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	$200,000
Total Project Cost	$400,000

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

Project Deliverables:
Status Report: December 31, 2011√
Status Report: June 30, 2012 √
Status Report: December 31, 2012 √
Final Report: September 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 (Tg) 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 there 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.

Semi-Annual Status Report – June 30, 2012

The goal of this project is to develop novel polyurethane resins based on ND renewable materials (i.e. vegetable oils such as soybean) for pultrusion composite processing. With successful synthesis, formulation, characterization, and larger-scale production of these renewable resins, the team also plans to demonstrate the utilization of these renewable resins in the pultrusion of composites at Tecton Products LLC. These composites would then be tested and compared in performance against currently produced pultruded composites.

Matching funds provided by the North Dakota Soybean Council and Tecton Products LLC along with funds provided by the NDIC-REP were used to fulfill the first year's project objectives and tasks. Investigators Dr. Webster, Dr. Wiesenborn, and Dr. Ulven of NDSU along with Robert Plagemann and Dr. Ravindran of Tecton met on a monthly basis to share results and ideas throughout the year. However, all of the investigators, students, and post-doctoral research associates involved in the project communicated seamlessly and continuously throughout the project to meet several deliverables and reach milestones. Described below are some of the major highlights achieved in the first year of the project, followed by additional detail specifically discussing the contributions made by the different groups working collaboratively in this project.

In the first year of the project, several proposed resin chemistries were evaluated and the most promising resin chemistries were fully synthesized and characterized for their appropriateness in the pultrusion process. Resins currently being used by Tecton as well as those being developed by NDSU have been and are continuing to be mechanically tested and compared for performance as resins and in composites. Strategies for scaling up resin manufacturing were developed and equipment was built at NDSU to start synthesizing new renewable resins in larger quantities over the next year of the project. Tecton provided all of the initial composite coupons for testing and a list of properties needed to be evaluated in order to establish baseline properties for comparison. These initial composite coupons were tested, characterized, and an in-depth summary report was completed for Tecton.

Specifically with regards to our previously stated goals in this project to the NDIC-REP, the PIs can report that we have established the knowledge base of a commercial bio-based polyurethane resin technology in Tecton's pultrusion composite applications which are needed to compare the resins being synthesized at NDSU for year two of the project. We have developed a suite of potential pultrusion resins at NDSU which contain 50%+ renewable content which will be scaled up and trialed in Tecton's pultrusion

process in the second year of the project. Finally, with the novelty of the resin chemistries developed and the high renewable content achieved, patent protection for this bio-based resin technology is currently being sought.

The following sections of key milestones reached for each of the teams working on this project provide more depth to the overall accomplishments reported in this semi-annual status report. Although the milestones are listed by teams separately, the collaboration between these teams was seamless during the first year of the project which led to several breakthroughs towards producing a bio-based resin appropriate for commercial production of pultruded composites in a ND composite manufacturing company.

Dean Webster's Group – CPM NDSU

1. Proposed resin chemistries were thoroughly evaluated for their potential cost (raw materials), ease of processing and expected outcome in terms of properties. Approaches were prioritized for lab work.
2. Resin chemistries based on methacrylated functionalized biobased resins were identified as the most promising approach and a series of resins were synthesized.
3. A standard curing catalyst and cure schedule was identified with assistance from Tecton for curing the experimental resins.
4. The viscosity of the resins was determined and resins were also blended with differing amounts of styrene diluent and the viscosity determined. A key finding is that with the biobased resin system lower amounts of styrene are required than are used with the petrochemical control resin system.
5. Resin systems were cured and their physical and mechanical properties were determined. These included tensile properties, thermal properties (glass transition temperature, thermal stability), and sol-content. From this data, structure-property relationships are being determined.
6. Samples of a biobased polyol were prepared for evaluation by Dr. Ulven's group.
7. From the structure-property data one or two of the resins will be selected for further evaluation in composite formulations.
8. An invention disclosure is being prepared for submission to the NDSU Technology Transfer Office.

Dennis Wiesenborn's Group – ABEN NDSU

1. Knowledge of the synthesis process technology was transferred from Dr. Webster's group to ABEN personnel.
2. A 45-L stainless steel separatory funnel and stand was fabricated for the pilot-scale refining of resin (designed for up to 10 kg resin batches).
3. An existing stainless steel, steam-jacketed kettle was modified for service as a reactor for resin synthesis (designed for up to 10 kg resin batches).
4. The effect of mixing, temperature, and hydrogen peroxide addition rates on a related synthesis was explored through a series of small-scale tests, in anticipation of the synthesis route that was later selected.
5. Most of the key raw materials were procured to begin production of test batches in 5 to 10-kilogram quantities this summer.

Chad Ulven's Group – ME NDSU

1. Testing standards for resins and pultruded composite properties of most interest to Tecton were identified and fixtures were developed to conduct all testing necessary.
2. Lab-scale resin curing and composite processing procedures were developed and used to manufacture test coupons using both experimental resins synthesized by Dr. Webster's group and commercially used resins by Tecton.

3. The thermal and mechanical properties of Tecton pultruded Polyurethane/fiberglass profiles were measured and reported.
4. The thermal and mechanical properties of control grade pultruded profiles from Tecton were measured and reported.
5. The thermal and mechanical properties of bio-based and petroleum based neat polyurethane were measured and reported.

Tecton Products LLC

1. Comprehensive test plan was supplied to Dr. Ulven's group to enable testing of materials for generation of baseline material properties. Tecton has also provided sample parts for testing.
2. Provided training to Dr. Ulven's group for usage of polyurethane starting materials for plaque preparation, and information on the same to support the generation of baseline material properties.
3. Provided information to Dr. Webster's group on resin cure conditions, desirable cure characteristics of the resin, and information on the mechanical properties of the resin to provide guidelines for the developmental work of the resin. Tecton is currently working on providing resin films that will be used for comparative property analysis.
4. Worked with Dr. Webster's group and Dr. Wiesenborn's group to identify resin compositions for scale-up based on processing requirements

Semi-Annual Status Report – December 31, 2012

Matching funds provided by Tecton Products LLC along with funds provided by the NDIC-REP were used to fulfill project objectives and tasks of the past six months. Investigators Dr. Webster, Dr. Wiesenborn, and Dr. Ulven of NDSU along with Robert Plagemann and Dr. Ravindran of Tecton met on a monthly basis to share results and ideas. However, all of the investigators, students, and post-doctoral research associates involved in the project communicated seamlessly and continuously throughout the project to meet several deliverables and reach milestones. Described below are some of the major highlights achieved in the last six months of the project, followed by more detail on the contributions made by the different groups working collaboratively in this project.

In the last six months of the project, two of the bio-resins developed at NDSU were selected for further evaluation in composite formulations using the structure-property data generated during the first year of the project. The two bio-resins chosen for scale-up potential include one composition of the methacrylated resin system and a biobased polyol for use in polyurethane formulations. The lab scale bio-resins are in the process of being scaled up to produce large batches for Tecton to trial in their production facility. Composite samples were produced in the NDSU labs for verification of properties when compared to the commercially produced composites by Tecton. Most recently, Tecton has started identifying activities related to trialing the new large batches of bio-resin such as safety, equipment modifications, and scheduling. Finally, patent protection for this bio-based resin technology continues to be sought through NDSU's technology transfer office.

A parallel approach for demonstrating the newly developed bio-resins has emerged and includes the use of a mini-pultruder to prepare samples for testing purposes. Tecton owns a mini-pultruder which is a basic laboratory scale set-up similar to the production equipment used for pultrusion. The mini-pultruder is typically used for developmental activities and not for production purposes. However, a considerable amount of work is required before the mini-pultruder can be used for the purpose that we envision for the project. The plan is to introduce the mini-pultruder as a senior design project for ME students for Spring 2013 so that it can be upgraded and commissioned for regular use. This is an

unexpected educational opportunity that has come about due to the collaborative nature of the project and which should be mutually beneficial to Tecton and NDSU.

The following sections of key milestones reached for each of the teams working on this project provide more depth to the overall accomplishments reported in this semi-annual status report. Although the milestones are listed by teams separately, the collaboration between these teams was seamless during the last six months of the project which led to progress towards producing a bio-based resin appropriate for commercial production of pultruded composites in a ND composite manufacturing company.

Dean Webster's Group – CNSE NDSU

1. From the previously measured structure-property data, two of the resins were selected for further evaluation in composite formulations. This included one composition of a methacrylated resin system and a biobased polyol for use in polyurethane formulations.
2. An invention disclosure was prepared for submission to the NDSU Technology Transfer Office.
3. The Webster group has provided assistance to the Wiesenborn group for the scale up of the candidate biobased resin systems

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Dennis Wiesenborn's Group – ABEN NDSU

1. Six batches (9 kg each) of epoxidized sucrose soyate resin were successfully produced with consistently good quality and yield. This resin is to be further modified by Dr. Webster's group to produce the biobased resins to be tested by Tecton.
2. The production (epoxidation and purification) time of a 9 kg batch was reduced from 8 days to 3 days. This was accomplished through the adaptation of a batch desolventizing unit (successfully tested) and the fabrication of a scale up of resin filtration unit.

Chad Ulven's Group – ME NDSU

1. 40% flax and 60% glass fiber (by volume) reinforced polyurethane composites were manufactured with polyurethane resins of Dr. Webster's group and commercially used resins by Tecton.
2. The thermal and mechanical properties of flax and glass fiber reinforced polyurethane composites were measured, reported, and discussed amongst the group.
3. The samples were polished in order to conduct microscopy, scanning electron microscopy, and nano-indentation characterization. Results will be reported and discussed amongst the group.

Tecton Products LLC

1. Tecton provided information on rovings and mats currently used in their system so that NDSU was able to mimic a pultruded profile (part) in terms of glass and resin loadings.
2. Tecton continued to support resin developmental efforts at NDSU by providing a list of tests for screening purposes to be performed on the newly developed bio-resins.
3. NDSU provided a sample of the bio-resin to Tecton that was used for preparation of mixes that can be eventually pultruded. The neat bio-resin had a higher overall cure time but there is a potential for reducing that by optimizing initiator combination/quantities. When the bio-resin was mixed with other materials required for processing in the lab at Tecton, some incompatibilities were observed that need to be addressed and a few approaches have been outlined for further work.
4. Tecton has started identifying activities related to trialing the new material and as a part of this effort Tecton has requested MSDS for the new bio-resins to get them approved from the Environment, Health, and Safety department.

April 18, 2013 - No-Cost Extension Request

A no-cost 3-month extension has been granted extending the date for filing the final report to September 30, 2013.

June 27, 2013