

CHEMICAL MODIFICATION OF LIGNOCELLULOSICS

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INTRODUCTION

Agro-based resources, also referred to as lignocellulosics, are resources that contain cellulose, hemicelluloses, and lignin. Lignocellulosics include wood, agricultural residues, water plants, grasses, and other plant substances. When considering lignocellulosics as possible engineering materials, there are several very basic concepts that must be considered. First, lignocellulosics are hygroscopic resources that were designed to perform, in nature, in a wet environment. Secondly, nature is programmed to recycle lignocellulosics in a timely way through biological, thermal, aqueous, photochemical, chemical, and mechanical degradations. In simple terms, nature builds a lignocellulosic from carbon dioxide and water and has all the tools to recycle it back to the starting

Biological Degradation	- Fungi, Bacteria, Insects, Termites
Enzymatic Reactions	- Oxidation, Hydrolysis, Reduction
Chemical Reactions	- Oxidation, Hydrolysis, Reduction
Mechanical	- Chewing
Fire Degradation	- Lightning, Sun
Pyrolysis Reactions	- Dehydration, Hydrolysis, Oxidation
Water Degradation	- Rain, Sea, Ice, Acid Rain, Dew
Water Interactions	- Swelling, Shrinking, Freezing, Cracking
Weather Degradation	- Ultraviolet radiation, Water, Heat, Wind
Chemical Reactions	- Oxidation, Hydrolysis
Mechanical	- Erosion
Chemical Degradation	- Acids, Bases, Salts
Chemical Reactions	- Oxidation, Reduction, Dehydration, Hydrolysis
Mechanical Degradation	- Dust, Wind, Hail, Snow, Sand
Mechanical	- Stress, Cracks, Fracture, Abrasion

Figure 1. Degradation reactions which occur when lignocellulosics are exposed to nature.

chemicals. We harvest a green lignocellulosic (for example, a tree) and convert it into dry products, and nature, with its arsenal of degrading reactions, starts to reclaim it at its first opportunity (Figure 1).

In order to produce lignocellulosic-based composite materials with a long service life, it is necessary to interfere with the natural degradation processes for as long as possible. This can be done in several ways. Traditional methods for decay resistance and fire retardancy, for example, are based on treating the product with toxic or corrosive chemicals which are effective in providing decay and fire resistance but can result in environmental concerns. There is another approach which is based on the premise that the properties of any resource are a result of the chemistry of components of that resource. In the case of lignocellulosics, cell wall polymers, extractives, and inorganics are the components that, if modified, would change the properties of the resource.

In order to make property changes, you must first understand the chemistry of the components and the contributions each play in the properties of the resource. Following this understanding, you must then devise a way to modify what needs to be changed to get the desired change in property.

Properties of lignocellulosics, such as dimensional instability, flammability, biodegradability, and degradation caused by acids, bases, and ultraviolet radiation are all a result of

Lignocellulosics exposed outdoors undergo photochemical degradation caused by ultraviolet radiation. This degradation takes place primarily in the lignin component, which is responsible for the characteristic color changes [Rowell 1984]. The lignin acts as an adhesive in the cell walls, holding the cellulose fibers together. The surface becomes richer in cellulose content as the lignin degrades. In comparison to lignin, cellulose is much less susceptible to ultraviolet light degradation. After the lignin has been degraded, the poorly bonded carbohydrate-rich fibers erode easily from the surface, which exposes new lignin to further degradative reactions. In time, this "weathering" process causes the surface of the composite to become rough and can account for a significant loss in surface fibers.

Lignocellulosics burn because the cell wall polymers undergo pyrolysis reactions with increasing temperature to give off volatile, flammable gasses. The hemicellulose and cellulose polymers are degraded by heat much before the lignin [Rowell 1984]. The lignin component contributes to char formation, and the charred layer helps insulate the composite from further thermal degradation.

CHEMICAL MODIFICATION SYSTEMS

For this discussion, chemical modification will be defined as a chemical reaction between some reactive part of a lignocellulosic and a simple single chemical reagent, with or without catalyst, to form a covalent bond between the two. This excludes all simple chemical impregnation treatments which do not form covalent bonds, monomer impregnation that polymerize in situ but do not bond with the cell wall, polymer inclusions, coatings, heat treatments, etc.

There are several approaches to chemically modifying the lignocellulosic cell wall polymers. The most abundant single site for reactivity in these polymers is the hydroxyl group and most reaction schemes have been based on the reaction of hydroxyl groups. Sites of unsaturation in the lignin structure can also be used as a point of reactivity as well as free radical additions and grafting. However, the most studied class of chemical reactions are those involving hydroxyl substitutions.

In modifying a lignocellulosic for property improvement, there are several basic principles that must be considered in selecting a reagent and a reaction system [Rowell 1975]. Of the thousands of chemicals available, either commercially or by synthetic means, most can be eliminated because they fail to meet the requirements or properties listed below.

If hydroxyl reactivity is selected as the preferred modification site, the chemical must contain functional groups which will react with the hydroxyl groups of the lignocellulosic components. This may seem obvious but there are several failed reaction systems in the literature using a chemical that could not react with a hydroxyl group.

The overall toxicity of the chemicals must be carefully considered. The chemicals must not be toxic or carcinogenic to humans in the finished product, and should be as nontoxic as possible in the treating stage. The chemical should be as noncorrosive as possible to eliminate the need for special stainless steel or glass-lined treating equipment.

In considering the ease with which excess reagents can be removed after treatment, a liquid treating chemical with a low boiling point is advantageous. Likewise, if the boiling point of a liquid reagent is too high, it will be very difficult to remove the chemical after treatment. It is generally true that the lowest member of a homologous series is the most reactive and will have the lowest boiling point. The boiling point range for liquids to be considered is 90-150°C. It is also possible to treat fibers with a gas system, however, there may be processing challenges in handling a pressurized gas in a continuous reactor.

Accessibility of the reagent to the reactive chemical sites is a major consideration. To increase accessibility to the reaction site, the chemical must swell the lignocellulosic structure. If the reagents do not swell the structure, then another chemical or co-solvent can be added to meet this requirement. Accessibility to the reactive site is a major consideration in a gas system unless there is a condensation step in the procedure.

Almost all chemical reactions require a catalyst. With lignocellulosics as the reacting

substrate, strong acid or base catalysts cannot be used as they cause extensive degradation. The most favorable catalyst from the standpoint of lignocellulosic degradation is a weakly alkaline one. The alkaline medium is also favored as in many cases these chemicals swell the cell wall matrix structure and give better penetration. The properties of the catalyst parallel those of reagents, i.e., low boiling point liquid, nontoxic, effective at low temperatures, etc. In most cases, the organic tertiary amines or weak organic acids are best suited.

The experimental reaction conditions which must be met in order for a given reaction to go is another important consideration. The temperature required for complete reaction must be low enough so there is little or no fiber degradation, i.e., less than 150°C. The reaction must also have a relatively fast rate of reaction with the cell wall components. It is important to get as fast a reaction as possible at the lowest temperature without lignocellulosic degradation.

The moisture present in the lignocellulosic is another consideration in the reaction conditions. It is costly to dry lignocellulosics to less than 1 percent moisture, but it must be remembered that the -OH group in water is more reactive than the -OH group available in the lignocellulosic components, i.e., hydrolysis is faster than substitution. The most favorable condition is a reaction which requires a trace of moisture and the rate of hydrolysis is relatively slow.

Another consideration in this area is to keep the reaction system as simple as possible. Multicomponent systems will require complex separation after reaction for chemical recovery. The optimum would be a reactive chemical that swells the lignocellulosic structure and acts as the solvent as well.

If possible, avoid byproducts during the reaction that have to be removed. If there is not a 100 percent reagent skeleton add-on, then the chemical cost is higher and will require recovery of the byproduct for economic and environmental reasons.

The chemical bond formed between the reagent and the lignocellulosic components is of major importance. For permanence, this bond should have great stability to withstand weathering. In order of stability, the types of covalent chemical bonds that may be formed are: ethers > acetals > esters. The ether bond is the most desirable covalent carbon-oxygen bond that can be formed. These bonds are more stable than the glycosidic bonds between sugar units in the lignocellulosic polysaccharides so the polymers would degrade before the grafted ether. It may be desired, however, to have the bonded chemical released by hydrolysis or enzyme action in the final product so that an unstable bond may be required from the modification.

The hydrophobic nature of the reagent needs to be considered. The chemical added to the lignocellulosic should not increase the hydrophilic nature of the lignocellulosic components unless that is a desired property.

If the hydrophilicity is increased, the susceptibility to micro-organism attack increases. The more hydrophobic the component can be made, the better the moisture exclusion properties of the substituted lignocellulosic will be.

Single site substitution versus polymer formation is another consideration. For the most part, a single reagent molecule that reacts with a single hydroxyl group is the most desirable. Crosslinking can occur when the reagent contains more than one reactive group or results in a group which can further react with a hydroxyl group. Crosslinking can cause the lignocellulosic to become more brittle. Polymer formation within the cell wall after initial reaction with the hydroxyl groups of the lignocellulosic components gives, through bulking action, dimensional stabilization. The disadvantage of polymer formation is that a higher level of chemical add-on is required for biological resistance than is required in the single site reactions.

The treated lignocellulosic must still possess the desirable properties of lignocellulosics. That is, the fiber strength should not be reduced, no change in color, good electrical insulation properties retained, final product not dangerous to handle, no lingering chemical smells, still glueable and finishable unless one or more of these properties are the object of change in the product.

A final consideration is, of course, the cost of chemicals and processing. In laboratory scale experimental reactions, the high cost of chemicals is not a major factor. For commercialization of a process, however, the chemical and processing costs are very important

factors. Laboratory scale research is generally done using small batch processing, however, rapid, continuous processes should always be studied for scale up. Economy of scale can make an expensive laboratory process economical.

In summary, the chemicals to be laboratory tested must be capable of reacting with lignocellulosic hydroxyls under neutral, mildly alkaline or acid conditions at temperatures below 150C. The chemical system should be simple and capable of swelling the structure to facilitate penetration. The complete molecule should react quickly with lignocellulosic components yielding stable chemical bonds, and the treated lignocellulosic must still possess the desirable properties of untreated lignocellulosics.

CHEMICAL MODIFICATION FOR PROPERTY ENHANCEMENT

As was stated before, because the properties of lignocellulosics result from the chemistry of the cell wall components, the basic properties of a fiber can be changed by modifying the basic chemistry of the cell wall polymers. Many chemical reaction systems have been published for the modification of agro-fiber. These chemicals include anhydrides such as, phthalic, succinic, malic, propionic and butyric anhydride, acid chlorides, ketene carboxylic acids, many different types of isocyanates, formaldehyde, acetaldehyde, difunctional aldehydes, chloral, phthaldehydic acid, dimethyl sulfate, alkyl chlorides, beta-propiolactone, acrylonitrile, epoxides, such as, ethylene, propylene, and butylene oxide, and difunctional epoxides [Rowell 1983, 1991].

By far, the most research has been done on the reaction of acetic anhydride with cell wall polymer hydroxyl groups to give an acetylated fiber. Many different types of lignocellulosic fibers have been acetylated using a variety of procedures including wood [Rowell 1983, Rowell et al 1986], bamboo [Rowell and Norimoto 1987, 1988], bagasse [Rowell and Keany 1991], jute [Callow 1951, Anderson and Tillman 1989, Rowell et al 1991], kenaf [Rowell 1993, Rowell and Harrison 1993], pennywort, and water hyacinth [Rowell and Rowell 1989]. Without a strong catalyst, acetylation using acetic anhydride alone levels off at approximately 20 weight percent gain (WPG) for softwoods, hardwoods, grasses, and water plants. While acetylation is not the only chemical modification procedure that has been shown to improve properties of lignocellulosics, it has been studied the most and will be used as an example in many cases.

Properties of Chemically Modified Fiber

Moisture sorption. By replacing some of the hydroxyl groups on the cell wall polymers with bonded chemical groups, the hygroscopicity of the lignocellulosic material is reduced. Table 1 shows the equilibrium moisture content (EMC) of several types of lignocellulosic fibers which have been reacted with several types of chemicals. Table 1 shows the EMC of pine wood fibers which have been reacted with different chemicals. In all cases, the EMC has been reduced as a result of modification. Both reactions with acetic anhydride and formaldehyde give the best results in lowering the EMC of the treated fiber. Table 2 shows the results of acetylating several different types of fibers on the EMC of the modified fiber. In all cases, as the level of acetyl weight gain increases, the EMC of the resulting fiber goes down. All types of fiber show the same level in the reduction in EMC as a function of level of acetyl weight gain (Rowell et al 1986).

If the reductions in EMC at 65% RH of acetylated fiber referenced to unacetylated fiber is plotted as a function of the bonded acetyl content a straight line plot results (Rowell and Rowell 1989). Even though the points represent many different types of lignocellulosic resources, they all fit a common curve. A maximum reduction in EMC is achieved at about 20% bonded acetyl. Extrapolation of the plot to 100% reduction in EMC would occur at about 30% bonded acetyl. This represents a value not too different from the fiber saturation point for water in these fibers. Because the acetate group is larger than the water molecule, not all hygroscopic hydrogen-bonding sites are covered so it would be expected that the acetyl saturation point would be lower than that of water. This finding would indicate that it does not matter which type of lignocellulosic resource is used to acetylate to make composites.

Table 1. EMC of control and chemically modified pine fiber.

Chemical	Weight Percent Gain	Equilibrium Moisture Content at 27C		
		30%RH	65%RH	90%RH
Control	0	5.8	12.0	21.7
Acetic	20.4	2.4	4.3	8.4
Anhydride				
Formaldehyde	3.9	3.0	4.2	6.2
Propylene	21.9	3.9	6.1	13.1
Oxide				
Butylene	18.7	3.5	5.7	10.7
Oxide				

Table 2. EMC of fiberboards made from control and acetylated fiber.

Fiber	Weight Percent Gain	Equilibrium Moisture Content at 27C		
		30%RH	65%RH	90%RH
Bagasse	0	4.4	8.8	15.8
	9.4	2.0	5.3	9.5
	13.0	1.7	4.4	7.7
	17.6	1.4	3.4	5.8
Kenaf	0	4.8	10.5	24.3
	18.4	2.6	5.8	11.3
Bamboo	0	4.5	8.9	14.7
	10.8	3.1	5.3	9.4
	17.0	2.0	3.7	6.8
Jute	0	5.8	9.3	18.3
	16.2	2.0	4.1	7.8
Pine	0	5.6	12.1	22.6
	6.3	4.5	10.2	19.5
	13.8	2.7	6.8	13.2
	18.2	2.1	5.1	9.9
Aspen	0	4.9	11.1	21.5
	8.7	3.1	7.7	14.9
	13.0	2.0	5.9	11.8
	17.6	1.6	4.8	9.4

The fact that EMC reduction as a function of acetyl content is the same for many different lignocellulosic resources indicates that reducing moisture sorption and, therefore, achieving cell wall stability are controlled by a common factor. The lignin, hemicellulose, and cellulose contents of all the materials are different. Earlier results showed that the bonded acetate was mainly in the lignin and hemicelluloses [Rowell 1982] and that isolated wood cellulose does not react with uncatalyzed acetic anhydride [Rowell et al 1994b].

Because these materials vary widely in their lignin, hemicellulose, and cellulose content,

because acetate is found mainly in the lignin and hemicellulose polymer, and because isolated cellulose does not acetylate by the procedure used, acetylation may be controlling the moisture sensitivity due to the lignin and hemicellulose polymers in the cell wall but not reducing the sorption of moisture in the cellulose polymer.

Pyrolysis properties. Chemical modification of agro-based fibers has some effect on the pyrolysis properties of lignocellulosics. In thermogravimetric analysis, control and chemically modified pine fibers pyrolyze at about the same temperature and rate (Table 3) [Rowell et al 1984]. Fibers reacted with propylene or butylene oxide have a slightly higher temperature of maximum weight loss. Fiber that was reacted with acetic anhydride or methyl isocyanate showed two peaks in the maximum weight loss data while both propylene and butylene oxides resulted in only one peak. Since the smaller, lower temperature peak represents the hemicellulose fraction in the fiber, the epoxide modified hemicelluloses seem to pyrolyze in the temperature range of the cellulose fraction. The heat of combustion and rate of oxygen consumption are higher for the epoxide modified fiber as compared to the control, acetic anhydride and methyl isocyanate modified fibers. This data would indicate that reacting fiber with acetic anhydride or methyl isocyanate is adding approximately the same carbon, hydrogen and oxygen content as the cell wall polymers. Reactive fire retardants could be bonded to the cell wall hydroxyl groups in reactions similar to this technology. The effect would be an improvement in dimensional stability, biological resistance as well as fire retardancy.

Table 3. Pyrolysis properties of control and chemically modified pine fiber.

Chemical	Weight Percent Gain	Temperature of Maximum Weight Loss C	Heat of Combustion KCal/g	Rate of Oxygen Consumption MM/g sec
None	0	335/375	2.9	0.06/0.13
Acetic Anhydride	21.1	338/375	3.1	0.08/0.14
Methyl Isocyanate	24.0	315/375	2.6	0.07/0.12
Propylene oxide	32.0	380	4.3	0.23
Butylene Oxide	22.0	385	4.1	0.24

PROPERTIES OF COMPOSITES MADE WITH CHEMICALLY MODIFIED FIBER

Dimensional Stability

Changes in dimensions, especially in thickness and in linear expansion, are a great problem in lignocellulosic composites because they not only undergo normal swelling (reversible swelling) but also swelling caused by the release of residual compressive stresses imparted to the board during the composite pressing process (irreversible swelling). Water sorption causes both reversible and irreversible swelling with some of the reversible shrinkage occurring when the board dries. Dimensional instability of lignocellulosic composites has been the major reason for their restricted use.

The EMC of different types of control and acetylated fibers are given in Table 2. The EMC and thickness swelling at three relative humidities for boards made from these fibers is shown in Table 4. Comparing the data in the two tables, it can be seen that the EMC for boards is slightly higher than for the fiber alone. The adhesive is more hydrophilic than the acetylated fiber.

Thickness swelling at the three levels of relative humidity is greatly reduced as a result of acetylation. Linear expansion is also greatly reduced as a result of acetylation (Krzysik et al 1992, 1933).

Table 4. Equilibrium moisture content (EMC) and thickness swelling (TS) of fiberboards made from control and acetylated fiber.

Fiber	Weight Percent Gain	EMC and TS at 27C					
		30% RH		65% RH		90% RH	
		EMC	TS	EMC	TS	EMC	TS
<.....%.....>							
Pine	0	4.5	3.6	9.4	6.6	19.7	29.2
	21.6	1.8	0.4	4.1	1.1	8.3	2.9
Bagasse	0	3.8	---	7.6	---	17.1	---
	17.6	1.8	---	4.0	---	7.9	---
Kenaf	0	4.8	3.0	10.5	9.6	26.7	33.0
	18.4	2.6	0.8	5.8	2.4	19.3	10.0
Bamboo	0	3.2	---	6.6	---	12.3	---
	18.0	1.6	---	4.1	---	7.9	---
Hemlock	0	3.3	1.0	7.2	3.1	19.8	11.2
	22.5	1.6	0.2	3.9	1.7	9.3	3.1

The rate and extent of thickness swelling in liquid water of fiberboards made from control and acetylated fiber is shown in Table 5. Both the rate and extent of swelling are greatly reduced as a result of acetylation. At the end of 5 days of water soaking, control boards swelled from 18 to 45% whereas boards made from acetylated fiber swelled from 3 to 10%. Drying all boards after the water soaking test shows the amount of irreversible swelling that has resulted from water swelling. Control boards show a greater degree of irreversible swelling as compared to boards made from acetylated fiber.

The results of both water vapor and liquid water tests show that acetylation of lignocellulosic fibers greatly improve dimensional stability of composites made from these resources.

Biological Resistance

Particleboards and flakeboards made from acetylated flakes have been tested for resistance to several different types of organisms. In a 2-week termite test using *Reticulitermes flavipes* (subterranean termites), boards acetylated at 16 to 17 WPG were very resistant to attack, but not completely so (Table 6) [Rowell et al 1979, 1988a]. This may be attributed to the severity of the test. However, since termites can live on acetic acid and decompose cellulose to mainly acetic acid, perhaps it is not surprising that acetylated wood is not completely resistant to termite attack.

Chemically modified composites have been tested with decay fungi in several ways. Control and chemically modified particleboards were exposed to a 12 week soil block test using the brown rot fungus *Gloeophyllum trabeum* and the white rot fungus *Trametes versicolor* (Table 7). All boards were made using a phenolic resin [Nilsson et al 1988, Rowell et al 1988a]. All of the bonded chemicals at a WPG over about 20 show good resistance to brown- and white-rot fungi except propylene oxide in the brown rot test. Propylene oxide is not effective in preventing attack by brown-rot fungi even though the same number of hydroxyl groups should be modified as were modified by reaction with butylene oxide, methyl isocyanate, acetic anhydride, beta propiolactone or acrylonitrile [Rowell et al 1988b]. This exception of propylene oxide to the protection rule is perhaps the key to understanding the mechanism of the resistance to attack by fungi by chemical modification. As was seen in Table 1, the EMC of propylene oxide modified fiber is higher than any other modified fiber and this may be the reason for the lower biological resistance.

Table 5. Rate and extent of thickness swelling in liquid water of fiberboards made from control and acetylated fiber and a phenolic resin [Resin content of boards: Kenaf - 8%, Bagasse - 5%, Bamboo - 6%, Hemlock - 8%, Pine - 8%]

Fiber	Percent Thickness Swelling at--								
	<---Minutes	-----			<-----	Hours	-----		
	15	30	45	1	2	3	4	5	6
Kenaf									
Control	15.5	17.1	21.1	22.6	24.7	26.8	31.1	32.6	34.0
18.4 WPG	6.7	6.8	6.8	7.0	7.0	7.0	8.0	8.1	8.3
Bagasse									
Control	19.2	20.2	21.0	21.6	22.0	22.7	23.0	23.6	24.0
17.6 WPG	1.8	2.0	2.2	2.3	2.7	2.9	3.3	3.5	3.8
Bamboo									
Control	4.0	7.3	8.4	10.2	12.6	13.8	14.0	14.8	15.0
18.0 WPG	1.5	1.7	1.9	2.3	2.3	2.3	2.4	2.4	2.4
Hemlock									
Control	11.2	11.8	12.3	12.5	14.1	15.2	16.2	16.8	17.0
22.5 WPG	2.6	3.3	3.7	3.8	3.9	4.0	4.0	4.1	4.2
Pine									
Control	25.7	29.8	30.7	31.6	32.9	33.5	33.8	33.9	34.0
21.6 WPG	0.6	0.9	1.1	1.2	1.6	1.9	2.1	2.2	2.5
Percent Thickness Swelling at--						Weight loss		Weight	
<----- Days ----->						after oven		loss after	
----- % -----								drying	
	1	2	3	4	5				
Kenaf									
Control	37.7	41.5	42.6	43.5	44.5	19.0		2.0	
18.4 WPG	8.5	8.5	8.7	8.8	9.0	0.7		2.8	
Bagasse									
Control	25.0	25.2	25.3	25.4	25.5	16.0		1.2	
17.6 WPG	5.0	5.0	5.1	5.2	5.2	1.5		1.4	
Bamboo									
Control	16.1	16.5	17.9	18.1	18.2	8.3		---	
18.0 WPG	2.5	3.1	3.2	3.2	3.3	2.2		---	
Hemlock									
Control	17.3	17.5	17.8	17.9	18.1	7.8		2.9	
22.5 WPG	5.2	5.6	5.8	6.0	6.6	1.7		1.9	
Pine									
Control	35.0	35.6	35.9	36.0	36.2	24.9		0.5	
21.6 WPG	3.7	4.0	4.2	4.3	4.5	2.6		1.1	

The mechanism of brown-rot fungi attack on lignocellulosics is thought to be as given in Figure 3 [Nilsson 1986]. The first biological attack on a lignocellulosic is an enzymatic reaction that results in a metal/peroxide chemical oxidation system. This oxidation system breaks down the large polymers into smaller pieces which results in an early and rapid strength loss as the degree of polymerization of the cellulose molecule is reduced. During this reaction phase, a second enzymatic system starts working in which carbohydrates and lignin are broken down. It is in this phase that weight loss occurs.

Table 6 Weight loss in chemically modified southern pine after 2 weeks exposure to *Reticulitermes flavipes*

chemical	Weight Percent Gain < % >	Wood Weight Loss
Control	0	31
Propylene oxide	9	21
	17	14
	34	6
Butylene oxide	27	4
	34	3
Acetic anhydride	10.4	9
	17.8	6
	21.6	5

Table 7. Biological resistance of chemically modified pine against brown- and white-rot fungi

Chemical	Weight Percent Gain <.....	Weight Loss After 12 Weeks	
		Brown-rot Fungus %	White-rot Fungus
		>	
None	0	68	7
Acetic Anhydride	17	<2	<2
Propylene oxide	25	<15	<2
Butylene oxide	22	<3	<1
Methyl Isocyanate	20	<3	<1
Formaldehyde	5	<3	<1
Beta Propiolactone	25	<2	<2
Acrylonitrile	25	<2	<2

ENZYMES--> HEMICELLULOSES

[Energy source for
generation of
chemical oxidation
system] ———> ACCESSIBLE CELLULOSE
(Strength losses)
[Energy source for
generation of beta-
glucosidases] —----> WEIGHT
LOSS

Figure 3. Mechanism of brown rot fungus attack on lignocellulosics

This mechanism is consistent with the data that strength losses occur long before weight losses in brown-rot fungi attacked wood [Rowell et al 1988b]. In this mechanism the key to brown-rot fungi resistance lies in the protection of the hemicellulose polymers. If that single component is protected, attack can not proceed.

Weight loss resulting from fungal attack is the method most used to determine the effectiveness of a preservative treatment to protect wood composites from decaying. In some cases, especially for brown-rot fungal attack, strength loss may be a more important measure of attack since large strength losses are known to occur in solid wood at very low wood weight loss [Couling 1961]. A dynamic bending-creep test has been developed to determine strength losses when wood composites are exposed to a brown- or white-rot fungus [Imamura and Nishimoto 1985].

Using this bending-creep test on aspen flakeboards, control boards made with phenol-formaldehyde adhesive failed in an average of 71 days using the brown-rot fungus *T. palustris* and 212 days using the white-rot fungus *T. versicolor* [Rowell et al 1988b]. At failure, weight losses averaged 7.8% for *T. palustris* and 31.6% for *T. versicolor*. Isocyanate-bonded control flakeboards failed in an average of 20 days with *T. palustris* and 118 days with *T. versicolor*, with an average weight loss at failure of 5.5% and 34.4%, respectively [Rowell et al 1988b]. Very little or no weight loss occurred with both fungi in flakeboards made using either phenol-formaldehyde or isocyanate adhesive with acetylated flakes. None of these specimens failed during the 300 day test period.

Mycelium fully covered the surfaces of isocyanate-bonded control flakeboards within 1 week, but mycelial development was significantly slower in phenol-formaldehyde-bonded control flakeboards. Both isocyanate- and phenol-formaldehyde-bonded acetylated flakeboards showed surface mycelium colonization during the test time, but the fungus did not attack the acetylated flakes so little strength was lost.

In similar bending-creep tests, both control and acetylated pine particleboards made using melamine-urea-formaldehyde adhesive failed because *T. palustris* attacked the adhesive in the glue line [Imamura et al 1988]. Mycelium invaded the inner part of all boards, colonizing in both wood and glue line in control boards but only in the glue line in acetylated boards. These results show that the glue line is also important in protecting composites from biological attack.

After a 16-week exposure to *T. palustris*, the internal bond strength of control aspen flakeboards made with phenol-formaldehyde adhesive was reduced over 90% and that of flakeboards made with isocyanate adhesive was reduced 85% [Imamura et al 1987]. After 6 months of exposure in moist unsterile soil, the same control flakeboards made with phenol-formaldehyde adhesive lost 65% of their internal bond strength and those made with isocyanate adhesive lost 64% internal bond strength. Failure was due mainly to great strength reductions in the wood caused by fungal attack. Acetylated aspen flakeboards lost much less internal bond strength during the 16-week exposure to *T. palustris* or 6-month soil burial. The isocyanate adhesive was somewhat more resistant to fungal attack than the phenol-formaldehyde adhesive. In the case of acetylated composites, loss in internal bond strength was mainly due to fungal attack in the adhesive and moisture, which caused a small amount of swelling in the boards.

Another test for biological resistance that has been done on acetylated composites is with brown-, White-, and soft-rot fungi and tunneling bacteria in a fungal cellar (Table 8). Control blocks were destroyed in less than 6 months while flakeboards made from acetylated furnish above 16 WPG showed no attack after 1 year. [Nilsson et al 1988, Rowell et al 1988a]. This data shows that no attack occurs until swelling of the wood occurs [Rowell and Ellis 1984, Rowell et al 1988a]. This is more evidence that the moisture content of the cell wall is critical before attack can take place.

Table 9 shows the data for chemically modified pine flakeboards in a marine environment [Johnson and Rowell 1988]. As with the termite test, all types of chemical modifications of wood help resist attack by marine organisms. Control flakeboards were destroyed in 6 months to 1 year, mainly because of attack by *Limnoria tripunctata*, while chemically modified flakeboards show little or no attack after 8 to 10 years.

Table 8. Fungal cellar tests of aspen flakeboards made from control and acetylated flakes [1,2]

Weight Percent Gain	Rating at intervals (Months) [3]							
	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/3
16.3	0	0	0	0	0	0	0	0
17.9	0	0	0	0	0	0	0	0

[1] Nonsterile soil containing brown-, white-, and soft-rot fungi and tunneling bacteria.

[2] Flakeboards bonded with 5% phenol-formaldehyde adhesive.

[3] Rating system: 0 = no attack; 1 = slight attack; 2 = moderate attack; 3 = heavy attack; 4 = destroyed; S = swollen.

Table 9. Ratings of chemically modified southern pine exposed to a marine environment [1]

Chemical	Weight Percent Gain	Years of Exposure	Mean rating due to attack by <i>Limnoriid</i> and <i>Teredinid</i> Borers	<i>Shaeroma</i> <i>terebrans</i>
Control	0	1	2-4	3.4
Propylene Oxide	26	11.5 3	10	3.8
Butylene Oxide	28	8.5	9.9 3	8.0
Butyl Isocyanate	29	6.5	10	
Acetic Anhydride	22	3	8	8.8

[1] Rating system- 10 = no attack; 9 = slight attack; 7 = some attack; 4 = heavy attack; 0 = destroyed

All laboratory tests for biological resistance conducted to this point show that acetylation is an effective means of reducing or eliminating attack by soft-, white-, and brown-rot fungi, tunneling bacteria, marine organisms, and subterranean termites.

Ultraviolet Resistance

Acetylation has also been shown to improve ultraviolet resistance of aspen fiberboards [Feist et al 1991a]. Table 10 shows the weight loss, erosion rate, and depth of penetration resulting from 700 hours of accelerated weathering. Control specimens erode at about 0.12 $\mu\text{m/hr}$ or about 0.02 %/hr. Acetylation reduces surface erosion by 50 percent. The depth of the effects of weathering is about 200 μm into the fiber surface for the un-modified boards and about half that of the acetylated boards. Table 11 shows the acetyl and lignin content of the outer 0.5 mm surface

and of the remaining specimen after the surface had been removed before and after accelerated Weathering. The acetyl content is reduced in the surface after weathering which shows that the acetyl blocking group is removed during

Table 10. Weight loss and erosion of aspen fiberboards made from control and acetylated fiber after 700 hours of accelerated weathering

Specimen	Weight loss	Erosion	Reduction in Erosion	Depth of Penetration of Weathering
	%/hr	µm/hr	%	µm
Control	0.019	0.121	---	199-210
Acetylated	0.010	0.059	51	85-105

weathering. W radiation does not remove all of the blocking acetyl group so some stabilizing effect to photochemical degradation still is in effect. The loss of acetate is confined to the outer 0.5 mm since the remaining wood has the same acetyl content before and after accelerated weathering. The lignin content is also greatly reduced in the surface as a result of weathering which is the main cell wall polymer degraded by UV radiation. Cellulose and the hemicelluloses are much more stable to photochemical degradation.

Table 11. - Acetyl and lignin analysis before and after 700 hours of accelerated weathering of aspen fiberboards made from control and acetylated fiber.

Specimen	Before weathering		After weathering	
	Surface	Remainder	Surface	Remainder
	Acetyl		Acetyl	
	<	%		>
Control	4.5	4.5	1.9	3.9
Acetylated	17.5	18.5	12.8	18.3
	Lignin		Lignin	
Control	19.8	20.5	1.9	17.9
Acetylated	18.5	19.2	5.5	18.1

In outdoor tests, flakeboards made from acetylated pine flakes maintain a light yellow color after one year while control boards turn dark orange to light gray during this time [Feist et al 1991b].

Strength Properties

The modulus of rupture (MOR), modulus of elasticity (MOE) in bending and tensile strength (TS) parallel to the board surface are shown in Table 12 for fiberboards made from control and acetylated pine kenaf and hemlock fiber. Acetylation results in a small

Table 12. Modulus of rupture (MOR), modulus of elasticity (MOE), and tensile strength (TS) parallel to the board surface of fiberboards made from control or acetylated fiber and phenolic resin [1].

Board	MOR <- MPa ->	MOE <- GPa ->	TS <- MPa ->
Pine			
Control	37.1	3.7	19.0
21.6 eWPG'	27.9	3.3	13.6
Kenaf			
Control	47.1	4.6	31.0
18.4 WPG	38.6	5.1	27.1
Hemlock			
Control	66.0	6.0	33.9
22.5 WPG	51.1	5.0	32.1
ANSI Stanard	31.0	---	10.3

[1] Resin content of boards: Pine 8%, Kenaf 8%, Hemlock 8%

decrease in MOR but about equal values in MOE and TS. All strength values given in Table 12 are above the minimum standard as given by the American Hardboard Association [ANSI 1982]. It has been shown that there is very little effect on strength properties of thin flakes as a result of acetylation [Rowell and Banks 1987]. The small decrease in some strength properties resulting from acetylation may be attributed to the hydrophobic nature of the acetylated furnish which may not allow the water soluble phenolic or isocyanate resins to penetrate into the flake. The adhesives used in these tests have also been developed for un-modified lignocellulose. Different types of adhesives may be needed in chemically modified boards [Vick and Rowell 1990].

It should also be pointed out that strength properties of lignocellulose are very dependent on the moisture content of the cell wall. Fiber stress at proportional limit, work to proportional limit, fiber stress at proportional limit, and maximum crushing strength are the mechanical properties most affected by changing moisture content by only +/- one percent below FSP [Rowell 1984, USDA 1987]. Since the EMC and FSP are much lower for chemically modified fiber than for control fiber, strength properties will be different due to this fact alone.

FUTURE OF LIGNOCELLULOSIC COMPOSITES

Fiber technology, high performance adhesives, and fiber modification can be used to manufacture structural lignocellulosic composites with uniform densities, durability in adverse environments, and high strength. Fiber modification can also be used to improve properties in composites made of both natural and synthetic resources used for geotextiles, filters, sorbents, packaging, and non-structural composites.

Products having complex shapes can be produced using flexible chemically modified fiber mats, which can be made by nonwoven needling or thermoplastic fiber melt matrix technologies. Within certain limits, the mats can be pressed into any desired shape, size, thickness, and density. With fiber mat technology, a complex product can be made directly from a lignocellulosic fiber blend. In general, the present technology requires the formation of flat sheets prior to the shaping of complex parts.

All of this technology can be applied to recycled lignocellulosic fiber as well as virgin fiber, which can be derived from many sources. Agricultural residues, all types of waste paper, yard waste, industrial fiber residues, residential fiber waste, and many other forms of waste lignocellulosic fiber can also be used to make property enhanced composites.

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