PROGRAM OBJECTIVE:

The objective of New Paper/Board composites program is to utilize recent advances in hydrophobic bonding to develop the next generation cellulosic composites that displace petroleum-based materials. The proposed program will utilize recent advances by Ragauskas et al. to develop heat-moldable fibrous composites containing 70% or greater amounts of cellulosic fibers that can be used as a replacement for a host of consumer-orientated disposable items, including: plastic cutlery, cups, and plates.

This industry directed program addresses a key research need of the Pulp and Paper Industry, as described in the Agenda 2020 Technology Platform and the IPST@GT Strategic Vision. These documents identified new cellulosic materials as a critical breakthrough technological needed for the industry including the creation of novel biopolymers, active functional surfaces, and new classes of materials with unique properties. The basic hypothesis of this program is that nano-structured particles and fibers can be engineered to deliver exceptional physical and optical properties for paper and paper-related materials that can not be readily achieved with macro-sized equivalent structures. In turn, these technologies will lead to new grades of paper and board applications.

PROJECT BACKGROUND:

Over the past few years, the principal investigator has demonstrated that the addition of a low-Tg polymer to a fiberous mat can lead to dramatic changes in composite sheet properties. As summarized in Figures 1a and 1b, for SW kraft linerboard handsheets impregnated with 0.5-4% PLA strength improvements of 20 – 35% were observed. The burst index values also benefited from the addition of PLA, increasing by 40 – 70% with increasing amounts of PLA. Hot pressing the testsheets with a press temperature of 130°C for 5 minutes was shown to enhance the tensile/burst index values for the PLA treated sheets. In comparison, the tear index values exhibited no changes with PLA treatment. The effects of hot pressing conditions (temperature, time pressure) on PLA treated testsheets are summarized in Figure 2. The tensile index data demonstrates that the effect of hot pressing kraft testsheets is primarily due to the addition of PLA, and not simply due to the hot pressing of the lignocellulosic fibers. The data presented in Figures 2b and 2c suggest that the improvements in tensile index on PLA treated sheets come about at even short press times and pressures when employing a press temperature of 130°C.
Comparable strength benefits were observed for PLA impregnation on the properties BCTMP sheets. To further explore the effects of the PLA treatment on the testsheets, a series of control and PLA treated and pressed testsheets were submitted for atomic force microscopy (AFM) analysis, as summarized in Figure 3.

Figure 3. Amplitude and phase AFM analysis of SW kraft linerboard with 0.0 and 2.5% PLA applied and hot pressed (Press Conditions: 130 °C, 2.30 x 10^3 kPa, 5 min.).

This fiscal year, the researchers have demonstrated the benefits of utilizing nano-sized resins and synthetic fibers to prepare a hydrophobic composite that is consists of 70% or greater SW ECF bleached kraft pulp. As summarized in Figure 4, the use of 60 nm polymethyl
methacrylate provided significantly enhanced water contact angles in comparison to 100 micron PMMA material, especially at a 10% charge.

![Bar graph showing water contact angles for 0%, 10%, and 30% PMMA heat-pressed to ECF bleached SW kraft pulp]

Figure 4. Water contact angles for 10% and 30% PMMA heat-pressed to ECF bleached SW kraft pulp

As reported at the January 2007 Research RAC review, the PMMA-pulp fiber composites also exhibited reduced water thickness swelling by 30-55% dependent upon the level of resin added. In all these studies, the nano-resin pulp composite yielded improved performance, due in part to improved dispersion prior to heat-pressing. Indeed, the control experiments with micron sized resins were frequently troubled with poor sheet formation and adhesion properties (see Fig. 5)

![Images of micron and nano polystyrene resins]

Figure 5. Variation in formation of PMMA-kraft pulp composites for nano-micron resin

Representative results from preparing paper-plastic composites are summarized in Table 1.
Table 1. Heat-pressed plastic - SW ECF kraft fiber composites

<table>
<thead>
<tr>
<th></th>
<th>Control 100%</th>
<th>10% Plastic 90% Fiber</th>
<th>20% Plastic 80% Fiber</th>
<th>30% Plastic 70% Fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 Micron Polystyrene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contact Angle</td>
<td>65.4°</td>
<td>83.1</td>
<td>81.2</td>
<td>83.3</td>
</tr>
<tr>
<td>2 h % Water Absorption</td>
<td>121</td>
<td>62.9</td>
<td>36.4</td>
<td>26.3</td>
</tr>
<tr>
<td>88 nm Nano Polystyrene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contact Angle</td>
<td>65.4°</td>
<td>82.6</td>
<td>74</td>
<td>69.2</td>
</tr>
<tr>
<td>2 h % Water Absorption</td>
<td>121</td>
<td>64.5</td>
<td>28.7</td>
<td>9.74</td>
</tr>
<tr>
<td>PLA Fiber (15 micron x 3 mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contact Angle</td>
<td>65.4°</td>
<td>39.0</td>
<td>40.9</td>
<td>44.8</td>
</tr>
<tr>
<td>2 h % Water Absorption</td>
<td>121</td>
<td>90.9</td>
<td>73.4</td>
<td>56.9</td>
</tr>
</tbody>
</table>

The data to-date demonstrates that the addition of nano-sized plastic resins particles are more effective in making a paper-plastic composites. The results of SEM analysis of the heated pressed materials would suggest this is due to significantly better dispersion of fiber and resin. Research studies for the remaining portion of this fiscal year will focus on identify the optimal plastic additive and size distribution for the preparation of paper-plastic composites. The project deliverables for FY 2007-08 leverage the success of this year’s program.

OVERALL PROGRAM DELIVERABLES:

The research deliverables for this program have been established through a series of collaborative industry discussion panels with industry leaders. The research program for FY 2007-08 will focus on addressing the remaining issues that need to be addressed before practical fiber composite manufacturing technologies can be pursued. These issues included:

- Optimization of fiber resource for composites (i.e., bleached HW vs. SW kraft)
- Effect of refined fibers on resin-fiber composite physical properties
- Application of resins with kraft linerboard and TMP to prepare a competitive alternative to plastic boxes.

The outcome of this program will be the development of break-through technologies for higher value-added paper platforms and new applications for kraft and mechanical pulps.

VALUE OF DELIVERABLES:

Based on the proposed research deliverables, and the recent Forest Products Nanotechnology workshop in Washington, it is anticipated that within a decade, greater than 50% of the total pulp and paper production in the U.S. (~104 million tons) will utilize assorted nanotechnologies in their manufacturing facilities and final products. The proposed program deliverables will be the cornerstone for new advanced materials, including kraft fibers composites reinforced with either nanoparticles or fibers of GRAS plastics (i.e., 2-5%
PLA: polylactic acid, PMMA: polymethyl methacrylate, modified starches) or for the manufacturing of innovative moldable fiber composites to displace current disposable plastic products, such as plastic cups, plates and forks.

Recent studies by Ragauskas have demonstrated that the strength of properties of TMP and kraft sheets can be increased by a factor of two or more by hot-pressing with polylactic acid or related flowable polymers.\textsuperscript{1} Based on typical product lifetimes of other products in pulp and paper, it is anticipated that the cellulosic composites developed in this program will be utilized within five years. Although the economic value of these new products cannot be accurately calculated at the present time, it is reasonable to anticipate the development of new, value-added markets that within a decade could readily be valued in the $100 million range. As summarized in Figure 6, over the past fifteen years, the growth in the packaging industry has been dominated by plastics.

![Material applications for packaging.](image)

Given the recent increased cost of petroleum and society’s renewed interest in sustainable technology, this program provides one of the most viable technological solutions to address the challenge that nonrenewable resources has imposed on paper-based product platforms.

**PROJECT GOALS:**

The goal of this research program is to provide its program sponsors a new product platform for kraft and mechanical pulps fibers. This is to be accomplished utilizing recent advances in low-Tg plastic resins and fibers that can be used to hydrophobically bond pulp fibers together. The resulting composite will retain the stiffness and cost-value of paper while exhibiting new water repellency and physical properties. The proposed product grade would facilitate the application of cellulosics in materials currently manufactured solely from petroleum products.
PROJECT APPROACH:

At the completion of this fiscal year, the researchers will have fully determined the viability of utilizing nanosized resin particles vs. plastic fibers as a means of manufacturing ECF bleached SW kraft pulp composites. In addition, we have already developed highly reproducible technique for heat-pressing fibrous composites together.

The key research tasks include,

Tasks:
1. Evaluate the performance of paper composites with fully bleached ECF SW and HW kraft pulps. Investigate product performance parameters (i.e., tensile, burst, thickness swelling) as a function of fiber resource (i.e., pine, spruce, maple, birch).
2. Evaluate the performance of paper composites with refined and unrefined fibers from section 1.
3. Identify optimal heat-pressing conditions to provide satisfactory paper-composite properties at minimal energy requirements. Evaluate the potential of a wood-plastic compatibilizer or plasticizer to yield improved properties while reducing energy needs.
4. Evaluate kraft linerboard or TMP pulp for paper-composite targeted as an alternative to plastic boxes.

REFERENCES