Results of chemical modification of lignocellulosic fibers for use in composites

Roger M. Rowell, Brenda A. Cleary, Jeffrey S. Rowell, Craig Clemons, and Raymond A. Young
USDA, Forest Products Laboratory, Madison, Wisconsin
University of Wisconsin, Department of Forestry, Russell Labs, Madison, Wisconsin

Abstract

Lignocellulosic fibers are biopolymer composites made up primarily of cellulose, hemicellulose, and lignin. Polymers make up the cell wall and are responsible for most of the physical and chemical properties exhibited by lignocellulosic fibers. Certain properties, among them dimensional instability to moisture, biodegradability, flammability, thermoplasticity, and degradability by ultraviolet light, acids, and bases, are the result of chemical reactions involving the cell wall. It is these properties that dictate the end use of lignocellulosics in composite formulation. By changing the basic chemistry of the cell wall polymers by esterification, it is possible to change the basic properties of lignocellulosic fibers leading to the production of high performance composites.

Introduction

A lignocellulosic is any substance that contains both cellulose and lignin. Lignocellulosics include wood, agricultural residues, water plants, grasses, and other plant substances. In general, lignocellulosics have been included in the term "biomass," but this term has broader implications than that denoted by lignocellulosics. Biomass includes living substances such as animal tissue and bones. Lignocellulosics have also been called "photomass" because they are a result of photosynthesis. A material is defined as a substance with consistent, uniform, continuous, predictable, and reproducible properties. An engineering material is defined simply as any material used in construction.

A composite is a reconstituted product made from a combination of one or more substances using some kind of mastic to hold the components together. The best known wood composites are plywood, particleboard, fiberboard, and laminated lumber. Wood is used as an engineering material because it is economical, low in processing energy, renewable, and strong. In some schools of thought, however, wood is not considered an engineering material because it does not have consistent, predictable, reproducible, continuous, and uniform properties. This is true for solid wood, but it is not necessarily true for composites made from wood.

For the most part, materials and composites can be grouped into two basic types: price-driven, for which costs dictate the markets, and performance-driven, for which properties dictate the markets. A few materials and composites might be of both types, but usually these two types are very distinct. In general, the wood industry has produced the price-driven type of composites. Even though the wood industry is growing, it has lost some market share to competing materials such as steel, aluminum, plastic, and glass. Unless something is done to improve the competitive performance of wood and other lignocellulosics, future opportunity for growth will be limited.

Materials and composites used by today's industry range from high performance-high cost to low performance-low cost. For example, the aerospace industry is very concerned about high performance in their materials and composites, and this results in high cost and low rate of production. The military is also concerned about performance, but their requirements are not as strict as those of the aerospace industry. Thus, the rate of production of military-type materials and composites is higher than that of aerospace materials and the cost is lower. In contrast, the wood industry depends on a high production rate and low cost. As a result, wood composites have lower performance as compared to aerospace and military composites.

Wood fiber can provide the wood industry with the opportunity to develop high performance materials and composites. The chemistry of wood and other lignocellulosic components can be modified to produce a material that has consistent, predictable, and uniform properties. As will be discussed later, properties such as dimensional instability, biodegradability, flammability, and degradation caused by ultraviolet light, acids, and bases can be altered to produce value-added, property-enhanced composites.

The perception that wood is not a material as defied

earlier is easy to understand. Wood is an isotropic (different properties in all three growing directions of a tree); it may contain sapwood, heartwood, latewood, earlywood, juvenile wood, reaction wood, knots, cracks, splits, and checks; and it may be bent, twisted, or bowed. These defects occur in solid wood but they need not exist in wood composites. The smaller the size of the components in the composite furnish, the more uniform the properties of the composite. For example, chipboard is less uniform than flakeboard, which is less uniform than particleboard, which is less uniform than fiberboard. Fiberboard made from wood fiber can be very uniform, reproducible, and consistent, and it is very close to being a true "material."

The properties of lignocellulosic composites can be modified to be consistent, predictable, reproducible, continuous, and uniform. Before we discuss how lignocellulosic properties can be modified, it is important to describe how the components of lignocellulosic composites interact.

Lignocellulosics change dimensions with changing moisture content because the cell wall polymers contain hydroxyl and other oxygen-containing groups that attract moisture through hydrogen bonding (17,26). The hemicelluloses are mainly responsible for moisture sorption, but the accessible cellulose, noncrystalline cellulose, lignin, and surface of crystalline cellulose also play major roles. Moisture swells the cell wall, and the lignocellulosic expands until the cell wall is saturated with water. Beyond this saturation point, moisture exists as free water in the void structure and does not contribute to further expansion. This process is reversible, and the lignocellulosic shrinks as it loses moisture.

Lignocellulosics are degraded biologically because organisms recognize the carbohydrate polymers (mainly the hemicelluloses) in the cell wall and have very specific enzyme systems capable of hydrolyzing these polymers into digestible units. Biodegradation of the high molecular weight cellulose weakens the lignocellulosic cell wall because crystalline cellulose is primarily responsible for the strength of the lignocellulosic (24). Strength is lost as the cellulose polymer undergoes degradation through oxidation, hydrolysis, and dehydration reactions. The same types of reactions take place in the presence of acids and bases.

Lignocellulosics exposed outdoors undergo photochemical degradation caused by ultraviolet light. This degradation takes place primarily in the lignin component, which is responsible for the characteristic color changes (18). The lignin acts as an adhesive in lignocellulosic 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 wood surface to become rough and can account for a significant loss in surface fibers.

Lignocellulosics burn because the cell wall polymers undergo pyrolysis react ions with increasing temperature to give off volatile, flammable gases. The hemicellulose and cellulose polymers are degraded by heat much before the lignin is degraded (18). The lignin component contributes to char formation, and the charred layer helps insulate the lignocellulosic from further thermal degradation.

If the fiber is reconstituted using a high performance adhesive, very strong and uniform lignocellulosic composites can be produced. However, properties such as dimensional instability, flammability, biodegradability, and degradation caused by acids, bases, find ultraviolet radiation are still present in the composite, which will restrict its use for many applications. If the properties of the composite do not meet the end-use performance requirements, then the question is: What must be changed, improved, and redesigned so that the composite does meet end-use expectations? Although such changes are regularly made in the textile, plastic, glass, and metal industries, they are rarely made in the lignocellulosic industry.

Because the properties of lignocellulosics result from the chemistry of the cell wall components, the basic properties of a lignocellulosic can be changed by modifying the basic chemistry of the cell wall polymers. Chemical modification technology can greatly improve the properties of lignocellulosics (14,15,20,25). Dimensional stability can be greatly improved by bulking the lignocellulosic cell wall either with simple bonded chemicals or by impregnation with water-soluble polymers (14). For example, esterification of lignocellulosic fiber using acetic, maleic, or succinic anhydride produces a fiber with reduced equilibrium moisture content (EMC), and composites made from this modified fiber have greatly improved dimensional stability as compared to that of a control composite (15,25). Acetylation of fiber greatly improves both resistance to biological attack and degradation due to ultraviolet radiation. Esterification does not seem to affect the fire properties of modified fibers.

Thermoformable composites are being made today that combine wood flour with thermoplastics. The wood flour is used mainly as a low-cost extender. If wood fiber were used in place of flour, it may be possible to use the strength of the wood fiber to greatly improve the mechanical properties of the wood-plastic composites made by extrusion technology, injection molding, or film blowing. Composites made from a combination of lignocellulosic fiber and plastics could have enhanced properties if the lignocellulosic could be made more thermoplastic or if compatibilization chemistry is applied.

Experimental

Esterification procedure. — Acetylation was performed using the simplified procedure published earlier (19). Attrition-milled aspen fiber was soaked in neat acetic anhy-

dride (AA) for 3 minutes. The fiber was then allowed to drain and placed in a reactor at 120°C for different periods of time to give different levels of chemical weight gain. After reaction, a vacuum was applied for 10 minutes to remove as much excess acetic anhydride and by-product acetic acid as possible. The esterified fiber was then ovendried at 105°C for 24 hours to further remove excess reagent and by product.

Modification of the fibers using maleic and succinic anhydride was performed using a hot xylene solution saturated with each of the anhydrides in a reaction vessel. When reflux temperature was reached, the aspen fiber was added and allowed to react for different lengths of time to give different levels of chemical weight gain. Excess anhydride was removed by extraction of the esterified fiber with xylenes for 4 hours. Excess xylene was removed by evaporation and then the fiber was ovendried for 24 hours at 105°C.

Scanning electron micrographs (SEM). — SEMs were taken with a Jeol 840 scanning electron microscope. All samples were coated with gold. A magnification of 750X was used.

Fiberboard production. — A liquid phenol-formaldehyde dry-process hardboard resin (GP 2341, 50% aqueous solution), was sprayed onto the esterified fiber. The fiber was hand formed into a mat approximately 6 by 6 inches and then pressed in a heated Carver press at 190ºC for 10 minutes to a predetermined thickness of ¼ inch and specific gravity of 0.7.

Moisture sorption. — Fiberboards were cut into 2- by 2-inch specimens and placed in separate rooms at 27°C and 30,65, or 90 percent relative humidity. Each specimen was weighed at the end of 21 days and the EMC determined. Duplicate samples were done and the results averaged.

Rate and extent of swelling. — Fiberboards cut into 2- by 2-inch specimens were soaked in water at room temperature and changes in board thickness was measured at 20,40, and 60 minutes, 1,2,3,4, and 5 hours, and every 24 hours from time zero for 5 days. The percentage increase in thickness was calculated based on the original ovendry thickness. Duplicate samples were run and averaged. The specimens were then ovendried again and the thickness and swelling redetermined. The specimens were then again immersed in water and the thickness measured. This cycle was repeated until specimens no longer increased in thickness from cycle to cycle.

Biological tests. — ***Soil*** block tests were done on ¾-in. square southern pine particleboard blocks according to ASTM standard D 1413 (1). Fungal cellar tests were done on 1-by ½-by3-inch southern pine and aspen particleboard blocks using nonsterile soil containing brown-, white-, and soft-rot fungi and tunneling bacteria (11). Triplicate samples were run and averaged.

Weathering tests. — Aspen waferboard specimens measuring 3 by 4 by ⅜ inch were used to evaluate accelerated weathering. Accelerated artificial weathering was conducted in a commercial chamber. The faces of all test specimens were exposed to a 6500-watt xenon arc light source (which closely approximates natural sunlight) in an enclosed chamber at 45° to 50°C and 50 percent relative humidity (4). Each 24-hour cycle of weathering consisted of 24 hours of light with 4 hours of distilled water spray. Exposure time is expressed as hours of exposure to light. Triplicate samples were run and averaged.

Results and discussion

Esterification chemistry. — Figure 1 shows the extent of modification achieved on aspen fiber with the three types

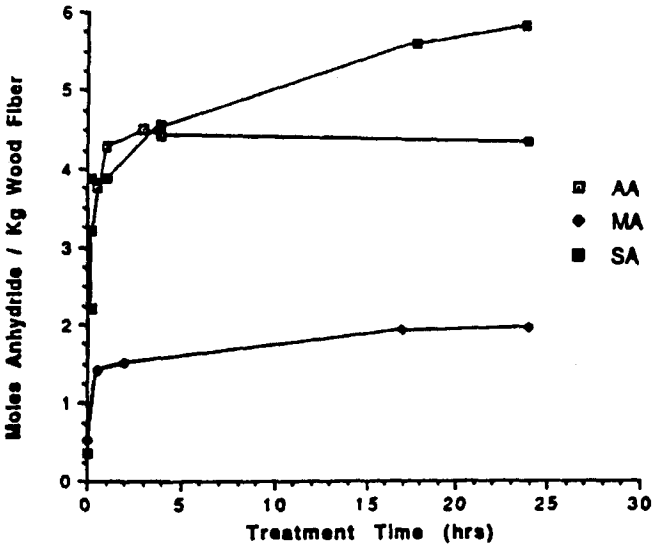

Figure 1. — Molar gains of aspen fiber esterified with acetic (AA), maleic (MA), and succinic (SA) anhydrides.

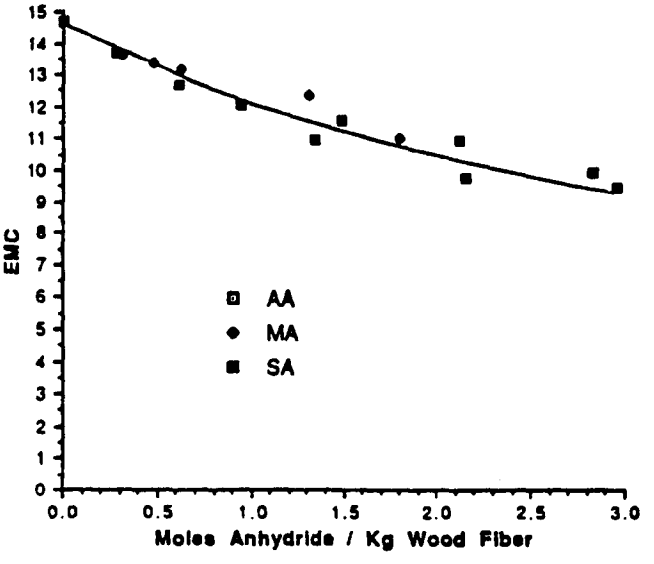

Figure 2. — EMC of aspen fiber esterified by reaction with acetic (AA), maleic, and succinic (SA) anhydrides (90% RH and27°C).

of anhydrides based on a molar addition. Maleic anhydride showed a much lower reactivity than succinic anhydride, which has the same structure except for the double bond in maleic anhydride. A possible explanation for this phenomena is that the rigidity of the maleic anhydride (created by the double bond) inhibits the penetration of the molecule into the cell wall and decreases the number of hydroxyl groups available for reaction. Acetic anhydride reacts faster than maleic anhydride and the same rate as succinic anhydride.

The ester contents of the maleic and succinic anhydride-modified aspen fibers were determined (2). Equivalent numbers were obtained when the ester content was calculated based on the acid value and the saponification value, indicating that the anhydride added as a monoester and not a diester for each reaction system. That is, the ester contents based on the number of free carboxyl groups and the total number of carboxyl groups present because of the anhydride modification indicated that the anhydrides added as a monoester. The ester content based on the acid and saponification values also agreed with the calculated weight percent gain for each reaction system.

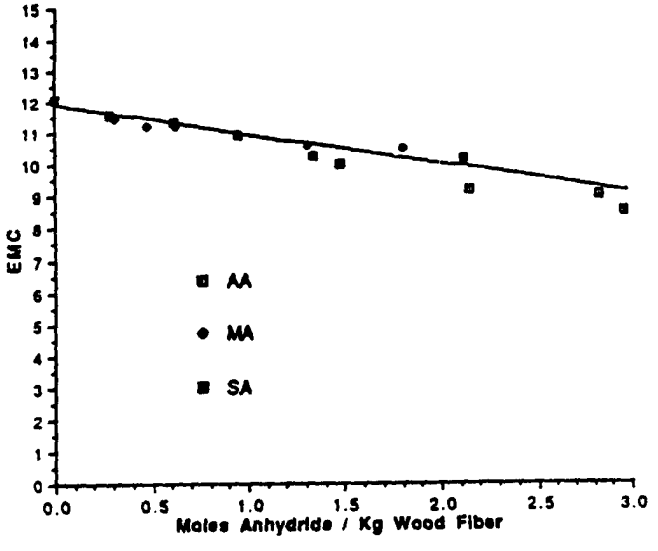

Figure 3. — EMC of aspen fiberboards made from fiber esterified by reaction with acetic, maleic, and succinic anhydrides (90% RH and 27°C).

Moisture sorption of esterified fiber and fiberboards. — Figure 2 shows that the EMC of the esterified fiber is independent of the type of esterification but is dependent on the molar gain of reacted ester in the wood fiber. A reduction in EMC was seen for each esterification as the level of modification was increased.

As with the esterified wood fiber, no significant difference was noted in the EMCs of the fiberboards made using phenol formaldehyde adhesive for each type of esterification but the level of modification significantly improved the EMC (Fig. 3). A proportional reduction in EMC was seen as the level of modification increased for each type of esterification. A 25 percent reduction in EMC was obtained at a molar gain of 3 moles of anhydride per kilogram.

Rate and extent of swelling of fiberboards in liquid water. — Increase in thicknesses due to liquid water swelling of the esterified specimens bonded with 5 percent phenol formaldehyde followed the same trends as the EMC of the humidified boards. Thickness increases were independent of the type of esterification but were dependent on the level of esterification. A 25 percent reduction in thickness swell was achieved at a level of modification of 3 moles of anhydride per kilogram.

Figure 4 shows the rate of fiberboard swelling in liquid water. While control boards swelled almost 25 percent in

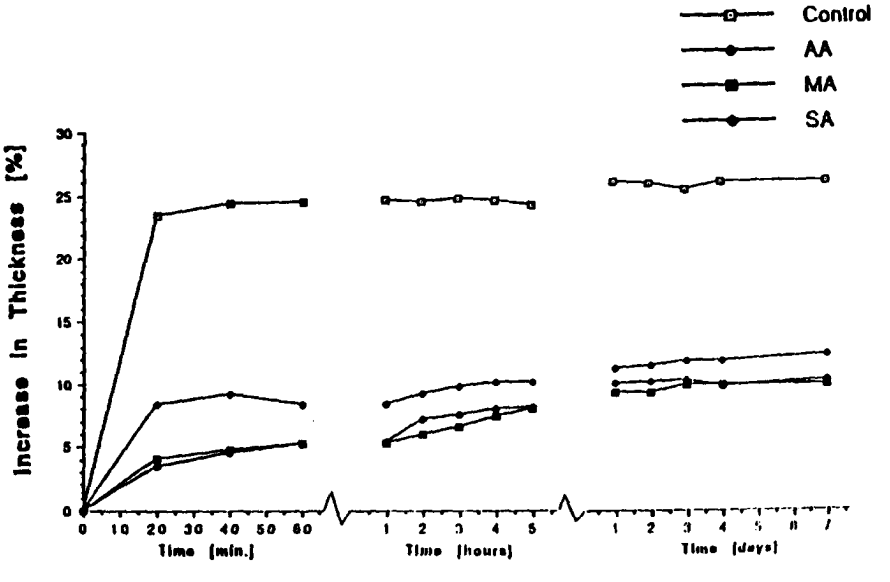

Figure 4. — Swelling history (water soaked specimens) of fiberboards of acetic, maleic, and succinic anhydride-modified aspen fiber and 5 percent phenol formaldehyde.

thickness in the first 20 minutes, all types of esterified boards swelled less than 10 percent. Acetic anhydride reduced the swelling to less than half of the control specimens while maleic and succinic anhydride modifications reduced the swelling further. The reduction in swelling can be attributed to the bulking of the cell wall and the reduction of the capillary action of the wood especially with the larger maleic and succinic anhydride molecules. A possible increase in thermoplasticity and subsequent increase in bond strength because of the increase fiber-to-fiber contact could also help explain the reduction in swell.

The results of cyclic wetting and drying tests on phenol-formaldehyde-bonded fiberboards are shown in Figure 5. Reversible swelling (normal swelling and shrinking of the fiber cell wall) has been reduced by all types of esterifications. Acetic anhydride shows a reversible swelling of about 8 percent while control boards show about 15 percent. Maleic and succinic anhydride have the same reversible swelling of about 10 percent. The major difference in the type of anhydride used is shown in the irreversible swelling (the permanent increase in the ovendry thicknesses over several cycles caused by relief of the stresses induced during pressing of the board). The specimens of acetylated fiber had less than half of the irreversible swelling compared with the unmodified boards. The maleic and succinic anhydride-modified boards showed a complete absence of irreversible swelling probably due to an increase in thermoplasticity of the esterified fiber which prevented stresses from being built up during pressing. These results suggest that the succinic and maleic anhydride-modified fibers undergo plastic deformation, the acetylated fiber recovers a portion of the induced deformation, and the control fiber recovers most or all of the plastic deformation created during pressing. Relatively low molar gains of succinic or maleic anhydride (approx. 2 moles anhydride per kg wood fiber) result in a complete absence of irreversible swelling.

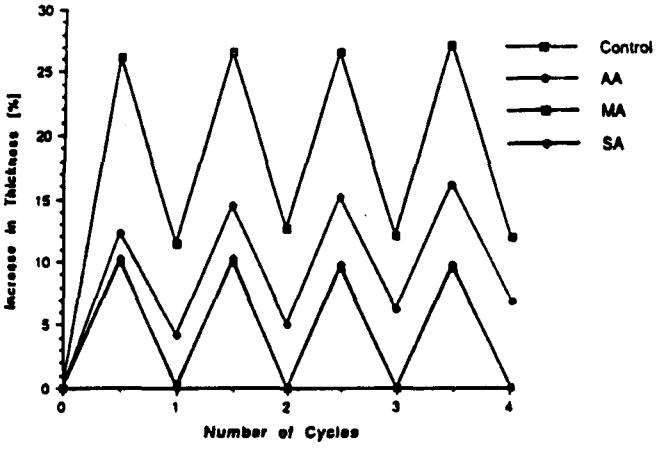

Figure 5. —Cyclic water swelling tests for fiberboards of acetic, maleic, and succinic anhydride-modified aspen fiber and 5 percent phenol formaldehyde.

Biological resistance, — Particleboard made from acetylated flakes have been tested for resistance to several different types of organisms. In a 4-week termite test using *Reticulitermes flavipes* (subterranean termites), boards acetylated at 16 to 17 weight percent gain were very resistant to attack, but not completely so (9,21,24). 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.

Esterified wood composites have been tested to decay fungi in several ways. Untreated aspen and pine particleboards exposed to white-, soft-, and brown-rot fungi and tunneling bacteria in a fungal cellar were destroyed in less than 6 months while particleboard made from acetylated furnish above 16 percent acetyl weight gain showed no attack after 1 year (Table 1) (21,24). In a standard 12-week single-culture soil-block test, aspen particleboard controls exposed to the white-rot fungus *(Trametes versicolor)* lost 34 percent weight, while acetylated particleboard (17% acetyl weight gain) lost no weight (12,21,24). Using the brown-rot fungi *(Tyromyces palustris),* aspen flakeboard controls lost 2 percent weight when a phenol-formaldehyde adhesive was used and lost 30 percent weight when an isocyanate adhesive was used. If the particleboard are water-leached before the soil-block test is run, control boards made with phenol-formaldehyde adhesive lose 44 percent weight with the brown-rot fungus *(Gloeophyllum trabeum)* (Table 2) (13,23,24). This

Table 1. — *Fungal cellar tests on aspen particleboards made from control and acetylated flakes (5% phenolic resin).*

Weight percent gain	Rating at intervals[a]					
	2 months	3 months	4 months	5 months	6 months	12 months
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
13.6	0	0	0	0	S/0	S/1
16.3	0	0	0	0	0	0
17.9	0	0	0	0	0	0

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

Table 2. — *Average weight loss in soil block tests for aspen particleboards made from control and acetylated flakes exposed for 12 weeks to* Gloeophyllum trabeum.

Weight percent gain	Average weight loss	
	Nonleached	Leached
	(%)	
0	28.5	44.1
7.3	3.0	22.4
11.5	1.2	13.9
13.6	0.4	2.6
16.3	1.2	0.6
17.9	1.0	0.1

shows that the adhesive can influence results of fungal toxicity, especially in a small, closed test container.

Weight loss resulting from fungal attack is the method most often 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 (3). A dynamic bending-creep test has been developed to determine strength losses when wood composites are exposed to a brown- or white-rot fungus (8).

Using this bending-creep test on aspen flakeboards, control boards made with phenol-formaldehyde adhesive failed in an average of 71 days with *T. palustris* and 212 days with *T. versicolor* (22). At failure, weight losses averaged 7.8 percent for *T. palustris* and 31.6 percent 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 percent and 34.4 percent, respectively (22). Very little or no weight loss occurred with both fungi in particleboard made using either phenol formaldehyde or isocyanate adhesive with acetylated flakes. None of these specimens failed during the test period.

Acetylated pine flakeboards have also been shown to be resistant to attack in a marine environment (10). Control flakeboards were destroyed in 6 months to 1 year, mainly because of attack by ***Limnoria tripunctata,*** while acetylated boards showed no attack after 2 years.

Table 3. — *Weight loss and erosion of acetylated aspen fiberboards after 800 hours of ultraviolet radiation (average of three specimens).*

Specimen	Weight loss	Erosion	Reduction in erosion compared to control	Depth of penetration of UV effects measured on cross section
	(%/hr.)	(μm/hr.)	(%)	(μm)
Control	0.019	0.121	--	190 to 210
Ac 12 WPG	0.013	0.081	33	170 to 190
Ac 18 WPG	0.010	0.059	51	85 to 105

Ultraviolet radiation resistance. — Table 3 shows the weight loss, erosion rate, and depth of penetration after 800 hours of accelerated weathering. Control specimens erode at about 0.12 μ/hr. or about 0.02% / hr. (6,7). The depth of the effects of weathering was about 200 μ into the wood surface (5). Acetylation to 12 weight percent gain reduced erosion by 33 percent and to 18 weight percent gain reduces erosion by 50 percent. The depth of penetration of ultraviolet radiation was also decreased as the level of acetylation increases.

Plasticization of esterified fibers. — Figure 6 shows SEMs of the faces of high density boards of both the unmodified and succinic an hydride esterified fiber made using no resins. All boards were pressed under identical conditions. The SEM of the control board shows almost no deformation of the fibers under the pressing conditions used. The SEM of the succinic anhydride fiberboard shows the fibers becoming flattened and spreading out. This indicates that thermoplasticity has been achieved. Plasticization was also achieved with modification using maleic anhydride but the amount of plasticization was not as great. This was probable due to the fact that maleic anhydride reacted to a much lower level than succinic anhydride.

Conclusions

Esterification using either acetic, maleic, or succinic anhydrides reduces EMC in aspen fiber regardless of the anhydride used. Fiberboards made from esterified fiber show greatly reduced reversible and irreversible thickness swelling. Irreversible swelling is completely eliminated in the case of fiber esterified with maleic and succinic anhydrides.

Biological resistance was greatly improved by esterification of fiber before fiberboard production. Modification of the cell wall polymers increases resistance as a result of lowering the EMC point below that needed for microorganism attack and changing the conformation and configuration requirements of the enzyme-substrate reactions.

Figure 6. — Scanning electron micrographs of the surface of aspen fiberboards. Control (left) and succinic anhydride modified (weight percent gain = 58)(right).

Resistance to degradation due to ultraviolet radiation was also greatly increased through esterification.

Both esterification with maleic and succinic anhydrides resulted in thermoplasticization of the wood fiber. Since succinic anhydrides reacts to much higher levels of chemical weight gains, it is more effective as a plasticizer than maleic anhydride.

Past research has shown that there is no change in the pyrolysis properties of esterified fiber (16).

Fiber technology, high performance adhesives, and fiber modification can be used to manufacture lignocellulosic composites with uniform densities, durability in adverse environments, and high strength.

Many different types of lignocellulosic fibers can be used to make composites. Wood fiber is currently used as the major source of fiber, but other sources can work just as well. Problems such as availability, collection, handling, storage, separation, and uniformity will need to be considered and solved. Some of these are technical problems whereas others are a matter of economics. Currently available sources of fiber can be blended with wood fiber or used separately. For example, large quantities of sugar cane bagasse fiber from sugar refineries, rice hulls from rice processing plants, and sunflower seed hulls from oil extraction plants are all available.

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 paper, yard waste, industrial fiber residues, residential fiber waste, and many other forms of waste lignocellulosic fiber base can be used to make composites. Recycled plastics can also be used as binders in both cost-effective and value-added composites. Thermoplastics can be used to make composites for nonstructural parts, and thermosetting resins can be used for structural materials.

Combining lignocellulosics with other materials such as glass, metals, inorganics, plastic, and synthetic fiber provides a strategy for producing advanced composites that take advantage of the enhanced properties of all types of materials. Chemical modification technology can be used to greatly enhance the properties of lignocellulosic fiber which can play a greater role in advanced materials. This allows the scientist to design materials based on end-use requirements within the framework of cost, availability, renewability, recyclability, energy use, and environmental considerations,

Literature cited

1. American Society for Testing and Materials. 1973. Standard method of testing wood preservatives by laboratory soil-block cultures. ASTM Standards D 1413. ASTM, Philadelphia, Pa.
2. Clemons, C., R.A. Young, and R.M. Rowell. Wood and Fiber Sci. (in press).
3. Cowling, E.B. Comparative biochemistry of the decay of sweetgum sapwood by white-rot and brown-rot fungus. 1961. USDA Forest Serv. Tech. Bull. No. 1258. 50 pp.
4. Feist, W.C. and R.M. Rowell. 1982. *In:* D.N.S. Hon, ed., Graft copolymerization of lignocellulosic fibers. Amer. Chem. Soc., Symp. Series No. 187, Washington, D.C. pp. 349-370.
5. _____ and D.N.-S. Hon. 1985. *In:* The Chemistry of Solid Wood. R.M. Rowell, ed. Advances in Chemistry Series, No. 207. Amer. Chem. Soc., Washington, D.C. pp. 401-451.
6. _____, R.M. Rowell, and W.D. Ellis. 1991. Wood and Fiber Sci. 23(1):128-136.
7. _____, _____, and J.A. Youngquist. 1991. Wood and Fiber Sci. 23(2):260-272.
8. Imamura, Y. and K. Nishimoto. 1985. J. Soc. Materials Sci. 34(38):985-989.
9. _____, _____, Y. Yoshida, S. Kawai, T. Sato, and M. Nakaji. 1986. J. Wood Res. 73:35-43.
10. Johnson, B.R. and R.M. Rowell. 1988. Material und Organismen 23(2):147-156.
11. Nilsson, T. and R.M. Rowell. 1982. Inter. J. Wood Preservation 2(3):119-121.
12. _____, _____, R. Simonson, A.-M. Tillman. 1988. Holzforschung. 42(2):123-126.
13. Rowell, R.M. unpublished data.
14. _____ and R.L. Youngs. 1981. Res. Note FPL-0243. USDA Forest Serv., Forest Prod. Lab., Madison, Wis. 8 pp.
15. _____. 1983. Commonwealth Forestry Bureau, Oxford, England. 6(12):363-382.
16. _____, R.A. Susott, W.G. De Groot, and F. Shafizadeh. 1984. Wood and Fiber Sci. 16(2):214-223.
17. _____ and W.B. Banks. 1985. Gen. Tech. Rept. FPL-GTR-50. USDA Forest Serv., Forest Prod. Lab., Madison, Wis. 24 pp.
18. _____, ed. 1985. The Chemistry of Solid Wood, Advances in Chemistry Series No. 207. Amer. Chem. Soc., Washington, D.C.
19. _____, A.-M. Tillman, and R. Simonson. 1986. J. Wood Chem. and Tech. 6(3):427-448.
20. _____ and P. Konkol. 1987. Gen. Tech. Rept. FPL-GTR-55. USDA Forest Serv., Forest Prod. Lab., Madison, Wis. 12 pp.
21. _____, G.R. Esenther, D.D. Nicholas, and T. Nilsson. 1987. J. Wood Chem. Technol. 7(3):427-440.
22. _____, J.A. Youngquist, and Y. Imamura. 1988. Wood Fiber Sci. 20(2):266-271.
23. _____ and M. Norimoto. 1988. Mokuzai Gakkaishi 34(7):627-629.
24. _____, G.R. Esenther, J.A. Youngquist, D.D. Nicholas, T. Nilsson, Y. Imamura, W. Kerner-Gang, L. Trong, and G. Deon. 1988. *In:* Proc. IUFRO Wood Protection Subject Group, Honey Harbor, Ont., Canada. Canadian Forestry Serv. pp. 238-266.
25. _____. *In:* Composites: Chemical and Physicochemical Aspects, T.L. Vigo and B.J. Kinzig, eds., Advances in Chemistry Series. Amer. Chem. Soc., Washington, D.C. (in press).
26. Stamm, A.J. 1964. Wood and Cellulose Science. The Ronald Press Co., N.Y.

In: Wood-fiber/polymer composites: Fundamental concepts, processes, and material options: Proceedings of 1st wood fiber-plastic composite conference; Madison, WI and 45th annual meeting of the Forest Products Society; New Orleans, LA Madison, WI: Forest Products Society; 1993: 121-127.

on recycled paper