the fiber wall influenced its extractability. Entrapment of hemicelluloses within a cellulose matrix was also the conclusion of Corbett and Kidd[30] from studies of alkali refining of pulps. Lindstrom et al.[31] measured the small amounts of hemicellulose released during beating and suggested that the material had been enclosed in microcavities of the pulp. Removal was aided by an electrostatic repulsion between charged molecules, they proposed. The same repelling force may be partly responsible for the increased extraction when alkali within a fiber is replaced by water during washing.

The potential for intimate intermixing of hemicellulose and cellulose was demonstrated by Clayton and Phelps[32] with sensitive measurements of labeled xylan and glucomannan. Sorption was conducted under very mild conditions in their experiments. Even at 20°C and a pH about 12 the intermixing of 0.05% alpha cellulose with 0.025% hemicellulose was sufficient in 30 s for detectable amounts of the sorbed xylan or glucomannan to resist extraction during 18 hours of soaking in 17.5% NaOH. The difficult removal of hemicellulose after much more severe conditions is understandable. Clayton and Phelps concluded that the hemicelluloses must have been sorbed on internal surfaces.

There is much evidence that hemicellulose contributes to sheet strength. One source of the benefit may be by reason of its location within the cell wall. A second benefit may be realized when external hemicellulose functions as a paper additive. Although many research reports do not make it apparent to what extent hemicelluloses are external to fibers or within fibers, it is quite clear from some reports that a primary function was as an additive. March[33] added dry hemicellulose before beating, Thompson et al.[34] added hemicellulose water solutions to prebeaten α-pulp, Toda et al.[35] sprayed a hemicellulose solution onto the wet sheet, Pettersson and Rydholm[36] added hemicellulose solutions at the beater and at the mould, and Mobarak et al.[37] added hemicellulose suspensions to beaten pulps. All of these authors measured substantial strength improvements. However, the positive effects of hemicellulose additives should not be fully equated with beneficial effects of hemicelluloses well within the fiber walls.

Summary and Conclusions

Uniformly obtained alkaline extracts of xylan and glucomannan from pulps were reproducible down to about 10-s extractions. These extractions distinguished qualitatively between hemicelluloses located on or near outer fiber surfaces and those

located on or near lumen (or large pore) surfaces because extractability from the latter was more dependent upon suction in short time periods. It was estimated that about half of an extract with suction came from the lumens and large pores. The water solubility of xylan argues against its simple adsorption on fiber surfaces.

An explanation for rapid extraction of some enclosed xylan and glucomannan may be that alkali rapidly opens surface pores that remain closed in water alone. A corollary to this suggestion is the possibility that some hemicellulose molecules may be partially embedded in the surface pore structure and partially exposed. Such molecules would be solubilized by water with difficulty but much more readily by alkali.

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