

Contract No. R-011-023
“Biobased Non-Isocyanate Urethane Hybrid Resins for Pultrusion Composites”

Submitted by North Dakota State University

Principal Investigator: Dr. Chad Ulven

PARTICIPANTS

Sponsor	Cost Share
North Dakota Soybean Council	\$ 80,000
Tecton	\$ 20,000
Tecton	\$100,000 (in-kind)
North Dakota Industrial Commission	<u>\$200,000</u>
Total Project Cost	\$400,000

Project Schedule – 24 months
Contract Date – July 1, 2011
Start Date – July 1, 2011
Completion Date – June 30, 2013

Project Deliverables:
Status Report: December 31, 2011v
Status Report: June 30, 2012
Status Report: December 31, 2012
Final Report: June 30, 2013

OBJECTIVE/STATEMENT OF WORK:

Funds for this project will be used to develop novel polyurethane resins based on ND renewable materials (i.e. vegetable oils) for pultrusion composite fabrication. If successful, the composites would be manufactured in Fargo at the Tecton facilities. Tecton is a subsidiary of Marvin Windows. The main source for feedstock for this project will be ND vegetable oils. If successful, the project would be commercialized very quickly as it would not require any plant modifications for Tecton.

This project will allow Tecton to meet a growing market demand for “green” composite materials. The product would have low or no VOC’s, creating a safer environment for ND employees. The product is also expected to have enhanced qualities compared to its traditional counterpart, including: less brittle, more durable, and lighter. The product is expected to have improved fabrication and fastening results.

The scope of work includes:

- Lab scale synthesis and characterization of hybrid resins through green routes using ND materials derived from soybean, canola, corn and sugar beets.
- Lab scale resin curing, composite fabrication and characterization at NDSU and Tecton.
- NDSU pilot plant resin scale-up and characterization.
- Pultrusion process trials of a prototype profile/component with the hybrid polyurethane resin at Tecton. Develop a good understanding of the manufacturability using the hybrid resin.
- Test prototypes to validate physical properties of the resulting composite at NDSU and Tecton.

STATUS

Contract has been signed and the work is underway.

Semi-Annual Status Report – December 31, 2011

The research group has been meeting monthly since September 2011 to better outline project sub-tasks, establish personnel in charge of meeting specific sub-tasks within sub-groups, and to establish proper lines of reporting and communication between all group members. The following sections outline specific details related to the current status of each sub-group.

Dean Webster's Group – New Biobased Resin Synthesis

Three approaches to novel biobased resins for pultrusions were selected for initial experimental work. Criteria for selection were 1) raw materials commercially available, 2) cost of raw materials is reasonable (and can meet project goals), and 3) synthesis processes are scalable. Tecton and NDSU exchanged information regarding curing conditions and commercially available initiators to use for initial evaluation of new resins. Initial experiments for several of the selected approaches were carried out and several resins were synthesized and characterized. Experiments to show the ability of the resins to cure were promising. Future work will involve broader exploration of the resin compositions, evaluation of the impact of diluents on viscosity, and curing of candidate resins and evaluation of their physical and mechanical properties.

Dennis Wiesenborn's Group – Scale-up Trial Resins

Although the process scale-up depends upon the lab-scale synthesis and characterization currently in progress, some initial scale-up activities are already underway. One key process step will be epoxidation. This step is somewhat difficult for three reasons: (1) The step involves the use of aqueous reactants (hydrogen peroxide and acetic acid) and a solid catalyst which must be maintained in intimate contact with the vegetable oil or oil derivative over the course of several hours. Thus, reactor mixing should be intense and efficient to achieve high conversion. (2) The addition of reactant hydrogen peroxide must be gradual and carefully controlled, and removal of reaction heat must also be adequate. (3) The resulting epoxy resin must be refined using several iterations of washing and separation to remove residual reactants. Recent tests with canola oil were very successful at the scale of 0.2 to 0.5 lb. resin. A stainless steel, stirred, jacketed reactor is being modified for production of batches of 9 to 11 lb. resin (4 to 5 kg). A separate refining unit will also be fabricated. This system will be completed in Spring 2012 and tested on both sucrose soyate ester and canola oil.

Chad Ulven's Group – Resin and Composite testing / Characterization

To establish protocol of testing the experimental resins and composites produced during the project, the mechanical properties of commercially available resin systems containing biobased resources were first investigated. This particular resin system includes polyols derived from soybean oil and a petroleum based isocyanate. The mix ratio of polyol to isocyanate is 100/74.3 (wt/wt). The neat polyurethane was processed using closed mold compression at room temperature under the 950 kPa for 12 hours. Some of the samples produced were post-cured using a simple process of heating in an oven at 80 °C for 3 hours. Some mechanical and thermal properties of the neat polyurethane were examined to evaluate properties both before and after post-curing. Mechanical properties (i.e. tensile strength, flexural strength, and impact strength) and thermal properties (i.e. heat distortion temperature - HDT, glass transition temperature - T_g , coefficient of linear thermal expansion - CLTE) all were found to increase after post-curing. The increase in thermal properties was more significant. The higher glass-transition temperatures (T_g) and HDT of the PU after post-curing were believed to be the result of increasing in crosslinking density. Future work will be in characterizing experimental resin systems developed by the research group and comparing their results to this initial commercial benchmark as well as some other commercial resin systems currently being used by Tecton and tested at NDSU.

Tecton Products - Establishment of testing protocol for benchmarking

During this phase, Tecton has provided materials for testing of mechanical properties to NDSU. The idea is to establish a set of material properties which will be used as a benchmark for the newly developed resin during the course of this project. Currently, two sets of samples have been tested and the test protocol is being continuously updated so that all mandatory new material qualification tests are

included in the test plan. NDSU is not equipped to carry out all the testing and so quotations are being obtained for testing at external agencies.

Tecton Products - Information sharing and access to Tecton facilities

Tecton has shared technical information for resin development with NDSU. This information will aid NDSU in testing the resins being developed and establish some baseline properties. Wiesenborn group members were given a tour of Tecton R&D scale-up capabilities to explore opportunities for use during the scale-up stage of the project.

Tecton Products - Other testing

Samples of unidirectional fiber reinforced plastic based on commercially available resin systems containing biobased resources was provided by NDSU for testing at Tecton. The testing was completed and the results were discussed between Tecton and NDSU. This is another material whose properties may be used for benchmarking purposes.

April 2, 2012