Canola-based Epoxy Resins for Bio-based Plastic Composites, ND43500

Progress Report for Year Two (2007-2008)

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OVERVIEW AND PROJECT IMPACT:

Our long-term goal is development of high-quality, affordable composite materials using canola oil-based resins and the transfer of this technology to industry. Briefly, we have already developed a process to prepare canola resin and techniques for incorporating this resin into composites; inclusion of up to 35% canola resin in a composite matrix has already been achieved in the first 18 months of this project. The performance of the canola resin and composite are competitive with 100% synthetic resin/composites. Key goals for the coming year are process scale-up, identification of industry needs and opportunities for canola resin, and development of composites targeted to specific industrial applications. This project is based on a unique partnership in composites research and is crucial to technical and commercial success of these types of materials. Composite Innovations, LLC recently requested a proposal on the use of our canola resin for the manufacture of splints for utility poles in North Dakota.

OBJECTIVES (as initially proposed):

Objective 1. Identify and optimize procedures for production of epoxy resins from canola oil and alcohol esters of canola oil, and characterize those epoxy resins.

Objective 2. Characterize resins and plastic composites produced from those resins, using standard industry techniques.

Objective 3. Analyze economic feasibility of and identify steps to transfer technology for canola-based resins.

COOPERATING INVESTIGATORS:

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NATURE OF WORK AND RESULTS:

Objective 1. Identify and optimize procedures for production of epoxy resins from canola oil and alcohol esters of canola oil, and characterize those epoxy resins. (Espinoza-Perez, under the direction of Wiesenborn).

A process for epoxidation was developed and rigorously tested, using a three-necked round bottom flask equipped with 1) a condenser, 2) a mechanical stirrer, and 3) an addition funnel. The flask was placed in a water bath to control the temperature at 50 °C (shown right). To start the reaction, 100 g (0.12 mol) of canola oil and solvent (when tested) was placed in the reactor and mixed 5 min. Next 20 g of Amberlite IR 120 resin and 15 g (0.25 mol) of glacial acetic acid were added. After that, 68 g (1 mol) of 50% H_2O_2 was gradually added over 30 min. The reaction was allowed to progress 3 h at maximum stirrer speed (500 rpm). Upon completion of the reaction time, the Amberlite was filtered off, the resin washed with 300 mL of saturated Na_2CO_3 solution at 50 °C followed by water at 50 °C, to reduce resin pH to 7. The resin was then dried overnight with anhydrous $MgSO_4$, filtered, and finally dried at 80 °C under vacuum (25 in Hg) for 30 min (Crivello and Narayan, 1992). A number of process parameters were evaluated to arrive at this procedure, such as method of agitation/stirring, reaction time and temperature, concentration and level of addition of H_2O_2, and type and use of solvent. The success of any one set of process parameters was gauged by measuring the oxirane oxygen content, although viscosity and iodine value were also monitored. We found that the stirring should be vigorous and that the reaction was essentially complete within 3 h. Although use of the solvent toluene is routinely reported in the literature, this solvent is a workplace hazard, and we achieved equally high-quality resin in the absence of toluene. As a result of these studies, it will now be possible to scale-up production for applications testing and to estimate production costs for a small commercial process.

Goals for year 3 are to increase the capacity of the reaction to 1 kg, and increase the amount of product recovered through identification of a compatible, inexpensive, green solvent.

Objective 2. Characterize resins and plastic composites produced from those resins, using standard industry techniques. (Tatlari, under direction of Ulven)

Epoxidized canola oil is not yet commercially available; therefore, this study was initiated by analyzing two commercially available epoxidized soybean oil resins and one experimentally produced epoxidized methyl ester resin derived from canola as potential matrix materials for fiber reinforced structural composites. Based on preliminary results, one type of epoxidized soybean oil was selected for complete composite material characterization. Because of curing problems associated with amine based hardeners, an anhydride based curing agent was chosen for the final composite system chosen. Ultimately, a low cost process was proven for vegetable oil-based epoxy composite manufacturing. Vacuum assisted resin transfer molding (VARTM) was shown to be cost-effective and would not need the same manpower and facilities as needed in processing methods such as hand lay-up, SFF, or pultrusion. In addition, the use of a heating blanket to provide the required thermal energy for cure eliminated the need for an oven. Additionally, the mechanical properties evaluated for vegetable oil-based epoxy composite were shown to be sufficient for structural applications. Composite samples made of 35% G-60 (soybean oil-based epoxy resin) blends showed nearly the same behavior as control samples in which no soybean oil-based epoxy resin was used. Tensile modulus and tensile strength dropped 4.2% and 10.2%, respectively, for 35% G-60 blends samples compared to control samples which were made of Resinfusion 8603 epoxy resin. Subsequently, we developed the capability to produce adequate amounts and quantity of epoxidized canola oil, and are in the process of confirming the properties using many of the same methods of composites manufacturing and testing.

A dynamic mechanical analyzer (DMA) was obtained this past year through a competitive equipment grant from the USDA National Research Initiative to assist this andrelated projects. The DMA performs highly sensitive, dynamic characterization of material properties over a wide temperature range. The DMA will ensure that the biobased composites developed will provide the needed functional properties.

Goals for year 3 are to determine the performance of canola/synthetic resin blends to that of soy/synthetic and 100% synthetic resin, evaluate alternative formulation and layup techniques to further improve composite performance, further develop analysis tools for cured composite samples.

Objective 3. Analyze economic feasibility of and identify steps to transfer technology for canola-based resins.

Composite Innovations and AGCO are two regional businesses that have already demonstrated significant interest in our canola resins. A proposal was recently submitted to Composite Innovations on the application of the resin in splints for wood utility poles, at the request of Composite Innovations. The accomplishments of the first 18 months were key in developing the confidence and rationale to consider applications testing in the coming year.

Publications:

Espinoza-Perez, J.D., D.P. Wiesenborn, K. Tostenson, C.A. Ulven, and M. Tatlari. 2007. Preparation and partial characterization of canola-based epoxy resins for bio-based plastic composites, paper 076079. ASABE Annual International Meeting, Minneapolis, MN, 17 - 20 June.

Espinoza-Perez, J., D. Wiesenborn, C. Ulven, C. Gustafson, K. Tostenson, and M. Tatlari. 2007. Canola-based epoxy resins applied to plastic composites, paper RRV-07129. ASABE/CSBE North-central Intersectional Conference, Fargo, Oct. 12-13.

Tatlari, M. 2008. Vegetable Oil-based Epoxy Resin for Structural Composite Material Manufacturing. M.S. Thesis under direction of C. Ulven, North Dakota State University, Fargo, ND