FINAL REPORT

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The goal of this project was 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 planned 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 Tecton Products, LLC and the North Dakota Soybean Council along with funds provided by the NDIC-REP were used to fulfill all of project objectives and tasks. Investigators Dr. Webster, Dr. Wiesenborn, and Dr. Ulven of NDSU along with Robert Plagemann and Dr. Ravindran of Tecton met with their respective teams on a monthly basis to share results and ideas. In addition, 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 the major highlights achieved in the project, while the following pages list in more detail the contributions made by the different groups working collaboratively in this project.

In the project, several bio-based resins formulated at NDSU were synthesized, processed into plastic and composite coupons, and tested for suitability in Tecton's composite pultrusion manufacturing processes during the first year of the project. The two bio-based resins chosen for scale-up potential included one composition of the methacrylated resin system and a bio-based polyol for use in polyurethane formulations. The lab scale synthesis of the methacrylated resin system developed was scaled up in the second year of the project to produce large batches for Tecton to trial in their production facility. Throughout the second year, composite samples were produced in the NDSU labs for verification of properties when compared to the commercially produced composites by Tecton. Tecton modified their large-scale pultrusion process to trial large batches of bio-based resin from NDSU. Finally, patent protection for this bio-based resin technology continues to be sought through the USPTO.

A parallel approach for demonstrating the newly developed bio-based resins also emerged through the use of a mini-pultruder to prepare samples for testing purposes. Tecton donated a mini-pultruder to NDSU 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 was required before the mini-pultruder could be used for the purpose envision for the project. Therefore, the mini-pultruder was initiated as a senior design project for Mechanical Engineering students in the spring semester of 2013 to upgrade and commission the system for regular use. This is an unexpected educational opportunity that evolved through this project due to the collaborative relationship developed between Tecton and NDSU.

Major Outcomes from the Project

- This project identified a novel highly functional bio-based resin system useful for pultrusion composites. The resin system developed results in similar properties and cost as current petrochemical resins, but has a bio-based content of approximately 50%. A provisional patent application has been filed.

- The resin system developed uses a lower amount of the hazardous styrene diluent compared to commercial resin systems. This reduces the cost and energy for capture and control of the styrene emissions during industrial scale processing. In the mix formulation in the third trial, a slight reduction in the overall styrene content was achieved. One aspect that was not explored on the plant scale was the reduction of styrene level in the NDSU base resin. There is a definite potential for significant reduction the styrene content, thereby improving the viscosity characteristics of the resin. This can be explored in future scale-up studies.

- The epoxidized sucrose soyate (ESS) base resin is a product of soybean oil and table sugar thus is 100% bio-based. ESS is produced with hydrogen peroxide, acetic acid, catalyst, sodium carbonate, and solvent. The residual hydrogen peroxide (approximately 60% of the initial sucrose soyate weight) breaks down to water. Acetic acid (13% of initial sucrose soyate weight), an oxygen carrier during the process is neutralized with sodium carbonate and properly discarded. The catalyst (18% of initial sucrose soyate weight) is a solid ionic exchange resin that can be recycled multiple times. The solvent (hexane) is used to reduce the viscosity during the washing step, and is then recycled. Therefore many of the steps and components to producing this resin have been developed with sustainable chemistry practices in mind.

- The pultruded glass fiber-reinforced thermosets based on the developed bio-based resin possesses tensile strength and modulus of 91% and 110%, flexural strength and modulus of 84% and 86%, v-notched shear strength and modulus of 82.2% and 58%, unnotched and notched impact energy of 93% and 87% and interlaminar shear strength of 72.4% as compared to Tecton Product's current pultruded composites. In addition, the glass transition and HDT of pultruded glass fiber-reinforced thermosets based on MAESS was 62% and almost 100% compared to Tecton's commercial samples. This proves the viability of using this bio-based resin in Tecton's products in the future if the resin can be commercially produced.

Specific Research Progress

The following sections of key milestones reached for each of the teams working on this project are described below. Although the milestones are listed by teams separately, the collaboration between these teams was seamless during the entire project which led 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

The focus of the effort by the Webster group was to design a resin system for pultrusion that was substantially bio-based, but have properties similar to that of a commercial petrochemical based resin system. Key properties needed are resin system viscosity, curing speed, stiffness, and strength. In addition, the cost needs to be comparable to resin systems currently on the market. The first year of the project, supported by matching funds from the North Dakota Soybean Council, focused on screening approaches to resin compositions and the second year was focused on scaling up and further optimizing the resin system.

At the outset of the project, a survey of the cost of the raw materials for the proposed approaches was carried out. It was found that several of the proposed raw materials were very expensive and would have made a resin based on these cost prohibitive and thus these approaches were removed from further consideration. Several approaches were screened initially, involving resin synthesis and characterization of the cured materials. From the initial screening, the project focused on a system involving functionalizing a novel bio-based epoxy resin previously developed at NDSU with reactive methacrylate groups. This system allows for the synthesis of resins having differing degrees of functionalization, yielding a range of performance properties. A complete study of the structure-property relationships of this system was carried out to fully map out the effect of resin functionality and diluent content on the properties of cured thermosets. It was found that the resin system allowed for the reduction in the amount of styrene reactive diluent compared to commercial systems, which can help reduce worker exposure to styrene.

In the second year of the project, we worked closely with Tecton to further optimize the resin system for use in their pultrusion system and prepare the resin for scale up in the ABEN pilot plant at NDSU. Based on the structure-property relationship study, a specific resin system in terms of functionality and styrene content was selected for further work. We then worked with Tecton to optimize the initiator system so that curing of the resin system could be achieved under their processing conditions. In preparing for scaling up of the resin synthesis, we optimized the catalyst used as well as the stabilizer used to maintain shelf stability of the resin system, ensuring that it did not inhibit the curing of the resin.

Finally, a rough estimate of the cost of the new bio-based resin system was carried out. While the cost of resin processing can be difficult to estimate until we were to work with a manufacturer, a reasonable cost estimate is $2.50/lb. This price is in the range of similar petrochemical resin technologies in use today. In addition, the bio-based content of the resin system is estimated to be approximately 50%

Dennis Wiesenborn's Group – ABEN NDSU

Pilot scale production of epoxidized sucrose soyate (ESS) and methacrylated ESS (MAESS) were carried out at the pilot plant. Knowledge of the synthesis process technology was transferred from Dr. Webster's group to ABEN personnel. Ten batches of ESS were produced at the NDSU Pilot Plant for Tecton formulation trials and related uses. A low epoxy equivalent weight (EEW) is preferred because it indicates that there are more epoxy or oxirane bonds in a given mass of resin. High percent solid content is preferred because it indicates that the percent volatile was very low.

Four batches (two 11.2 kg, one 9.3 kg, and one 6.7 kg) of MAESS were produced at the pilot plant. After adding 30% of styrene to each batch, a total 54.9 kg of MAESS with styrene was produced. All the batches had the desired acid number less than 4 and were transferred to Tecton for the manufacturing of pultruded composite materials.

Before the pilot scale production of ESS, a series of small-scale tests were carried out to explore the effect of mixing, temperature, and hydrogen peroxide addition rates on a related synthesis, in order to select the synthesis route for pilot scale reactor and funnel design.

An existing stainless steel, steam-jacketed kettle was modified for service as a reactor for resin synthesis (designed for up to 10 kg ESS resin batches and 20 kg of MAESS resin batches). There were four major modifications on the kettle to suit the purpose of resin production. These modifications were to retain

reaction content within the reactor, improve mixing and transfer of reactor content, and improve temperature control.

A 45-L stainless steel refining unit was fabricated for the pilot-scale separation, washing, and filtration of resin. The unit was designed for up to 10 kg resin batches.

The production (epoxidation and purification) time of a 7-10 kg batch was reduced from 8 days to 3 days. This was accomplished through the above refining unit and adaptation of a batch desolventizing unit from on existing solvent extraction unit at the pilot plant.

Chad Ulven's Group – ME NDSU

Throughout the project, we have assessed the mechanical and thermal properties of the bio-based composites produced from the various bench top and industrial scale trials for comparison and to provide direction for formulation modification. Mechanical and thermal properties of pultruded glass fiber-reinforced polyester composites that are currently produced and used in Tecton Product's materials were also assessed as the control to compare with the novel glass fiber-reinforced bio-based composites produced throughout the project.

Since the last report, we received three samples sets produced during industrial trials at Tecton. These samples were nominally designated as (1) Control, (2) Trial 1 (with carb), and (3) Trial 3. The Control grade is a standard pultruded profile, Trial 1 (with carb) and Trial 3 are pultruded glass fiber-reinforced bio-based polyester composites. The mechanical and thermal properties of pultruded glass fiber-reinforced bio-based polyester composites were assessed and reported in the attached confidential report. These mechanical properties include: Tensile strength and modulus, flexural strength and modulus, interlaminar shear strength (ILSS), v-notched shear strength and impact energy (toughness) were tested according to ASTM standards. The thermal properties include: Glass transition temperature (Tg), and Heat Distortion Temperature (HDT). All properties are reported for longitudinal fiber orientation. The experimental techniques and the technical testing standards are described in the Methods section of the confidential property report.

Tecton Products LLC

Tecton supported the Senior Design Project students in the Mechanical Engineering Department at NDSU by providing inputs about the minipultruder as well as supplying certain materials to be able to run pultrusions. Tecton also supported some trials with a new test material on the mini pultruder.

Tecton conducted intensive lab-scale testing with the resins supplied by NDSU and shortlisted formulations to be tried in the plant. This was followed by three trials in the plant with different mix formulations and in two instances; the part was coated as well. From the pultrudability aspect, the final mix was the best mix. Due to confidentiality reasons, the details of the tests and trials are only included in the confidential report.