PERFORMANCE DRIVEN COMPOSITES FROM LIGNOCELLULOSIC RESOURCES

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Lignocellulosic resources have played a major role throughout human history. Even the earliest humans used lignocellulosic resources, such as wood, to make shelters, cook their food, construct tools, and make weapons. Collectively, society learned very early the great advantages of using a resource that was widely distributed, multi functional, strong, east to work, aesthetic, and renewable.

Up until about 1920, the Western world greatly depended on the use of lignocellulosic resources for materials. With the coming of plastics, high performance metals, ceramics, and other synthetics, the use of lignocellulosic derived materials lost market share.

As we start the 21st century, there is a greater awareness of the need for materials in an expanding world population and increasing affluence. At the same time, we also face the fact that our non-renewable resources are being used up. Our attention is being drawn to renewable, biodegradable and sustainable resources for materials.

Lignocellulosic Materials, such as wood, are generally sold as high volume, low performance products. For the most part, we have designed and used lignocelulosic materials accepting limitations such as dimensional instability, ultraviolet and biological degradation, and thermal instability. However, with a better understanding the relationship between chemistry, properties, and performance of lignocellulosics, we can produce a new generation of value added composites that will be performance driven rather than cost driven.

A single lignocellulosic fiber is a three dimensional, hydroscopic composite composed mainly of cellulose, hemicelluloses, and lignin with minor amounts of protein, extractives and inorganics. These fibers were designed, after millions of years of evolution, to perform, in nature, in a wet environment. Nature is programmed to recycle these resources, in a timely way, back to basic building blocks of carbon dioxide and water through biological, thermal, aqueous, photochemical, chemical, and mechanical degradations.

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

Lignocellulosic resources are degraded biologically because organisms "recognize" the carbohydrate polymers (mainly the hemicelluloses) in the cell wall and have both non-specific chemical and highly specific enzyme systems capable of hydrolyzing these polymers into digestible units. Biodegradation of both the matrix and the high molecular weight cellulose weakens the fiber cell wall. Strength is lost as the matrix and cellulose polymer undergoes degradation through oxidation, hydrolysis, and dehydration reactions. As degradation continues, removal of cell well content results in weight loss.

Lignocellulosic resources exposed outdoors undergoe photochemical degradation caused by ultraviolet radiation. This degradation takes place primarily in the lignin component, which is responsible for the characteristic color changes. The surface becomes richer in carbohydrate polymer content as the lignin degrades. In comparison to lignin, carbohydrate polymers are much less susceptible to ultraviolet degradation. After the lignin has been degraded, the poorly bonded carbohydrate-rich fibers erode easily from the surface, which exposes new lignin to undergo 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.

Lignocellulosic resources burn because the cell wall polymers undergo pyrolytic reactions with increasing temperature to give off volatile, flammable gasses. The hemicelluloses are the first to be thermally degraded followed closely by the cellulose polymer. The most thermally stable polymer in the cell wall is lignin. This is not surprising since oil and coal deposits are sources of prehistoric lignin. The lignin and carbohydrate components contribute to char formation, and the charred layer helps insulate the composite from further thermal degradation.

We traditionally think of lignocellulosic-based composites as solid, i.e. wood. We know solid, we trust solid, we understand solid. There has been, however, a trend away from solid wood for many traditional applications toward smaller member composites. The new products started with glue laminated beams, to plywood, to flakeboard, to particleboard, and, finally, to fiberboard. These new products introduced new concepts of to be learned and understood such as adhesion, stress transfer, and VOC (volatile organic compound) emissions, and required new standards and codes.

The biggest advantage of the fiber level is that most defects have been removed from the resource, you have more consistency in the resource, you have the ability to form products In any shape you desire, and you have easy access to the cell wall for modification. Solid and flat sheets are no longer limits in fiber-based technologies.

We are not limited to just one type of lignocellulosic fiber-based resource. The world is full of many varieties of renewable natural fibers (see Table 1). We are no longer limited by shape, density, size, or texture. New product lines become possible, such as geotextiles, filters, sorbents, structural composites, non-structural composites, molded products, packaging, and combinations with other resources,

For many applications, lignocellulosic fiber composites can be used with nothing more than a better understanding of the materials science and chemistry of the resource with respect to the desired application. However, in cases of use in adverse environments, performance properties need to be improved if lignocellulosic materials are to be used for long term applications. The natural degradation reactions must be prevented to increase the lignocellulosic fiber composite useful lifetime.

Table 1. Dimensions and chemical composition of some common agro-fibers

Type of Fiber	Cellulose (%)	Lignin (%)	Fiber Dimension (mm) Mean Length	Mean Width
Cotton	85-90	0.7-1.6	25	0.02
Seed Flax	43-47	21-23	30	0.02
Hemp	57-77	9-13	20	0.022
Abaca	56-63	7-9	6.0	0.024
Coniferous Wood	40-45	26-34	4.1	0.025
Sisal	47-62	7-9	3.3	0.02
Bamboo	26-43	21-31	2.7	0.014
Kenaf	44–57	15-19	2.6	0.02
Jute	45-63	21-26	2.5	0.02
Esparto	33-38	17-19	1.9	0.013
Papyrus	38-44	16-19	1.8	0.012
Sugar cane Bagasse	32-37	18-26	1.7	0.02
Cereal straw	31-45	16-19	1.5	0.023
Corn straw	32-35	16-27	1.5	0.018
Wheat straw	33-39	16-23	1.4	0.015
Rice Straw	28-36	12-16	1.4	0,008
Esparto	42-54	17-19	1.2	0.013
Deciduous wood	38-49	23-30	1.2	0.03
Coir	35-62	30-45	0.7	0.02

Listed by Increasing mean fiber length

Properties such as dimensional instability, flammability, biodegradability, and degradation caused by acids, bases, and ultraviolet radiation are all a result of chemical degradation reactions (hydrolysis, oxidation, dehydration, and reduction) which can be prevented or, at least, slowed down if the cell well chemistry is altered. This approach is based on the premise that the properties of any resource are a result of the chemistry of the components of that resource. In the case of lignocellulosic resources, cell wall polymers, extractives, and inorganics are the components that, if modified, would change the properties of the resource. Based on performance requirements, chemical modifications can be carried out to change the chemistry of the resource which will result in a change in performance. The desired performance changes may be to improve dimensional instability, decay resistance, ultraviolet resistance, chemical resistance, and/or thermal stability. The chemistry can also be changed for thermoplasticity, hardness, toughness, appearance, density, sound insulation, and many other performance properties. All of this

chemistry is targeted to change or improve some specific performance requirement resulting in composites that are designed for Improved performance.

Chemical modification is 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. In general, the chemicals used 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.
Many chemicals have been used including anhydrides, acid chlorides, ketene carboxylic acids, isocyanates, aldehydes, b-propiolactone, acryionitrile, epoxides, [1-3].
By far, the most research has been done on the reaction of acetic anhydride with cell wall polymer hydroxyl groups in lignocellulosics to give an acetylated fiber (Fig 1). This one modification will be used as an example of the changes that can take place using a simple chemical reaction system on pine fibers.

Wood-OH + $CH_3C(=O)-O-C(=O)-CH_3$ --—>
Wood -O-C(=O)-CH3 + $CH_3C(=O)-OH$

Fig 1. Reaction of acetic anhydride with wood.

By replacing some of the hydroxyl groups on the cell wall polymers with acetate groups, the hygroscopicity of the lignocellulosic material is reduced. Table 2 shows the reduction in equilibrium moisture content (EMC) of pine wood fibers that have been acetylated using acetic anhydride.

Table 2. EMC of acetylated pine fiber

	Weight Percent Gain	EMC at 27C (%)		
		30% RH	65% RH	90% RH
Control	0	5.8	12.0	21.7
Acetylated	20.4	2.4	4.3	8.4

Changes in dimensions, especially in thickness and in linear expansion, are a great problem in lignocellulosic composites. Reaction of the fiber with acetic anhydride before fiberboard production results in a fiberboard that swells much less in water compared to an un-modified control (Table 3).

Table 3. Thickness swelling of pine fiberboard after 5 days of water soaking (Phenolic resin,

	Increase in thickness (%)
Control	24.9
Acetylated	2.6

Acetylation also greatly Improves the resistance to both brown- and white-rot fungi (Table4).

Table 4. Biological resistance of acetylated pine against brown- and white-rot fungi

	Weight Loss After 12 Weeks	
	Brown-rot Fungus	White-rot Fungus
	……%……	
Control	53	7
Acetylated	<2	<2

There is very little change in the mechanical properties of pine fiberboards due to the acetylation (Table 5.

Table 5. Mechanical properties of pine fiberboards (900 Kg/m^3) made from control and acetylated fiber (10% phenolic resin.

	MOR (MPa)	MOE (GPa)	IBS (MPa)
Control	53	3.7	2.3
Acetylated	61	4.1	2.3

MOR - Modulus of rupture
MOE - Modulus of elasticity
IBS - Internal Bond Strength

Control or chemically modified fibers can be formed into flexible mats by several techniques such as carding, thermobonding or needle punching. In carding, the fibers are combed, mixed and physically entangled into a felted mat. In thermobonding, a meltable mastic is added to the fiber matrix to form a mat which is held together by thermowelding. A needle punched mat is produced in a machine which passes a randomly formed machine made web through a needle board in which the fibers are mechanically entangled. The density of this type of mat can be controlled by the amount of

fiber going through the needle board or by Overlapping needled mats to give the desired density. During any one of these mat forming technologies, an adhesive can be added by dipping or spraying of the fiber before mat formation or added as a powder during mat formation. The mat is then shaped and densified by pressing in a hot press using a mold of the desired shape in the press. Within certain limits, any size, shape, thickness, and density is possible.

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

Products having complex shapes can be produced using flexible chemically modified fiber mats. Within certain limits, the mats can be pressed into any desired shape, size, thickness, and density.

Lignocellulosic fibers can also be combined with other resources such as plastics, glass, metals and synthetics. The objective is to combine two or more materials in such a way that a synergism between the components results in a new material that is much better than the individual components. All of this technology can be used to make a new generation of performance driven composites.

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