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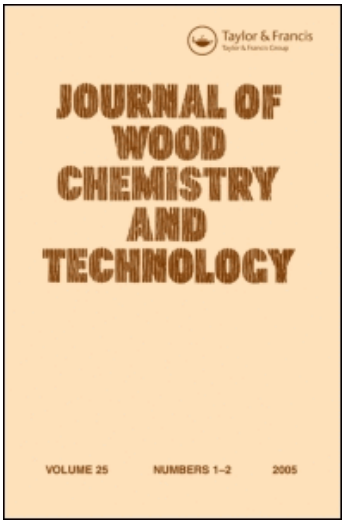

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MOLECULAR WEIGHTS OF LIGNOSULPHONATE AND CARBOHYDRATE LEACHED FROM SULPHITE CHEMIMECHANICAL PULP

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ABSTRACT

The molecular weights of both the lignosulphonate and carbohydrate fractions leached from sulphite chemimechanical pulps increased as the leaching proceeded. Lignosulphonate molecular weights rose from 11000 to 61000. Values for the carbohydrate fractions were lower, ranging from 6000 to 17000. For the lignin, the diameter of the equivalent sphere corresponding to the whole sample leached was considerably higher than the medium-pore diameter of the fiber. This discrepancy indicated that the lignosulphonate macromolecule in the fiber wall adopted a flat conformation.

INTRODUCTION

When high yield sulphite chemimechanical pulp is suspended in water, lignin and carbohydrate are leached from the fibers[1]. The leaching process appears to be diffusion controlled[1]. The rate of leaching also depends on the degree of swelling of the fiber, being faster when the fiber is more swollen[2]. Thus the mechanism

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seems to be one of restricted diffusion of lignosulphonate and carbohydrate macromolecules through the pores in the fiber wall.

If the above picture is correct it would be expected that greater quantities of the low molecular weight material would be released first with more of the larger molecules being removed in the later stages of leaching. There should also be some correlation between the size of the molecules and the dimensions of the pores in the fiber wall. Such trends have been noted in the leaching of lignin from the fibers of unbleached kraft pulp[3].

The purpose of the present work was to measure the molecular weight of fractions of lignosulphonate and carbohydrate removed from the fibers at different stages of leaching and to compare the size of the leached macromolecules with the size of the pores in the wall. Samples were isolated at various intervals in the leaching process and the lignosulphonate and carbohydrate fractions separated by electrophoresis-convection[4]. Molecular weights were determined by sedimentation equilibrium[5]. For the lignin, a comparison was made between the effective hydrodynamic diameter of the dissolved macromolecules and the pore size of the water-swollen fiber wall.

EXPERIMENTAL AND RESULTS

The pulp sample used for the present investigation was an ultra high yield sulphite chemimechanical pulp (CMP) of 92% yield obtained from a newsprint mill. The chip stock consisted of 45%

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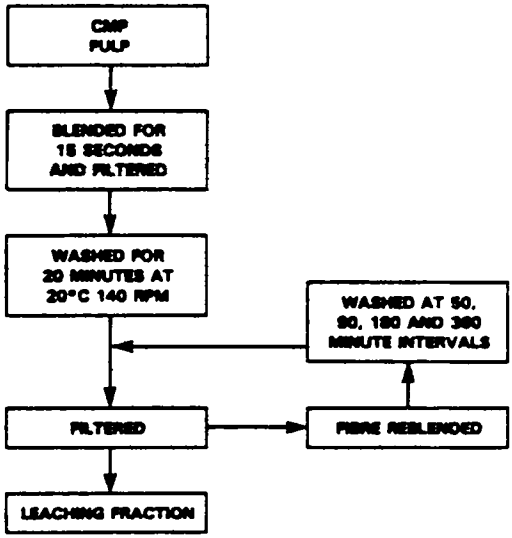

FIGURE 1 Preparation of leachate fractions at various washing intervals at 20°C.

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spruce, 45% balsam and 10% pine. Chips were presteamed and then cooked at 155-160°C for 40 min. in a sulphite liquor of pH 7.8. The process by which the sample was produced as well as various properties of the pulp are given in more detail in an earlier paper[1].

The procedure used to isolate fractions of leachate at different intervals of washing is shown in Figure 1. An accurately weighed 10 g oven-dry sample of CMP was blended in 500 mL of chilled distilled water for 15 seconds to remove extraneous cooking liquor. The suspension of pulp fibers was rapidly filtered through a coarse sintered glass filter, and the washed pad of pulp reblended with 500 mL of distilled water equilibrated at 20°C.

The pulp suspension was then quickly added to a further 500 mL of 20°C water contained in the washing vessel previously described[1,6], and the stirring rate immediately adjusted to 140 RPM. After 20 minutes of leaching, the entire suspension was removed from the washing vessel and rapidly filtered through a coarse sintered-glass filter. A fresh liter of water was allowed to equilibrate at 20°C, the pad of fiber reblended, and the washing resumed at 140 RPM. Similarly, a fresh liter of leachate was obtained at 50, 90, 180 and 360 minutes of washing.

This procedure was repeated five times. Thus, 5 L of leachate were collected at each time interval. Each fraction was evaporated down to 20 mL and then filtered through a 0.2 μm polycarbonate membrane to remove the accumulated fines. The samples were kept frozen until they were analyzed. The samples isolated at different intervals of leaching were diluted to 25 mL, and an aliquot taken for the analysis of the total lignin and carbohydrate content. The remaining solution was neutralized with 0.1 N sodium hydroxide, diluted to 30–50 mL with distilled water, and subjected to three cycles of electrophoresis-convection. In this method the solution is held in a nylon dialysis tube about 5 cm in diameter and 40 cm in length, suspended vertically in a water bath. A horizontal electrical field is applied radially in the tube. The lignosulphonate molecules migrate electrophoretically to the inner surface of the tube, producing a layer of increased density. This layer falls convectionally, thus causing the lignosulphonate to concentrate at the bottom of the tube. The

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uncharged carbohydrate molecules do not migrate in the field and therefore are not concentrated with the lignin. After several hours, the lower layers in the tube yield a fraction rich in lignosulphonates, while the supernatent liquid is rich in carbohydrate. The method is described in greater detail in a previous publication[4]. The lignin and carbohydrate fractions were recovered by freeze-drying.

As described previously[7], the lignin and carbohydrate content of each fraction was determined by means of ultraviolet spectrophotometry and orcinol colourimetry, respectively. The compositions of the whole and fractionated samples are given in Table I.

Molecular weights were determined with a Spinco Model E ultracentrifuge, using the short column sedimentation equilibrium technique previously developed in this laboratory[5]. The molecular weight results are given in Table I. Integral values are weight averages of all fractions. Insufficient sample remained after the electrophoretic separation of the second fraction (20-50 minute interval of leaching) to perform sedimentation equilibrium. Consequently, the molecular weights of fractions L-2 and C-2 could not be determined.

In a separate experiment, a whole sample was prepared by collecting a single sample after six hours of leaching. The composition and molecular weight of this sample are also reported in Table I. The weight of the lignin and carbohydrate leached were, respectively, 1.46 mg and 0.70 mg per gm oven dry weight of pulp.

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TABLE I

Composition and Weight Average Molecular Weights of the Lignin and Carbohydrate Fractions Isolated at Different Intervals of Leaching at 20°C

Leaching interval (min)	Percent of Total Leached		Lignin Fraction*			Carbohydrate Fraction*	
	Lig.	Carb.	Lignin (%)	Mw (g mol^{-1})	d (nm)	Carb. (%)	Mw (g mol^{-1})
0-20	42	25	83	11000**	3.4	67	6000**
20-50	20	30	70	16000**	3.8	50	7000**
50-90	10	13	76	29000	4.7	60	9000
90-180	16	19	72	26000	4.5	54	10000
180-360	12	13	78	61000	6.0	52	17000
Integral	100	100	77	22000	4.2	57	9000
Whole Sample	-	-	81	17000	3.9	63	10000

*In each fraction the percentage of lignin plus the percentage of carbohydrate equals 100.
**Values from mid-interval lines (Figure 2).

DISCUSSION

As shown in Table I, the molecular weights of both lignosulphonate and carbohydrate increased with time of leaching. The trend is shown clearly in Figure 2, in which the molecular weight is plotted against the mid-interval time. As expected, the larger molecules diffuse more slowly through the fiber wall and are removed in the later stages of leaching.

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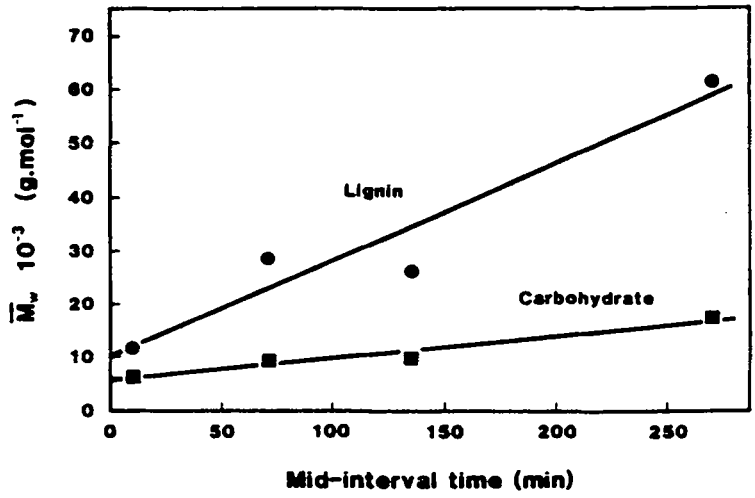

Figure 2 The variation of the weight average molecular weight of leached lignosulphonate and carbohydrate fractions with mid-interval time of leaching.

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Integral values of the weight average molecular weight and the compositon of the lignin and carbohydrate samples were calculated. In Table I these data are given, together with the experimentally determined values for the whole sample. In view of the uncertainties involved in the preparation of the fractions, the agreement is fairly good.

In an earlier paper it was shown that the rate of intrafiber diffusion of lignosulphonate macromolecules in CMP was about six orders of magnitude less than their free diffusion rate[1]. The most important cause of the effect is probably the entrapment of the macromolecules in the pores of the fiber, thereby restricting diffusion through the fiber wall. A similar phenomenon was

observed in the leaching of lignin from unbleached kraft pulp[6], and a theory was developed in which the slowing down of the diffusion was related to the difference in dimensions of the pores and the macromolecules[8].

The size of the lignosulphonate macromolecules can now be compared with the size of the pores in the fiber wall. From the molecular weight of the lignin fractions, the diameter, d, of the equivalent sphere was calculated by the method described previously[3]. Values of d are given in Table I. For all fractions and for the whole sample, they exceed the median pore width of 2.3 nm as measured by solute exclusion[9]. Note that these calculations must be considered only approximate since, on average, about 20% of the lignin fraction was carbohydrate.

Using the equation derived previously by Favis and Goring (Equation 8 in Reference 8) it can be shown that, for the whole fraction, the molecular width should exceed the pore diameter by 18% in order to reduce the free diffusion coefficient by six orders of magnitude. This corresponds to a molecular width of 2.7 nm. As shown in Table I, the diamter of the equivalent sphere for the lignosulphonate of the whole fraction is 3.9 nm. This suggests that the lignin macromolecules diffusing through the fiber wall adopted a flat rather than a spherical conformation. The concept of a flat, or disk-like conformation for lignin has been proposed previously[8,10]. Note, however, that in contrast to the above results, lignin molecules removed during pulping appear to escape from pores that are approximately the size of the equivalent sphere[11].

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An analysis such as the one given above for the lignosulphonate was not attempted for the carbohydrate fraction. Most of the wood polysaccharides are essentially linear chain molecules[12] and probably exist in an extended conformation in the cell wall[13]. The assumption of an equivalent sphere or a flat disk-like conformation would be unwarranted for such molecules. Furthermore, the carbohydrate fractions contained, on average, about 40% lignin. Therefore, speculation as to their size in comparison with the porous structure of the wall was not justified.

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