OPPORTUNITIES FOR VALUE-ADDED BIO-BASED COMPOSITES

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ABSTRACT

There are many opportunities to add value to biobased composites. Improving properties within a framework of cost effectiveness is the most obvious. Improving dimensional stability alone can lead to many new options for biobased composites. If other property improvements can be achieved, such as biological resistance, resistance to ultraviolet degradation, fire resistance, and greater stability in acid and base conditions, in a cost effective way, even more markets could open up. One very attractive line of current research is to improve properties through chemical modification. This chemistry can be done as a separate processing step or done during the thermo-pressing process so that all chemistry and molding can be done in one step. If properties can be adjusted so that a consistent, predictable, uniform, and reproducible material can be produced, biobased fiber could be used in place of many higher priced non-renewable fiber. Biobased fiber can be blended or alloyed with other material to produce an entirely new generation of composites: biobased/plastics, biobased/glass, biobased/metal, and biobased/synthetic fiber. Another option to add value to biobased composites is to optimize performance through the use of a wide variety of biobased fiber options. Many long agricultural fibers could provide improved strength to complex shaped composites as well as substitute for fiber glass in technologies such as resin transfer molded products.

INTRODUCTION

From my perspective as a researcher, I would like introduce four basic concepts in considering value added biobased composites. The way each person or company evaluates these concepts will determine their attitudes in this field. The first consideration is a concept of composite versus material, the second is the type of composite or material, the third is flat sheet versus shaped technologies, and the fourth is market opportunities for composites or materials. I feel that many decisions concerning value added composites have been made without fully considering the implications of these concepts. I would like to explain and expand on each of these four concepts in this paper.

The implications of these four concepts are that in order to seriously consider value added products in the biobased industries, there must be a fundamental change in research planning, product consideration, and marketing. Those changes must focus on materials rather than composites, materials that are performance-driven rather than price-driven, materials that are shaped in the press, and products targeted for non-traditional wood markets. This does not imply that traditional markets for reconstituted wood products would or should change. I only want to point out that value added thinking requires a completely different set of considerations than are presently used in the traditional production and marketing of wood products. There will always be markets for solid wood and commodity wood composites, but there are many opportunities for new value added biobased materials.

I will use the terms wood, lignocellulosic, and biobased interchangably in this paper to remind the reader that wood is not the only fiber source available to the wood industry. In spite of problems associated with storage, the time of harvesting, the regional nature of some crops, and the bulky, low density of many different types of biobased fiber, agricultural, waste, and recycled fiber can enhance an overall product strategy by combining fibers of different aspect ratios.

COMPOSITES OR MATERIALS

The first concept can be described in two simple definitions: A composite is a reconstituted product made from a combination of two or more substances using some kind of a mastic to hold the components together. A material is a substance (could be a composite) with consistent, uniform, continuous, predictable and reproducible properties [Caulfield and others 1990, Rowell and others 1992]. Using these definitions, the reconstituted wood industry is more in tune with concepts in composites rather than materials. Wood composites such as flake-, strand-, and particleboards are not homogenous so their properties vary within each board. Fiberboards are much more consistent in properties within each board and come the closest to a biobased material.

It is interesting to note that information on wood and other lignocellulosics is not included in most university courses in materials science. While this may seem strange, considering wood is one of the most common "materials" used for building, the fact that it is perceived as not being consistent, uniform, etc., has kept it out of most academic considerations. Most materials science classes deal mainly with metals, and to a lesser extent, ceramics, glass, and plastics, depending on the background of the professor.

While solid wood may never be accepted as a material as defined earlier because of its inconsistent properties, bio-based fiber conceivably can conform to the definition of a material. By converting wood and other lignocellulosics into fiber, knots, splits, checks, cracks, twists, bends, etc., are removed and sapwood, heartwood, springwood, latewood, etc., are mixed to produce, a consistent fiber furnish.

Even given the possible uniformity that can be derived from a fiber composite, problems still exist both in the academic community and among the general public about the acceptance of lignocellulosic composites. In the early days of wood composites, products such as particleboard developed a bad reputation mainly due to failures in fasteners and to swelling under moist conditions. This led to public skepticism about the use of wood composites. The markets that were developed for wood composites were all price driven with few claims for performance. For the most part, this is still true even though much of the more expensive furniture, for example, is made from veneered composites in which higher performance is gained by using composite cores.

In a broad sense, the general public remains skeptical about the use of adhesives. Since they have personal experience with hammer and nails (and screws), they tend to put their trust in mechanical fastners rather than "glues". This is another preception that must be changed in order for wood composites to truly emerge as materials. This perception is not only held by the general public but in the minds of many wood products people.

PRICE- VERSUS PERFORMANCE-DRIVEN COMPOSITES

Composites and materials can be grouped into two basic types: price-driven, for which costs dictate the markets, and performance-driven, for which properties dictate the markets. In general, the wood industry has produced the price-driven or commodity types of composites where low cost is the main concern. There are many opportunities for performance-driven or value-added composites and materials but the mind set of low cost (i.e. low performance) must be readjusted to fit into a materials framework along with other materials i.e. plastics, glass, metals, and synthetics.

If a biobased fiber is blended with a high performance adhesive, very uniform lignocellulosic composites (approaching materials) can be produced. However, properties such as dimensional instability, flamability, biodegradability, and degradation due to acids, bases, and 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 for the targeted performance-driven materials market, then the properties must be changed, improved, or redesigned so that it does meet end use materials expectations. While such changes are made everyday in such industries as textiles, plastics, glass, and metals, it is rarely done or even considered in the lignocellulosic industries.

Chemical modification of lignocellulosics

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 [Rowell and Konkol 1987, Rowell and Youngs 1981, Rowell 1983, Rowell 1992].

Dimensional stability can be greatly improved by bulking the lignocellulosic cell wall either with simple bonded chemicals or by impregnation with water soluble polymers [Rowell and Youngs 1981]. For example, acetylation of the cell wall polymers using acetic anhydride produces a lignocellulosic composite with a dimensional stability of 90 to 95 percent as compared to a control composite [Rowell and others 1986]. The same level of stabilization is achieved by using water-soluble phenol-formaldehyde polymers followed by curing [Rowell and Youngs 1981].

Biological resistance 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 [Rowell and others 1988]. Toxic chemicals can also be added to the lignocellulosics 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 [Rowell 1984].

Fire retardants can be bonded to the lignocellulosic cell wall to greatly improve the fire performance of lignocellulosic composites [Rowell 1984]. 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 lignocullulosic composite can be greatly improved in several ways. Lignocellulosic 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 [Rowell 1984]. For example, composites impregnated with methyl methacrylate 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.

There are already examples of the application of chemical modification in the wood industry today. Japan is clearly the leader in this field. Daiken Trade and Industry Company, Ltd., produces a product called "alpha-wood" which is an acetylated wood used in high performance sound system speakers, bath tubs, and bathroom doors. Another acetylated product combined with an in situ polymerized organic monomer is marketed for kitchen floors and for use in high-class flooring for heavy traffic walkways. Acetylated fiber is now in a pilot plant study in both the United Kingdom and Sweden to product exterior grade commercial siding, doors and windows, interior automobile parts, and furniture. There is a great deal of continuing research in Japan, United Kingdom, Sweden, Denmark, Netherlands, United States, China, Canada, New Zealand, and Germany to improve the properties of lignocellulosics through chemical modification.

The real break through in chemical modification will come when the changes in chemistry can be performed during the hot pressing process. This will greatly simpify the process and reduce the time and costs needed for the modification. Continuous process chemical modifications will also help reduce time and costs. These are presently under study in Japan [Hongo 1990] and the United Kindgom [Sheen 1992].

Lignocellulosics in combination with other materials

Before 1980, the words blend and alloy were essentially unknown in the plastics industry. Today, there are more than 1000 patents relating to plastic blends and alloys and it is estimated that one out of every five kilograms of plastic sold is an alloy or blend [Wigotsky 1988]. In the plastic industry, the word blend is defined as a mechanical mixture of two or more plastics and an alloy is an actual molecular bonding of the chemical elements within the plastics. Blends and alloys have revolutionized the plastics industry as they offer new materials with properties never before available and materials that can be tailored for specific end uses. The same opportunities for new materials and markets are available to the biobased industries if they are willing to take the risks in research and marketing.

It is possible to combine, blend, or alloy lignocellulosics with other materials such as glass, metals, plastics, and synthetics to produce a completely new class of materials [Youngquist and Rowell 1989]. 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. For example, a dimensionally stabilized wood fiber could be combined with other stable materials to form light weight. stiff, durable engineering materials. This concept is only viable if one considers that the wood fiber can be stabilized and the resulting products can be marketed in a cost effective way as performance-driven materials.

One of the biggest new areas of research in the value added area is in combining lignocellulosics with thermoplastics. Since prices for plastics have risen sharply over the past few years, adding a lignocellulosic powder or fiber to plastics provides a cost reduction to the plastic industry (and in some cases a performance reduction as well) but to the lignocellulosic industry, this represents an increased value for the biobased component.

Combining lignocellulosics with thermoplastics can be done in several ways. In one case, thermoplastics are simply mixed with biobased powder or fiber (nut shell powder or wood fiber are presently used) and the mixture heated. The plastic melts, but the wood fiber and plastic components remain as distinct separate phases. One example of this technology is reinforced thermoplastic composites, which are light weight, have improved acoustical, and heat reformability properties, and cost less than comparable products made from plastic alone. These advantages make possible the exploration of new processing techniques, new applications, and new markets in such areas as packaging, furniture, housing, and automobiles.

A second way to combine wood fiber and plastics is to use a compatibilizer to make the hydrophobe (plastic) mix better with the hydrophil (wood). 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 wood fiber/plastic blends.

A final combination of wood fiber and thermoplastics is in products that can best be described as wood-plastic alloys. In this case the wood and plastic have become one material and it is not possible to separate them. Wood-plastic alloys are possible through fiber modification and grafting research. This can be done if you consider that biobased fibers consist of a thermoset polymer (cellulose) in a thermoplastic matrix (lignin and the hemicelluloses). The glass transition temperature (GIT), however, of the thermoplastic matrix is higher than the decomposition temperature of the fiber. If the GIT were lowered through chemical modification, it should be possible to thermoplasticize the lignin and the hemicelluloses at temperatures below decomposition. If a reactive thermoplastic is then reacted with the modified biobased fiber, it should be possible to form biobased fiber/thermoplastic alloys. Chemical modifications using neat maleic and succinic anhydrides result in thermoplasticization of the biobased fiber [Rowell and Clemons In Press]. Results indicate that only the hemicelluloses and lignin have been modified. It is also possible to thermoplasticize cellulose but then the strong, stiff. re-inforcing thermoset structure is lost. But, if the cellulose were also plasticized, it would be possible to produce lignocellulosic films and foams [Matsuda 1985, Hon 1989, Shiraishi 1991].

Metal films can be overlayed on to smooth, dimensionally stabilized lignocellulosic fiber composite surfaces or applied through plasma technology to produce durable coatings. Such products could be used in exterior construction to replace all aluminum or vinyl siding, markets where wood has lost market share. Metal fibers can also be combined with stable biobased 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 wood fiber mat, which is then pressed into various shaped sections.

Wood-glass 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. Long biobased fibers such as jute and kenaf can be used to replace or in combination with glass fiber in resin transfer molding (RTM) technology. Problems of dimensional stability and compatibility with the resin must be addressed but this could also lead to new markets for property enhanced biobased materials.

FLAT VERSUS SHAPED COMPOSITES

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. If the final shape can be produced during the pressing step, then the secondary manufacturing profits can be realized by the primary board producer. This is another way to achieve a value added product.

Flat sheet lignocellulosic fiber composite products are made by making a gravity formed mat of fibers with an adhesive and then pressing. This technology can be used to make value added products as described earlier. However, there are opportunities to form complex shaped, deep drawn composites by first making a nonwoven mat which can be pressed into composites of any desired size and shape.

Nonwoven mat technologies involve room temperature air mixing of lignocellulosic fibers with a long binder fiber which can be a biobased fiber such as jute, cotton, or kenaf, a synthetic fiber such as a polyester, or a thermoplastic fiber. The resultant mixture passes through a needling step that produces a low-density mat in which the fibers are mechanically entangled. The mat is then shaped and densified by a thermoforming step. With this technology, the amount of lignocellulosic fiber can be greater than 90 weight percent. In addition, the lignocellulosic fiber can be precoated with a thermosetting resin: for example, phenol-formaldehyde.

Numerous articles and technical papers have been written and several patents have been issued on both the manufacture and use of nonwoven fiber webs containing combinations of textile and lignocellulosic fibers. This technology is particularly well-known in the consumer products industry. For example, Sciaraffa and others [1982] were issued a patent for producing a nonwoven web that has both fused spot bonds and patterned embossments for use as a liner material for disposable diapers. Brooks [1990] published a review of the history of technological development for the production and use of moldable wood products and air-laid, nonwoven, moldable mat processes and products.

There are opportunities for value added biobased composites using the nonwoven mats themselves. One interesting application for low-density fiber mats is for mulch around newly planted seedlings (geo-textiles). 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 [Crutchfield and others 1985]. 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. Low-density fiber mats can also be used to replace dirt or sod for grass seeding around new homesites or along highway embankments. The grass seed can be incorporated in a wood or jute fiber mat. Fiber mats promote seed germination and good moisture retention. High-density fiber mats can be used for air filters or other types of filters. The density of the mats can be varied, depending on the material being filtered and the volume of material that passes through the mat per unit of time. Medium and high density mats can also be used for oil spill clean up pillows.

These same mats can be formed using a chemically modified fiber with a high performance adhesive to produce value added shaped materials. Products can be produced for use as interior automotive parts, reusable (and nestable) packaging of high cost products, construction materials for wall, flooring, and ceilings of modular housing, and many other applications. It also possible to combine other materials in this technology as was suggested earlier. Exterior automotive parts, for example, could be made by combining a glass fiber surface (made from a glass fiber mat) with a stable/compatibilized biobased core.

NEW MARKETS FOR COMPOSITES

Finally, when considering "new" markets for wood-based composites, the wood industry mainly considers replacing one wood product with the new wood product rather than consider markets where wood has lost to other materials or markets that wood has never been in before. I call this the industrial wooden pie . . . make one piece bigger by making another piece smaller. We need to make the whole pie bigger!

I have given examples in this paper where new markets can be created for value added biobased composites and especially biobased performance driven materials. Until about the 1920's. we relied almost completely on wood, brick, and steal for our materials. Since then, modern metal, glass and petroleum technologies have emerged to give us materials such as high carbon and stainless steel, structural aluminum alloys, organometalics. ceramics, and various plastics. These have become the materials of choice for performance driven applications. It is possible to use property enhanced, shaped biobased materials to replace or combine with these materials to create new markets. This will require vision, creativity, planning, and conviction on the part of the wood industry for this to become a reality.

CONCLUSIONS

There must be a paradigm change in the wood industry in order to make changes necessary to shift from a largely commodity based industry to enlarge their share of value added markets. Changes must focus on considerations of many different types of biobased fibers for product diversification, materials rather than composites, materials that are performance-driven rather than price-driven, materials that are shaped to final form in the press, and products targeted for non-traditional wood markets.

Taking advantage of lignocellulosic cell wall modification chemistry and combining lignocellulosics 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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