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Roger M. ROWELL

CHEMICAL MODIFICATION: A NON-TOXIC APPROACH TO WOOD PRESERVATION

Reaction of wood with anhydrides, isocyanates, and epoxides reduces the moisture content of the cell wall and increases the resistance of the modified wood to attack by fungi. As the level of bonded chemical increases. the cell wall equilibrium moisture content decreases and the resistance to attack by white- and brown-rot fungi increases. There is a direct relationship between the decrease in cell wall moisture content and resistance to fungal attack The mechanism of the effectiveness of chemical modification to provide decay resistance seems to be due to the reduction of moisture content in the modified wood.

Keywords: chemical modification, reaction systems, moisture content, decay resistance

Introduction

For the most part, we have used wood putting up with the "natural defects" that nature has given to us, such as dimensional instability and degradations due to moisture, heat, ultraviolet radiation and decay. Wood is a hygroscopic resource that was designed to perform, in nature, in a wet environment and nature is programmed to recycle wood in a timely way through biological, thermal, aqueous, photochemical, chemical, and mechanical degradations back to its building blocks of carbon dioxide and water. The properties of any resource are, in general, a result of the chemistry of the components of that resource. In the case of wood, the cell wall polymers (cellulose, hemicelluloses, and lignin) are the components that, if modified, would change the properties of the resource. If the properties of the wood are modified, the performance of the modified wood would be changed. This is the basis of chemical modification of wood to change properties and improve performance. Many chemicals have been used to chemically modify natural fibers to improve performance including anhydrides, isocyanates, and epoxides.

Roger M. ROWELL, University of Wisconsin, Madison, WI 53706, USA

While wood is a preferred building material for many applications, it has been restricted from many markets mainly due to its moisture sensitivity, dimensional instability and biodegradability. Traditional methods for decay resistance are based on treating the product with toxic chemicals which are effective in providing decay resistance but can result in environmental concerns. Dimensional instability and biodegradability, are a result of chemical degradation reactions which can be prevented or, at least, slowed down if the cell wall chemistry is altered [Rowell 1975, 1983, 1984, 2005].

There is a very close relationship between the moisture content of wood and its biodegradability. Dry wood does not decay. Chemical modification decreases amount of moisture wood will pick up from its environment and is effective in reducing attack by fungi. These two phenomenons are interrelated, that is, the decrease in moisture content due to chemical modification is thought to be the reason the modified wood is more decay resistant [Rowell 2005]. The purpose of this paper is to study the relationship between decay resistance as a function of the reduction in moisture content resulting from chemical modification.

Chemical Reaction Systems

Several chemical modification systems have been studied to covalently bond chemicals to the cell wall polymer hydroxyl groups that bulk the cell wall. The reaction of:

anhydrides [Rowell 1983, 1984, 2005]

WOOD-OH + R-C(=O)–O-C(C=O)-R→ WOOD-O-C(=O)-R+R-C(=O)-OH

isocyanates (Rowell and Ellis 1981)

WOOD-OH + R-N=C=O → WOOD-O-C(=O)-NH-R

and epoxides (Rowell and Ellis 1984)

WOOD-OH + R-CH(-O-)CH_2 → WOOD-O-CH_2-CH(OH)-R

have been extensively studied. The bulking chemical reactions take place mainly on hydroxyl groups in lignin and the hemicelluloses (Rowell 1980,1982).

Table 1 shows that these three chemical modification systems result in a lowering of the equilibrium moisture content of pine particles. Reaction with acetic anhydride and methyl isocyanate are the most effective in reducing the cell wall equilibrium moisture content. Propylene and butylenes oxides are not as effective in reducing equilibrium moisture content as the other chemical reaction systems due to the formation of a new hydroxyl group when the epoxide reacts with the cell wall hydroxyl group.

Table 1. Equilibrium moisture content of control and chemically modified pine particles
Tabela 1. Wilgotność równowagowa w próbach kontrolnych i chemicznie modyfikowanych wiórów sosnowych

Chemical *Srodek chemiczny*	WPG	EMC at 27°C 30% RH	65% RH	90% RH
Control *Kontrola*	0	5.0	8.5	18.9
Acetic Anhydride *Bezwodnik octowy*	20.4	2.4	4.3	8.4
Methyl Isocyanate *Izocjanek metylu*	20.4	3.3	4.9	9.6
Propylene Oxide *Tlenek propylenu*	21.9	3.9	6.1	13.1
Butylene Oxide *Tlenek butylenu*	18.7	3.5	5.7	10.7

Table 2 shows the weight loss due to attack by either a brown- or a white-rot fungi in a 12 week standard ASTM test on control and chemically modified particleboards. All three chemical modifications are effective in reducing the attack by white-rot fungi but propylene oxide reacted wood is not as resistant to brown-rot attack as are the rest of the reaction systems.

Table 2. Weight loss due to fungal attack of control and chemically modified pine particleboard (5% phenolic resin)
Tabeta 2. Utrata masy na skutek ataku grzybowego w kontrolnych i chemicznie modygikowanych sosnowych plytach wiórowych (5% żywica fenolowa)

Chemical ***Srodek chemiczny***	WPG (%)	Brown-rot Fungus *Grzyb brazowej zgnilizny* (%)	White-rot Fungus *Grzyb bialej zgnilizny* (%)
Control *Kontrola*	0	61.3	7.8
Acetic Anhydride *Bezwodnik octowy*	17.8	1.7	1.1
Methyl isocyanate *Izocjanek metylu*	20.4	2.8	0.7
Propylene Oxide *Tlenek propylenu*	25.3	14.2	1.7
Butylene Oxide *Tlenek butylenu*	22.1	2.7	0.8

The most research has been done on the reaction of acetic anhydride with wood and there is already a commercial process in Japan and there soon will be in the United Kingdom and the United States [Rowell et al. 1986]. For this reason, the remainder of this paper will deal with the reaction of acetic anhydride with pine particles and the resulting equilibrium moisture content and resistance to attack by fungi of the acetylated particleboards.

Table 3 shows the relationship between weight gain due to acetylation and the reduction in equilibrium moisture content on pine particleboards made using a 5% phenolic resin. The table shows that as the acetyl content increases, the equilibrium moisture content decreases.

Table 3. Equilibrium moisture content of control and acetylated pine particleboards
Tabela 3. Wilgotność równowagowa w próbach kontrolnych i acetylowanych sosnowych plyt wiórowych

WPG	Equilibrium Moisture Content at 27°C *Wilgotność równowagowa przy 27°C* 30% RH	65% 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 4 shows the resistance of acetylated particleboards to attack by brown- and white-rot fungi as a function of the weight gain due to acetylation. As the weight gain increases, weight loss due to fungal attack decreases. Acetylated pine particleboards become resistant to attack by white-rot fungi at about 11% weight gain and to brown-rot fungi at about 15% weight gain.

Table 4. Resistance of control and acetylated pine particleboard against brown- and white-rot fungi (using 5% phenolic resin)
Tabela 4. Odporność kontrolnych i acetylowanych sosnowych plyt wiórowych na grzyby brazowej i bialej zgnilizny (przy zastosowaniu 5% żywicy fenolowej)

WPG	Weight Loss After 12 Weeks *Strata masy po 12 tygodniach* Brown-rot Fungus *Grzyb brazowej zgnilzny* (%)	White-rot Fungus *Grzyb bialej zgnilizny* (%)
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

A fungal cellar was set up using unsterile soil that contained white-, brown- and soft-rot fungi and tunneling bacteria [Nilsson et at. 1988]. Particleboards made using control and acetylated particles, at various levels of bonded acetyl groups, were tested over a 144 month period. Table 4 shows the results of a long term fungal cellar test. Control particleboards were swollen at the first 2 month inspection, some fungal attack was observed and the boards failed at 6 months. Swelling was detected in the 7.3% weight gain acetylated particleboards at 2 months but no fungal attack was observed until 3 months and failure occurred at 12 months. Swelling was observed in the 11.5% weight gain acetylated particleboards at 4 months but no decay was detected until 5 months and the boards failed at 24 months. Swelling was observed in the 13.6% weight gain acetylated particleboards at 6 months but no fungal attack was detected until 12 months and failure was at 36 months. Particleboards acetylated above 16% weight gain did not swell or decay in the 144 month test.

Table 5. Fungal cellar test on control and acetylated pine particleboards

Tabela 5. Grzybowy test piwniczny przeprowadzony na kontrolnych i acetylowanych sosnowychplytach wiórowych.

Weight Gain *Przyrost wagi*	Rating[1] at intervals (Months) *Ocena w przedzialach miesieczych*									
Pmmt *Procent*	2	3	4	5	6	12	24	36	72	144
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	0	0
17.9	0	0	0	0	0	0	0	0	0	0

Rating system[1] - 4 = Destroyed, 3 = Badly attacked, 2 = Some attack, 1 = Evidence of attack, 0 = No attack, S = Swollen

System oceny[1] - 4 = Zniszczony, 3 = Mocno zaatakowany, 2 = Lekko zaatakowany, 1 = Objawy ataku, 0 = Brak objawów ataku, S = Napecznialy

Combining the data from Tables 3, 4 and 5, Table 6 shows the relationship between equilibrium moisture content at 90% relative humidity and the performance of the equivalent control or acetylated particleboard in the soil block and fungal cellar tests.

Table 6. Comparison of equilibrium moisture content at 90% relative humidity and swelling, decay and failure of control and acetylated pine particleboards
Tabela 6. Porównanie zawartosce wilgotnosci rownowagowej przy 90% wilgotnosci wzglednej oraz pecznienia, gnicia i uszkodzenia kontrolnych i acetylowanych sosnowych plyt wiórowych

WPG	EMC at 90% RH	Months to board: *Miesiecy, zeby ptyta:*		
		Swelling[1] *Napeczniala[1]*	Decay[2] *Zgnila[2]*	Failure[3] *Ulegla uszkodzeniu[3]*
0	22	<2	2	6
6 - 7.3	17	2	3	12
10.4 – 11.5	14	4	5	24
13.6 – 14.8	12	6	12	36
16.3 - 20.4	9	>144	>144	>144

[1] Swelling first observed
[1] *Pierwsze objawy pecznienia*
[2] Start of decay
[2] *Poczatek gnicia*
[3] Reached a rating of 4
[3] *Osiagniecie oceny 4*

Conclusions

Reaction of wood with anhydrides, isocyanates and epoxides are effective in reducing the equilibrium moisture content of the modified wood.

Reaction of wood with anhydrides, isocyanates and epoxides are effective in reducing attack by white- and brown-rot fungi.

As the weight gain due to reaction with acetic anhydride increases, equilibrium moisture content decreases and resistance to attack by white- and brown-rot fungi increases.

Using the data derived from the acetylation of wood particles and particleboards made using acetylated particles, it can be concluded that as the level of bonded acetyl increases, equilibrium moisture content decreases and resistance to attack by white- and brown-rot fungi increases.

Acetylated pine particleboards above a weight gain of approximately 16% show the lowest equilibrium moisture content and are very resistant to attack by white-, brown-, and soft-rot fungi and tunneling bacteria.

Finally, the data suggests that the mechanism of resistance to attack by fungi by chemical modification is due to a reduction in the cell wall moisture content.

Acetylation of wood provides protection from fungal attack of wood without the use of toxic chemicals.

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CHEMICZNA MODYFIKACJA JAKO SPOSÓB NIETOKSYCZNEJ OCHRONY DREWNA

Streszczenie

Reakcja drewna z bezwodnikami, izocyjanianami i epoksydami zmniejsza wilgotność śiany komórkowej i zwieksza odporność modyfikowanego drewna na atak grzybów. W miare wzrostu ilości zwiazanych chemikaliów, maleje wilgotność równoważna ściany komórkowej i zwieksza sie jej odporność na atak grzybów rozkladu bialego i brunatnego.. Pomiedzy obniżaniem sie wilgotności Sciany komórkowej i odporności na atak grzybów istnieje bezpośrednia żaleznośc. Wydaje sip, że mechanizm efektywnego oddzialywania modyfikacji chemicznej, wyrażajacej sie w przeciwdzialaniu rozkiadowi biologicznemu polega na redukcji wilgotności zmodyfikowanego drewna.

Slowa kluczowe: modyfikacja chemiczna, systemy reakcji, Wilgotność, odporność na zgnilizne.

Tlum.: Zbigniew Śniataia