TECHNOLOGY SUMMARIES

In an effort to increase benefits to all CELL division members, including those who are not able to attend the national meeting, we will feature Technology Summaries in the division newsletters. These summaries are written by experts in their respective Gelds and are intended to be a brief overview of the state-of-the-art in a specific topical area. If you have specific technical areas that you would like to see reviewed or if you are willing to write a brief technology summary please contact Tor P. Schultz, Forest Products Lab, Mississippi State University, Mississippi State, MS 39762-9820, Phone (601) 325-3136. E-mail: schultz@fpl.msstate.edu

The attached review is in the area of lignocellulosic/plastic composites, and is authored by Anand Sanadi (University of Wisconsin-Madison), and Daniel Caulfield and Roger Rowell (USDA-Forest Products Laboratory). For further information, contact Dr. Sanadi at: e-mail: arsanadi@facstaff.wisc.edu; fax: 608-231-9262; or phone: 608-231-9421.

LIGNOCELLULOSIC/PLASTIC COMPOSITES

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Newer materials and composites that have both environmental and economic benefits are being developed for applications in the automotive, building, furniture and packaging industries. Agro and forest resources have always played an important role in the plastics industry. The earliest phenolic products were filled with wood flour to lower the cost and improve the processibility of the resin. Enormous quantities of agro-wastes have subsequently been used as fillers in thermosets.

The use of lignocellulosics as fillers and reinforcements in thermoplastics has been gaining acceptance in commodity plastics applications in recent years. It is interesting to point out that the interest in using lignocellulosics as fillers and reinforcement in plastics is not new, and there are plenty of published papers and patents dating back several decades. The resurgence of interest in the 1990s is probably due to increasing plastic costs, and environmental aspects of using renewable materials. Automotive interiors using wood flour-polypropylene composites have been produced commercially since the mid- 1970s. In this case the wood flour acts as a filler, where no significant strengthening benefit is achieved. In all probability, this figure is likely to increase as a deeper understanding of the interaction between the lignocellulosics and non-polar plastics is reached and these materials are used as reinforcements (and not just as a filler) in thermoplastics. If proper techniques are developed whereby greater volume fractions of agro-based materials can be incorporated, without sacrificing property enhancement, there will be considerable potential for the large scale use of these composite materials. An added benefit is the potential for recycling the materials, by re-processing the products for the same r related applications. These materials are low cost, lower density than conventional non-renewable inorganic filler/reinforcements. Fundamental knowledge of agro-materials thermoplastic composites and appropriate processing techniques will make it possible to &place some glass fiber applications with these environmentally acceptable agro-materials. The use of thermoplastics as the matrix instead of thermosets adds the potential of product recycling. Although thermoplastics have their limitations due to their tendency to creep and therefore limited load bearing ability, they have unique processing advantages and do not have the volatile emissions associated with formaldehyde based adhesives.

In general lignocellulosics can be classified into two categories, particulate and fibrous. Particulates have an aspect ratio (ratio of the length to diameter) of approximately unity. In general no significant strengthening is expected, although the elastic modulus and some other properties may be improved. Wood flour, ground rice hulls, ground corncob, etc. can be classified as particulate. Fibers can be considered to be short when the aspect ratios vary between that of the particulates and that of continuous fibers. Wood fibers are the most widely used short fibers, but can also be obtained from agro-bases from different parts of the plant such as bast, seed or leaf fibers. The actual strengthening benefit to the composite due to the fibers will depend on the stress transfer efficiency from the matrix to the fibers. The stress transfer efficiency varies according to the fiber length distribution present in the composite and the type of fiber- matrix interfacial interactions occurring.

A recent conference "Wood-Plastics Conference" held in Madison, WI, dealt exclusively on the combination of lignocellulosics with polymers, and fundamental and applications were concurrently held and a summary of the proceedings follows.

FIBER RESEARCH

A significant amount of the work on lignocellulosic- thermoplastic composites has been on the use of wood flour or pulp fibers. Processing generally leads to significant fiber breakage resulting in very short fibers which do not reach their full reinforcing potential. Attempts to maximize wood-fiber lengths are underway for such composites. although the maximum possible reinforcement is limited due to the low initial lengths of wood fibers.

Non-wood, agro-based bast fibers have the advantage of being available in long fiber strands (bundles), where the individual ultimate fibers, are in general longer than wood fibers, and are held together in a matrix of natural polymers. The use of these long fiber strands, will afford the possibility of longer fiber reinforcement and hence improved composite properties. Furthermore, the agro-based fibers, may contribute a significantly different surface chemistry and/or have unique extractives that could affect the processing, compatibility, internal lubrication, and ultimately composite properties. Research at the University of Wisconsin and the Forest Products Laboratory does suggest that kenaf (Hibiscus cannabinus) , a bast fiber, may have some unique chemistry or presence of extractives that help in internal lubrication during the blending process.

As compared to the properties of wood fibers, little is known of the properties of agro-based fibers. Researchers at USDA- Southern Station (Pineville), University of Wales and University of Maine are studying the physical and chemical properties of individual bast fibers. A great deal of damage was observed in the fibers. and that could partially explain the significant variation in properties such as the fiber strength and modulus. The presence of certain types of extractives of the different agro-based fibers could affect the processing, compatibility and internal lubrication, and ultimately composite properties. It is well known that the presence of moisture effects the properties of the fibers, and recent work at the Silsoe Research Institute also shows evidence of a relationship between te modulus, damage and relative humidity. This could have implications in the separation of fibers from their source (wood, bast, leaf or fruit) to ensure minimum damage.

PROCESSING

The processing of fiber/thermoplastic composites involves heating the thermoplastic to above its melting point and providing sufficient shearing agitation to ensure intimate mixing between fiber and plastic matrix. the heating and shearing action may be accomplished by a number of different types of plastic processing equipment. Much of the initial research has involved the use of extruders and thermokinetic mixers. In thermokinetic mixers, a unique processing equipment that may be suitable for blending lignocellulosic with commodity plastics, the shearing action of the high speed impeller blades generates sufficient heat to both melt and mix the blend. But the commercialization of fiber/plastic composites has developed almost exclusively with the utilization of plastic extrusion technology. There are already several commercial enterprises in the business of selling compounded woodfiber/plastic composite manufactured on extruders. These businesses were represented at the conference.

Although both heat and agitation are necessary for compounding thermoplastics and fibers, both the heat and the shearing action can have detrimental effects on the incorporated fibers. Although heating to above the melting point of the thermoplastic may be necessary, exposure of the fibers to the pyrolytic, degrading effects of heat should be minimized. This usually requires processing at temperatures lower than those conventionally used with neat polymers or with inorganic-filled polymers. Because of the high temperatures employed, and the moisture sensitivity of cellulosic fibers, pre-drying of fibers prior to compounding (or other moisture control methods) are necessary.

The shearing action which is necessary for intimate mixing of fiber/ thermoplastic composites also has detrimental effects on the fiber-length distribution. Aggressive sharing elements in an extruder can effectively change the reinforcing characteristics of a fiber to those of a non- reinforcing filler. Furthermore, shearing tends to expose new surfaces of the fiber in melt blending techniques, and the level of shearing would determine whether the exposed surface is rich in lignin or hemicellulose.

Maximum reinforcement is gained by incorporating large volume fractions of high modulus fibers in matrices. The requirement for a high volume fraction of fibers poses practical processing difficulties. Although the maximum volume of perfectly aligned cylindrical fibers that can be packed into a composite is theoretically about 91%, in practice lower limits are reached because of the inability of matrix to wet and infiltrate the fibers. Flexible fibers twist and rotate in many complex ways and each fiber effectively occupies an extended volume from which other fibers are excluded. During processing, when two fibers approach, collisions may occur, but fibers need not actually touch in order to affect each others paths. At very low fiber fractions, the whole of the suspension is occupied, and no free rotation is possible. Interaction between fibers is evidenced in the final composite in two ways: fiber alignment and fiber clumping. As the concentration of fibers increases, their rotations are affected, and fibers even at low concentrations under shear will assume a preferred orientation in the direction of shear. This orientation becomes more apparent as the fiber content increases as the result of the multiple collisions and correlated orientations between fibers. At higher concentrations. fiber clumping occurs.

COMPOSITES

The major factors that govern the properties of the composite are fiber dispersion, fiber length distribution and fiber orientation. It is of great importance that fibers are dispersed uniformly in the plastic. This is sometimes difficult due to the hydrophilic nature of the fibers and the vastly different non-polar plastics such as polyethylene and polypropylene. Clumping and agglomeration must be avoided to produce efficient composites. The efficiency of the composite also depends on the amount of stress transferred to the fibers from the matrix. This stress transfer efficiency can be maximized by improving the interaction and adhesion between the plastic matrix and the fibers, and also by maximizing the fiber length distribution. Using very long fibers during the compounding stage will result in higher fiber length distribution in the final blend. However, long fibers sometimes increase the amount of clumping giving areas that are rich in fibers and areas with excessive matrix; this ultimately reduces the composite efficiency. Uniform fiber dispersion therefore cannot be compromised, and a careful selection of the initial fiber lengths, process conditions and processing aids are needed to obtain good fiber dispersion and optimized fiber lengths.

The stress transfer between the plastic matrix and the fiber depends on several factors including the fiber and matrix surface energetics, interface interaction and the characteristics and properties of the interphase. Interesting work on the surface properly characterization and modification using enzymes is ongoing at the Royal Veterinary and Agricultural University of Denmark. Although wetting analysis is time consuming, and the complexity of the test enhanced due to the non-homogeneous nature of natural fibers, some useful information can be obtained. This information may be pertinent when producing composites using non-woven fiber mats of agro-based and polypropylene fibers that are then compression molding, a practice being used for producing automotive interiors in Europe.

Dynamic mechanical analysis has been used to study the interactions between the fibers and polymer matrix. Work at the Southern Research Station (Forest Service) and Washington State University shows some unique characteristics since the wood fibers are considered as a reactive medium in polyurethanes and have been viewed as interpenetrating networks and work on engineering the interphase to improve composite properties is continuing. Researchers at the University of Kassel (Getmany) are using dynamic mechanical analysis to show the effect of an improved interphase in natural fiber reinforced epoxy when using coupling agents. The importance of having a good interphase to reduce the detrimental effect of moisture is clearly indicated in their work.

The use of maleated polyolefins to improve the adhesion and interaction between the lignocellulosic and polyolefin and composite thereby improve performance is well known. University of Toronto researchers suggest that the improvement in composite properties are due to several factors such as surface energy effects, improved fiber dispersion, improved fiber orientation and improved interfacial adhesion through mechanical interlocking. Toughness improvement, a major need for expanding the use of lignocellulosic/plastic composites is being studied by several groups. Cooperative work between the Forest Products Laboratory and Lulea University of Technology, Sweden, was reported using maleated elastomeric polymers such as ethylene/propylene/diene terpolymers to improvement impact properties in blends of wood flour and polypropylene. The Agrotechnical Research Institute's (ARI, Netherlands) work includes the use of lignocellulosic materials for filling engineered polymers which could increase the use of lignocellulosics in new applications. Engineering polymers need higher processing temperatures. and ARI'S work indicate that the reinforcing effect of the fibers is preserved at processing temperatures of about 260 C. Reaction injection molding of cellulose fiber mats using polyurethanes and various combination with polyureas is being done at Louisiana State University. Significant property enhancement can be achieved when using cellulose fiber mats and research is being conducted to optimizing processing conditions. Higher performance thermoplastics such as styrene-maleic anhydride are also being studied as matrices for lignocellulosics at Oregon State University. The presence of the maleic anhydride group could significantly enhance adhesion between the fibers and matrix although no evidence of any chemical reaction has been observed. Research in Brazil tends to focus on different fibers as reinforcing fibers in plastics and focuses on the automotive industry. It is interesting to note that the Brazilian automotive industry has been utilizing jute-polypropylene composites in automotive applications for several years, and the first composites were made from discarded polypropylene and jute bags that had been used for shipping coffee and green bean.

Considerable work has been done at the Forest Products Laboratory, USDA and the University of Wisconsin. Wood based and agro based polyolefin composites have been studied and this work has resulted in creation of several industries that produce these blends for injection molders. Ongoing studies includes fracture toughness, dynamic mechanical properties, creep and stress relaxation behavior and tailored interphases for property modification. Preliminary work has been conducted on the effect of removing extractives on composites performance, but results are difficult to analyze because of the inherent variability of fiber mechanical properties. The importance of improved interphase properties on long term moisture related effects are again clearly evident. Research is continuing on the effect of particle size of wood flour in order to optimize processing condition and properties.

FUTURE RESEARCH AND UTILIZATION

In the past two decades, considerable interest has been generated in the potential use of biodegradable thermoplastics to help solve some of the problems associated with municipal solid waste; litter and landfill disposal. The high cost of biodegradable thermoplastics, however, has prevented their adoption for packaging and other wide-scale applications, where disposal is expected shortly after a limited useful lifetime. The necessary low-cost nature of disposable products requires both a cost efficient processing system and inexpensive raw materials. Melt- processing (i.e. extrusion and injection molding) of thermoplastic biodegradable polymers that are highly loaded (with cheap biodegradable fillers) affords both an inexpensive process and materials' cost-savings without sacrificing biodegradability. In addition, if the filler consists of suitable agro-fibers, considerable reinforcement of the plastic can be achieved which enhances the mechanical properties of the composite during its useful lifetime. These improved mechanical properties may have the potential for justifying some of the later disposal costs.

Future research goals include using engineering thermoplastics to expand the use of lignocellulosic composites to higher performance applications. Studying and improving the impact toughness, creep, and other long term performance is ongoing, although a great deal of work needs to be conducted before these composites are accepted in more stringent applications. Higher filling levels without significant embrittlement could greatly increase the use of the renewable fibers in composite applications. Initial work at the University of Wisconsin and Forest Products Laboratory suggests that high filling levels, 75 % or more by weight, may be possible although the lack of toughness is a major drawback of these composites. Retaining fiber length is an important aspect of making efficient composites and work is being done in several laboratories. Wood and lignocellulosic fibers are themselves composites, with crystalline cellulose as the reinforcing element in a matrix of lignin and hemicellulose. Thermoplasticization of the lignin-hemicellulose matrix of wood to make a moldable lignocellulosic without the use of an external polymer matrix is an interesting idea Several groups are working in this area, although the real benefit is to develop techniques that do not use environmental hazardous solvents or chemicals to create a moldable lignocllulosic composites.

FUTURE PROGRAMMING

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BOSTON, MA
August 23-28,1998

Four copies of abstract (original on ACS Abstract Form) due April 15, 1998

Cellulosics in Cosmetics and Pharmaceutical Applications. M. El-Nokaly, Procter & Gamble, MVL-ON162, P.O. Box 398707, Cincinnati, OH 45239-8707. Phone: 513-627-1482; Fax: 513-627-0055; R.Y. Lochhead, U. of Southem Mississippi, Hattiesburg, MS 39406-0076. Phone: 601-266-4868; Fax 601-266-5504; e-mail: lochhead@ocean.st.usm.edu

Application of New Imaging Techniques to Lignocellulosic Materials. T.C. Rials, Southern Research Station, 2500 Shreveport Hwy., Pineville, LA 71360. Phone: 318-473-7274; Fax: 318-473-7246.

Polymers from Renewable Resources. (Cosponsored with POLY). K.J. Edgar, Eastman Chemical Company, P.O. Box 511, Kingsport, TN 37662. Phone: 423-229-4396; Fax: 423-229-1434, e-mail: kjedgar@eastman.com

Historic Textile and Paper Materials. J. Cardamone, ERRC, USDA-ARC, 600 Mermaid Lane, Wyndmoor, PA 19038; Phone: 215-233-6680; Fax: 215-233-6795

ANAHEIM, CA
March 21-25, 1999

Anseime Payen Award Symposium
Advances in Analytical Methodologies in Lignocellulose Chemistry. J. Han, USDA Forest Products Lab, One Gifford Pinchot Drive, Madison, WI 53705-2398. Phone: 608-231-9424; Fax: 608-231-9262
Tentative Topics:
Entrepreneurial Opportunities for Biopolymer Technologies (Cosponsored with CARB)
Cyclodextrins and Water Soluable Carbohydrates (Cosponsored with CARB)

NEW ORLEANS, LA
August 22-26, 1999

Biosynthesis and Modification of Polysaccharides. M. Brown, University of Texas, Austin, TX

THE FIBRIL ANGLE

SPRING 1998 NEWSLETTER

CELLULOSE, PAPER, AND TEXTILE DIVISION, of the AMERICAN CHEMICAL SOCIETY

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Schedule of Symposia in Dallas, Texas, March 29-April 2, 1998

CELLULOSE, PAPER AND TEXTILE DIVISION Stephen S. Kelly, Program, Chair					
	Sun.	Mon.	Tues.	Wed.	Thur.
TUTORIAL: Recent Advances in Lignin Chemistry	A,P				
Anselme Payen Award Symposium - Honoring Joseph McCarthy		A,P	A,P	A,P	
Modification and Characterization of Cellulose and Lignocellulosics					A,P

A - technical session in the morning.
P - technical session in the afternoon.
E - Evening poster session

The division's board meeting, which is open to CELL members, will be held at 2:00-6:00 p.m. on Saturday, March 28th. See the CELL home page for the location.