Project Title: Innovative Pulp Fiber-Plastic Composites

GT Project Staff:
Principal Investigator: Art. J. Ragauskas

PROJECT OBJECTIVE:

The primary objective of this program is to develop new, low cost, pulp fiber reinforced thermoplastics suitable for innovative load bearing structural applications. The market potential for pulp in wood fiber reinforced nylons and polyesters exceed 1 billion pounds per year. Fiber reinforced thermoplastic use is growing more than 10% annually. The use of pulps fibers to reinforce structural thermoplastics is economically justifiable as currently, fiber-reinforcing technology is dependent on costly fiberglass (~$0.80/lb). This program directly addresses the technical challenges established in the "Setting the Industry Technology Agenda", (TAPPI Press) in the New Forest Based Materials agenda, with a goal of increasing the returns from processing pulp and wood by at least 20%.

PROJECT BACKGROUND:

This project focuses on developing ***new markets for SW TMP and kraft pulp***. Specifically, pulp used to reinforce thermoplastics to obtain plastic products suitable for structural applications. Currently, most wood fiber reinforced thermoplastics are actually wood flour filled polyolefins (polyethylene and polypropylene).[1] A commercial product called Fiberon® has a flexural strength of 19 MPa (2,800 psi), and flexural modulus of 3.9 GPa (560,000 psi). Since the matrix is recycled polyethylene, it is sensitive to creep. As the filler is wood flour, it is very low strength. Consequently, this commercial material is suitable for deck surfaces but not for the support structure for the deck.[2] The materials developed in this project will be suitable for the support structure. These materials will be suitable for replacing chemically treated wood, which is gradually being removed from the market place.

This project will accomplish this goal by developing low cost pulp fiber reinforced thermoplastics suitable for innovative structural applications. Specifically, these materials require a tensile strength exceeding 70 MPa (10,000 psi) and a tensile modulus exceeding 5 GPa (700,000 psi). In addition, these composites should have low creep, good impact resistance, high service temperature, and resistance to rotting and infestation. These attributes are not found in commercially prevalent wood flour filled polyolefins. In order to achieve the desired properties, the wood fibers must be well dispersed in, and bonded to, the thermoplastic matrix, while retaining a high aspect ratio. A high fiber aspect ratio is a critical component for improved strength performance. This nation's softwood furnish is a key parameter to the overall success of this program. To meet these requirements, pulping and refining are necessary to recover high aspect ratio fibers with low fiber-fiber bonding capabilities and enhanced hydrophobic surfaces.

Although the latter goal can be achieved, to some extent, with chemical additives[3,4] the thrust of this program is to develop low-cost kraft and TMP pulp fibers that have maximum lignin surface coverage. In this manner, we will be able to maximize the interfacial attractive forces between pulp fibers and nylon. At the same time, we will minimize fiber-fiber bonding that leads to detrimental interactions (i.e., floc formation) in pulp/plastic composites. Finally, our research studies will focus on employing long-fiber SW TMP and liner board kraft pulps with post-consumer sources of nylon and/or polyesters to maximize the structural reinforcing properties of the fiber component. As such, this program will provide SW kraft and TMP manufacturers new, patent protected markets for their pulping operations.

The specific sources of recycled polymers to be investigated include post consumer carpet and post consumer polyester bottles. Currently more than 8 billion lb/yr of post consumer carpet is landfilled. Wellman, Invista and other companies sort post consumer carpet by face fiber (mostly nylon 6 and 66 and some polypropylene and polyester). These companies sort, shred, and grind the carpet in route to recovering and purifying the expensive nylons. After purification these nylons are just as expensive as virgin nylons so they have very modest market volumes. In this investigation, sorted and shredded carpet will be used without extensive purification, leading to a feedstock cost in the range of $ 0.10/lb. This shredded carpet typically contains about 75 wt % face fiber. The recycled polyester bottles are over 90 % purity, hence this source of matrix is often more than $ 0.20/lb.

In preliminary work, performed this year by Drs. Muzzy and Ragauskas, a mixture of 40 % southern SW kraft liner board and recycled post consumer carpet containing approximately 77 % nylon 6 was mixed, and injection molded into test specimens (see Figure 1.). These specimens achieved a flexural strength of 49 MPa and flexural modulus of 4.3 GPa. A similar mixture with 40 % SW thermomechanical pulp achieved a flexural strength of 53 MPa and flexural modulus of 4.7 GPa , as summarized in Table 1.

Figure 1. Picture of Recently Developed Kraft Pulp-Nylon 6 Post Consumer Carpet Composite Prepared by Injection Molding.

These stiffness values approach commercial goals but additional research is needed to provide product specifications demanded by the market. Product analysis of the IPST@GT composites indicated that fiber-flock formation occurs in the pulp/plastic

composite. This is a source of structural weakness which will be eliminated in this research program.

Table 1: Preliminary Physical Testing of Nylon 6 – Pulp Fiber Composite Boards Prepared at GT.

	Recycled Nylon 6 & 40% Kraft Linerboard Pulp	Recycled Nylon 6 & 40% TMP Pulp	Virgin Nylon 6 & 40% Kraft Linerboard Pulp
Flexural Strength	49 MPa (7,110 psi)	52 MPa (7,540 psi)	101 Mpa (14,650 psi)
Flexural Modulus	3.5 GPa (510,000 psi)	4.7 GPa (680,000 psi)	3.2 GPa (460,000 psi)
Tensile Strength (5,700 psi)	38 MPa (5,510 psi)	30 MPa (4,360 psi)	57 MPa (8,270 psi)
Tensile Modulus	3.2 GPa (460,000 psi)	2.9 GPa (420,000 psi)	3.4 GPa (490,000)

As summarized in Table 1, our fiber/nylon composites exhibit much better strength properties than the 19 MPa for the commercial plastic lumber. In some cases the modulus is lower than the 3.9 GPa measured for the commercial plastic lumber because the plastic lumber has 50 % wood flour. The virgin nylon 6 composite has a flexural strength 5X better than the plastic lumber. These properties are noteworthy, and commercially promising.

A careful examination of the pulp-nylon composites indicates that the current materials suffer from some degree of "pulp fiber pull-out" and fiber flocculation. Both of these issues are due to interfacial pulp fiber-nylon compatibility. A basic hypothesis of this program is that current pulping technologies can be modified to maximize pulp fiber-plastic interface bonding interactions. This will be accomplished by modifying current pulping technologies to maximize surface lignin coverage will retaining a high fiber aspect ratio.

Prior Studies: Our research group has developed a unique research capability in pulp/nylon composites. Although the use of wood flour in plastics is a well developed commercial product, and the benefits of employing pulp fibers in polypropylene have been documented; few studies have examined the use of pulp/nylon composites or pulp/polyester composites. The reason nylon and polyester composites have not been studied is the high melt temperatures of these polymers (225 – 265 ^{o}C). As the results in Table 1 demonstrate, it is possible to successfully compound pulp with nylon 6 despite its 225 ^{o}C melting point. As discussed, the field of pulp-nylon composite is an attractive field of research with short term practical benefits available. Researchers have examined alternative technologies to integrate lignocellulosics into nylon products including:

- Wood chips impregnated with resin and curing in the presence of reinforcing nylon fibers.[5]

- Press-formed composites employing 40-60 wt.% polymer waste as the binder, and the balance as wood chips. [6]
- Cotton linter pulp was soaked in water and mixed with 6,6-nylon to give nanocomposite powder, which was made into chips, then hot-pressed to give a uniform sheet.[7]
- Hot press technique was used to prepare nylon-wood fiber and polypropylene-wood fiber composites. An increase in tensile strength and elastic modulus was observed in the wood fiber/nylon composite, indicating that interfacial bonding occurs. (Note: strength benefits were less than in this program employing extrusion technologies)[8]

There have been numerous studies of surface modification and interfacial bonding in natural fiber composites. This topic was reviewed recently by Mohanty *et al*.[9] many of these studies focused on using maleated polyethylene and polypropylene as coupling agents since polyethylene and polypropylene matrices are so prevalent. An alternative approach that has been reported utilizes isocyanates for wood fiber surface treatments. Consequently, we have compared a urethane based sizing from Hydrosize, Inc. in our nylon composite studies. To date this size has not led to improved physical properties. As part of this program we will demonstrate that the hydrophobic pulp-plastic composites out-perform sized-pulp:plastic composites in physical properties and economic considerations.

DELIVERABLES:

In year one of this three year program, the researchers will identify kraft and TMP pulping conditions that maximize surface lignin coverage of pulp fibers and provide optimal fiber:plastic bonding properties for (1) Pulp/nylon composites and (2) Pulp/polyester composites. These pulping studies represent a key component of this innovative research program and will maximize the strength properties of these composites. The fundamental fiber to plastic interface physical chemistry properties involved in bonding will be characterized employing advanced material science techniques including thermogravimetric analysis, (TGA), differential scanning calorimetry (DSC), scanning electron microscope (SEM) and solid-state nuclear magnetic resonance (NMR).

The composites will be manufactured employing 20 – 60% pulp fibers using a newly acquired 30 mm screw diameter extruder. Because this extruder has been built to our specifications we expect improvements in fiber dispersion as well as good retention of high fiber aspect ratios. During year one, a unique wood pulp feeding system will be built for the twin screw extruder. This feed system will facilitate good fiber dispersion in the matrix. Wood fiber stabilization and devolitilization will be explored; both as a fiber preparation step and as a task integrated into the extrusion compounding process. Reactive extrusion to enhance interfacial adhesion will also be investigated.

Another task started during year one is the integration of extrusion compounding with compression molding. This approach is less expensive than separate compounding and

molding operations which require drying and reheating the intermediate compounded material. This approach is particularly attractive for large thick structures. Some examples include bumper beams for cars, railroad ties, and form boards for pouring concrete.

In year two of this program, researchers will build on the results of year one to characterize the complete profile of composite physical properties, including: tensile, flexure and impact properties. Since the composite is intended for static load applications, the flexural modulus of attractive candidates will be determined up to 2,000 hours. This analysis will be used in an iterative process of modifying the extrusion process to improve composite board product quality. This data, and an economic assessment of pulp/nylon and pulp/polyester composites boards will be provided to the program sponsors at the completion of year two.

Also during year two biopolymer matrices will be investigated as alternative matrices. The primary candidate for evaluation is polylactic acid (PLA) from Cargill-Dow since this is produced in commercial quantities. Another partial biopolymer, Dupont's polytrimethylene terephthalate (Sorona®), will be investigated. Both these polymers are polyesters with lower melting points than the polymers studied in year 1. Since these biopolyesters are expensive (more than $ 1/lb), a key feature for wood fiber reinforcement is to maintain or improve mechanical properties while achieving a lower composite cost than the matrix.
In year three, the researchers will employ pilot plant facilities to verify the commercial viability of laboratory studies. Continuous board products will be produced to permit testing as structural support beams. A detailed process design and economic analysis will be prepared to assess the profitability of this technology. Additional applications for this technology will be identified.

VALUE OF DELIVERABLES:

The program investigators anticipate that upon completion of this program, innovative composite board products and molded products will be available for commercial testing. The sponsoring companies will also have access to the fundamental knowledge as to how kraft and mechanical pulping technologies can be modified to maximize their integration into plastic composites. Process design features and successful compounding conditions will be known using 30 mm and 50 mm twin screw extruders. Board extrusion, compression molding and injection molding conditions will be established. These results will be established with nylon and polyester matrices principally derived from post consumer sources. The processing and performance of renewable polymeric matrices, like polylactic acid and polytrimethylene terephthalate, will be assessed.

As discussed, the market for fiber reinforced plastics is in excess of 1 billion pounds and is growing annually by 10%.[10] The primary reinforcing agent is fiberglass and on a cost, weight, and physical performance basis wood fibers exhibit superior properties. Currently, the construction and automobile markets consume greater than 50% of the

fiber reinforced plastic manufactured per annum. On a cost basis, pulp fibers should be able to readily penetrate this market as they provide a substantial cost advantage over glass fibers[11] which sell for more than $ 1,600/ton. This is provided that differences in interfacial surface properties between pulp fibers and plastic are resolved. The researchers' anticipate that pulp manufacturers could readily demand 50-60% of the cost of glassfibers for these specialized wood fibers (i.e., $800-900/ton). A preliminary estimate using sorted post-consumer nylon carpet at $ 0.10/lb, wood fiber at $ 0.40/lb and selling a 2" x 8" board at $ 0.90/lb leads to a rate of return close to 50 %. Most plastic decking board sells for more than $ 1.25/lb.

To illustrate the value of integrated compounding and compression molding consider a car bumper beam which weighs 10 pounds and has a fabricated cost over $ 25. Using 50 % recycled nylon at $ 0.10/lb, 30 % wood fiber at $ 0.40/lb and 20 % long glass fiber at $ 0.80/lb, the projected cost of a 10 pound bumper is under $ 12 per bumper. This is just one example of a high volume molded product where the addition of wood fiber and the use of integrated manufacturing is very attractive.

Once this program addresses these technical issues, the researchers' anticipate a rather rapid introduction of pulp/nylon and pulp/polyester products into the market place. It is readily anticipated that within 1-2 years of completion of this project, wood fiber reinforced nylon and polyester composites will displace ~ 3-5% of the glassfiber market and exhibit a 10 – 15% growth in market demand for the following decade, with a projected market demand in excess of 1 billion lbs.

PROJECT GOALS:

The first goal is to make wood fiber reinforced nylon and polyester composites by extrusion compounding where the fibers have a high aspect ratio and are well dispersed. By achieving this goal, the desired stiffness and strength can be realized for using these composites in structural applications, such as support beams. The second goal is to maximize interfacial adhesion in order to maximize composite strength. The third goal is to demonstrate that these composites can be produced profitably, at a cost well below glass fiber composites.

PROJECT APPROACH:

The research program for year one will involve the following:

1. Modified kraft and TMP pulping softwood furnish to maximize surface lignin.
2. Pulp stabilization for high melt temperature processing.
3. Developing a unique fiber feeding system to minimize fiber attrition.
4. Optimizing extrusion compounding conditions.
5. Demonstration of integrated extrusion and compression molding as a low cost fabrication method.

Our current studies in this field indicate that the more lignin a wood fiber has, the better it performs in composite board performance tests. This behavior has been attributed the presence of surface lignin.

Analysis of pulps will be initially accomplished with batch mixing trials. For preferred systems, we will scale up to the twin screw extruder. A 30 mm diameter twin screw extruder is available for these studies. This extruder has multiple ports for venting and adding material along the length of the barrel. Experimental parameters to be examined include:

- Screw design
- Fiber feed system design
- Screw speed
- Processing aids
- Venting and feed port locations
- Die design
- Temperature level and profile

It is important, from an economic perspective, to demonstrate the ability to go from sorted and shredded thermoplastic recyclate directly to an extruded or molded product. This integrated manufacturing approach significantly reduces the cost of the final product. The objective of this program is to retain long reinforcing fiber lengths and achieve good mixing to obtain the best properties from reinforcing with wood pulp. Therefore, we will work on the process design and extruder operation to improve these features. We will modify the fiber feed system to minimize fiber damage when the fiber first contacts the molten resin. To prepare test specimens and prototypes, we will use both injection molding and compression molding. Since the extruder is next to a compression press, we will do compression molding by charging the mold with hot extrudate from the twin screw extruder. This method is a very low cost route to molded products.

REFERENCES

1 Cellulose pulp-reinforced plastic composites. Watanabe, Shigeru; Suzuki, Masao; Ishii, Masayoshi. Jpn. Kokai Tokkyo Koho, CODEN: JKXXAF JP 04209631 A2 19920731 (1992).

2 Lumber substitutes made from fiber-reinforced plastics and method for manufacture. Heikkila, Kurt E.; Garofalo, Anthony L., Jpn. Kokai Tokkyo Koho, CODEN: JKXXAF JP 08336905 A2 19961224 (1996).

3 Lumber containing thermoplastic resins and antimicrobial agents. Kawase, Shigeki; Yamatomi, Mitsuyo. Synthetic Jpn. Kokai Tokkyo Koho, CODEN: JKXXAF JP 2003147871 A2 20030521 CAN 138:364179 AN 2003:387080 (2003).

4 Sustainable composites from renewable resources. Wool, R. P.; Khot, S. H.; LaScala, J. J.; Williams, G. I.; Bunker, S. P.; Morye, S. S. Composites in the Transportation Industry, Proceedings of the ACUN-2: International Composites Conference, 2nd, Sydney, Australia, Feb. 14-18, 2, 619-627 (2000).

5 Manufacture of plastic-wood composites. Xu, Jie. Faming Zhuanli Shenqing Gongkai Shuomingshu, CODEN: CNXXEV CN 1096730 A 19941228 Application: CN 93-107129 19930622. CAN 126:158494 AN 1997:154897 (1994).

6 Polymeric molding mixture with wood chips and fiber waste. Negmatov, Sajibzhan S.; Abdiraimov, Isamiddin; Tulyaganov, B. Kh.; Khvan, Boris N.; Kazakov, Bajburi T., CODEN: URXXAF SU 1792950 A1 19930207(1993).

7 Manufacture of cellulose-thermoplastic composites with good thermoformability. Yamane, Chihiro; Okajima, Kunihiko. (Asahi Kasei Corporation, Japan). Jpn. Kokai Tokkyo Koho, CODEN: JKXXAF JP 2003128791 A2 20030508 Patent written in Japanese. Application: JP 2001-331118 20011029 (2003).

8 Composite materials based on wood and nylon fiber. McHenry, E.; Stachurski, Z. H. Department of Engineering, The Australian National University, Canberra, Australia. Composites, Part A: Applied Science and Manufacturing (2003), 34A(2), 171-181.

9 Surface modifications of natural fibers and performance of the resulting biocomposites: An overview. Mohanty, A.K., Misra, M., Drzal, L.T., Composite Interfaces, Vol 8, no 5, 313-343 (2001).

10 Success of plastics recycling and its future. Ettefagh, Tamsin. Your Ticket to Outstanding Color and Additives, [Conference Papers], Arlington, VA, United States, Sept. 17-19, 2000, 12/i, 12/1-12/27.

11 Recycled fiberglass composite as a reinforcing filler in post-consumer recycled HDPE plastic lumber. George, S. D.; Dillman, S. H. Annual Technical Conference - Society of Plastics Engineers (2000), 58th(Vol. 3), 2919-2921.