CELLULOSE CHEMISTRY AND TECHNOLOGY

CHEMICAL MODIFICATION OF WOOD TO PRODUCE STABLE AND DURABLE COMPOSITES

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Dimensionally stable solid wood and wood composites can be achieved by several methods, including cell wall bulking, cell wall polymer crosslinking and removal of hygroscopic components in the cell wall. Bulking the cell wall with bonded chemicals produces dimensionally stable products that can withstand wet and dry cycles. Crosslinking with a short difunctional chemical, such as formaldehyde, can produce dimensionally stable products that can also be used in wet-dry cycles and the amount of chemical add-on is very small (4 to 6%), but the wood is brittle. Wood heated to temperatures where the hygroscopic hemicellulose polymers are degraded produces a dimensionally stable product, but with reduced strength. Controlling the moisture content in the cell wall is one of the keys to biological resistance. If the equilibrium moisture content in the cell wall is below that required for a microorganism to attack wood, the chemically modified wood is then resistant to attack. The modification of the configuration and conformation of the substrate polymers, so that enzyme recognition cannot take place, may also be part of the protection mechanism.

Keywords: chemical modification, composites, heat treatments, crosslinking, acetylation, formaldehyde, bulking, dimensional stability, decay resistance, equilibrium moisture content

INTRODUCTION

If we look into the future of materials, we need to reduce our dependence on non-renewable resources and increase our use of renewable resources. To replace many non-renewable materials, stable and durable biomass materials will be used. For many countries, the biomass will be wood.[1]

Wood is a porous three-dimensional, hydroscopic, viscoelastic, anisotropic biopolymer composite, composed of an interconnecting matrix of cellulose, hemicelluloses and lignin, with minor amounts of inorganic elements and organic extractives. There are several key words in this definition that need to be addressed to produce stable and durable building materials: porous, hydroscopic, anisotropic and biopolymer composite.[2]

In terms of moisture sorption and biological degradation, hemicelluloses are a key element. Hemicelulose polymers are accessible, hydroscopic and contain sugar residues that may be the recognition point for microorganisms to start the degradation of the wood. The pressure exerted when wood swells is enormous. The measured swelling pressure is of 91 MPa with a theoretical value of 158 MPa. This large swelling pressure was used by the Egyptians to split granite.

The properties of any resource are, for the most part, a result of the chemistry of the resource, and if you change the chemistry, you change properties, and if you change properties, you change performance. The stable and durable properties of wood can be changed by changing the chemistry at the molecular level.[3]

CHEMICAL MODIFICATION TO IMPROVE STABILITY

Three approaches will be covered to improve the stability of wood using chemical modification: 1) cell wall bulking – bulk the cell wall with chemical back to its green volume (acetylation), 2) crosslinking – interconnect cell wall polymers with short chain difunctional chemical (formaldehyde), and 3) heating – heat at high temperatures to remove hygroscopic cell wall polymers (hemicelluloses).[4,5,6,7]

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Cell wall bulking

The cell wall can be bulked with non-bonded or bonded chemicals. An example of the non-bonded would be polyethylene glycol (PEG), but the obtained products could only be used for dry applications, otherwise the chemical will leach. In bonded chemicals, there is a chemical reaction with cell wall hydroxyl groups to form stable bonds. The products from this type of technology can be used in highly humid conditions and wet/dry cycles. The bulking chemicals occupy space in the cell wall, bulking it back to its green volume without exceeding the elastic limit of the cell wall. Where bonding takes place is not important. One example of this chemistry is the reaction of wood with acetic anhydride.[8]

$$\text{WOOD-OH} + \underset{\text{Acetic Anhydride}}{\text{CH}_3\text{C(=O)-O-C(=O)-CH}_3} \rightarrow \underset{\text{Acetylated Wood}}{\text{WOOD-O-C(=O)-CH}_3} + \underset{\text{Acetic Acid}}{\text{CH}_3\text{C(=O)-OH}}$$

All woods contain acetyl groups: softwoods – 0.5-1.7%, and hardwoods – 2-4.5%. Table 1 shows the change in volume in wood from green to dry to acetylated.

The elastic limit of cell wall was not exceeded and the acetylated wood reached back its original green volume. The equilibrium moisture content (EMC) is reduced as the level of acetyl weight gain increases. Table 2 shows the reduction in EMC as a function of acetyl weight gain.

Table 3 shows the dimensional stability resulting from the acetylation of solid pine wood and for a fiberboard made from acetylated pine fiber.

Table 1
Change in volume in wood from green to dry to acetylated

Green volume (cm^2)	OD volume (cm^2)	Change (%)	Ac (%)	Ac volume (cm^2)	Change (%)
38.84	34.90	-10.1	22.8	38.84	+10.1

Table 2
Equilibrium moisture content of acetylated pine

Weight Percent Gain (WPG)	Equilibrium Moisture Content (EMC) at 27 °C		
	30% RH	64% RH	90% RH
0	5.8	12.0	21.7
6.0	4.1	9.2	17.5
10.4	3.3	7.5	14.4
14.8	2.8	6.0	11.6
18.4	2.3	5.0	9.2
20.4	2.4	4.3	8.4

Table 3
Dimensional stability of acetylated wood (24 h water soak)

Solid Pine	EMC	S	ASE
Control	21.7	13.8	-
Acetylated	8.4	4.2	69.3
Pine fiberboard*			
Control	20.2	21.3	-
Acetylated	3.4	2.1	90.1

*5% phenolic resin, S = Swelling coefficient, ASE = Antishrink efficiency

Crosslinking

When wood is reacted with formaldehyde, crosslinking takes place between two hydroxyl groups in the cell wall polymers. Because of the short crosslinking distance, the two polymers are locked in a rigid structure. The locking of the polymers does not allow the cell wall to expand when it gets wet.

WOOD-OH + H-C(=O)-H → WOOD-O-C(OH)-H_2 + WOOD-OH → WOOD-O-CH_2-O-WOOD
Formaldehyde Hemiacetal Acetal

The two hydroxyl groups can come from (1) hydroxyls within a single sugar unit, (2) hydroxyls on different sugar residues within a single cellulose chain, (3) hydroxyls between two different cellulose chains, (4) same as 1, 2 and 3 except the reaction occurring on hemicelluloses, (5) hydroxyl groups on different lignin residues, and (6) interaction between cellulose, hemicelluloses and lignin hydroxyls. The potential crosslinking combinations are large and, theoretically, all of them are possible. Since the reaction is a two-step mechanism, some of the added formaldehyde will be in a non-crosslinked hemiacetal form. These chemical bonds are very unstable and would not survive long after the reaction.

If the reaction with wood and formaldehyde is carried out at 160 °C with no catalyst, very little reaction takes place and very little dimensional stability is achieved. If, however, the reaction is done at 160 °C with a mineral acid catalyst, there is approximately a 3.5% weight gain, resulting in a 50% reduction in EMC and dimensional stability up to 80-83%, but the wood is brittle.[9]

Heating

When wood is heated, a wide variety of reactions take place. The hemicelluloses are the first to thermally degrade, followed by cellulose. Lignin is stable over a wide range of temperatures.[10]

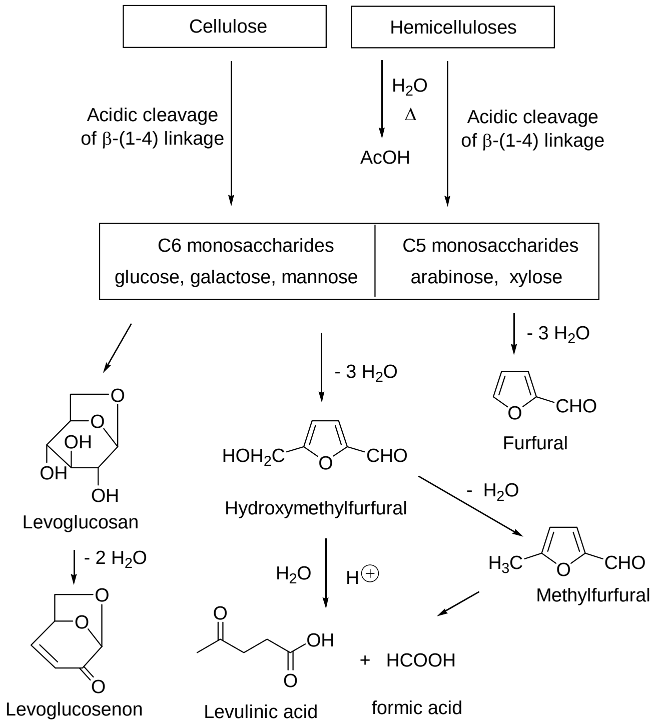

Figure 1: Possible thermal degradation mechanism of cellulose and hemicelluloses

Table 4 shows the weight loss due to heating at different temperatures. As the temperature and time increase, weight loss also increases.

Table 5 shows the loss of cell wall polymers as a result of heating wood for 8 hours at 240 °C.

The majority of weight loss occurs in the hemicellulose polymers.

Table 6 shows the decrease in EMC as a function of time and temperature. As the time and temperature increase, EMC decreases to about 50%.

When *Pinus sylvestris* is heated to 220 °C for 1 to 3 hours, there is a 50% reduction in antishrink efficiency.

It can, therefore be concluded that dimensional stability can be achieved by three different mechanisms: 1) bulking, which reacts wood back to its green volume, 2) crosslinking, which prevents expansion, and 3) heating, which leads loss of hygroscopic hemicelluloses.[3,4,5]

Table 4
Weight loss due to heating wood at different times and temperatures

Heating temperature (°C)	Time (h)	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	0.5	7
240	8	21

Table 5
Loss of cell wall polymers before and after heating for 8 hours at 240 °C

	Lignin (%)	Glucose (%)	Xylose (%)
Control	22.7	44.0	14.2
Heated (21% wt loss)	38.0	35.5	5.5

Table 6
Reduction in EMC as a function of time and temperature

Temperature (°C)	Time	EMC 90% RH (%)
25	0	18.9
220	8 min	13.1
220	1 hour	9.3
190	2 hour	9.1

CHEMICAL MODIFICATION TO IMPROVE DURABILITY

The same three mechanisms will now be studied as means to improve wood durability: 1) bulking cell wall (acetylation), 2) crosslinking cell wall polymers (formaldehyde), and 3) high temperature heating.[3]

The mechanism of brown-rot fungal attack on wood is thought to start with some recognition in the hemicellulose polymers. Specifically, it may be arabinose that is the only hemicellulose sugar that exists in a strained 5-membered ring. The first reaction is an enzymatic reaction on hemicellulose polymers, which generates the chemical reactions that start degrading cell wall polymers. So, in theory, if you protect the hemicelluloses or remove them, durability should increase.

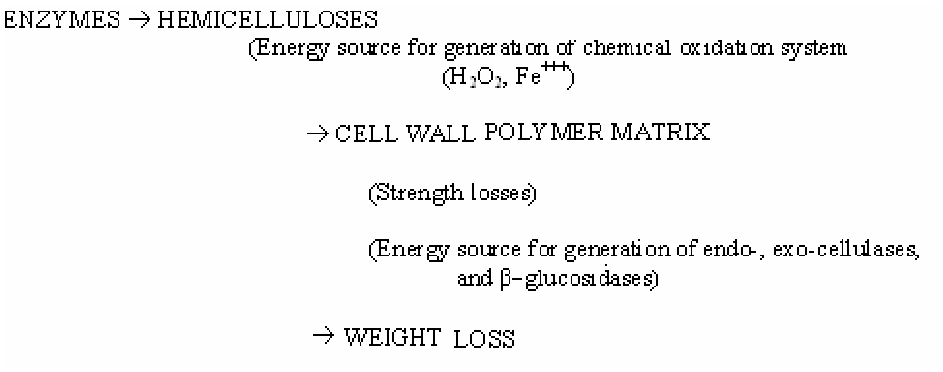

Figure 2: Possible mechanism of wood degradation by brown-rot fungus

Table 7
Weight loss of acetylated wood in a soil block test

Acetyl WPG (%)	Weight loss after 12 weeks	
	Brown-rot fungus (%)	White-rot fungus (%)
0	61.3	7.8
6.0	34.6	4.2
10.4	6.7	2.6
14.8	3.4	<2
17.8	<2	<2

Table 8
Resistance of formaldehyde crosslinked wood attacked by brown- and white-rot fungi

Formaldehyde weight gain (%)	Weight loss (%)	
	Brown-rot	White-rot
2	Low	High
6	Medium	High

Cell wall bulking

Table 7 shows the weight loss values for acetylated wood in a standard 12 week ASTM soil-block test using brown- and white-rot fungi. As the level of acetyl goes up, the weight loss decreases. A greater effect is observed for white-rot fungus, as compared to brown-rot fungus. At approximately 15% acetyl weight gain, the acetylated wood is resistant to the attack of white-rot fungus and at 17% it is resistant to brown-rot fungus.

Crosslinking

There is very little data in the literature on the resistance of formaldehyde crosslinked wood to the attack of brown- and white-rot fungi. Table 8 shows a summary of the available data. Crosslinked wood shows good resistance to white-rot fungus attack, but less resistance to brown-rot fungus.

Heating

Heating wood also has an effect on its resistance to brown- and white-rot fungi. Table 9 shows an increase in the resistance of heat-treated wood to brown-rot fungus, but no resistance to white-rot fungus. In fact, heat-treated wood is less resistant to the attack of white-rot fungus than unheated wood.

Table 9
Resistance of heat-treated wood to attack by brown- and white-rot fungi

Process	Weight loss (%)	
	Brown-rot fungus	White-rot fungus
Control	31.0	5.1
Plato	10.0	6.8
Premium	16.0	9.0
NOW	13.3	7.8
OHT	7.4	5.6

NOW = New option wood
OHT = Oil Heated

CONCLUSION

Resistance to the attack of fungi can be achieved by three different mechanisms:

- Bulking – no water molecule at the glycosidic bond for hydrolysis and changes in the conformation and configuration on the substrate,
- Crosslinking – not very effective, which may be caused by the bonding so tight and strong that water molecules can not get to the glycosidic bond,
- Heating – consisting in the removal of hemicelluloses, so no substrate is left to get the degradation started.

Increase in durability can be achieved by the same three mechanisms, but:

- Bulking depends on where bonding takes place,
- Crosslinking depends on what polymers are involved,
- Heat treatment depends on loss of hygroscopic cell wall polymers.

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