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AGRO-FIBER BASED COMPOSITES: EXPLORING THE LIMITS

Roger M. Rowell

USDA Forest Service, Forest Products Laboratory, Madison, WI and Departments of Biological Systems Engineering, Forestry and The Engineering Research Center for Plasma Aided Manufacturing, University of Wisconsin, Madison, WI

ABSTRACT

In any investigation where you are exploring the limits of a technology, the first task is to define what the limits are and on what they are based. In the area of agro-fiber based composites, there are two general types of limits: One is based on human limits and the second, is based on technological limits of the resource. Included in the human limitations are tradition, misinformation, lack of fundamental scientific knowledge of the resource, and bias. Included in the technological limitations of the resource are physical and chemical properties and testing/evaluation methodologies. Fundamental understanding of the resource, its performance characteristics, chemistry, materials properties, and failure mechanisms are essential. Once we understand, however, we must move on to modifications and manipulations of the chemistry and performance properties before agro-fiber based composites can reach their highest potential.

1. INTRODUCTION

There is a greater awareness of the need for materials in an expanding world population and increasing affluence. It took all of recorded history for the world population to reach 1 billion by 1830. In 1930, it had doubled to 2 billion. While it took one hundred years to increase human population by 1 billion during this time period, at the present rate, the population increases by 1 billion people every eleven years. Agro-based composites provide an opportunity to fill this growing need for materials within an acceptable environmental framework.

We have used agro-based composites, like wood, for so long, as a building material, that we tend to accept its failures and limitations in use. By accepting these failures and limitation, we also limit our expectations of performance, which, ultimately, limits our ability to accept new concepts for improved performance. This is interesting as we have accepted completely new materials such as metal alloys, ceramics, and plastics that have limitations in their performance but we tend to overlook any deficiencies they may have because our expectations of these materials are higher than those we have for agro-based composites. Maybe it is because we think we know everything there is to know about agro-based composites because it is a familiar material used by common people for low cost markets. Agro-based composites have been used by people for centuries and its use is like the old expression, “what was good enough for grandpa, is good enough for me”. If we live by this old saying in the area of materials, we have limited our expectations of agro-based composites to a time long gone while years of advances in chemistry and materials science research have been taking place.

In order to explore the limits of using agro-fiber based composites, we must first explore the limits of our understanding of the chemistry and materials properties of agro-based resources and then explore the limits of the resource itself.

2. LIMITS OF OUR UNDERSTANDING OF THE RESOURCE

One way to determine where each of us are in our understanding of agro-based resources, is to investigate our knowledge base of the resource and where/how we obtained that knowledge. First, we need to determine at what level of understanding we are comfortable with. That is, do you understand agro-based resources at the macroscopic level, microscopic level, or molecular level? Understanding properties and performance are very different at each level. At the macroscopic level, for example, we understand information such as color, texture, defects, and effects of growing conditions on properties. At the microscopic level, we understand vessels, tracheids, rays, pits, resin canals, density, and cell wall architecture. At the molecular level, we understand the chemistry of carbohydrate polymers, such as cellulose and the hemicelluloses, the chemistry of the lignin polymer, the extractives and inorganic, and the matrix the cell wall components are in.

	STRENGTH	DECAY	BURNING	MOISTURE
MACROSCOPIC LEVEL	DEFECTS	ACCESS	COMBUSTION	ACCESS
MICROSCOPIC LEVEL	ARCHITECTURE	ACCESS	VOLATILE	ACCESS
MOLECULAR LEVEL	CELLULOSE POLYMER	RECOG-NITION	PYROLYSIS	H-BONDING

Fig.1 -Properties of agro-based resources at three levels of understanding.

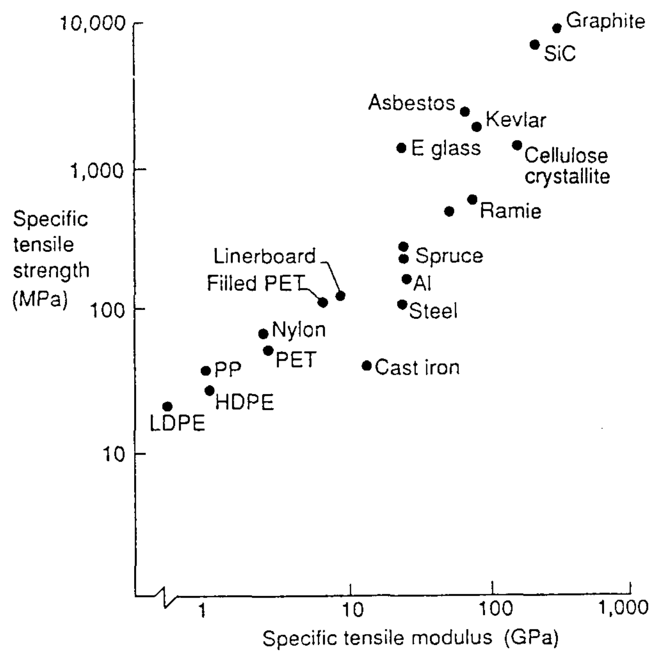

Fig 2- Comparison of specific tensile strength and modulus of various materials.

If we use these levels to investigate, for example, strength properties of agro based resources (Figure 1), we would understand that at the macroscopic level, strength is controlled by defects, at the microscopic level, by cell wall architecture, and at the molecular level, by the matrix and by the high molecular weight, crystalline cellulose polymer. In terms of tensile strength, the cellulose molecule is ten times stronger than a wood fiber which is ten times stronger than a piece of solid wood. With reference to specific tensile strength, the cellulose crystallite is stronger than nylon, steel, and aluminum, similar to e glass and kevlar (Figure 2.)

3. TECHNOLOGICAL LIMITS OF THE RESOURCE

There are many different types of agro-fibers: (1) bast or stem fibers, which are the fibrous bundles in the inner bark of the plant stem running the length of the stem such as jute, flax, hemp, kenaf, ramie, roselle, and urena; (2) leaf fibers, which run the length of leaves such as banana, sisal, henequen, abaca, pineapple, cantala, caroa, mauritius, and phorrnium; (3) seed-hair fibers such as coir, cotton, kapok, and milk weed floss; (4) core, pith or stick fibers, which form the low density, spongy inner part of the stem of plants such as kenaf and jute; and (5) all other plant fibers not included above such as roots, leaf segments, flower heads, seed hulls and short stem fiber.

Agro-based fiber resources have many advantages. They are renewable, widely distributed, recyclable, versatile, easily available in many forms, aesthetic, biodegradable, combustible, compostible, and reactive, and have high strength to weight ratio and good insulation properties (sound and thermal). Some might consider part of these as disadvantages, such as biodegradable and combustible, but these features provide a means of predictable and programmable disposal not easily achieved with other resources.

A single ago-fiber is a three dimensional, hydroscopic composite composed mainly of cellulose, hemicelluloses, and lignin with minor amounts of protein, extractives and inorganic. These fibers were desiemed, 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. In order to expand the use of agro-fiber based composites in adverse environments, it is necessary to interfere with natures recycling chemistry. Before that is possible, it is essential we understand the mechanisms of degradation in order to derive methods to prevent them.

BIOLOGICAL DEGRADATION - Hemicelluloses > Accessible Cellulose > Non-Crystalline Cellulose > Crystalline Cellulose > Lignin
MOISTURE SORPTION - Hemicelluloses > Accessible Cellulose > Non-Crystalline Cellulose > Lignin > Crystalline Cellulose
THERMAL DEGRADATION - Hemicelluoses > Cellulose > Lignin
UTRAVIOLET DEGRADATION - Lignin > Hemicelluloses > Accessible Cellulose > Non-Crystalline Cellulose > Crystalline Cellulose
STRENGTH - Crystalline Cellulose > Matrix [Non-Crystalline Cellulose + Hemicelluloses + Lignin] > Lignin

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Fig. 3 Cell wall polymers responsible for the properties of agro-based resources

Figure 3 shows a summary of the cell wall polymers responsible for loss of performance properties due to environmental degradation chemistries.

Agro-based resources 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. Agro-based composites exposed to moisture frequently are not at equilibrium 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, agro-fiber based composites undergoes cyclic swelling and shrinking as moisture levels change resulting in more severe moisture effects than those encountered under steady moisture conditions.

Agro-based 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 wall content results in weight loss.

Agro-based resources exposed outdoors undergoes 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.

Agro-based resources bum because the cell wall polymers undergo pyrolysis 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.

4. MODIFICATION FOR ENHANCED PERFORMANCE

For many applications, agro-based fiber composites can be used with nothing more than a better understanding of the materials science and chemistry of the resource. However, in cases of use in adverse environments, performance properties need to be improved. The natural degradation reactions must be prevented to increase the agro-based fiber composite useful lifetime.

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 wall 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 agro-based resources, cell wall polymers, extractives, and inorganic are the components that, if modified, would change the properties of the resource. Based on performance requirements, modifications can be carried out to change what needs to be changed to get the desired change in property and, therefore, change in performance.

There are many references to property improvement through chemical modification. In general, two types of modification chemistries have been studied: surface and bulk. Surface modifications change surface properties, such as adhesion, and rate properties, such as moisture sorption, and are usually done using liquid dipping procedures, gas systems, or cold plasma technologies. Bulk modification mainly change equilibrium properties, such as dimensional stability and are usually done using liquid vacuum/pressure technologies. Because of the large surface area, short distance of penetration required, and ease of reagent removal, fiber modifications are easily done. Through a better understanding of the natural degradation chemistries it is possible to greatly improve the performance of agro-based composites in use by tailoring specific chemical reactions to stop the undesirable natural degradations from occurring.

One of the most studied chemistries to improve performance properties of agro-fiber based composites involve reactions with acetic anhydride (acetylation). Chemical modifications of this type react with accessible hydroxyl groups on the cell wall polymers. These are the same hydroxyl group involved in the natural degradation chemistries. The addition of a simple acetate group on the natural fiber changes both rate and equilibrium properties. Table 1 shows a summary of some of the properties changed through this simple chemistry. Moisture sorption

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Agro-based fiber-OH + CH_3-CO-O-CO-CH_3 ---> Agro-based fiber-O-CO-CH_3 + CH_3-CO-OH

Fig 4- Acetylation of agro-based fiber using acetic anhydride.

Table 1 - Equilibrium moisture content (EMC), thickness swelling (TS), biological resistance modulus of rupture (MOR), modulus of elasticity (MOE), and tensile strength (TnS) parallel to the board surface of fiberboards made from control and acetylated pine fiber (8% phenolic resin).

Weight Percent Gain %	EMC and TS at 27C 90% RH EMC %	TS %	Weight Loss After 12 Weeks Brown-rot Fungus %	White-rot Fungus %	MOR MPa	MOE GPa	TnS MPa
0	19.7	29.2	68	7	37.1	3.7	19.0
19.6	8.2	2.7	<2	<2	32.9	3.3	15.6

is greatly reduced as evidenced by a reduced equilibrium moisture content in the cell wall. Cell wall swelling has been reduced by a factor of 10 and attack by both brown- and white-rot fungi has been eliminated. Mechanical properties have been somewhat reduced but not significantly. Many other chemistries have been used with similar results.

Limitation in performance of agro-fiber based composites can be greatly improved through chemical modification techniques. While we apply these chemistries everyday to change the properties of synthetics (textiles, carpeting, etc), we do not apply these same technologies to ago-based resources. We have only begun to explore property enhancement chemistries of agro-fiber based composites.

5. CONCLUSIONS

Limits in the development of high performance composite materials based on agro-fiber resources are mainly due to a lack of understanding of the resource.

Surface and bulk fiber modification can be used to improve adhesion and performance properties of the resource.

High performance adhesives along with fiber modification can be used to manufacture structural ago-fiber based composite materials with uniform densities, durable in adverse environments and high strength.

Chemical modification technology can be tailored to the life cycle of the product.
Products having complex shapes can be produced using flexibly chemically modified fiber mats.

Many products can be made from natural or modified agro-fibers alone. Many other products can be produced which have a natural or modified agro- fibers as a component of the composite.

What are the limits of agro-fiber based composites? Are there any?

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