CHAPTER 8
WOOD DURABILITY AND STABILITY WITHOUT TOXICITY

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INTRODUCTION

Part of a sustainable future for wood products depends on extending the lifetime of wood used in adverse environments. For some products such as the daily news paper, the average life of the products is one day. For packaging, the products average life time may be as few days to a few weeks. For pallets and wooden containers, the lifetime may be several months. For construction, the lifetime may be many, many years. For those products with a long expected life, especially when used outdoors, there is a need to protect them from environmental degradation. The need to protect wood from decay has been an issue ever since humans first used wood. There are references in the Old Testament to the use of decay resistant wood.

While there are wood preservatives that can protect wood for many years of outdoor use, the present wood preservatives are effective based on toxicity to the attacking organisms. In a sustainable future for wood, protection must be based on renewable, sustainable enbirnmentally friendly technologies.

When wood preservation was in its infancy, the approach for protection was focused only on toxicity. Salts of arsenic, chromium, copper and tin have been used along with toxic organic chemicals such as pentachlorophenol and creosote. The wood was treated with these chemicals at various loading levels using various solvents and most did provide long-term effectiveness against fungal attack. Unfortunately, these chemicals are broad spectra toxins that are also toxic to humans and other life forms

With a greater awareness of the persistence of some of these toxic wood preservative chemicals in nature and the concern for our ecosystem, less toxic or narrow spectra toxins have been explored and developed into commercial products. Less toxic and narrower toxicity also has resulted in less effectiveness.

Another approach, which was not followed in the early studies of wood preservation, is to study the mechanisms of fungal attack to determine if preservative methods could be based on metabolic differences between fungi and humans. For example, humans do not possess enzymes capable of breaking down cellulose, a major enzyme system in fungi.

There are several other ways to approach wood preservation without using toxicity as the mechanism of effectiveness. One approach is to interfere with the organisms metabolism. Fungi contain the polysaccharide chitin in their "skin" and interfering with the metabolic formation of chitin would be lethal to fungi and not affect humans. Micro-organisms have enzyme systems that can metabolize cellulose. Since humans do not have cellulase enzymes, then blocking cellulose breakdown in fungi would be an effective tool in wood preservation. Chemicals that interfere with the organism's energy or life cycle is another way to achieve the goal of wood preservation without relying on use of toxic chemicals.

Another approach to wood protection is to change the cell wall chemistry such that attacking organisms can not recognize the wood as a source of food or reduce the cell wall moisture content to a level too low for fungal attack. Chemical modification of wood results in a modified wood that is not toxic to humans but is resistant to attack by micro organisms. There are several approaches to modification for protection and two of them (acetylation and heat treatments) will be presented in this chapter.

There are several misunderstandings about wood. First, wood is not renewable. It comes from a tree so for wood to be sustainable, the emphasis must be placed on healthy ecosystems to ensure a continuous supply of the resource. Second, there is a lot of waste wood and other bioresources that are free for the taking. Nothing is free. To move anything from one place to another requires handling and shipping costs. And, as soon as a market is found for the "waste" resource, it then has a value. Third, wood was designed by Nature as a building material. Wood was designed over millions of years to perform wet not dry. Water in the wood is the plasticizer that allows a tree to move in the wind without breaking. A final misconception is that wood was designed by Nature to be durable. Nature had a very efficient recycling system of five basic chemistries to degrade wood back to its original building blocks of carbon dioxide and water. The five chemistries are oxidation, hydrolysis, dehydration, reduction and free radical decomposition.

WOOD IN ADVERSE ENVIRONMENTS

The properties of wood vary depending on what part of the tree it came from. Sapwood, heartwood, latewood, earlywood, juvenile wood, growth rate, hardwood, softwood, and bark along with drying defects (cracks and splits), grain direction and age of the tree all contribute to a product with non-uniform properties and inconsistent performance.

Wood changes dimension with changing moisture content because the cell wall polymers contain hydroxyl and other oxygen-containing groups that attract moisture through hydrogen bonding. The hemicelluloses are mainly responsible for moisture sorption, but the accessible cellulose, noncrystalline cellulose, lignin, and surface of crystalline cellulose also play roles. Moisture swells the cell wall which expands until it is saturated with water (fiber saturation point, FSP). Beyond this saturation point, moisture exists as free water in the void structure and does not contribute to further swelling. This process is reversible, and the fiber shrinks as it loses moisture below the FSP Wood exposed to moisture frequently is not at equilibrium having wetter areas and drier areas within the same board. This exacerbates the moisture problem resulting in differential swelling followed by cracking and/or compression set Over the long term, wood undergoes cyclic swelling and shrinking as moisture levels change resulting in more severe moisture effects than those encountered under steady moisture conditions.

The pressure exerted when wood swells is very large and must be taken into consideration when wood is used in increasing moisture contents. The maximum swelling pressure of wood has been measured (Tarkow and Turner 1958). It was measured by inserting wooden dowels into steel restraining rings equipped with a strain guage. The wooden dowels of different densities were then wetted with liquid water and the swelling pressure measured as a function of density. Extrapolation of the curve of swelling pressure vs density to the density of the cell wall (1.5) gave value of 91 MPa (1 3,200 psi). A theoretical value based on an osmotic pressure theory, gave a theoretical value of 158 MPa at room temperature. The difference between the actual and the theoretical values was thought to be due to hydroelastic factors. These factors are associated with the fact that restrained wood has a lower moisture content as compared to un-restrained wood.

The best example of using the swelling pressure of wood to practical use goes back to the Egyptians. On a trip to Egypt in 2001, the author saw the evidence first hand. On the edge of a shear granite cliff, holes about 15 cm long, 5 cm wide and 10 cm deep had been chiseled into the rock. Dry wooden wedges the size of the cavities were driven into these holes. Water was then poured onto the dry wood and allowed to swell. The swelling pressure caused the granite to split down the chain of holes resulting in a giant obelisk or other large building blocks. Figure 1 (left) shows the series of holes that were chiseled into a large rock and Figure 1 (right) shows the result of the splitting process.

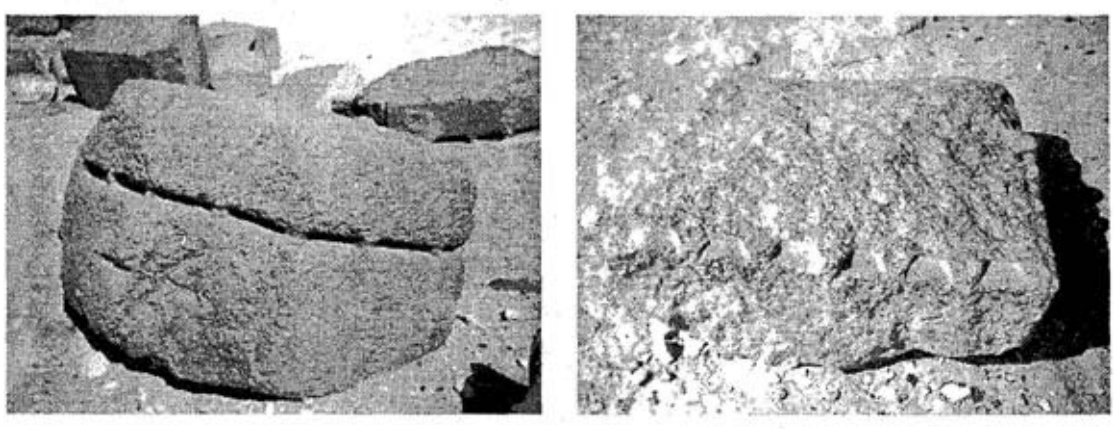

FIGURE 1 – Rocksplit by using the swelling pressure of wood (Egypt 2001).

Wood is degraded biologically based on an oganisms' ability to recognize a potential food source, mainly in the carbohydrate polymers (more specifically the hemicelluloses) in the cell wall. Microorganisms have both non-specific chemical hadn highly specifric enzyme systems capable of hydrolyzing these polymers into digestible units (Figure 2). Biodegradation of both the matrix and the high molecular weight cellulose weakens the fiber cell wall. Strength is lost as the matrix and cellulose polymer undergoes degradation through oxidation, hydrolysis, and dehydration reactions. As degradation continues, removal of cell wall content results in weight loss. All of these biological reactions take place in a high humidity condition.

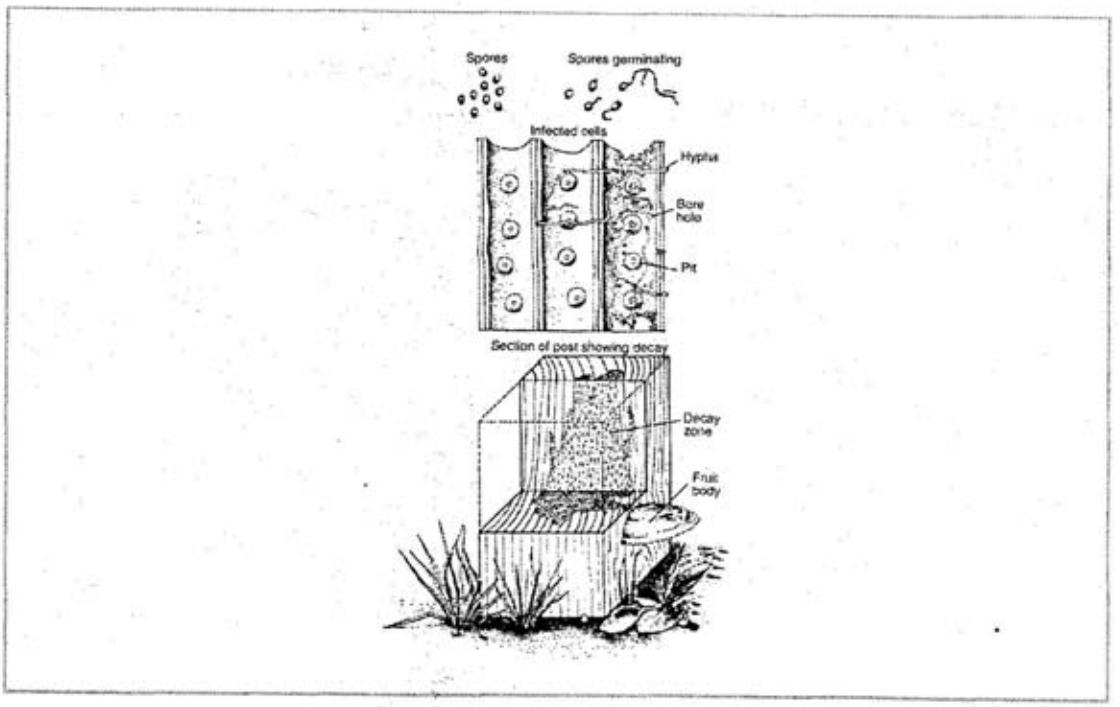

FIGURE 2 - Microorganism attack on wood.

PROPERTY AND PERFORMANCE ENHANCED BIOMATERIALS

With an increased awareness of the fragility of our environment and the need for durability in wood products, new technologies have been developed to increase the service life of wood materials without the use of toxic chemicals. Issues of sustainability, carbon sequestration and performance converge in this search for environmentally friendly methods of wood preservation.

Heat treatments of wood and chemical modification using acetic anhydride to acetylate wood have been studied for many years and are now both commercial. Both methods result in increased decay resistance and improved dimensional stability to different degrees. Strength properties of the wood is also affected mainly by heat treatments.

HISTORY

HEAT TREATMENTS

Heating wood to improve performance dates back many thousands of years. The Kalvträsk wooden ski was bent using heat by the Saami and used in northern Sweden over 5200 years ago (Åström 1993, Insulander 1999). From hieroglyphic pictures of furniture in Egypt between 2500 and 3000 BC, there are chairs made using heat bent wood members (Rivers and Umney 2005). The Egyptians also bent wood for bows using hot water around 1900 BC as shown on tomb paintings (Ostergard 1987). In the 11th century, the Viking shipbuilders also bent wood using heat for parts of the ship (Olsen and Crumlin-Pedersen 1967). In the Norwegian stave churches, large beams were bent using heat and joined (Bugge, 1953, Holan 1990). Finally, the wooden cask makers knew how to heat-bend wood 2000 years ago (Twede 2005). A picture of a wooden cask is shown on the wall of a 2690 BC Egyptian tomb (Kirby 1971). Wooden casks were also made by the Romans to store wine (Twede 2005).

In the early part of the 20th century it was found that drying wood at high temperature increased dimensional stability and a reduction in hygroscopicity (Tiemann, 1915, Stamm and Hansen 1937). Later, it was found that heating wood in molten metal at temperatures between 140° and 320° C reduced swelling in Sitka spruce by 60% and also increased resistance to microbiological attack (Stamm et al. 1946). They also found that the increase in stability and durability also increases brittleness and loss in some strength properties including impact toughness, modulus of rupture and work to failure. The treatments usually cause a darkening of the wood and the wood has a tendency to crack and split.

Burmester studied the effect of temperature, pressure and moisture on wood properties (1973). He found that the optimum conditions for pine were 160 °C, 20-30% moisture and 0.7 MPa pressure. He reported high dimensional stability and resistance to brown-rot fungi attack and minimal loss of strength. He named his process as FWD (Feuchte-Wärme-Druck).

More recently, Norimoto et al. (1993) and Ito et al. (1998) heated wet wood to improve dimensional stability. Inoue et al. (1993) heated wet wood to fix compression set in wood.

Over the years, several names have been given to the various heat treated products and treatments for wood. Including Staypak and Stabwood in the United States (using dry wood); Lignostone and Lignofol from Germany (using dry wood), Jicwood and Jablo from the UK, Thermowood in Finland (using water vapour), Plato in The Netherlands (using water), Perdure from Canada (using steam), Oil Heat Treated (OHT) from Germany (using oil) and New Option Wood/Retification in France (using nitrogen) (Hill 2006).

ACETYLATION

The acetylation of wood was first performed in Germany by Fuchs (1928), using acetic anhydride and sulfuric acid as a catalyst. Fuchs found an acetyl weight gain of over 40%, which meant that he decrystalized

the cellulose in the process. He used the reaction to isolate lignin from pine wood. In the same year, Horn (1928) acetylated beech wood to remove hemicelluloses in a similar lignin isolation procedure. Suida and Titsch (1928) acetylated powdered beech and pine using pyridine or dimethylaniline as a catalyst to yield an acetyl weight gain of 30 to 35 percent after 15 to 35 days at 100 °C. Tarkow (1945) first demonstrated that acetylated balsa was resistant to decay. Tarkow (1946) first described the use of wood acetylation to stabilize wood from swelling in water. Since the 1940s, many laboratories around the world have looked at acetylation of many different types of woods and agricultural resources.

Acetylation of wood using acetic anhydride has mainly been done as a liquid phase reaction. The early work was done using acetic anhydride catalyzed with either zinc chloride or pyridine. Through the years, many other catalysts have been tried both with liquid and vapor systems. Some of the catalysts used include urea-ammonium sulphate, dimethylformamide, sodium acetate, magnesium persulfate, trifluoroacetic acid, boron trifluoride and X-rays. The reaction has also been done without catalyst and by using an organic co-solvent. Gas phase reactions have also been reported using both ketene and acetic anhydride, however, the diffusion rate is very slow so this technology has only been applied to thin veneers (Rowell 2005). Most acetylation reactions done today are done without the use of a catalyst.

Acetylated wood is now sold by Titanwood in Arnhem, The Netherlands. It is sold under the name of accoya® and available in several species of wood in Europe, North America and Asia.

CHEMISTRY

HEAT TREATMENT

There are a variety of thermal modification processes that have been developed. The results of the process depend on several variables including time and temperature, treatment atmosphere, wood species, moisture content, wood dimensions and the use of a catalyst (Stamm 1956, Millett and Gerhards 1972). Temperature and time of treatment are the most critical elements and treatments done in air result in oxidation reactions not leading to the desired properties of the treated wood. Wood degrades faster when heated in either steam or water as compared to dry conditions (MacLean 1951, 1953, Millett and Gerhards 1972, Hillis 1975). Stamm (1956) showed that wood heated in the presence of oxygen degraded more rapidly that wood heated in a oxygen-free atmosphere. As the treatment time increases, embrittlement of the wood increases (Yao and Taylor 1979, Edlund 2004). Generally, weight loss occurs to a higher extent in hardwoods as compared to softwoods which may be due to the higher content of acetyl groups in hardwoods releasing more acetic acid during heat treatment contributing to the acid hydrolysis (MacLean 1951, 1953, Millett and Gerhards 1972, Hillis 1975).

As the wood is heated, the first weight loss is due to the loss of water, followed by a variety of chemistries that produce degradation products and volatile gasses (Shafizadeh and Chin 1977). As the temperature increases, wood cell wall polymers start to degrade. Pyrolysis of the hemicelluloses takes place about 270 °C followed closely by cellulose. Lignin is much more stable to high temperature (Stamm 1956). In

the early stages of degradation, 83% of the weight loss is water (Mitchell et al. 1953). The hemicellulose polymers are the first to degrade followed by the cellulose resulting in the formation of furans such as furfural and hydoxymethyl furfural (Figure 3). The hemicellulose and cellulose are also degraded to internal ethers and other rearrangement products. The optimum amount of waterthat can be lost is three molecules of water from two anhydroglucose units or 16.7 percent of the carbohydrate polymers or 12 percent of the wood (Stamm and Baechler 1960).

Table 1 shows the weight loss resulting from heating wood at different temperatures in the presence of moisture. As the temperature increases, so does the weight loss,

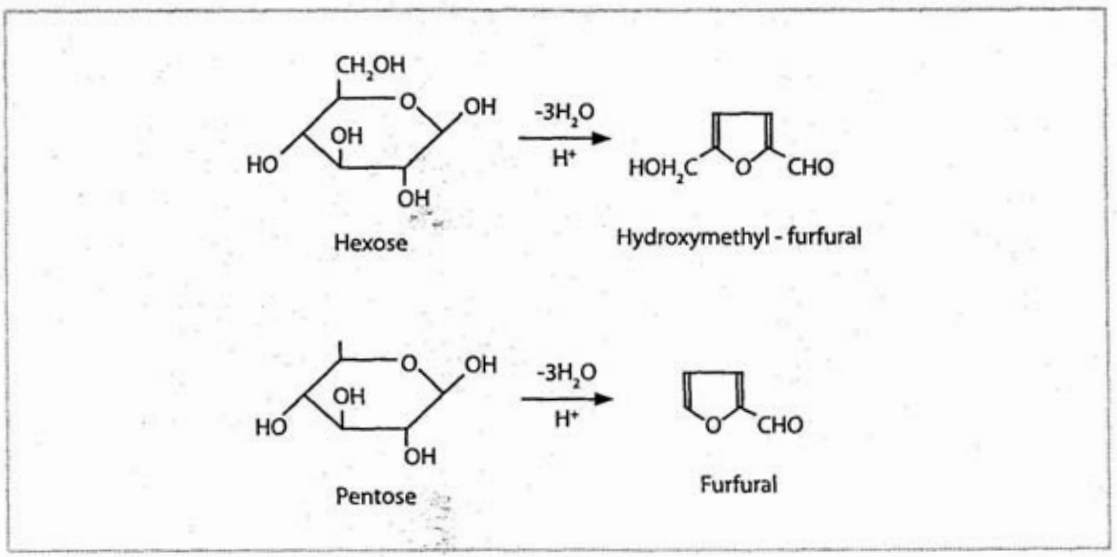

FIGURE 3 - Formation of hydroxymethyl furfural from hexoses and furfural from pentoses as a result of heat treatments of wood.

TABLE 1 - Weight loss due to heating wood in the presence of moisture

Heating Temperature (°C)	Time (hrs)	Weight Loss(%)
120	2	2-3
120	10	5
180	10	10-12
190	2	4-7
190	12	5-10
200	10	10-17
220	1	6-7
235	4	25
240	5	7

Table 2 shows the sugar analysis before and after treating aspen with high pressure steam (220 °C) for 8 minutes. The data shows that in the very early stages of weight loss, the hemicellulose polymers are breaking down and cellulose remains unchanged. Over half of the arabinan and rhamnans are lost during this initial heating.

TABLE 2 - Sugar analysis of aspen before and after heating at 220 °C for 8 minutes.

Wt Loss (%)	Total Carbohydrate (%)	Arabian (%)	Galactan (%)	Rhamnan (%)	Glucan (%)	Xylan (%)	Mannan (%)
0	61.8	0.56	0.68	0.30	42.4	16.3	1.6
2.2	59.2	0.20	0.58	0.14	42.2	14.6	1.5

ACETYLATED

The reaction of acetic anhydride with wood results in esterification of the accessible hydroxyl groups in the cell wall, with the formation of by-product acetic acid. The by-product acid must be removed from the product as the human nose is quite sensitive to the odor of acetic acid. While this is easily done in the case of wood particles and fiber, it is somewhat difficult to do in solid wood.

Acetylation is a single-addition reaction, which means that one acetyl group is on one hydroxyl group with no polymerization:

$$\text{WOOD–OH} + \underset{\text{ACETIC ANHYDRIDE}}{CH_3\text{–C(=O)–O–C(C=O)–CH}_3} \rightarrow \underset{\text{ACETYLATED WOOD}}{\text{WOOD–O–C(=O)–CH}_3} + \underset{\text{ACETIC ACID}}{CH_3\text{–C(=O)–OH}}$$

Thus, all the weight gain in acetyl can be directly converted into units of hydroxyl groups blocked. This is not true for a reaction where polymer chains are formed (epoxides and isocyanates, for example). In these cases, the weight gain cannot be converted into units of blocked hydroxyl groups.

Isolated lignin reacts faster with acetic anhydride as compared to hemicelluloses and holocellulose (Kumar and Agawal 1983, Rowell et al. 1994). Kumar and Agawal (1983) reported that at an acetyl weight percent gain of 13.5, 86.4% of the lignin was acetylated, 21.6% of the hemicelluloses and 9.3% of the cellulose. Reacting wood at 120 °C with acetic anhydride and no catalyst, at an acetyl weight gain of 16 to 19%, theoretically about 90% of the lignin is esterified, and 25% of the holocellulose (Rowell 1982). It is assumed that 100% of the hemicellulose hydroxyl groups are substituted and no cellulose hydroxyl substituted There may be a small amount of hydroxyls esterified on the surface hydroxyls in the amorphous regions of cellulose. This conclusion is based on the observation that pure cotton cellulose cloth can be used to hold wood fiber and no weight gain is observed in the cotton cloth after several acetylation reactions.

MOISTURE AND DIMENSIONAL STABILITY

HEAT TREATMENT

Because of the loss of hygroscopic hemicellulose polymers during heat treatment, the equilibrium moisture content (EMC) is reduced (Table 3). Dimensional stability of heat treated wood was first thought to be due to a cross-linking of cellulose chains (Stamm and Hansen 1937). The furan intermediates that form from the decomposition of the hemicelluloses have poor hygroscopicity and have little effect on the EMC.

TABLE 3 - Equilibrium moisture content (27 °C) of aspen heat treated at 220 °C

Time (min)	EMC at		
	30% RH	65% RH	90% RH
	%		
0	4.7	10.3	8.9
8	2.8	6.2	13.1

Table 4 shows a summary of recent results on EMC resulting from heat treatments from various authors. In most cases, a 50% reduction in EMC is observed. In most examples given, the process was done in a vapor atmosphere between 190 and 220 °C with a relative humidity of 35 to 65%.

TABLE 4 - Reduction in EMC as a result of heating wood.

Wood species	Conditions	Reduction in EMC (%)	Reference
Pinus pinaster	190 °C | 8-24 hrs	50	Esteves et al. 2006
Pinus sylvestris	220 °C | 1-3 hrs	50	Thermowood handbook 2003
Eucalyptus globulus	190 °C | 2-24 hrs	50	Esteves et al. 2006
Pinus sylvestris	Plato process	50-60	Tjeerdsma 2006

Table 5 shows the reduction in swelling of wood (reported as antishrink efficiency ASE) that has been heat treated.

TABLE 5 - Dimensional stability of various woods as a result of heat treatment.

Wood species	Conditions	ASE (%)	Reference
Pinus pinaster	170 °C | WL[1] 2%	50	Esteves et al. 2006
Eucalyptus globulus	190 °C | WL 2%	77	Esteves et al. 2006
Eucalyptus globulus	200 °C | WL 10%	60	Esteves et al. 2006
Pinus sylvestris	220 °C	40	Rapp Sailer 2001

[1] WL = Weight loss

ACETYLATED

Acetylation of wood reduces the number of hydroxyl groups that can sorb moisture so the equilibrium moisture content (EMC) and fiber saturation point (FSP) are reduced and the dimensional stabilization increases with increasing weight gain due to acetylation (Rowell et al. 1986, Rowell 2005). Table 6 shows the reduction in EMC and FSP and ASE as a result of acetylation. Table 7 shows the reduction in EMC and Table 8 shows the dimensional stability for different species.

TABLE 6 - Antishrink efficiency (ASE) of control and acetylated pine (Rowell 2005).

WPG	EMC 27 °C			FSP	ASE
	30%RH	65%RH	90%RH		
0	5.8	12.0	21.7	45	---
6.0	4.1	9.2	17.5	24	
10.4	3.3	7.5	14.4	16	
14.8	2.8	6.0	11.6	---	
18.4	2.3	5.0	9.2	14	
20.4	2.4	4.3	8.4	10	83.2

TABLE 7 – Reduction in equilibrium moisture content as a result of acetylation.

Species	WPG	Reduction in EMC (%)	Reference
Pinus sylvestris	20	50	Minato et al. 2003
Pinus elliotti	20	50	Hillis 1984
Populus tremula	20	50	Rowell 2005
Pinus sylvestris	20	70	Epmeier et al. 2004

Figure4 shows the sorption isotherm for control and acetylated spruce. It is interesting to note that that the acetylated samples show a difference in sorption and desorption just as seen in the control spruce.

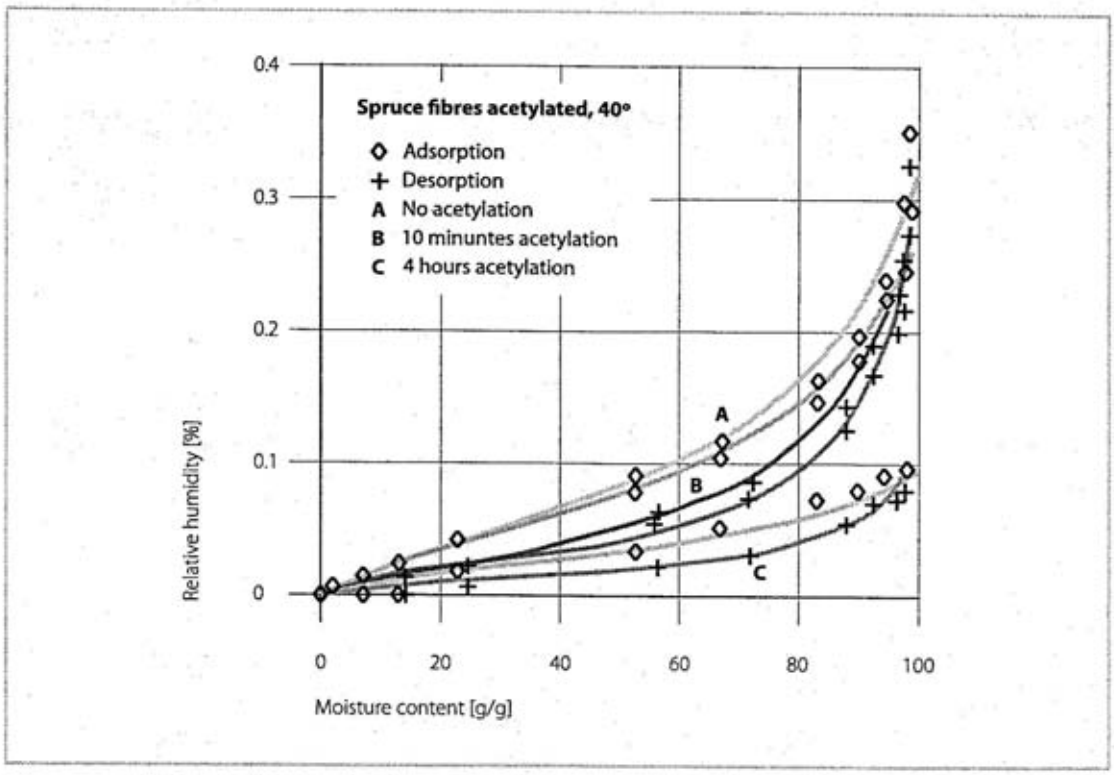

FIGURE 4 – Sorption isotherm of control and acetylated spruce.

TABLE 8 - Antishrink efficiency of several types of acetylated wood.

Species	WPG	ASE	Reference
Pinus elliotti	15	60	Rowell 1983
Pinus sylvestris	20	70	Epmeier et al. 2004
Pinus strobus	22	70	Rowell 2005

DECAY RESISTANCE

It is well documented that brown-rot fungi degrade softwoods mainly attacking and degrading the carbohydrate polymers in the cell wall. What is not so well understood is how they recognize the carbohydrate polymers and how the degrading chemistry starts.

Figure 5 shows the mode of attack of a brown-rot fungus on a softwood. The degradation process starts with fungal enzymes attacking the hemicellulose polymers. Little or no weight or strength losses occur during this initial stage. This is followed by a chemical oxidation system (H_2O_2, Fe^{+++}) generating free radicals that degrades both the hemicellulose and cellulose polymer matrix resulting in strength losses

and a drop in pH (Cowling 1961). This oxidation system then provides the energy source for the generation of ß-glucosidases (indo- and exo-cellulases) that continue the attack on the carbohydrate polymers ultimately resulting in weight loss. The fungi colonize and the attack is now well underway.

The loss in DP results in strength losses before there is very much weight loss. As the weight loss increases, the carbohydrate polymers are badly degraded which results in matrix loss.

ENZYMES → HEMICELLULOSES
(Energy source for generation of chemical oxidation system and drop in pH)
+ CELL WALL POLYMER MATRIX
(Strength losses, Energy source for generation of ß-glucosidases, and colonization)
→ **WEIGHT** LOSS

FIGURE 5–Proposed mechanism of brown-rot attack of softwoods.

Figure 6 shows that the major cell wall polymers lost during brown-rot fugal attack are the carbohydrates. Lignin is also attacked by brown-rot fungi but to a much lesser degree as compared to the carbohydrate polymers.

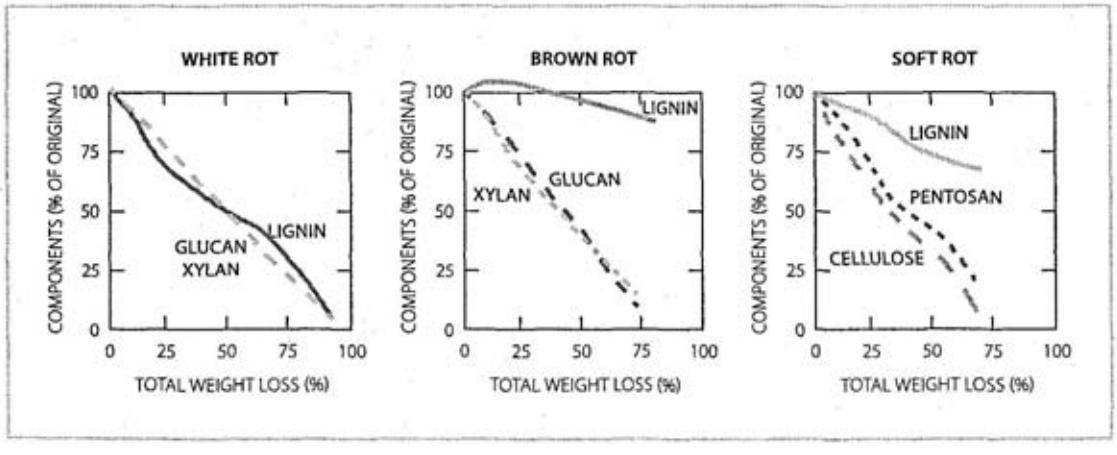

FIGURE 6–Weight loss of cell wall polymers in wood attacked by a brown-rot fungus.

HEAT TREATMENT

As dimensional stability increases and hygroscopicity decreases in heat treated wood, resistance to decay also increases (Stamm et al. 1946, Stamm and Bacchler 1960). Table 9 shows the data of Stamm et al. 1946). A reduction in swelling over 40% results in no weight loss in the decay test. Similar results were obtained when the test fungus was *lenzites trabea* 517 (Stamm and Bacchler 1960).

Table 10 shows fungal resistance of two types of heat treated wood (Rapp and Sailer 2001). Pine (*Pinus sylvestris*) and spruce (*Picea abies*) were heated in oil or air at three different temperatures and the treated blocks were tested for decay for 19 weeks in the EN 113 (1996) decay test using *Coniophora pureana* fungus. The data shows that heating in oil is more effective in reducing attack by fungi than heating in air. This may be due to the presence of the oil in the samples.

TABLE 9 -Relationship between reduced swelling and decay resistance of white pine using *Trametes serialis* fungus (Stamm *etal.* 1946).

Reduction in swelling (%)	Weight loss due to decay (%)
30-33	12
33-38	4.5
40 or more	0

TABLE 10 - Fungal resistance of pine and spruce heated in oil or air

Temperature (°C)	Oil Heated		Air Heated	
	Pine	Spruce	Pine	Spruce
	Wt loss (%)	Wt loss (%)	Wt loss (%)	Wt loss (%)
Control no heat	40	48	--	--
180	13	15	25.0	31.2
200	1.9	13.1	15.8	26.7
220	2.0	0.0	11.0	5.5

Welzbacher and Rapp compared different types of industrially heat treated products using several different fungi in laboratory tests and in different field and compost conditions (2007). Table 11 shows the weight loss during an EN 113 test using three different fungi. The heat treatment in oil was the most effective but the effect of the oil is not known in the decay test.

TABLE 11 - Weight loss (%) of different woods and different heat-treating processes' due to attack by *Poria placenta, Coriolus versicolor and Coniophora puteana*

Material	P. placenta	C. versicolor	C. puteana
Pine control	31.0	5.1	47.5
Douglas fir control	14.0	2.6	27.4
Oak control	0.8	14.3	3.9
Plato	10.0	6.8	3.7
Premium	16.0	9.0	1.9
NOW	13.3	7.8	12.2
OHT	7.4	5.6	3.4

[1] Plato = Heat treated (The Netherlands), Premium = Heat treated (Finland), NOW = New Option Wood, OHT = Oil-heated wood.

The same authors also determined mass loss in a 32-week test with two different soils according to EN-807 (1997). Table 12 shows the results of that test.

TABLE 12 - Average mass loss (%) after 32 weeks exposure to two different types of soil.

Material	Compost soil	Field soil
Pine control	21.9	21.7
Douglas fir control	14.2	12.0
Oak control	38.7	39.7
Plato	9.6	4.4
Premium	9.5	5.8
NOW	5.7	4.2
OHT	6.5	4.2

The same authors also placed control and heat-treated stakes in the ground according the EN-252 (1990) For 5.5 years and determined the mass loss and the type of fungi that was attacking the wood. Using a Rating system of 0 = no decay, 1 = slight attack, 2 = moderate attack, 3 = severe attack and 4 = destroyed They found that pine control had a rating of 3.8; Douglas fir, 3.3; oak, 3.6; Plato, 3.1; Premium, 3.5; NOW, 2.9; and OHT, 2.3. All samples were attacked by white- and soft-rot fungi but white-rot was the dominate fungus found for the heat-treated woods.

Resistance to decay in heat-treated wood is probably due to the loss of hemicelluloses polymers in the cell wall. As was shown earlier, the more weight loss in the heating process, the more durable the heat-treated wood.

ACETYLATED

Over the years, several mechanisms have been put forward to explain the resistance to brown-rot fungal attack provided by acetylated wood. The earliest ideas centered around the modification of the con-Formation and configuration of the substrate such that the specific enzymatic attack could not take place Stamm and Baechler 1960, Talajasjo et al. 1989a,b, Takahashi 1996). Another theory is based on The bulking effect of the covalently bonded acetyl group (Foster et al. 1997, Foster 1998). Another was Advanced that the mechanism was based on the physical blocking of the cell wall micropores so enzy-me penetration can not take place (Papadopoulas and Hill 2002, Hill 2002, Hill et al. 2005). Highley et al. (1 994) showed that the smallest enzyme of a brown-rot fungi is too large to penetrate the cell wall. The average size of a cellulitic enzyme is about 5 nm and the smallest pore size in wood is < 3.8 nm. Mohebby (2003) speculated that there are very small regions in the cell wall that are not acetyated due to the size of the acetate group but that are accessible to free radicals produced by the fungi.

Table 13 shows the resistance of acetylated wood to brown- and white-rot fungi in a 12 week standard ASTM (1976) soil block test. While the control pine blocks lost an average of 61% weight, the acetylated blocks list less than 2% due to brown-rot fugal attack.

TABLE 13 - Resistance of acetylated pine against brown- and white-rot fungi in an ASTM standard 12 week soil block test. Rowell et al. 1987).

WPG	Weight Loss After 12 Weeks	
	Gloeophyllum trabeum	Trametes versicolor
	(%)	
0	61.3	7.8
17.6	1.7	1.1

Table 14 shows the correlation between weight loss due to decay and increasing acetyl content. As the acetyl content increases, resistance to decay increases to a weight gain of about 18 weight percent gain at which point fungi can no longer attack the acetylated wood. Table 14 also shows the EMC as a function of weight loss due to fungal attack. As the EMC decreases, decay decreases. An EMC of 9 or below results in decay resistance.

TABLE 14 -Correlation between cell wall moisture content and fungal attack of control and acetylated pine.

WPG	EMC	Weight loss	
	90%RH	Brown-rot Fungus	White-rot Fungus
	%		
0	21.7	61.3	7.8
6.0	17.5	37.6	5.1
10.4	14.4	8.7	3.3
14.8	11.6	3.0	<2
18.4	9.2	<2	<2
20.4	8.4	<2	<2

Table 15 shows the results of a fungal cellar test using control and acetylated flakeboard samples at increasing levels of acetyl content (Nilsson et al. 1988).

TABLE 15 - Fungal cellar tests of aspen flakeboards made from control and acetylated flakes (Nonsterile soil containing brown, white and soft-rot fungi and tunneling bacteria).

WPG	Rating at intervals (months)							
	2	3	4	5	6	12	24	36
0	S/2	S/3	S/3	S/3	S/4	--	--	--
7.3	S/0	S/1	S/1	S/2	S/3	S/4	--	--
11.5	0	0	S/0	S/1	S/2	S/3	S/4	--
13.6	0	0	0	0	S/0	S/1	S/2	S/4
16.3	0	0	0	0	0	0	0	0
17.9	0	0	0	0	0	0	0	0

RATING SYSTEM: **0** = no attack; **1** = slight attack; **2** = moderate attack; **3** = heavy attack; **4** = destroyed; **S** = swollen.

The present authors have postulated that the mechanism of decay resistance in acetylated wood is based on moisture exclusion due to the fact that the equilibrium moisture content of a highly modified wood is too low to support fungal attack, i.e. no water molecules at the site of a glycosidic bond that the fungal enzymes need for hydrolysis (Rowell, 1983, Ibach and Rowell 2000, Ibach et al. 2000). Another idea is that the mechanism is based on the modification of the hemicellulose fraction in the cell wall. Maybe even more specific, the modification of the arabinose sugar in the hemicelluloses considering that this is an **L**-pentose sugar in the hemicelluloses and it is the only sugar in a strained five-membered ring. Why is this sugar present in this strained ring form? Could it be the trigger that Mother Nature uses as a point of attack to start the entire degradation process? Is the mechanism of resistance as simple as protecting arabinose from hydrolysis?

It is interesting to note that all woods contain acetyl groups: softwoods from 0.5 to 1.7% and hardwoods from 2 to 4.5%. Why they are present is unknown. Acetylation of wood to an acetyl level of about 17 to 20% renders the wood resistant to attack by both brown-rot, white-rot and soft-rot fungi.

Table 16 shows the results of the moisture sorption at 30%, 65% and 90% RH before the soil block test and the weight loss after the soil block test. In the solid wood specimens, the control sample lost 65.8% weight and had an EMC at 90% of 20.2%.

TABLE 16 - Equilibrium moisture content of southern pine solid wood before and after attack and weight loss due to brown-rot fungal attack.

	BEFORE DECAY				AFTER DECAY		
Acetyl %	EMC at:			Weight loss %	EMC at:		
	30% RH	65% RH	90% RH		30% RH	65% RH	90% RH
0	4.2	9.4	20.2	65.8	---	---	---
5	2.9	7.0	16.5	58.8	3.9	7.5	11.8
12	2.4	5.2	13.0	44.9	3.4	6.9	10.3
14	1.8	4.6	11.4	35.6	3.2	6.2	9.7
19	1.1	3.7	8.6	5.0	2.3	4.6	7.2

As the % acetyl increased, the EMC decreased as did the weight loss due to fungal attack. At 19 %acetyl, the weight loss was only 5% and the EMC at 90% RH was 8.6%. Also, as the % acetyl increased, the pH of the wood decreased from 4.5 to 3.7.

Table 16 shows the EMC of solid wood before and after the soil block test and the weight loss in the soil block test. The control sample has an EMC at 90% RH of 20.2% and a loss of 65.8% due to fungal attack. As the % acetyl increased, the weight loss due to fungal attack decreased. At an acetyl % of 19, the EMC at 90% RH was 8.6% and the weight loss was only 5.0%. In all cases, the EMC decreased at all RH levels after the decay test which may indicate that moisture sensitive hemicelluloses were lost during the brown-rot fungal attack.

TABLE 17 - Equilibrium moisture content of southern pine fiber before and after attack and weight loss due to brown-rot fungal attack.

	BEFORE DECAY				AFTER DECAY		
Acetyl %	EMC at:			Weight loss %	EMC at:		
	30% RH	65% RH	90% RH		30% RH	65% RH	90% RH
0	2.9	7.9	12.4	51.7	8.5	10.6	13.8
5	2.2	6.2	10.1	26.5	4.9	7.9	11.4
9	1.6	5.2	8.5	5.9	3.8	6.6	9.8
15	0.9	3.5	5.9	0.7	2.5	4.4	6.1

Table 17 shows the EMC of wood fiber before and after the soil block test and the weight loss in the soil block test (Rowell et al. 2007). The control sample has an EMC at 90% RH of 12.4 % and a loss of 51.7% due to fungal attack. The EMC for the fiber control was much lower than for the solid wood possibly indicating surface extractives or resin. As with solid wood, as the % acetyl increased, the weight loss due to fungal attack decreased. At an acetyl % of 15, the EMC at 90% RH was 5.9% and the weight loss was

only 0.7%. In all cases, the EMC increased slightly at all RH levels after the decay test which may indicate only a small loss of hemicelluloses during the brown-rot fungal attack.

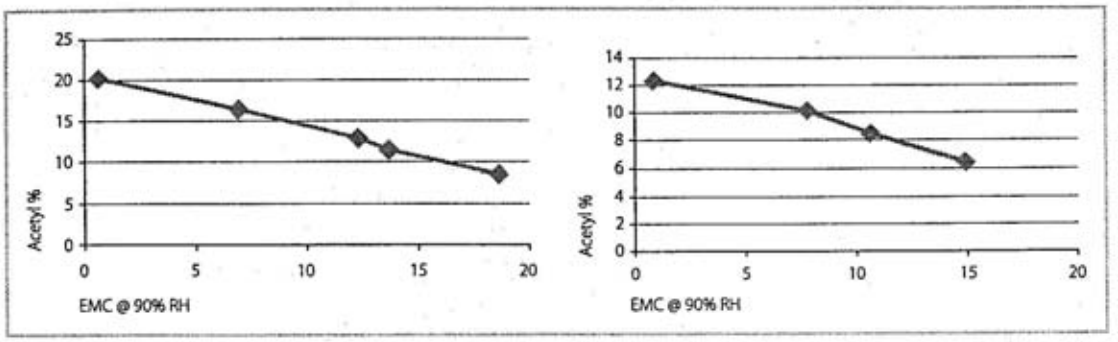

FIGURE 7 –Acetyl content before brown-rot attack as a function of equilibrium moisture content: solid wood (left) and wood fiber (right)

Figure 7 shows that there is a linear relationship between the increase in acetyl content and the decrease in EMC for both solid wood and wood fiber. Table 18 shows that there is very little loss of acetyl in both sold wood and wood fiber due to brown-rot fungal attack. This would indicate that the mass lost during decay has little or no bonded acetyl.

TABLE 18 - Acetyl content before and after attack by brown-rot fungus.

Solid Wood			
WPG	Acetyl Before (%)	Acetyl After (%)	Weight loss (%)
0	0.63	0.22	65.8
19	18.60	17.67	5.0
Fiber			
0	0.81	0.39	51.7
15	14.96	14.75	1.4

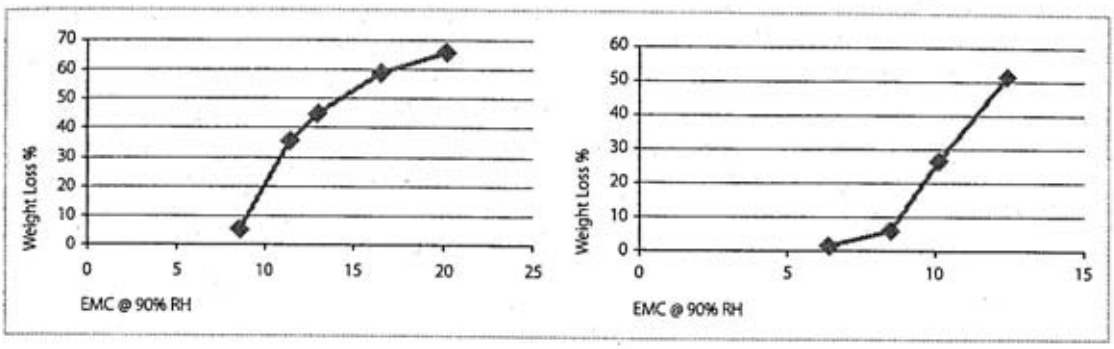

FIGURE 8 –Weight loss due to brown-rot fungal attack as a function of equilibrium moisture content: Solid wood, left; wood fiber, right.

While there was a linear relationship between acetyl and EMC, Figure 8 shows that there is a non-linear relationship between weight loss and EMC. This might indicate that it is the last and, perhaps the most hindered, hydroxyls to react are the critical ones that result in resistance to attack by the brown-rot fungus.

TABLE 19 – Carbohydrate analysis after brown-rot degradation of solid wood,

Solid Wood WPG	Weight Loss (%)	Total Carbo Lost (%)	Araban Lost (%)	Galactan Lost (%)	Rhamnan Lost (%)	Glucan Lost (%)	Xylan Lost (%)	Mannan Lost (%)
0	65.8	88.0	86.7	66.8	75.0	89.0	84.3	93.5
19	5.0	18.0	27.4	17.5	16.7	18.0	11.1	20.9

Table 19 shows the loss of carbohydrates during the brown-rot attack of solid wood. The non-acetylated wood has a total carbohydrate loss of 88% and most of the mannans, xylans, glucans, and arabans are lost. This shows a major loss of both hemicelluloses and cellulose. In the acetylated sample at 19% acetyl, there is only a 18% loss of carbohydrates with the arabans losing the most weight.

TABLE 20 - Carbohydrate analysis after brown-rot degradation of wood fiber.

Wood Fiber WPG	Weight Loss (%)	Total Carbo Lost (%)	Araban Lost (%)	Galactan Lost (%)	Rhamnan Lost (%)	Glucan Lost (%)	Xylan Lost (%)	Mannan Lost (%)
0	51.7	85.8	87.9	71.9	90.0	83.8	90.6	92.5
15	1.4	13.2	89.0	55.2	70.0	0	38.3	42.0

Table 20 shows the loss of carbohydrates in the wood fiber. The non-acetylated fiber loses 85.8% carbohydrate with major weight loss in all sugars except the galatans. The acetylated sample at 15 % acetyl shows only 13.2% total carbohydrate loss, no loss of cellulose (glucans) but major losses of arabans and rhamnans.

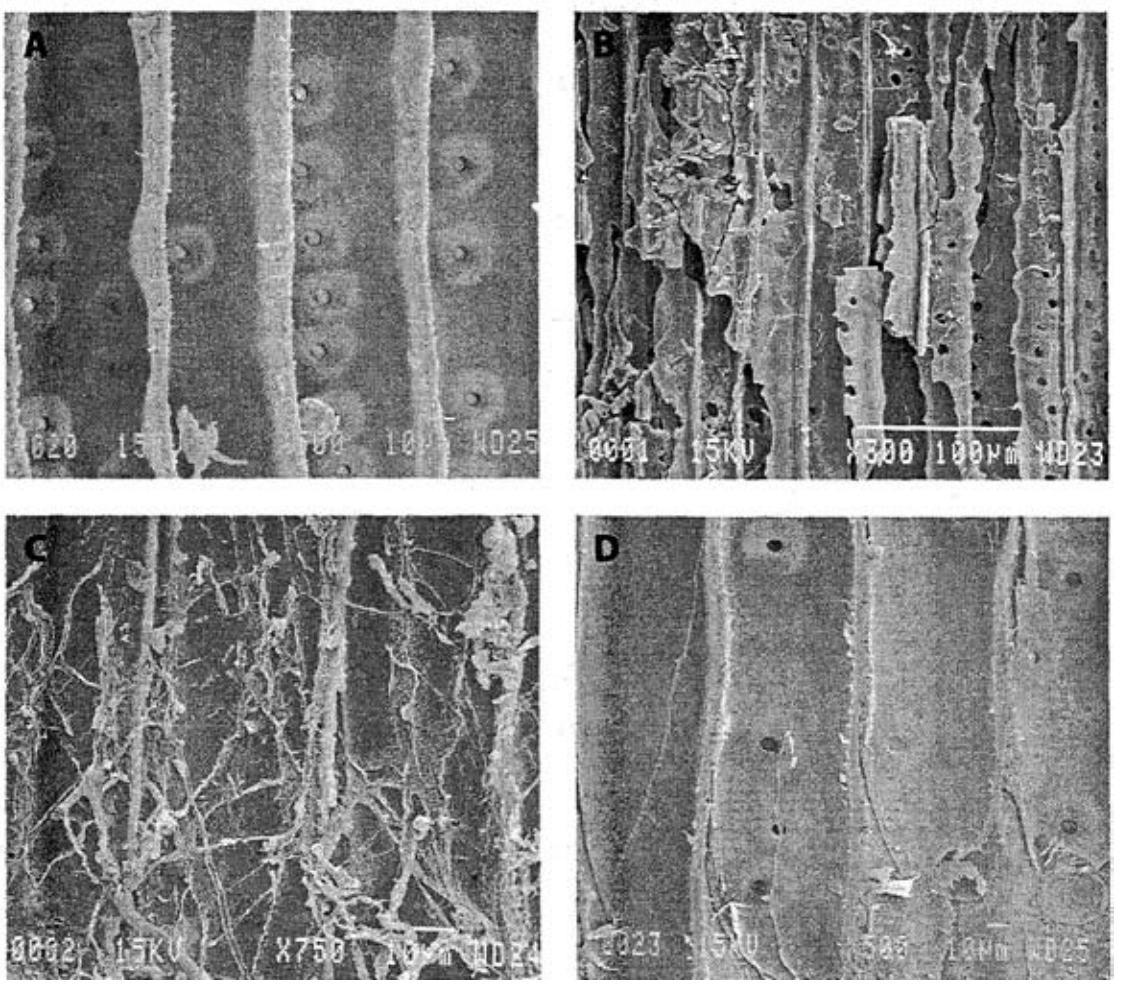

FIGURE 9 - Southern yellow pine before acetylaltion (A), non-acetylated wood after attack by brown-rot fungi (weight loss 65%) (B), hyphae growing on non-acetylated wood (C), hyphae growing on acetylated wood (19 %acetyl) (D).

Figure 9 shows the scanning electron micrographs of (A) solid wood before acetylation, (B) non-acetylated wood after brown-rot fungal attack, (C) hyphae growing on non-acetylated wood and (C) hyphae growing on acetylated wood. Figure 9B shows that the wood is badly degraded and Figure 9C shows hyphae growing all over the degraded wood. Figure 9D shows a few hyphae on the acetylated wood indicating that the wood is not toxic to the organism.

STRENGTH

HEAT TREATED

Stamm et al. (1946) were the first to report a loss of mechanical properties as a result of heat treatments of wood. They heated wood at 320 °C for one minute or 150 °C for a week and found a 17 percent reduction in modulus of rupture (MOR) when heated in molten metal and 50 percent when heated in air. Under the same conditions, there was less loss in modulus of elasticity (MOE).

Mitchell (1988) found that losses in strength properties were much less when wood was heated dry as opposed to wet. Figure 10 shows the loss in MOR when loblolly pine was heated at different temperatures wet and dry and Figure 11 shows the loss in MOE under the same Conditions (Mitchell 1988, Hill 2006).

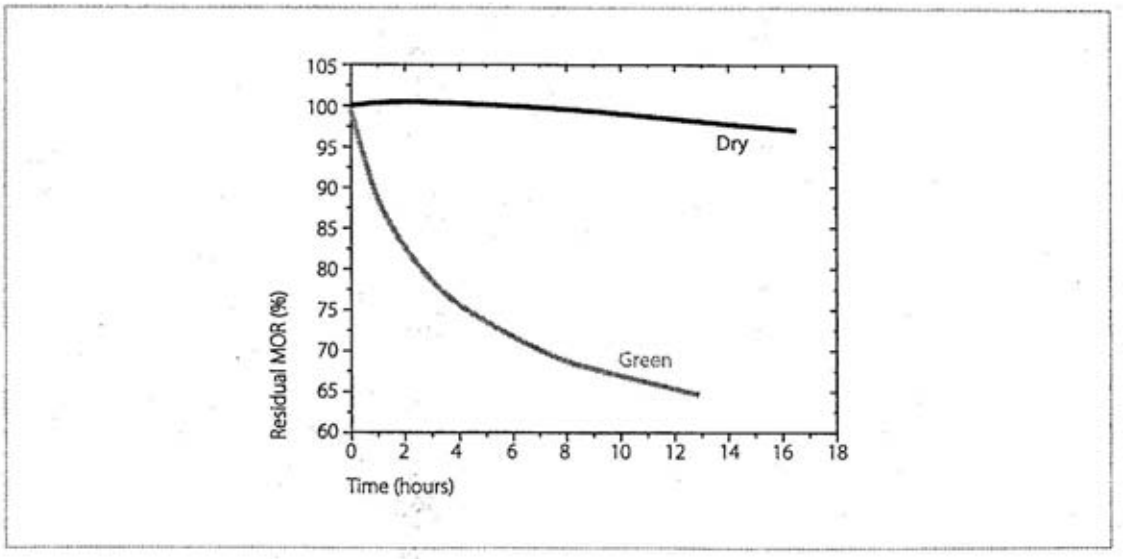

FIGURE 10 -Changes in MOR resulting from wet or dry heating of loblolly pine (Mitchell 1988, Hill 2006).

Rapp and Sailer (2001) heated pine and spruce at 180 to 220 C for various times in air and in oil and determined MOR and MOE in a three point bending test. The highest MOE was 11,000 N/mm^2 in oil heating and little loss in MOE in both air and oil heating. MOR, however, decreased 30% in oil heating and impact bending strength decreased and the wood became brittle. Oil-heated wood lost about 50% and air-heating lost over 70% of the impact strength compared to controls.

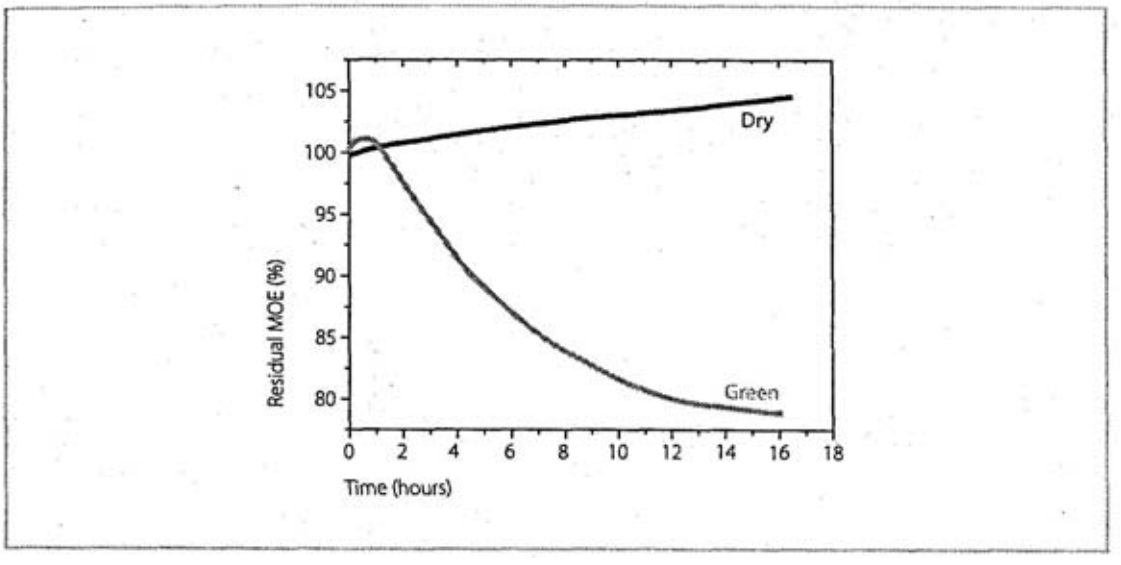

FIGURE 11 -Changes in MOE resulting from wet or dry heating of loblolly pine (Mitchell 1988, Hill 2006).

Table 21 gives a summary of other data on strength changes in heat-treated wood. In all cases, there was only a small decrease in MOE but major changes in MOR depending on temperature, time and atmosphere.

TABLE 21 - Change in MOR as a result of heat treatment of various woods.

Species	Treatment	MOR (%)	Reference
Betula pendula	Vapor, 200 °C	-43	Johansson and Moren 2005
Beech, spruce	Vapor 200 °C	-50	Yildiz et al. 2006
Pinus sylvestris	OHT 220 °C	-30	Rapp and Sailer 2001
Pinus pinaster	O2 180-200 °C	-6 - -25	Esteves et al. 2006

ACETYLATED

Narayanamurti and Handa (1953) acetylated some woods from India and found a slight decrease in MOE of acetylated wood as compared to controls. The Koppers company found that acetylated southern and ponderosa pine showed no loss of impact bending strength as compared to controls (1961). Dreher et al. studied the strength properties of acetylated pine, oak and maple boards. Compressive strength, hardness, fiber stress at proportional limit and work to proportional limit were higher in acetylated boards than in controls. MOR increased by acetylation in pine but decreased in oak and maple. MOE was unchanged while shear strength parallel to the grain was decreased in all three acetylated species. Table 22 shows the bending stiffness [MOE] and bending strength of [MOR] of acetylated radiate pine. The table shows strength properties are retained even after of acetylation.

TABLE 22 - Bending stiffness [MOE] and bending strength of [MOR] of control and acetylated radiata pine.

Sample	Before Acetylation		After Acetylation	
	MOR N/mm2	MOE N/mm2	MOR N/mm2	MOE N/mm2
Radiata Pine	63.6	10,540	--	--
Acetylated Radiata pine	--	--	64.4	10,602

This data shows (within experimental error) that there is no strength or stiffness loss due to the acetylation process. Finite span tensile strength of thin strips of pine and lime showed no significant difference in tensile strength between control and acetylated wood (Rowell and Banks 1987).

Table 23 shows the wet and dry strength of acetylated radiata pine wood. Non-acetylated pine loses over 60 percent of its dry strength and over 35 percent of its dry stiffness when wet. Acetylated radiata pine, on the other hand, only loses 10 percent or less in MOR and MOE when wet.

TABLE 23 -Wet and dry strength and stiffness of solid radiata pine and acetylated radiata pine.

Sample	Dry Strength MOR N/mm2	Dry Stiffness MOE N/mm2	Wet Strength MOR N/mm2	Difference (%)	Wet Stiffness MOE N/mm2	Difference (%)
Radiata Pine	63.6	10,540	39.4	-62	6760	-36
Acetylated Radiata Pine	64.4	10,602	58.0	-10	9690	-8.6

CONCLUSION

Modification of wood using heat treatments or by chemical modification using acetic anhydride result in wood that is dimensionally stable and resistant to attack by fungi without the use of toxic chemicals that could leach into the environment. These may be the treatments of the future for protection of wood used in adverse conditions.

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PORTO **2010**

SUSTAINABLE DEVELOPMENT
IN THE FOREST PRODUCTS INDUSTRY

Roger M. Rowell :: Fernando Caldeira :: Judith K. Rowell

edições UNIVERSIDADE FERNANDO PESSOA

FICHA TÉCNICA

TITULO Sustainable Development in the Forest Products Industry
EDITORS Roger M. Rowell Fernando Caldeira, Judith K. Rowell

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COMPOSIÇÃO Oficina Gráfica da Universidade Fernando Pessoa
IMPRESSÃO E ACABAMENTOS Sersilito Empresa Giáfica, Lda

DEPOSITO LEGAL 311521/10

ISBN 978 989 643-052-8

OS CONTEUDOS DOS CAPITVLOS SÃO DA INTEIRA
RESPONSABILIDADE DOS AUTORES

CATALOGAÇÃO NA PUBLICAÇÃO
.....

SUSTAINABLE DEVELOPMENT IN THE FOREST PRODUCTS INDUSTRY
Sustainable development in the forest products industry : eds Roger M Rowell Fernando Caldeira Judith K. Rowell -Porto Edições Universidade Fernando Pessoa 2010, 284 p.; 25 cm
ISBN 978-989-633-052-8

Biomassa -- Sustentabilidade

CDU 620.95
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