

# Influence of Degree of Polymerization of Cellulose and Hemicellulose on Strength Loss in Fire-Retardant-Treated Southern Pine<sup>1)</sup>

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## Keywords

Fire-retardant  
Strength loss  
Degree of polymerization  
Hemicellulose

## Summary

Southern pine boards, both untreated and treated with a fire retardant, were exposed to either a room temperature or high temperature (66°C (150°F)) environment. Strength properties were measured after 1 and 1-1/2 years of exposure, respectively. The degree of polymerization and the chemical composition of  $\alpha$ -cellulose isolated from the exposed wood were measured. Little relationship was found between degree of polymerization and strength. However, a strong relationship was found between the amount of mannan in the  $\alpha$ -cellulose isolated from the wood and the modulus of rupture and the work-to-maximum load of solid wood. This correlation leads to the conclusion that hemicellulose plays an important role in determining the strength of wood.

## Introduction

Fire-retardant- (FR) treated wood that has been exposed to elevated temperatures can incur substantial strength loss. The magnitude of this problem has been reported (APA 1989; Still *et al.* 1991; NAHB 1989, 1990). FR-treated strength loss has been studied as a function of exposure temperatures (LeVan *et al.* 1990; Winandy 1995), and kinetic models have been developed to quantify this strength loss (Woo and Schniewind 1987; Pasek and McIntyre 1990; Winandy *et al.* 1991; Winandy and Lebow 1996). Although the role of hemicelluloses and the chemical mechanism by which this occurs have been studied (LeVan *et al.* 1990; Winandy 1995), neither is well understood. This study examined the role of the degree of polymerization (DP) of cellulose and the degradation of the constituents in side-chains and the mainchains of hemicelluloses in the strength loss of FR-treated wood.

## Background

Although a substantial amount of research has looked at the effect of FR treatment on wood strength and exposure to high temperatures on wood strength, it is only recently that the combined effects have been studied.

Gerhards (1970) reviewed eight studies that were conducted from 1944 to 1969 at the USDA Forest Service, Forest Products Laboratory (FPL). These studies involved

treatment of small, clear wood specimens and structural-sized specimens with proprietary, commercial fire retardants. In each of the eight FPL studies, the modulus of rupture (MOR) of FR-treated wood that had been kiln dried after treatment was 6% to 19% less than for matched untreated specimens, with an average 13% reduction in MOR. The modulus of elasticity (MOE) was reduced by 7% compared with matched untreated, non-redried controls.

A similar study was performed at Oregon State University (Johnson 1967). Douglas-fir was commercially treated and kiln dried with two different fire retardants. Specimens treated with one formulation and kiln dried after treatment exhibited a reduction in MOR of 14%, compared with untreated controls. The other formulation resulted in a 15% reduction in MOR. Johnson also found that FR-treated wood that was air dried after treatment, instead of kiln dried, showed little to no strength loss.

The strength of untreated wood exposed to high temperatures was described by MacLean (1951), Davis and Thompson (1964) Thompson (1969) and Millett and Gerhards (1972). This work clearly showed that high-temperature strength loss in wood was directly related to exposure temperature and duration.

Luther (1921) reported work on the effects of zinc chloride and various high-temperature exposures on wood strength. At one time, zinc chloride was used as a wood preservative, and at higher concentrations as a fire retardant. Zinc chloride-treated and untreated wood were conditioned at 24°C (75°F), 38°C (100°F), and 66°C (150°F) for up to 2 years. Luther found that the MOR of the treated wood was reduced by 0%, 18%, and 49%, respectively. Luther also concluded that there existed a safe temperature below which the fire retardant had little or no effect on the strength of the treated wood.

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The most ambitious and comprehensive studies on the effects of FR-treated wood exposed to elevated temperatures have taken place at the FPL. The effect of six different fire retardants on the bending properties of wood at elevated temperatures was examined by LeVan *et al.* (1990) and Winandy (1995). The initial reductions in MOR, MOE, and work to maximum load (WML) were attributed to fire-retardant treatment. Low (27°C) and moderate (54°C) temperature exposures caused little further strength loss after 5 months of exposure. At higher temperature exposures (66°C or 82°C), wood treated with each of the fire-retardant formulations and untreated wood experienced progressively greater strength loss over duration of exposure. When thermal degradation was initiated, the rate of strength loss was similar for all the formulations, including the untreated material. With increasing exposure to higher temperatures over time, a progressive reduction in the content of hemicellulosic sugars was measured along with a corresponding reduction in strength. Arabinose showed the greatest decrease, followed by galactose, then mannose and xylose. Cellulose and lignin were generally unaffected. However, these data were limited in that the analysis was based on residual sugars of the wood after exposure to high temperatures. It did not include an examination of the polymeric chains from which the sugars were isolated.

#### Model of wood strength

Wood fiber is the basic building block of wood. Solid wood is composed of a huge number of wood fibers that are mostly oriented in the same direction and bound together by lignin. To understand the strength of wood, it is necessary to understand the structure and strength of the wood fiber, or cell. The cell wall is composed of a thin, outer primary wall and a much thicker, inner secondary wall. The secondary wall is composed of the  $S_1$  layer, a thick middle  $S_2$  layer, and an inner  $S_3$  layer. The hollow area inside of the  $S_3$  layer is known as the cell lumen. The middle lamella is the lignin-rich area between each fiber and together with the two adjacent primary walls forms the compound middle lamella.

All regions of the cell wall contain varying amounts of cellulose, hemicellulose, and lignin (Fig. 1). The middle lamella contains mostly lignin, with small amounts of hemicellulose and cellulose. The primary wall has proportionally more cellulose and hemicellulose than the middle lamella, but less than the secondary wall. Proceeding from the  $S_1$  layer through the  $S_3$  layer, the percentage of lignin decreases. The  $S_1$  layer is made of mostly lignin, with hemicellulose and cellulose comprising the rest. The largest component of the  $S_2$  layer is cellulose, followed by hemicellulose and lignin. The  $S_3$  layer still contains mostly cellulose, but with a larger fraction of hemicellulose and little lignin.

On the molecular level, aggregations of cellulose chains are hydrogen bonded into a long, thin chain called a microfibril. These microfibrils are encrusted in the lignin-hemicellulose matrix. It is believed that lignin, a large

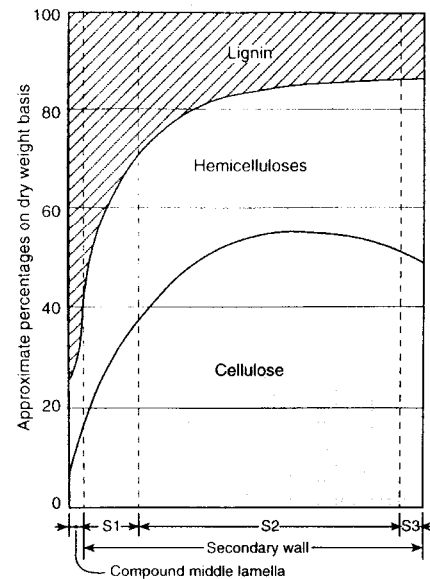


Fig. 1. Distribution of the principal chemical constituents within the various layers of the cell wall in conifers (Panshin and de Zeeuw 1970).

amorphous polymer, is covalently bonded to hemicellulose (Whistler and Chen 1991). It is also thought that hemicellulose is associated with the cellulose microfibrils, either by physical proximity or hydrogen bonding. LeVan *et al.* (1990) and Winandy (1995) showed that hemicelluloses are the most thermal-chemically sensitive component of wood and that changes in the hemicellulose content and structure are primarily responsible for initial strength loss.

Lignin is thought to serve as a stiffener for the fiber. It has often been speculated that the long, linear cellulose molecules are primarily responsible for the strength of the fiber. However, a single microfibril or a group of microfibrils cannot entirely account for the strength of an entire fiber (Winandy and Rowell 1984). The chemical-mechanical linkages between the cellulose microfibril and the lignin-hemicellulose matrix and then the next microfibril allow a lateral load to be shared among both microfibrils. When the cellulosic microfibrils and lignin-hemicellulose matrix act as a continuum, internal stress can be efficiently distributed across the cell wall and throughout the entire fiber. It is this ability for intrafiber stress distribution and load sharing that enables wood fibers to functionally act as a composite material.

#### Microfibril compared with matrix failure

Previous studies have shown that both untreated and FR-treated wood exposed at elevated temperatures can undergo strength reductions (LeVan *et al.* 1990; Winandy 1995). Several mechanisms for thermal- or thermochemical-induced strength loss in wood have been proposed, but only limited data exist to support these hypotheses. Based on the model of wood strength previously outlined, two possible theories seem likely.

One theory suggests that the acids in wood, especially when accelerated by acidic FR-treatments and/or exposures to high temperatures, hydrolyze the cellulose chains. Cellulose is often thought to be primarily responsible for the strength of the wood fiber, therefore reducing the length of the cellulose molecules (DP) would cause a reduction in macro-strength properties. This theory of hydrolytic cellulose depolymerization was advanced by Ifju (1964) and is widely accepted (Mark 1967; Kass *et al.* 1970).

The other mechanistic theory is that the hemicellulose is hydrolyzed, causing cleavage of covalent bonds, first in the sidechains, then in the backbones of hemicellulose polymers. Cleavage of hemicelluloses prior to attack on cellulose would disrupt the intrafiber load sharing and should result in reduced strength properties. Leopold and McIntosh (1961) examined the tensile strength of individual loblolly pine fibers and could establish no correlation between fiber strength and the DP of cellulose. In addition, wood treated with acid (Kass *et al.* 1970) showed a convincing correlation between MOR and pentosan content. LeVan *et al.* (1990) proposed that cleavage of hemicellulosic sidechains within the lignin-hemicellulose matrix caused disruption of load-sharing capacity and, therefore, might be responsible for the observed strength losses. Under this proposed theory, some load-sharing capacity would not only be due to covalent or secondary chemical bonding, but to mechanical entanglements between hemicellular sidechains and zones of amorphous cellulose or other matrix components.

Woo and Schniewind (1987) performed differential scanning calorimetry on FR-treated wood and found that the lowest temperature exothermic peak corresponded to the depolymerization of hemicellulose. This idea was pursued further (Berndt *et al.* 1990), and the authors attempted to correlate the area of this exothermic peak with the strength loss of FR-treated wood. The correlation between toughness and area of the exothermic peak was very high; however, the correlation between MOR and the area under the exothermic peak was somewhat lower.

Leopold and McIntosh (1961) measured the tensile strength of individual fibers, which may or may not extrapolate to indicate the strength behavior of solid wood. They found no relationship between DP and strength. In contrast, Ifju (1964) examined larger specimens—thin microtomed sections, cut into 2.5- by 100-mm rectangles. Random cellulose depolymerization was induced by gamma irradiation, followed by strength tests. He postulated that the lignin should have been unaffected by the irradiation due to its aromatic structure. However, hemicellulose, which should have been at least as susceptible to radiation-induced depolymerization as cellulose, was not measured. After irradiation, the cellulose was nitrated and isolated from the lignin and hemicellulose. Although it is certainly true that a reduction in the DP of cellulose was observed along with a reduction in tensile strength, it is unclear whether the reduction in cellulose DP was causative or merely incidental to the strength loss. Another explanation, but unmeasured, could be that the initial strength loss was primarily caused by reductions in the hemicellulose DP.

Such an interpretation agrees with the findings of Davis and Thompson (1969), who showed that heat treatments primarily affected hemicelluloses as toughness decreased.

### Objectives

The objectives of this research were to (1) measure the DP of  $\alpha$ -cellulose isolated from FR-treated and untreated clear wood and (2) determine the relationship between changes in strength properties, specifically MOR, and changes in the DP of cellulose and chemical composition.

### Methods

The wood for this study had already been cut, treated, dried, conditioned, and its mechanical properties non-destructively and destructively measured as part of studies by LeVan *et al.* (1990) and Winandy (1995). In that work, small, clear, straight-grained southern pine boards free from defects were used. Specimens were cut to 35 by 16 by 305 mm (1-3/8 by 5/8 by 12 in.), with a vertical grain orientation. After conditioning to 12% moisture content, a group of specimens was pressure treated to approximately 55 kg/m<sup>3</sup> (3.4 lb/ft<sup>3</sup>) with monoammonium dihydrogen phosphate (MAP).

The test specimens were treated by placing the wood under vacuum of -90 kPa (27 in-Hg) for 30 minutes, introducing the treating solution, then applying 1.0 MPa (145 lb/in<sup>2</sup>) of pressure for 60 minutes. After treatment, the specimens were dried in a kiln at 49°C (120°F) until the average moisture content of the specimens reached 13%. After kiln drying, one group of treated and one group of untreated specimens were placed in a conditioning chamber at 66°C (150°F) and 75% relative humidity (RH) for 590 days. Another group of treated and another group of untreated specimens were placed in a conditioning chamber for 365 days at 27°C (80°F) and 30% RH. After conditioning, each specimen was tested in flat-wise bending with a center point load over a 222-mm (8.75-in.) span. This yielded the 14:1 span-to-depth ratio specified in ASTM (1996) D-143-94. The mechanical properties of MOE, MOR, and WML of each specimen were determined.

### Isolation of $\alpha$ -cellulose

A portion of each specimen was removed and ground in a Wiley mill to pass a 40-mesh screen. The ground wood meal was extracted with 95% ethanol for 6 hours. The extracted wood meal was then delignified for 4 hours using the acid chlorite method (Browning 1967). The hemicellulose was removed from the holocellulose by alkali extraction (ASTM 1978). The sugar units and any residual acid soluble and Klason lignin content were determined using the procedures of Pettersen and Schwandt (1991), TAPPI (1982), and Effland (1977), respectively.

### Measured molecular weight

The molecular weight distribution of cellulose was determined by the method of Wood *et al.* (1986). The cellulose was dissolved in pyridine and reacted with phenyl isocyanate for 48 hours to form cellulose tricarbanilate. A portion of this mixture was removed, and the solvent was evaporated under nitrogen. The cellulose tricarbanilate was then dissolved in tetrahydrofuran, and the molecular weight distribution was measured by gel permeation chromatography. The DP was determined by dividing the measured molecular weight of the cellulose tricarbanilate by the molecular mass of a single cellulose tricarbanilate unit.

### Results

The specific gravity and the mechanical properties (MOR, MOE, WML) of each specimen and their group averages

**Table 1.** Effect of thermal-chemical processing treatment and high-temperature exposure on mechanical properties

FR treatment	Exposure temperature (°C)	Duration (days)	Density air dry (kg/m <sup>3</sup> )	MOE (GPa)	MOR (MPa)	WML (kJ/m <sup>3</sup> )
Untreated	27	0	251	12.3	109.2	90.0
Untreated	27	0	264	13.4	115.6	118.5
Untreated	27	0	254	12.8	106.9	92.5
Untreated	27	0	302	15.4	126.6	102.0
Untreated	27	0	282	15.1	131.2	123.6
Group Average			270	13.8	117.9	105.3
MAP-treated	27	0	282	11.9	89.1	61.3
MAP-treated	27	0	276	14.2	107.2	86.0
MAP-treated	27	0	300	8.3	86.0	131.0
MAP-treated	27	0	311	14.0	113.8	96.1
MAP-treated	27	0	286	13.0	97.5	77.2
Group Average			291	12.3	98.7	90.3
Untreated	66	560	261	14.3	95.7	73.8
Untreated	66	560	265	14.7	83.2	30.8
Untreated	66	560	297	12.2	80.8	35.6
Untreated	66	560	289	15.1	108.7	62.8
Untreated	66	560	281	16.0	112.4	67.1
Group Average			2794	14.5	96.2	54.0
MAP-treated	66	560	231	9.2	33.9	10.3
MAP-treated	66	560	271	13.2	44.1	9.3
MAP-treated	66	560	252	11.1	19.0	1.9
MAP-treated	66	560	293	13.1	39.4	8.1
MAP-treated	66	560	267	10.2	24.3	4.0
Group Average			2638	11.4	32.1	6.7

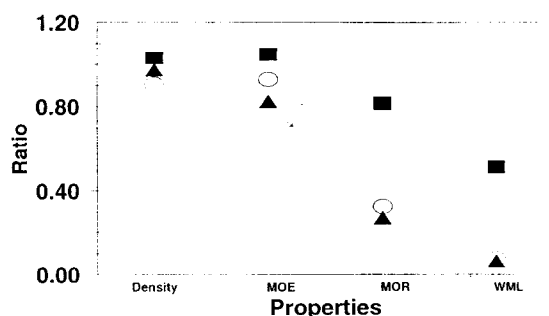
are given in Table 1. Both MOR and WML were reduced by both FR-treatment and high temperature exposure (Fig. 2). The MOE of untreated material was unaffected, and the MOE of FR-treated material was affected to a much lesser degree than was MOR or WML (Fig. 2).

Table 2 contains the results of the carbohydrate/sugar and lignin analyses and the DP of the  $\alpha$ -cellulose. The DP, lignin content, and most carbohydrate/sugars decreased after FR-treatment and/or high temperature exposure (Fig. 3). The apparent increase in the amount of glucan in the high-temperature and treated specimens was probably

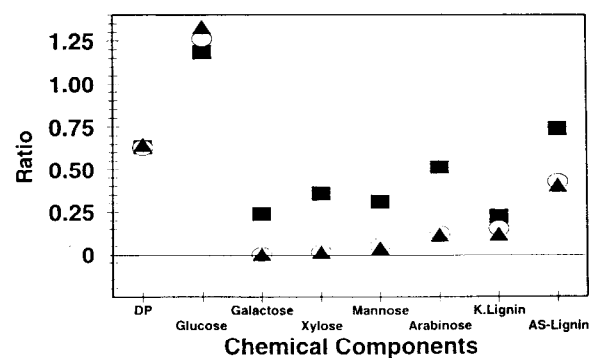
due to an on-going removal of lignin and hemicellulose during thermal degradation. In other words, as lignin and hemicelluloses are removed or destroyed, the remaining proportion of cellulose increases.

## Discussion

Each matched specimen underwent an identical pre-treatment and treatment processing. Therefore, it was initially reasonable to assume that differences reported between sugar analysis of holocellulose and  $\alpha$ -cellulose should be



**Fig. 2.** Ratios of various physical and mechanical properties for untreated material (unexposed to exposed for 365 days at 66°C), MAP-treated material (unexposed to exposed for 560 days at 66°C), and untreated-unexposed material to MAP-treated material exposed for 560 days at 66°C. ■ Untreated (560 vs 0 days); ○ FR-treated (560 vs 0 days); ▲ FR/560 days to untreated/0 days.



**Fig. 3.** Ratios of various chemical constituents for untreated material (unexposed to exposed for 365 days at 66°C), MAP-treated material (unexposed to exposed for 560 days at 66°C), and untreated-unexposed material to MAP-treated material exposed for 560 days at 66°C. ■ Untreated (560 vs 0 days); ○ FR-treated (560 vs 0 days); ▲ FR/560 days to untreated/0 days.

**Table 2.** Effects of chemical processing and high-temperature exposure on composition of  $\alpha$ cellulose

FR treatment	Exposure (°C)	Duration (days)	DP of Cellulose	Arabinose (%)	Galactose (%)	Xylose (%)	Mannose (%)	Glucose (%)	Klason lignin (%)	Acid soluble lignin (%)	Total (%)
Untreated	27	0	1430	0.4	2.2	2.4	11.7	72.9	2.86	3.30	95.8
Untreated	27	0	1720	0.4	1.5	2.5	13.1	72.3	3.24	3.06	96.1
Untreated	27	0	1500	0.5	1.6	2.2	12.9	72.6	3.34	3.23	96.4
Untreated	27	0	1190	0.4	1.3	2.7	11.6	73.3	2.91	2.81	95.0
Untreated	27	0	1410	0.4	1.2	2.4	13.5	72.1	3.35	3.06	96.0
Group Average			1450	0.4	1.6	2.4	12.6	72.6	3.14	3.09	95.9
MAP-treated	27	0	2170	0.3	1.1	1.8	11.0	77.2	2.26	2.72	96.4
MAP-treated	27	0	1420	0.3	1.3	1.5	12.5	76.6	2.58	3.14	97.9
MAP-treated	27	0	1370	0.3	1.4	2.1	13.5	73.2	3.04	3.18	96.7
MAP-treated	27	0	1440	0.3	1.1	2.3	11.2	75.9	2.52	2.93	96.3
MAP-treated	27	0	1070	0.4	1.2	1.3	10.5	80.2	2.02	2.72	98.3
Group Average			1494	0.3	1.2	1.8	11.7	76.6	2.48	2.94	97.1
Untreated	66	560	1120	0.1	0.4	0.7	6.0	89.3	0.60	2.05	99.2
Untreated	66	560	1020	0.1	0.6	0.9	6.3	84.8	0.53	2.40	95.6
Untreated	66	560	600	0.1	1.0	0.8	5.2	84.7	0.83	2.36	95.0
Untreated	66	560	650	0.1	0.4	0.7	6.8	86.2	1.00	2.34	97.5
Untreated	66	560	1210	0.1	0.4	0.7	8.0	85.6	0.59	2.32	97.7
Group Average			920	0.1	0.6	0.8	6.5	86.1	0.71	2.29	97.0
MAP-treated	66	560	960	0	0.0	0.1	1.6	97.4	0.27	1.29	100.7
MAP-treated	66	560	990	0	0.0	0.1	1.5	96.0	0.65	1.31	99.6
MAP-treated	66	560	960	0	0.1	0.1	1.3	96.1	0.33	1.16	99.1
MAP-treated	66	560	990	0	0.0	0.1	1.6	96.2	0.33	1.32	99.6
MAP-treated	66	560	800	0	0.0	0.1	1.4	97.7	0.33	1.71	100.7
Group Average			940	0	0.0	0.1	1.5	96.7	0.3	81.26	99.9

**Table 3.** Change in chemical composition (expressed as a ratio) between  $\alpha$ -cellulose specimens from this study when compared with matched holocellulose specimens previously reported by LeVan *et al.* (1990) and Winandy (1995)

FR treatment	Exposure temperature (°C)	Duration (days)	Ratio for				
			Arabinose	Galactose	Xylose	Mannose	Glucose
Untreated	27	0	0.32	0.63	0.34	1	1.56
MAP-treated	27	0	0.35	0.57	0.30	1	1.78
Untreated	66	560	0.25	0.27	0.14	0.59	2
MAP-treated66	560	— <sup>a</sup>	0	0.04	0.25	2.25	

<sup>a</sup> Undefined (zero/zero).

related to the additional steps used in the isolation procedures to go from holocellulose to  $\alpha$ -cellulose. We originally assumed that the  $\alpha$ -cellulose isolation procedure would affect hexose and pentose sugars similarly and that each of the individual components of the various hemicelluloses might be similarly degraded.

The ratios presented in Table 3 show that results from previous carbohydrate analysis of holocellulose of matched material (LeVan *et al.* 1990; Winandy 1995) were systematically different than results from the  $\alpha$ -cellulose used in this study. The reasons and implications of these differences must be understood prior to independently discussing the results. The ratios presented in Table 3 strongly suggest that the  $\alpha$ -cellulose isolation procedures

primarily affected the pentose-rich araboglucuronoxylan (AGUX) hemicelluloses and was significantly less invasive toward hexose-rich galactoglucomannan (GGM) hemicelluloses. We noted that the reported levels of the hexose-based components associated with GGM hemicelluloses (i.e., galactose, glucose and mannose) were similar to those initially reported by Winandy (1995) (Table 3). Note that for treated and untreated material, not exposed to elevated temperature, that mannose levels are reportedly unchanged between  $\alpha$ -cellulose and holocellulose, glucose levels are increased, and galactose levels are reduced at a 2 for 3 ratio. These results seem sensible because mannose exist in the mainchain of the GGM hemicellulose. Glucose exists both in the mainchain of the GGM

hemicellulose and as cellulose. Galactose primarily exists as GGM sidechains and thereby seem most susceptible to hydrolysis. Contrast these results with the reported levels of the components associated with pentose-based AGUX hemicelluloses (i.e., arabinose and xylose) that were reduced by more than 65% (a 1 for 3 ratio) when compared with those previous matched values (Table 3). Note that at room temperature both the pentose components affected by the  $\alpha$ -cellulose isolation procedure at more than twice the rate of a sidechain hexose like galactose. When exposed to 66°C for 1-1/2 years, few differences exist between pentose and sidechain hexoses, but major differences exist in the residual pentose versus mainchain hexoses. Our results seem to confirm the results of Kass *et al.* (1970), who suggested that this might be related to the more chemically-susceptible pentosan character of AGUX-hemicellulose when compared with GGM-hemicellulose.

Sweet (1995) found that correlation between strength loss and losses in mannose content were greater than between strength and other carbohydrates. We attribute this to his use of  $\alpha$ -cellulose rather than holocellulose. The direct relationship between reductions in mannose content and strength loss, which is evident in Sweet's (1995) study, was not as strongly evident in previous studies that examined the carbohydrate composition of non-isolated holocellulose (LeVan *et al.* 1990; Winandy 1995). Those previous studies showed stronger relationships between arabinose and galactose contents and strength properties than did mannose, glucose, or xylose contents. However, we believe this apparent contradiction actually provides confirmation of some facets of the hypothesis put forth by LeVan *et al.* (1990) and Winandy (1995). They reported that initial strength loss first appeared to be related to the removal of sidechain hemicelluloses, thereafter followed by attack of mainchain hemicellulosic components. Accordingly, we believe that the  $\alpha$ -cellulose isolation procedures actually give us insight into the second stage of the proposed mechanism by LeVan *et al.* (1990) and Winandy (1995). Our data clearly shows that the pentosan hemicelluloses (arabinose and xylose) are preferentially removed and the hexosan sidechain (galactose) is also removed during the  $\alpha$ -cellulose isolation procedure (Table 3). Thus, post-  $\alpha$ -cellulose isolated analytical results, which have higher proportions of hexose-based mainchain hemicelluloses like glucans and mannans, yield specific insight into at the second phase of that previously noted mechanistic hypothesis.

The direct relationship between the mannan content of  $\alpha$ -cellulose and MOR and WML in this study supports previous conclusions that GGM-hemicelluloses play an important role in the strength loss of FR-treated southern pine wood (LeVan *et al.* 1990, Winandy 1995). The reason for this correlation is likely due to the composition of softwood hemicellulose. The GGM-hemicellulose in southern pine, like other softwoods, is made up of a mannan/glucose backbone. By measuring the mannan content, we were really measuring the degree to which the GGM-hemicellulose backbone was still intact. For untreated wood conditioned at low temperatures, a good deal of hexose-

hemicellulose remains in the  $\alpha$ -cellulose even after alkali extraction. For degraded wood, a larger fraction of hemicellulose can be removed using the same procedure because various hemicelluloses are more physically assessable and chemically susceptible (Sweet 1995).

The measurement of mannan in the  $\alpha$ -cellulose allows us to determine the amount of "residual intact hemicellulose" that is present in wood, which correlates to the amount of strength in the particular specimen. Treatment with fire retardants and/or high temperature exposure will reduce the amount of "intact hemicellulose," thus reducing the strength of the wood. Because we think the mannan content in the  $\alpha$ -cellulose is thought to represent the "backbone" of the GGM-hemicellulose in the wood, had holocellulose been evaluated rather than  $\alpha$ -cellulose, then the xylan backbone of AGUX would have also been strongly related to strength loss based on previous results of LeVan *et al.* (1990) and Winandy (1995).

Overall, these results lead us to support the hypothesis that progressive degradation of the hemicellulose between microfibrils (i.e., matrix failure) is the primary mechanism of hydrolytic strength loss in FR-treated and untreated wood. Initially, sidechain constituents, involving sugars like arabinose in AGUX and galactose in GGM, are cleaved, especially in non-isolated material. Later, mainchain constituents like mannose, glucose, and xylose are degraded.

The DP of the cellulose seems to have little impact on the initial loss in strength properties, which agrees with the findings of Leopold and McIntosh (1961). Although these data seemingly contradict the conclusions of Ifju (1964), that contradiction may be related to differences between the actual and the assumed degrade mechanism that resulted in his data. We believe that had the degree of "residual intact hemicellulose" been accounted for by Ifju (1964), widely different conclusions might have been drawn.

## Conclusions

In this study, several physical and chemical properties (specific gravity, sugar content, DP of cellulose) were used to relate the mechanical strength of FR-treated and untreated southern pine wood. Reductions in the DP of cellulose did not appear to be related to wood strength loss under thermal degradation. The extent to which the hemicellulose mainchains, especially the mannans in GGM, were left undamaged after treating, thermal exposure, and isolation/extraction procedures for the  $\alpha$ -cellulose were related to residual MOR and WML. These wood chemistry-strength relationships appear to be predictive and such work is currently underway.

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Received March 19th 1998

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