A STATE-OF-THE-ART PAPER

RELATING WOOD CHEMISTRY AND STRENGTH: PART II. FUNDAMENTAL RELATIONSHIPS BETWEEN CHANGES IN WOOD CHEMISTRY AND STRENGTH OF WOOD

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Abstract.   In Part I of this series, the relationship between physical properties and chemistry and anatomy of wood were reviewed (Winandy 2016). This Part II article explores a fundamental relationship between the mechanical properties and the chemical composition of wood and how degradation of its individual chemical components affects strength loss. It then presents a proposal for a universal theory as to the fundamental mechanism between wood strength loss and changing wood chemistry. That theory purports that the desequencing of the complex lignocellulosic structure of woody materials involves the same systematic series of processes during either biological, chemical, or thermal deterioration. The goal of this article is to create a better understanding of how changes in wood chemistry fundamentally influence wood strength.

Keywords: Chemistry, mechanical properties, decay, treatments, thermal effects.

INTRODUCTION

In Part I of this series (Winandy 2016), the relationship between the chemistry and anatomy of wood and its physical properties were reviewed. The implications of changes in cellular anatomy, and particularly in the chemical composition of the various levels of cellular anatomy, must be understood to relate changes in engineering properties. The explanations about the chemical and anatomical composition of wood presented in Part I were intended to provide a means to visualize the complex macro, micro, and molecular structures governing the fundamental relationship between wood chemistry, structural anatomy, and the mechanical properties of wood.

Part I reviewed relationships between the physical/mechanical properties of wood as a function of changes in its chemistry and anatomical structure. The objective of this Part II article will be to detail strength loss-to-wood chemistry relationships when softwoods are exposed to hydrolytic chemical agents, exposure to elevated temperatures, and/or enzymatic decay.

An array of studies in the last 25 yr has indicated that early events related to strength loss in softwood lumber can be correlated almost exclusively to degradation of hemicellulose(s), especially degradation of the branched monomers such as D-galactose and L-arabinose that serve as branched sidechains along the hemicellulose main chains. This article will review the results of those studies and show that when they are viewed as a series, they provide evidence of systematic relationship supporting the hypothesis of a unified model for strength loss in

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softwood lumber exposed to severe thermal, chemical, or biological exposures.

BACKGROUND

Wood is often best visualized as a system of tubular elements collectively known as wood cells. Each of the three major types of wood cells serves a different function (USDA 2010). The source of strength in solid wood is this system of interconnected, multifunctional wood cells. The woody cell wall is a multilaminate structure with the S_2 layer having nearly perpendicular outer and inner layers (S_1 layer and S_3 layer, respectively) wound around the S_2 layer, and thus creating the cell lumen. Each layer of the cell wall has a distinct orientation and most importantly, a distinct chemistry (Winandy and Rowell 2013). Because not all cellulose bonds are perfectly aligned, these three dimensional cellulose structures possess alternating crystalline regions and nonaligned (noncrystalline) amorphous regions. Other carbohydrate and phenolic polymers, like hemicelluloses and lignin, then intermingle within and bulk up these amorphous regions (Stamm 1964; Mark 1967; Sjostrom 1981; Bodig and Jayne 1982; Fengel and Wegener 1984; Rowell 1984).

At a molecular level, the cell wall of each cell type has a unique laminated structure, composed of varying quantities and arrangements of three polymer types: cellulose, hemicelluloses, and lignin. The carbohydrates, cellulose and hemicellulose, are composed of glycosidic pyran- or furan-ringed structures with methoxyl and/or hydroxyl subunits of each carbon in the ringed structure. The placement of each of these subunits is positioned slightly different for each carbohydrate (Fig 1). These positional differences control the access of hydrolytic agents to the critical glycosidic bonds between the pyran- or furan-ringed monomers within the polymer structures. On the basis of the structural characteristics of each sugar, Sjostrom (1981) ranked the lability of the glycosidic bonds of each of these carbohydrates (from highest to lowest) as arabinose, xylose, galactose, mannose, and glucose. This order was attributed to the relative positions of the respective hydroxyl units bonded around the pyran- or furan-ringed structures and how those hydroxyl positions protect both the pyran- or furan-ringed structures and the glycosidic linkages between those monomer structures that in turn create the hemicellulose and cellulose polymers (Sjostrom 1981).

Two basic types of hemicelluloses occur in wood, arabinoxylans and galactoglucomannans. The backbone of the arabinoxylans is xylan with branched sidechains of arabinan and acetyls. The backbone of the galactoglucomannans is alternating mannan and glucan units at a 3-4:1 ratio with branched sidechains of galactans. In both cases, the branched sidechains provide an additional element of defense against hydrolytic attack of the main-chain structure. Also note that for both the arabinoxylans and galactoglucomannans, the sidechains sugars are more labile than the sugar(s) comprising the main chain.

In the chemistry of wood pulping, these relationships of hemicellulose degradation at the earliest stages of the pulping process have been known for years (Harris 1975; Sjostrom 1981). Sjostrom (1981) states, *Hemicelluloses are attacked more easily than cellulose mainly because of their amorphous state and low degree of polymerization. . . . their glycosidic bonds are more labile toward acid hydrolysis than . . . cellulose. . . . Galactose residues are easily hydrolyzed . . . Arabinofuranose . . . are extremely labile toward acid hydrolysis.* This cause-and-effect relationship of changes in the chemistry of wood affecting wood pulp properties are consistent with the chemical action from fire-retardant (FR) treatments or preservative treatments, or from thermal hydrolytic attack, or from biological decay as they have been described in this review article.

The basic concept that reductions in the strength of wood and wood-based composites were a direct function of changes in the wood chemistry and/or anatomy were first postulated by others, such as Stamm (1964), Mark (1967), and Rowell (1984). However, these concepts were never
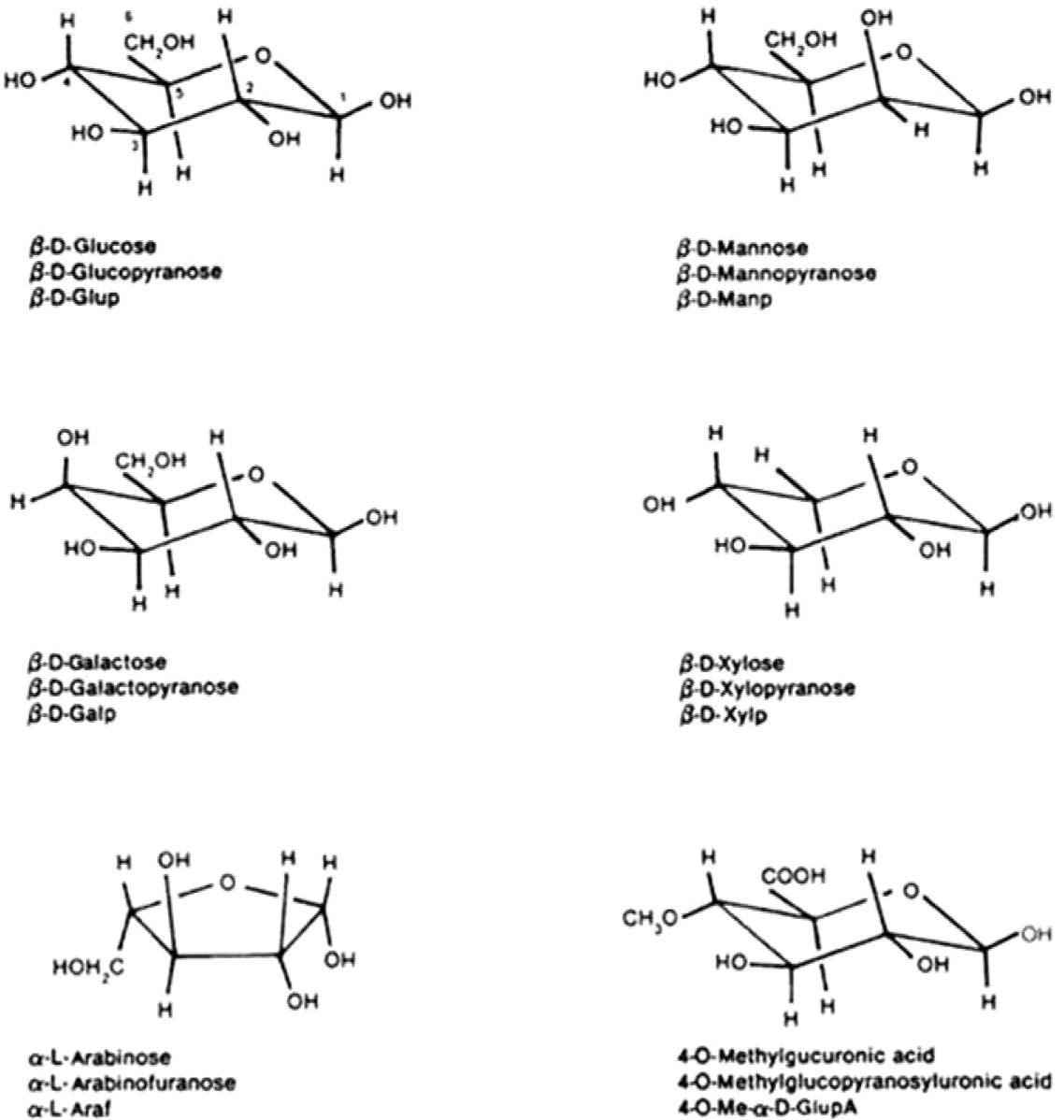
Figure 1.   Representation of the individual carbohydrate entities making up hemicellulose and cellulose (Rowell et al 2013).

comprehensively correlated and coalesced into a qualitative theory. We will now try to do so.

THERMAL-CHEMICAL DEGRADATION

The effect of FR treatment on wood strength over time of exposure at elevated temperatures has been extensively studied in a series of studies at Forest Products Laboratory (LeVan et al 1991; Winandy 1995; Winandy and Lebow 1996; Lebow and Winandy 1999). That work found that the magnitude and rate of strength loss over time at high temperatures was quantitatively proportional to time-at-temperature and the level of acidity (ie pH) of the FR chemical systems studied (Figs 2 and 3). Therefore,
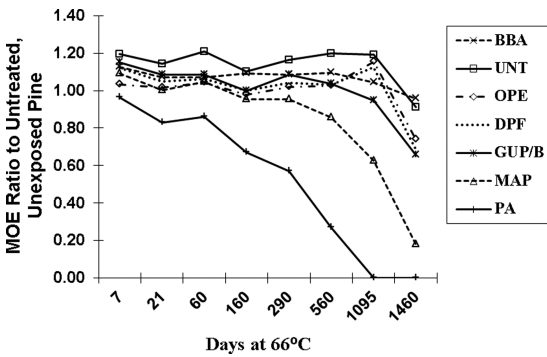
Figure 2. Loss in MOE over time at 66°C for seven different treatments each with a progressively higher pH (Lebow and Winandy 1999).

because it exhibited a direct cause and effect relationship, it could be modeled (Lebow and Winandy 1999). In Figs 2 and 3, the six FRs and one matched untreated (UNT) group are ordered for their pH from lowest pH (phosphoric acid) to highest pH (borax and boric acid) and were selected to evaluate a range of wood pH from 2.5 to 8.0. Note that bending strength (MOR) as shown in Fig 3 deteriorates faster and that deterioration occurs at a reduced duration of exposure at 66°C than does the deterioration in MOE (Fig 2). Also note that for both MOE and MOR, the relationship between time at temperature and wood pH was consistent over the time-pH vs strength-stiffness continuum.

In similar studies, untreated lumber exposed at high temperatures indicated that the kinetics-based models of Lebow and Winandy (1999)
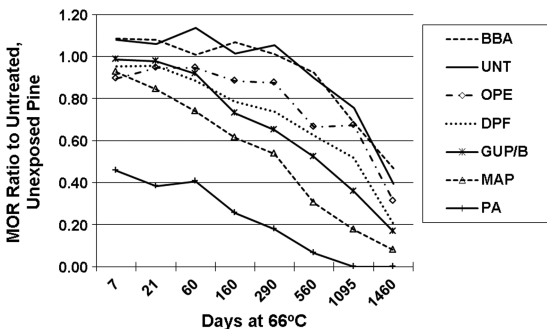
developed for small specimens correlated well with the untreated lumber findings (Green et al 2003) (Fig 4). They too monitored changes in wood chemistry and their results for the lability of individual sugar types, magnitude of their deterioration, and rate of those changes in wood chemistry for untreated lumber of various wood species and grades closely paralleled the results and model parameters reported for kinetic models (Lebow and Winandy 1999) and for chemical-compositional models (Winandy and Lebow 2001) for small clear specimens of untreated pine. Thus, the trends for thermal-induced strength loss and its correlation to changes in wood chemistry for small, clearwood specimens or lumber were quite similar. In addition, extended exposure of chromated copper arsenate (CCA) preservative-treated pine lumber at elevated temperatures also caused similar time-at-temperature effects on wood strength and similar progressive changes in chemistry (Winandy 1994). In another study monitoring wood composites, it was shown that extending the duration of high-temperature hot pressing of medium density fiberboard (MDF) fibers resulted in similar thermal effects in wood fiber and on the resulting MDF properties, and caused similar changes in the compositional chemistry of those fibers as had earlier been found for solid wood and lumber (Winandy and Krzysik 2007).
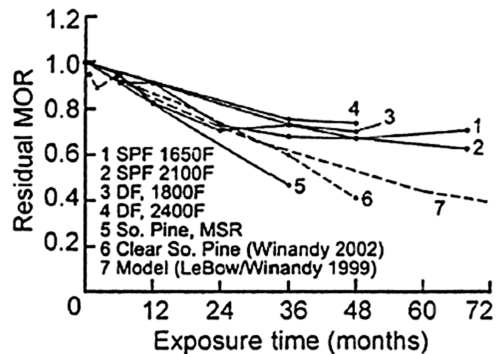

Figure 4. Residual MOR values for small clear southern pine (LeVan et al 1990; Winandy and Lebow 2001) and analytical model of Winandy and Lebow (2001) compared with results of solid sawn 2 × 4 lumber exposed at 66°C (Green et al 2003).

Figure 3. Loss in MOR over time at 66°C for seven different treatments each with a progressively higher pH (Lebow and Winandy 1999).

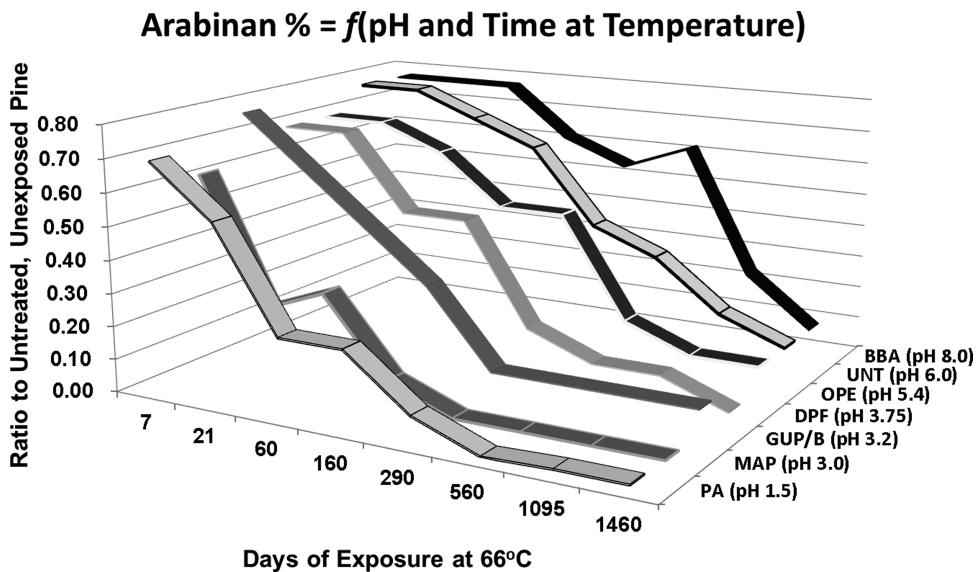## Arabinan % = *f*(pH and Time at Temperature)

Figure 5.   Ratio of treated-to-untreated loss in arabinan over time of exposure at 66°C (Winandy and Lebow 2001).

Each study listed above also monitored and correlated the changes in wood chemistry to strength. The critical finding in this coordinated series of studies of LeVan et al (1991), Winandy (1994, 1995), Winandy and Lebow (1996), Lebow and Winandy (1999), Green et al (2003), and Winandy and Krzysik (2007) was that changes in wood chemistry caused by thermal or thermo-chemical degradation could be directly related to strength loss and it was quantitative. That coordinated series of studies showed that under extended thermal and/or thermochemical conditions that degraded the wood, the wood deteriorated in a systematic sequence of events and those events progressed in a consistent and orderly manner. The first phase included significant
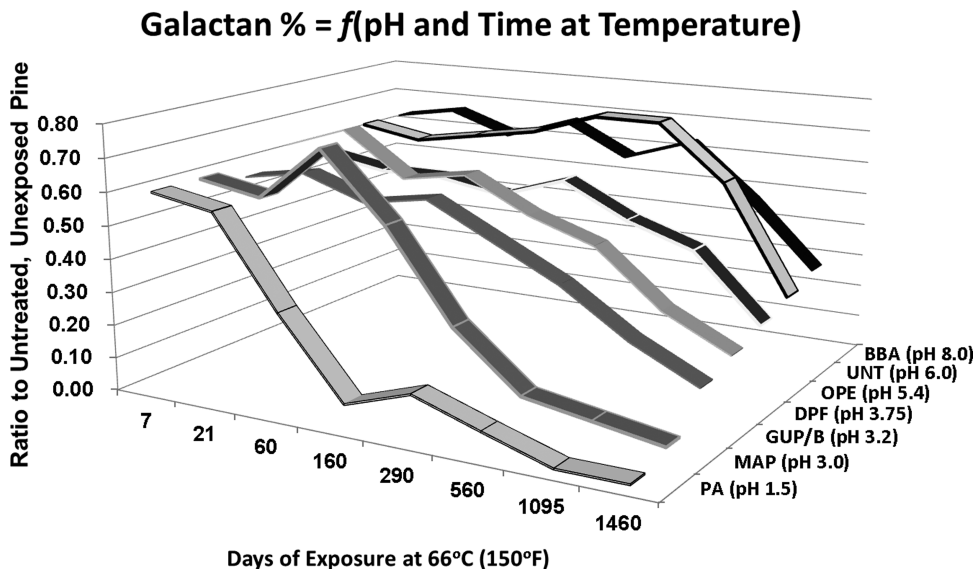
Galactan % = *f*(pH and Time at Temperature)

Figure 6.   Ratio of treated-to-untreated loss in galactan over time of exposure at 66°C (Winandy and Lebow 2001).
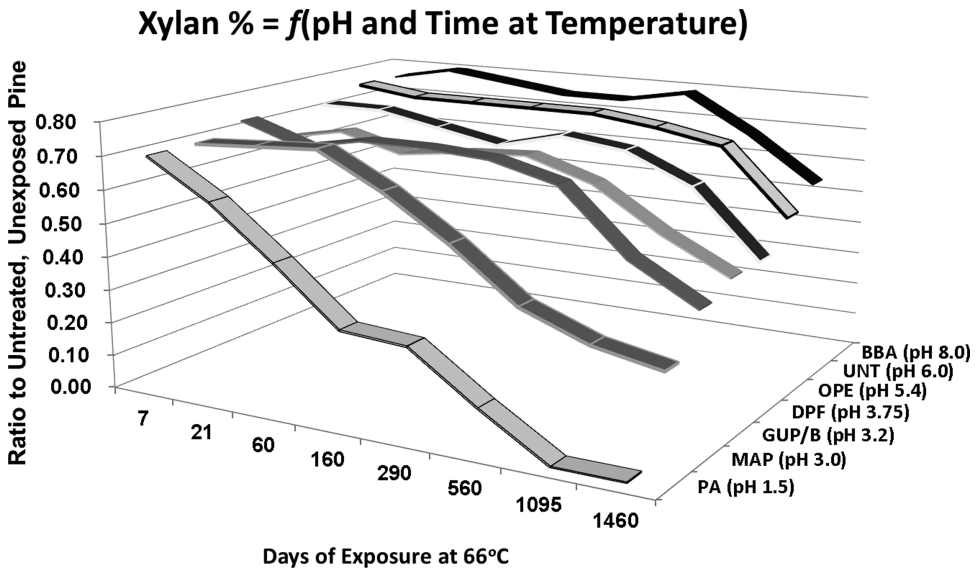
Xylan % = *f*(pH and Time at Temperature)

Figure 7.   Ratio of treated-to-untreated loss in xylan over time of exposure at 66°C (Winandy and Lebow 2001).

arabinan and galactan degradation (eg side chains of hemicelluloses) that occurred prior to attack on mannan, xylan, or glucan (eg main chains of hemicelluloses and cellulose, respectively) (Figs 5-9). They also found that the arabinan and galactan degrade was quantitatively related to the earliest loss in bending strength (Figs 5 and 6).

They noted that no discernible loss in mannan or xylan could be noted until the deterioration of arabinan and galactan approached 25-50% of its initial values (Figs 7 and 8). They then noted that no discernible loss in glucans could be noted until the deterioration of mannans and xylans approached 25-50% of their initial values. Finally,
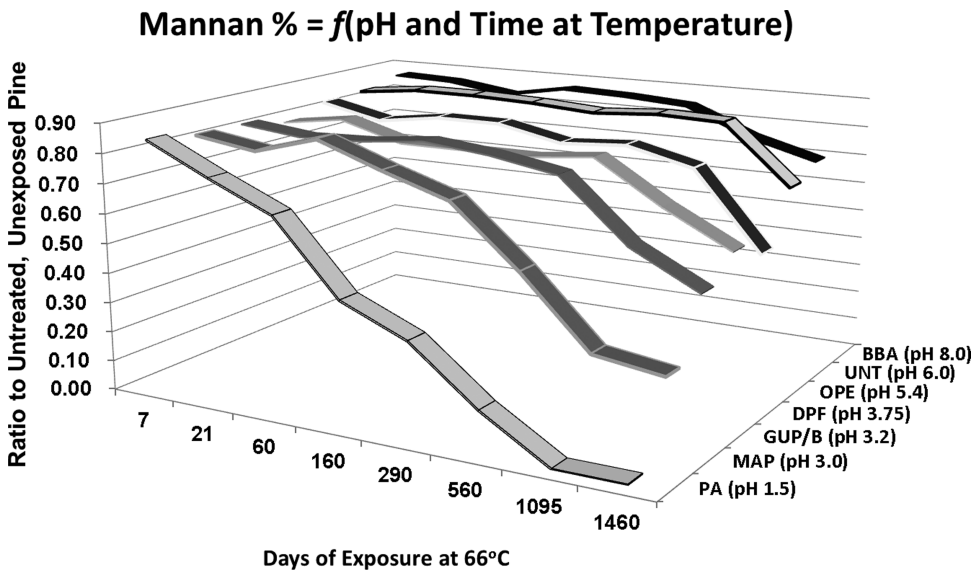
Mannan % = *f*(pH and Time at Temperature)

Figure 8.   Ratio of treated-to-untreated loss in mannan over time of exposure at 66°C (Winandy and Lebow 2001).

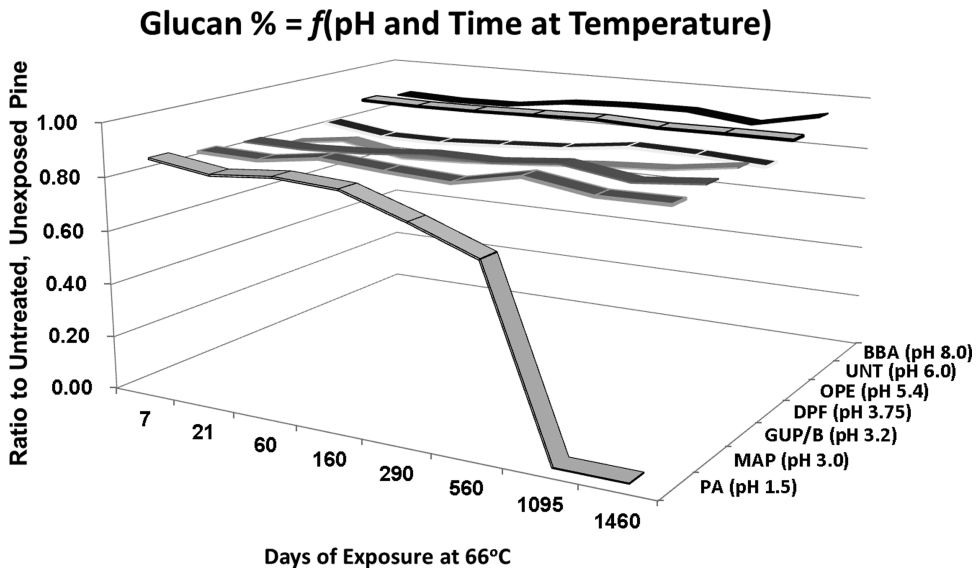## Glucan % = *f*(pH and Time at Temperature)

Figure 9.   Ratio of treated-to-untreated loss in glucan over time of exposure at 66°C (Winandy and Lebow 2001).

only after strength losses had exceeded 50-75% did noticeable degradation of the glucan components begin (Fig 9).

This series of coordinated studies taken as a whole eventually led to the development of predictive kinetics-based models for strength of untreated and treated clearwood and lumber based on time and temperature (Lebow and Winandy 1999; Green et al 2003) and theoretical degradation models for strength loss as a function of changes in the chemistry of wood as they are related to strength loss (Winandy and Lebow 2001).

The fundamental concept that these relationships of strength loss from thermal and thermochemical exposures being quantitative functions of the changes in wood chemistry, naturally has led to the hypothesis that they could also apply to biological deterioration and its effects on loss of wood strength.

BIOLOGICAL DEGRADATION

The ratio of rate-of-strength-loss to rate-of-mass-loss varies by exposure conditions and natural variation in wood resistance, but it has long been reported that a ratio of strength loss-to-mass loss

of wood varies from 3:1 to 6:1 (Wilcox 1968, 1978). Winandy and Morrell (1993) developed a test methodology to monitor these biological-strength relationships and found that in brown-rot decay of Douglas-fir significant arabinan and galactan degradation occurred prior to attack on mannan, xylan, or glucan (Fig 10). They also found that arabinan and galactan degrade was closely related to the earliest loss in bending strength. They noted that no discernible loss in mannan or xylan could be noted until the arabinan and galactan degrade approached 25-50%.
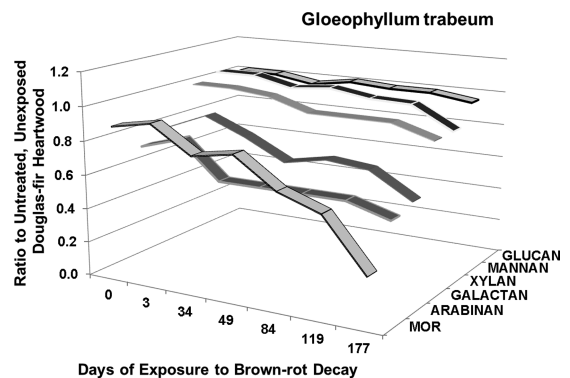

Figure 10.   Effects of *Gloeophyllum trabeum* decay fungi on loss of various carbohydrates, lignin, and strength over time of decay exposure (Winandy and Morrell 1993).
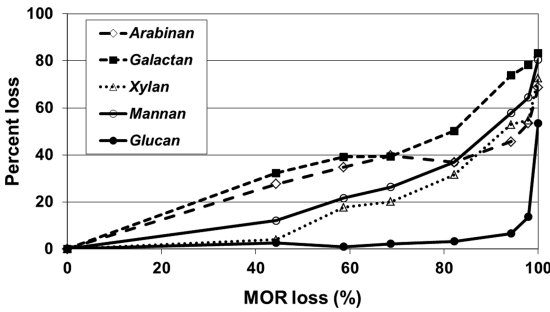
Figure 11. Effects of *Gloeophyllum trabeum* brown-rot decay fungi on loss of various carbohydrates vs loss in MOR as decay progresses (Curling et al 2002).

A virtually identical magnitude and order of events for the initial loss in bending strength during brown-rot decay being strongly related to just the loss in arabinan and galactan was confirmed by Curling et al (2002) using a slightly different and then newly developed biological test method (Fig 11). Later, Clausen and Kartal (2003) further confirmed those same trends for the magnitude and order of events of early strength loss being a primary function of degradation of arabinan and galactan for both compression strength (Fig 12) and bending strength (Fig 13).

The obvious conclusion for each of these studies dealing with early biological decay was that the causes of early bending strength loss were exclusively related to the loss in arabinan and galactan during the earliest stages of decay. Another striking fact was that the progressive
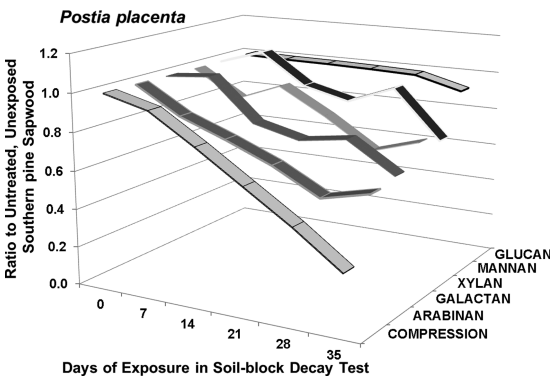

Figure 12. Change in radial compression strength and carbohydrate content as decay progresses (Clausen and Kartal 2003).
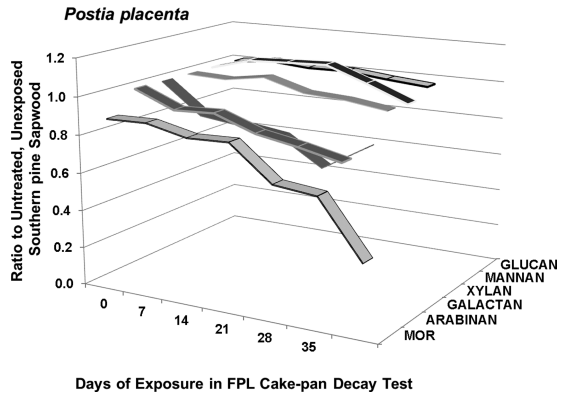

Figure 13. Change in bending strength (MOR) and carbohydrate content as brown-rot decay progresses (Clausen and Kartal 2003).

order of changes in wood chemistry and their relative effect on wood strength during the early stages of decay were virtually identical to those previously noted for thermal and/or thermochemical degradation of wood strength.

Given that the fundamental relationships of initial loss in wood strength under biological, thermal, and/or thermochemical degradation results almost exclusively from the degradation of arabinan and galactan before any other carbohydrate degradation, it is a reasonable certainty that a singular mode and sequence of carbohydrate deterioration is at work. Whether concerned about biological, thermal, and/or thermochemical degradation of the wood, carbohydrate degradation results from the systematic desequencing (ie an orderly piece by piece disassembly) of the complex lignocellulosic structure.

Accordingly, it is more than likely that earlier models, such as those proposed for the effects of wood strength for FR-treated and untreated wood under high-temperature thermal degradation (Winandy and Lebow 2001) or for lumber (Green et al 2003) are likely candidate models from which to begin the study of development of a *Universal Wood-Strength Degrade Model*. Development of such a concept is beyond the scope of this article and the capabilities of its author, but the overwhelming evidence presented in this article leads to the belief that the concept

of a *Universal Wood-Strength Degrade Model*, somehow similar to that shown in Fig 12 as proposed by Winandy and Lebow (2001), is highly probable as a means to define the fundamental relationships of loss in wood strength under biological, thermal, and/or thermochemical degradation. The evolution of such a model is inevitable.

SUMMARY

The goal of this article was to review the findings of a number of different authors who over the last couple of decades have systematically studied the effects of chemical treatments, elevated temperatures, and/or biological decay on the mechanical properties of wood and wood composites. It has presented a hypothesis that there exists a singular relationship for the strength loss in wood and wood-based materials caused by a uniform and progressively systematic desequencing (first affecting the side-chain units of the hemicellulose, then main-chain units of the hemicellulose, then finally the cellulose itself) of the carbohydrate chemistry of wood. This systematic desequencing of that carbohydrate chemistry and its similar effects on the woody microstructure occur under chemical, thermal, or biological attack.

The results of these different studies by different authors were reviewed and discussed, relative to their observations and evaluations on the fundamental "strength loss-to-change in chemistry" relationships. Each study individually found that as wood properties were affected by chemical or thermal agents or by biological deterioration, the magnitude of the strength loss was directly related to both the sequence of individual chemical changes and the magnitude of those losses in individual carbohydrates. Viewed as a composite, the reviewed literature showed that the earliest portion of strength loss in wood under all three modes of deterioration mentioned earlier was initially related to deterioration and loss of the side-chain components of the hemicellulose. Then, after a measureable amount of loss in arabinan and/or galactan components had occurred, the degradation of the main-chain hemicellulose components (ie mannans, xylans) was observed. Finally after significant degradation of the main-chain hemicelluloses occurs, they each report deterioration of glucan-rich amorphous areas of cellulose and even lignin.

The overriding conclusion from the coordinated series of studies reviewed in this article is that the overall sequence of events causing a loss in strength under biological, thermal, and/or thermochemical actions is as follows:

1. Directly related to the rate of hydrolytic deterioration of side-chain hemicelluloses such as arabinan and galactan.
2. Subsequent hydrolytic deterioration of the main-chain hemicellulose monomers such as mannan and xylan.
3. Eventual hydrolytic deterioration of glucan-based cellulose and lignin.

The next generation of wood scientists will surely further study this phenomenon and then develop quantitative models.

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