

Canola-based Epoxy Resins for Bio-based Plastic Composites
Progress Report for Year One (2006)

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Project Duration: 3 years (currently finishing year 1)

Amount Requested from NCRP/North Central CRP: \$81,450
\$24,150 in year 1, \$29,750 in year 2, \$27,550 in year 3

NCRP Priority Addressed: A. Bio-diesel/Bio-products

Summary: Canola-based resins were produced and analyzed in our lab, and blended with synthetic resin at up to 20% to prepare composite samples. These initial blends decreased ability to withstand bending, but improved impact resistance compared to 100% synthetic resins. However, performance of canola-based resins we develop will likely at least equal that of soy-based resins by the end of year 2, because of the insights that have been gained in year 1. The experience being gained with these materials will enable us to develop suitable product applications, project costs, and transfer this technology to private industry. A minor addition to the original proposal is needed to characterize and inhibit resin crystallization during storage, but does not require a change in the budget.

Research Results: The overarching objectives are to identify the types of plastic composite applications for which canola-based resins are best suited, and to transfer affordable processes for canola-based resins and plastic composites to private industry. Year one focused on the first two of three proposed objectives (original proposal in addendum).

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.

Epoxy resin was produced first from canola methyl ester (ECME) and later from canola oil (ECO). Epoxidation methods which were evaluated thus far were epoxidation with (1) m-chloroperoxybenzoic acid (m-CPBA; Zhu et al., 2004), and (2) hydrogen peroxide and glacial acetic acid, in the presence of ion-exchange resin catalyst and toluene solvent (Crivello and Narayan, 1992). ECME was found to have a much lower viscosity than ECO (Table 1); therefore the reaction, purification and transfer of ECME is more easily accomplished. Use of m-CPBA was found to be the most direct method; however, the cost of m-CPBA was prohibitive for preparing more than the bare minimum amount of resin required for Objective 2. The second method achieved a resin of very good quality, and can be readily scaled up to provide a sufficient amount of resin for Objective 2.

Table 1. Characteristics of epoxy resins developed or acquired for this study.

Sample	Method ^a	Oxirane Content (%)	Viscosity (mPa-s) at 23-24°C
ECME	m-CPBA	6	17
	H ₂ O ₂ /acetic acid	6	23
ECO	m-CPBA	6	149
	H ₂ O ₂ /acetic acid	6	150
Commercial A ^b		5	197
Commercial B ^b		5	167

^a Epoxide resin samples were prepared at NDSU either directly using a peroxyacid (m-CPBA), or by using a mixture of hydrogen peroxide and acetic acid (H₂O₂/acetic acid).

^b A and B were PLASTHALL[®] ESO and PARAPLEX[®] G-60, respectively, provided by CP Hall.

Oxirane content should be maximized to achieve high cross-linking, with the maximum possible being limited by the level of unsaturation. Canola and soybean oil have similar levels of unsaturation, and thus ECME, ECO and the other resins in this study have similar upper limits for oxirane content (Table 1). Vegetable oil-based resins were found to slowly crystallize during storage, thereby interfering with their use in composite applications. However, crystallization was reversed by gently heating the resin and then cooling to room temperature.

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

Current industry practice is to blend a vegetable oil-based resin with a synthetic resin, and then cure the resin by addition of a hardener. Our goal is to produce composites that incorporate as much canola-based resin as possible, while also maintaining a flexural strength (ability to withstand bending) similar to 100% synthetic resin. But flexural modulus should be reduced to improve impact resistance. Hardened sample with up to 10% ECME was prepared. The flexural strength of the hardened sample was less than the 100% synthetic sample; however, flexural modulus showed the desired decrease (Figure 1). Recently, hardened samples with 20% ECO were prepared and show promise, but these have yet to be evaluated for flexural strength and flexural modulus.

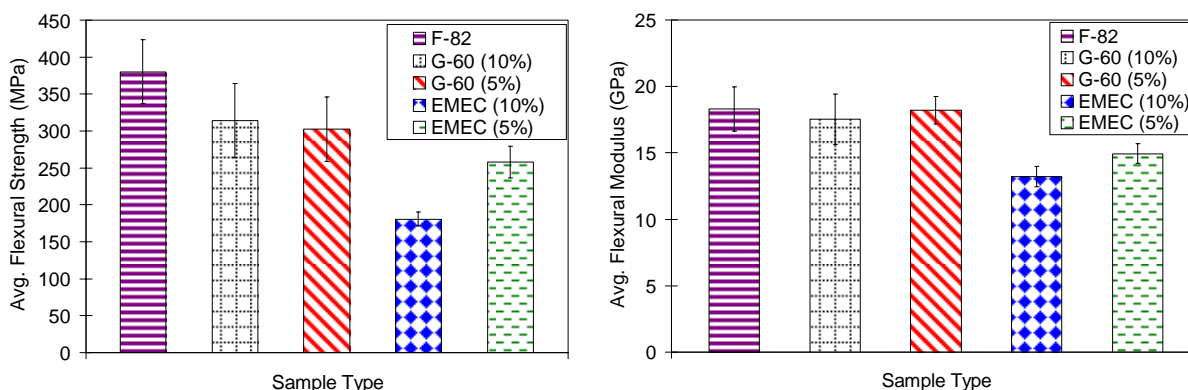


Figure 1. Average flexural strength (left) and flexural modulus (right) calculated for composite samples of E-glass/100% synthetic (F-82), E-glass/5% and 10% soybean oil-based epoxy (G-60) with synthetic epoxy (F-82) blends, and E-glass/5% and 10% epoxidized methyl ester derived from canola oil (EMEC) with synthetic epoxy (F-82) blends. Error bars denote standard deviation.

Publications

Tatlari M, Sailer N, Ulven CA, Wiesenborn DP, Tostenson K, Polansky P, and Krog A. (2006) Vegetable Oil-Based Epoxy Resin for Structural Composite Material Manufacturing. The American Society for Composites (ASC) 21st Annual Technical Conference, Dearborn, MI, Sept. 17th – 20th, Paper #170, CD-ROM Proceedings.

Tatlari M, Ulven CA, Sailer N, Wiesenborn DP, Tostenson K, Polansky P, and Krog A (2006) Vegetable Oil-Based Epoxy / E-Glass Composite Materials: Properties and Synthesis. Society for the Advancement of Materials and Process Engineering (SAMPE) Fall Technical Conference, Dallas, TX, Nov. 6th – 9th, CD-ROM Proceedings.