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A NEW GENERATION OF COMPOSITE MATERIALS FROM AGRO-BASED FIBER

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INTRODUCTION

Agro-based fibers are classified according to what part of the plant they come from. Five different fiber classifications will be used in this report: (1) bast or stem fibers, which are the fibrous bundles in the inner bark of the plant stem running the length of the stem; (2) leaf fibers, which run the length of leaves; (3) seed-hair fibers; (4) core, pith or stick fibers, which form the low density, spongy inner part of the stem of certain plants; and (5) all other plant fibers not included above. Examples of bast or stem fibers include jute, flax, hemp, kenaf, ramie, roselle, and urena. Leaf fibers include banana, sisal, henequen, abaca, pineapple, cantala, caroa, mauritius, and phormium. Seed-hair fibers include coir, cotton, kapok, and milk weed floss. Core fibers represent the center or pith fibers of such plants as kenaf and jute and can represent over 85 percent of the dry weight of these plants. The remaining fibers include roots, leaf segments, flower heads, seed hulls and short stem fiber.

While individual single fibers in all of these classes are quite short (except for flax, hemp, ramie, cotton, and kapok), fiber bundles can be quite long. For example, hemp, jute, and kenaf can have fiber bundles as long as 400 cm and abaca, mauritius, and phormium are about half this length. Considering all plant fiber types, there is a vast array of potential long and short fibers for composite production.

PLANT UTILIZATION FOR COMPOSITES

Scheme 1 shows possible processing pathways that lead to the composite products identified in this report that can come from each fraction of the plant. The entire plant (leaves, stock, pith, roots) can be used directly to produce structural and non-structural composites. By using the entire plant, processes such as retting, fiber separation, fraction purification, etc. can be eliminated which increases the total yield of plant material and reduces the costs associated with fraction isolation. This also gives the farmer a different option in their crop utilization. That is, bringing in the entire plant to a central processing center and not having to get involved in plant processing.

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WHOLE PLANT -------->LONG FIBER ---->MATS
     |          |          |                |
     |          |          Combinations     Filters,
[Fiberize]      PITH       with other       Geotextiles,
     |          |          resources        Packaging,
     |          |                           Molded
     |          |                           composites,
Structural      Sorbents,
Non-structural  Packing,
composites      Light weight composites,
                Insulation
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Scheme 1- Possible processing pathways from each plant fraction.

Another option is to separate the higher value long fiber from the other types of shorter fiber and use it in combination with other materials to make value added structural composites. When the long fiber is separated, the by-product is a large amount of short fiber and pith material that can be used for such products as sorbents, packing, light weight composites, and insulation. By utilizing the by-product from the long fiber isolation process, the overall cost of long fiber utilization is reduced.

The isolated long fiber can then be used to make mats which have value added applications in filters, geotextiles, packaging, molded composites, and structural and non-structural composites.

POTENTIAL COMPOSITES FROM AGRO-RESOURCES

For this report, a composite will be defined as any combination of two or more resources held together by some type of mastic or matrix. Composites can be classified in many ways: by their densities, by their uses, by their manufacturing methods, or other systems. For this report, they will be classified by their uses. Eight different use classes will be covered: (1) geotextiles, (2) filters, (3) sorbents, (4) structural composites, (5) non-structural composites, (6) molded products, (7) packaging, and (8) combinations with other materials Rowell 1993). There is some overlap between these areas. For example, once a fiber web has been made, it can be directly applied as a geotextile, filter, or sorbent or can be further processed into a structural or non-structural composite, molded product, used in packaging, or combined with other resources. Within each composite made there are opportunities to improve the performance of that composite by improving the performance of the fiber going into the composite.

(1) Geotextiles

The long bast or leaf fibers can be formed into flexible fiber mats, which can be made by physical entanglement, nonwoven needling or thermoplastic fiber melt matrix technologies. The two most common types are carded and needle punched mats. In carding, the fibers are combed, mixed and physically entangled into a felted mat. These are usually of high density but can be made at almost any density. A needle punched mat is produced in a machine which passes a randomly formed machine made web through a needle board that produces a mat 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.

Numerous articles and technical papers have been written and several patents have been issued on both the manufacture and use of nonwoven fiber mats containing combinations of textile and lignocellulosic fibers or lignocellulosic fibers alone. This technology is particularly well-known in the consumer products industry. Medium-to high-density fiber mats can be used in several ways. One is for the use as a geotextile. Geotextiles derive their

name from the two words geo and textile and, therefore, mean the use of fabrics in association with the earth.

Geotextiles have a large variety of uses. These can be used for mulch around newly planted seedlings. The mats provide the benefits of natural mulch: in addition, controlled-release fertilizers, repellents, insecticides, and herbicides can be added to the mats as needed. Research results on the combination of mulch and pesticides in agronomic crops have been promising.

The addition of such chemicals could be based on silvicultural prescriptions to ensure seedling survival and early development on planting sites where severe nutritional deficiencies, animal damage. insect attack, and weed problems are anticipated. Medium density fiber mats can also be used to replace dirt or sod for grass seeding around new homesites or along highway embankments. Grass or other type of seed can be incorporated in the fiber mat. Fiber mats promote seed germination and good moisture retention. Low and medium density fiber mats can be used for soil stabilization around new or existing construction sites. Steep slopes, without root stabilization, lead to erosion and loss of top soil.

Medium and high density fiber mats can also be used below ground in road and other types of construction as a natural separator between different materials in the layering of the back fill. It is important to restrain slippage and mixing of the different layers by placing separators between the various layers. Jute and kenaf geotextiles have been shown to work very well in these applications but the potential exists for any of the long agro-based fibers.

(2) Filters

Medium and high density fiber mats can be used for air filters. The density of the mats can be varied, depending on the size and quantity of material being filtered and the volume of air required to pass through the filter per unit of time. Air filters can be made to remove particulate and/or can be impregnated or reacted with various chemicals as an air freshener or cleanser.

Medium to high density mats can also be used as filtering aids to take particulate out of waste and drinking water or solvents.

(3) Sorbents

Tests are presently underway to to use agro-based sorbents to remove heavy metals, pesticides, and oil from rain water run off in several cities in the United States. Medium and high density mats can also be used for oil spill clean up pillows. It has been shown that agro-based core material from kenaf will preferentially sorb oil out of sea water when saturated with water. There are many other potential sorbent applications of agro-fiber/core resources such as removal of dyes. trace chemicals in solvents and in the purification of solvents.

It is also possible to use core materials as sorbents in cleaning aids such as floor sweep. While this is not a composite, as such, but it does represent another way agro-based resources can be used as sorbents.

(4) Structural Composites

A structural composite is defined as one that is required to carry a load in use. In the housing industry, for example, these represent load bearing walls, roof systems, subflooring, stairs, framing components, furniture, etc. In most, if not all cases, performance requirements of these composites are spelled out in codes and/or in specifications set forth by local or national organizations.

Structural composites can range widely in performance from high performance materials used in the aerospace industry down to wood-based composites which have lower performance requirements. Within the wood-based composites, performance varies from multi-layered plywood and laminated lumber to low cost particleboard. Structural wood based composites, intended for indoor use, are usually made with a low cost adhesive which is not stable to moisture while exterior grade composites use a thermosetting resin that is higher in cost but stable to moisture.

Performance can be improved in wood-based as well as agro-based composites by using chemical modification techniques. fire retardant and/or, decay control chemicals, etc.

(5) Non-Structural Composites

As the name implies, non-structural composites are not intended to carry a load in use. These can be made from a variety of materials such as thermoplastics, textiles, and wood particles, and are used for such products as doors, windows. furniture, gaskets, ceiling tiles. automotive interior parts, molding, etc. These are generally lower in cost than structural composites and have fewer codes and specifications associated with them.

(6) Molded Products

The present wood based composite industry mainly produces two dimensional (flat) sheet products. In some cases, these flat sheets are cut into pieces and glued/fastened together to make shaped products such as drawers, boxes, and packaging. Flat sheet wood fiber composite products are made by making a gravity formed mat of fibers with an adhesive and then pressing. If the final shape can be produced during the pressing step, then the secondary manufacturing profits can be realized by the primary board producer. Instead of making low cost flat sheet type composites, it is possible to make complex shaped composites directly using the long bast fiber.

In this technology, fiber mats are made similar to the ones described for use as geotextiles except during mat formation an adhesive is 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 a thermoforming step. Within certainlimits, any size, shape, thickness, and density is possible.

These molded composites can be used for structural or non-structural applications as well as packaging, and can be combined with other materials to form new classes of composites. This technology will be described later.

(7) Packaging

“Gunny” bags made from jute have been used as sacking for products such as coffee, cocoa, nuts, cereals, dried fruits, and vegetables for many years. While there are still many applications for long fiber for sacking, most of the commodity goods are now shipped in containers. These containers are not made of agro-fibers today but there is no reason why they cannot be. Medium and high density agro-based fiber composites can be used for small containers, for example, in the tea industry and for large sea-going containers for commodity goods. These composites cart be shaped to suit the product by using the molding technology described previously or made into low cost, flat sheets and made into containers.

Agro-based fiber composites can also be used in returnable containers where the product is reused several times. These containers can range from simple crease-fold types to more solid, even nestable, types. Long agro-fiber fabric and mats can be overlayed with thermoplastic films such as polyethylene or polypropylene to be used to package such products as concrete, foods, chemicals, and fertilizer. Corrosive chemicals require the plastic film to make them more water resistant and reduce degradation of the agro-based fiber. There are also many applications for agro-based fiber as paper sheet products for packaging. These vary from simple paper wrappers to corrugated, muti-folded, multi-layered packaging.

(8) Combinations with Other Resources

It is possible to make completely new types of composites by combining different resources. It is possible to combine, blend, or alloy leaf, bast and/or stick fiber with other materials such as glass, metals, plastics, and synthetics to produce new classes of materials. The objective will be 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.

Agro-based fiber/glass fiber composites can be made using the glass as a surface material or combined as a fiber with lignocellulosic fiber. Composites of this type can have a very high stiffness to weight ratio. The long bast fibers can also be used in place of glass fiber in resin injection molding (RIM) or used to replace, or in combination with, glass fiber in resin transfer molding (RTM) technologies. Problems of dimensional stability and compatibility with the resin must be addressed but this could also lead to new markets for

property enhanced agro-based materials.

Metal films can be ovedayed on to smooth, dimensionally stabilized fiber composite surfaces or applied through cold plasma technology to produce durable coatings. Such products could be used in exterior construction to replace all aluminum or vinyl siding, markets where agro-based resources have lost market share.

Metal fibers can also be combined with stabilized fiber in a matrix configuration in the same way metal fibers are added to rubber to produce wear-resistant aircraft tires. A metal matrix offers excellent temperature resistance and improved strength properties, and the ductility of the metal lends toughness to the resulting composite. Application for metal matrix composites could be in the cooler parts of the skin of ultra-high-speed aircraft. Technology also exists for making molded products using perforated metal plates embedded in a phenolic-coated fiber mat, which is then pressed into various shaped sections.

Bast or leaf fiber can also be combined in an inorganic matrix. Such composites are dimensionally and thermally stable, and they can be used as substitutes for asbestos composites. Inorganic bonded bast fiber composites can also be made with variable densities that can be used for structural applications.

One of the biggest new areas of research in the value added area is in combining natural fibers with thermoplastics (Sanadi et al 1994,a,b,c). Since prices for plastics have risen sharply over the past few years, adding a natural powder or fiber to plastics provides a cost reduction to the plastic industry (and in some cases increases performance as well) but to the agro-based industry, this represents an increased value for the agro-based component. Most of the research has concentrated on using a compatibilized to make the hydrophore (plastic) mix better with the hydrophil (lignocellulosic). The two components remain as separate phases, but if delamination and/or void formation can be avoided, properties can be improved over those of either separate phase. These types of materials are usually referred to as natural fiber/thermoplastic blends.

Another combination of fiber and thermoplastics is in products that can best be described as fiber-plastic alloys (Rowell et al 1994). In this case the fiber and plastic become one material and it is not possible to separate them. Fiber-plastic alloys are possible through fiber modification and grafting research. This can be done if you consider that agro-based fibers consist of a thermoset polymer (cellulose) in a thermoplastic matrix (lignin and the hemicelluloses). The. glass transition temperature (Tg), however, of the dry natural thermoplastic matrix is higher than the decomposition temperature of the fiber. If the Tg were lowered through chemical modification, it should be possible to thermoplasticize the lignin and possibly the hemicelluloses to be able to do thermomolding at temperatures below decomposition. If a reactive thermoplastic is then reacted with the modified biobased fiber, it should be possible to form fiber/thermoplastic alloys. It is also possible to thermoplasticize cellulose but then the strong, stiff. reinforcing thermoset structure is lost. But, if the cellulose were also plasticized, it would be possible to produce agro-based films and foams.

CHEMICAL MODIFICATION FOR PROPERTY IMPROVEMENT

The performance of any lignocellulosic fiber composite is restricted by the properties of the fiber itself. Agro-based composites will change dimensions with changes in moisture content, be degraded by organisms. be degraded by ultraviolet radiation. and burn. If these negative properties of the natural fiber can be improved, all types of agro-based composites could have greatly improved performance. To understand how agro-based fiber can be used in property enhanced composites. it is important to understand the properties of the components of the cell wall and their contributions to fiber and fiber composite properties.

All agro-based fibers are three-dimensional. polymeric composites primarily made up of cellulose, hemicelluloses, lignin, and small amounts of extractives and ash. The cell wall polymers and their matrix make up the cell wall and in general are responsible for the physical and chemical properties of the agro-based fiber. Properties such as dimensional instability, flammability, biodegradability, and degradation caused by acids. bases, and ultraviolet radiation are a result of the environment trying to convert the natural composites back into their basic building blocks (carbon dioxide and water).

Composites made from agro-based resources change dimensions 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 major roles. Moisture swells the cell wall, and the fiber 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 fiber shrinks as it loses moisture.

Agro-based composites 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 fiber cell wall because crystalline cellulose is primarily responsible for the strength of the cell wall. Strength is lost as the cellulose polymer undergoes degradation through oxidation, hydrolyses, and dehydration reactions. The same types of reactions take place in the presence of acids and bases.

Agro-based composites 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. 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.

Agro-based composites bum because the cell wall polymers undergo pyrolysis reactions with increasing temperature to give off volatile, flammable gases. The hemicellulose and cellulose polymers are degraded by heat much before the lignin is. The lignin component contributes to char formation, and the charred layer helps insulate the composite from further thermal degradation.

Because the properties of the agro-based fiber 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 (Rowell 1983, 1990)

Dimensional stability can be greatly improved by bulking the fiber cell wall either with simple bonded chemicals or by impregnation with water soluble polymers. For example, acetylation of the cell wall polymers using acetic anhydride produces a fiber composite with greatly improved dimensional stability and biological resistance The same level of stabilization can also be achieved by using water-soluble phenol-formaldehyde polymers followed by curing.

Biological resistance of fiber-based composites can be improved by several methods. Bonding chemicals to the cell wall polymers increases resistance due to the lowering of the equilibrium moisture content point below that needed for microorganism attack and by changing the conformation and configuration requirements of the enzyme-substrate reactions. Toxic chemicals can also be added to the composite to stop biological attack. This is the basis for the wood preservation industry.

Resistance to ultraviolet radiation can be improved by bonding chemicals to the cell wall polymers, which reduces lignin degradation, or by adding polymers to the cell matrix to help hold the degraded fiber structure together so water leaching of the undegraded carbohydrate polymers cannot occur. Fire retardants can be bonded to the fiber cell wall to greatly improve the fire performance of composites. Soluble inorganic salts or polymers containing nitrogen and phosphorus can also be used. These chemicals are the basis of the fire retardant wood treating industry.

The strength properties of a fiber composite can be greatly improved in several ways. The finished composites can be impregnated with a monomer and polymerized in situ or impregnated with a preformed polymer. In most cases the polymer does not enter the cell wall and is located in the cell lumen. By using this technology, mechanical properties can be greatly enhanced. For example, composites impregnated with acrylates, methacrylate, epoxy, or melamine monomers and polymerized to weight gain levels of 60 to 100 percent, show increases (compared to untreated controls) in density of 60 to 150 percent, compression strength of 60 to 250 percent, and tangential hardness of 120 to 400 percent. Static bending

tests show increases in modulus of elasticity of 25 percent, modulus of rupture of 80 percent, fiber stress at proportional limit of 80 percent, work to proportional limit of 150 percent, and work to maximum load of 80 percent, and at the same time a decrease in permeability of 200 to 1,200 percent.

CONCLUSIONS

Fiber from a wide variety of plants can be used to produce a wide variety of composites. These composites range from value added speciality products to very large volume commercial materials. High performance composite materials with uniform densities, durability in adverse environments, and high strength can be produced by using ago-based fiber, high performance adhesives, and fiber modification to overcome dimensional instability, biodegradability, flammability, and degradation caused by ultraviolet light, acids, and bases. Products with complex shapes can also be produced using flexible fiber mats, which can be made by nonwoven needling or thermoplastic fiber melt matrix technologies. Taking advantage of fiber cell wall modification chemistry and combining bast fiber with other materials provides a strategy for producing advanced composites and materials that take advantage of the enhanced properties of all types of materials, and it allows the scientist to design materials based on end use requirements within the framework of cost, availability, renewability, recyclability, sustainability, energy use, and environmental considerations.

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