

# PRODUCTION AND CHARACTERIZATION OF EPOXIDIZED CANOLA OIL

J. D. Espinoza Pérez, D. M. Haagenon, S. W. Pryor, C. A. Ulven, D. P. Wiesenborn

**ABSTRACT.** Epoxidized canola oil may be well suited to the partial replacement of petroleum products in composite matrices; however, a process is needed to obtain this material from canola oil at sufficient conversion and scale to assess product properties. Therefore, canola oil was epoxidized in a solvent-free process with a heterogeneous catalyst; a fractional factorial design was used to determine the impact of processing conditions and their two-factor interactions on epoxy group content of epoxidized canola oil. The studied parameters were: molar ratio of acetic acid to unsaturation, molar ratio of hydrogen peroxide to unsaturation, concentration of hydrogen peroxide, concentration of catalyst, and temperature. Epoxidized canola oil with up to 98.5% conversion was produced. The parameters molar ratio of acetic acid to unsaturation, concentration of hydrogen peroxide, temperature, and their interactions were found to be significant in the defined design space. Process conditions that achieved the highest conversion were scaled to 300 g to compare the conversion, production yield, and rheological and melting properties of products of the epoxidation of both canola and soybean oil with and without solvent. Epoxidized canola oil crystallized at room temperature; at 40 °C it was shear-thinning with an apparent viscosity of 140 to 150 mPa·s. Elimination of solvent in the epoxidation process decreased the yield 10% but did not reduce the conversion to epoxy groups. Therefore, the scaled-up, solvent-free process is proposed as a green alternative for sufficient epoxidized canola oil to test composite applications.

**Keywords.** Bio-composites, Bio-products, Composites, Epoxidation of vegetable oils, Epoxidized soybean oil, Epoxy resins, Green chemistry, Thermosetting resins.

Vegetable oils provide consumer-friendly and environmentally friendly substitute products for petrochemicals. From the wide variety of potential vegetable oil products, this study is focused on epoxidized canola oil. Epoxidized vegetable oils are widely used as a plasticizers and stabilizers of PVC, and they also can be used as part of the matrix in the preparation of composites. The matrix will typically be reinforced by a fiber such as E-glass. Thermosetting resins, which crosslink in presence of a hardener, are widely applied as matrices in composites. Epoxy resins, which include epoxidized vegetable oil, are one of the most common types of thermosetting resins. Epoxy resins contain epoxides as functional groups. Therefore, the degree of epoxidation will influence the properties of the final polymer. Although epoxidized vegetable oil is not a new material, much remains to be learned about the process and product characterization. Innovation with vegetable oils is needed to compete in applications currently dominated by

petroleum (Chen et al., 2002; Liu and Erhan, 2005; Liang et al., 2005; Boquillon, 2006; Güner et al., 2006). A number of studies have evaluated key factors for epoxidation of soybean and other oils, including concentration of reagents, reaction temperature, and reaction time, but little has been reported for epoxidized canola oil (Sinadinovik-Fiser et al., 2001; Rangarajan et al., 1995; Vicek and Petrovic, 2006; Goud et al., 2006; Goud et al., 2007; Mungroo, et al., 2008, Campagnella et al., 2009). In studies where many factors are involved, fractional factorial designs can be applied to identify those factors with large effects (Myers and Montgomery, 2002).

Epoxides, also known as oxiranes or epoxy groups, are cyclic ethers with a three-membered ring structure. Due to this highly strained ring structure, epoxy groups are more reactive than other ethers, making them important intermediates for a variety of products (Goud et al., 2006). Epoxidation of vegetable oils consists of adding a single oxygen atom to each unsaturation (carbon-carbon double bond) in the fatty acid chain using percarboxylic acids or organic and inorganic peroxides as oxidizing agents; the original unsaturation is thus converted into an epoxy group. A high content of unsaturation in the vegetable oil is desirable during the epoxidation reaction. Therefore, the vegetable oil fatty acid profile can be used to predict the content of unsaturation and formation of epoxy groups. The conversion of unsaturation to epoxy groups can be directly monitored with the oxirane oxygen content, and indirectly with the iodine value (Parreira et al., 2002).

The canola oil fatty acid profile differs from that of soybean oil, the most commonly epoxidized vegetable oil. Canola oil is rich in monounsaturated oleic acid (62%), while

---

Submitted for review in March 2009 as manuscript number FPE 7965; approved for publication by the Food & Process Engineering Institute Division of ASABE in June 2009.

The authors are **Judith D. Espinoza Pérez**, ASABE Member Engineer; Graduate Student, **Darrin M. Haagenon**, Research Specialist, and **Scott W. Pryor**, ASABE Member Engineer, Assistant Professor, Department of Agricultural and Biosystems Engineering, **Chad A. Ulven**, Assistant Professor, Department of Mechanical Engineering and Applied Mechanics, and **Dennis P. Wiesenborn**, Professor, Department of Agricultural and Biosystems Engineering, North Dakota State University, Fargo, North Dakota. **Corresponding author:** Dennis P. Wiesenborn, Department of Agricultural and Biosystems Engineering, North Dakota State University, P.O. Box 6050, Fargo, ND 58108-6050; phone: 701-231-7277; fax: 701-231-1008; e-mail: D.Wiesenborn@ndsu.edu.

soybean oil has a higher content of polyunsaturated linoleic acid (53%). Another significant difference between these oils is the content of saturated fatty acids. Canola oil has a lower content of saturated fatty acids (6%) in comparison with soybean oil (15%) (Ackman, 1990). Saturated fatty acids cannot be epoxidized and thus cannot participate in the preparation of polymers. This characteristic of the fatty acid profile of canola oil makes it well suited to the development of new epoxy resins.

The degree of epoxidation has an effect on the resin physical properties, such as viscosity and crystalline melting temperature. These physical properties determine the application and processing of the resin. The composites industry requires resin viscosities less than 500 cP for liquid molding operations because higher viscosities cause voids and increase infusion and production time (La Scala and Wool, 2005).

Industrially, epoxidized vegetable oils are mainly prepared from peracid formed *in situ* from the reaction of hydrogen peroxide with acetic acid or formic acid. The use of formic acid does not require a catalyst, but it is more expensive than acetic acid. Acetic acid requires an acid catalyst, which can be homogenous (liquid) or heterogeneous (solid). Homogeneous catalysts are not expensive, but they are not easily reused and their side reactions promote epoxy-group degradation (especially to hydroxyl groups). Heterogeneous catalysts are easily removed from the product and recycled, decreasing the environmental impact and the production cost. Heterogeneous catalysts, such as ion exchange resins, also reduce side reaction production, decreasing epoxy-group degradation (Gunstone, 1997; Hang and Yang, 1999; Campanella and Baltanás, 2005). Organic solvents such as hexane, heptane, benzene, and toluene are used in the epoxidation of vegetable oils to decrease the epoxy-group degradation and to facilitate sample purification (Rangarajan et al., 1995; Goud et al., 2007; Campanella et al., 2009). Associated health hazards, as well as increased time and cost of organic solvent use and recovery, are disadvantages.

Epoxidation of canola oil was recently reported by Campanella et al. (2009) and Mugroo et al. (2008). In the first study, canola oil was epoxidized using performic acid in the presence of benzene with a conversion of 95%. In the second study, a small sample of canola oil (23 g) was epoxidized in a solvent-free process using a heterogeneous catalyst with acetic acid and formic acid. Use of acetic acid resulted in better conversion of unsaturated groups to epoxy groups (90%) compared to formic acid. The catalyst showed little loss of activity upon reuse. This environmentally friendly approach is worth pursuing; however, higher conversion and scale are needed, as well as additional information about the processing and properties of epoxidized canola oil, to evaluate epoxidized canola oil for composite material applications. Therefore, one objective of this study was to develop the production of epoxidized canola oil via a solvent-free, heterogeneous-catalysis process, using a fractional factorial design to identify the significant process factors to improve conversion. A second objective was to scale the process to 300 g and then compare the conversion, production yield, and rheological and melting properties of products of the epoxidation of both canola and soybean oil with and without solvent.

## MATERIALS AND METHODS

### MATERIALS

Commercial edible-grade canola and soybean oil were acquired locally. The catalyst Amberlite IR120 H resin (ion exchange capacity = 1.8 eq L<sup>-1</sup>; mean particle size: 0.62 to 0.83 mm) used as received was purchased from Acros Organics (Morris Plains, N.J.). Glacial acetic acid, aqueous solutions of hydrogen peroxide (30% and 50%), and anhydrous sodium carbonate were purchased from EDM Chemicals (Gibbstown, N.J.). Anhydrous magnesium sulfate was acquired from Mallinckrodt Baker, Inc. (Phillipsburg, N.J.). Toluene was purchased from BDH (Muskegon, Mich.). All other chemicals used in this study were of analytical reagent grade.

### SOLVENT-FREE EPOXIDATION OF CANOLA OIL

Epoxidation of canola oil was carried out in a 1 L three-necked round bottom flask equipped with (1) a thermometer, (2) an addition funnel, and (3) a mechanical stirrer. A semi-circular Teflon stirrer blade (long-groove keyhole) of 75 mm diameter on a glass shaft was connected to the mechanical stirrer (Arrow Engineering Co., Inc., Hillside, N.J.). The flask was placed in a water bath to control the temperature. Canola oil (50 g) containing 0.221 moles of unsaturation, acetic acid, and catalyst was first added to the flask in accordance with the experimental design (table 1). Flask contents were mixed for 5 min prior to dropwise (2 mL min<sup>-1</sup>) addition of the aqueous solution of hydrogen peroxide (30% or 50%) to the flask. After hydrogen peroxide addition, the reaction was carried out for 5 h at 500 rpm. The catalyst was then filtered off using cheesecloth, and the filtrate was held in a separatory funnel for 2 h; the lower (aqueous) layer was discarded. The organic layer was washed three times with 150 mL of saturated sodium carbonate solution at 50 °C, and then three times with 150 mL of water at 50 °C. The organic layer was dried overnight with 10 g of anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration under vacuum with Whatman No. 4 filter paper. All treatments were carried out in duplicate. Oxirane oxygen content, iodine value, conversion, selectivity, and FTIR spectroscopy were used to characterize the epoxidation products. The conditions in table 1 were selected on the basis of a fractional factorial design with five factors.

### FATTY ACID PROFILE DETERMINATION

Fatty acid profiles of canola oil and soybean oil were determined by gas chromatography according to the method described by Zheljzkov et al. (2008). In a 2 mL vial, 2 µL of oil were mixed with 1 mL of hexane/chloroform/0.5 M sodium methoxide in methanol (75:20:5, v/v/v). The sample (1 µL) was injected into a Hewlett-Packard model 5890 Series II gas chromatograph containing a DB-23 capillary column (30 m × 0.25 mm, J&W Scientific, Folsom, Cal.) and equipped with a flame ionization detector. The column was initially maintained at 190 °C for 4 min and was increased at a 15 °C min<sup>-1</sup> rate to 220 °C. After 1 min at 220 °C, the temperature was increased to 240 °C at a rate 25 °C min<sup>-1</sup> and was held at 240 °C for 1 min, for a total run time of 8.8 min. The injector and detector temperatures were 230 °C and 250 °C, respectively. The carrier gas was helium at a flow rate of 1.9 mL min<sup>-1</sup> and a split flow of 100 mL min<sup>-1</sup>. Peak identification was performed by comparing the relative retention times with those of a commercial standard mixture of fatty

**Table 1. Experimental design and reaction conditions of the solvent-free epoxidation of canola oil.**

Treatment	Factor <sup>[a]</sup>					Reagent Amounts		
	A	B	C	D	E	AA	HP	Catalyst
	AA:U Molar Ratio	HP:U Molar Ratio	HP (% wt)	Catalyst (% wt)	Temperature (°C)	AA (mL)	HP (g)	Catalyst (g)
1	1:1	2:1	50	35	60	12.6	30.1	14.9
2	0.5:1	2:1	50	35	50	6.3	30.1	12.7
3	1:1	1.5:1	50	35	50	12.6	22.5	12.3
4	0.5:1	1.5:1	50	35	60	6.3	22.5	10.1
5	1:1	2:1	30	35	50	12.6	50.1	22.0
6	0.5:1	2:1	30	35	60	6.3	50.1	19.7
7	1:1	1.5:1	30	35	60	12.6	37.6	17.6
8	0.5:1	1.5:1	30	35	50	6.3	37.6	15.4
9	1:1	2:1	50	25	50	12.6	30.1	10.7
10	0.5:1	2:1	50	25	60	6.3	30.1	9.1
11	1:1	1.5:1	50	25	60	12.6	22.5	8.8
12	0.5:1	1.5:1	50	25	50	6.3	22.5	7.2
13	1:1	2:1	30	25	60	12.6	50.1	15.7
14	0.5:1	2:1	30	25	50	6.3	50.1	14.1
15	1:1	1.5:1	30	25	50	12.6	37.6	12.6
16	0.5:1	1.5:1	30	25	60	6.3	37.6	11.0

<sup>[a]</sup> A = Acetic acid (AA) : unsaturation (U) molar ratio (AA:U).  
 B = Hydrogen peroxide (HP) : unsaturation (U) molar ratio (HP:U).  
 C = Concentration of the aqueous solution of hydrogen peroxide (% wt).  
 D = Concentration of catalyst as percentage of the combined weight of acetic acid and hydrogen peroxide (% wt).  
 E = Temperature (T, °C).

acid methyl esters purchased from Nu-Chek Prep, Inc. (Elysian, Minn.), and fatty acid concentrations were expressed as a weight percentage of the total fatty acids.

**IODINE VALUE, HYDROXYL VALUE, AND OXIRANE OXYGEN CONTENT**

The iodine value (IV) was determined on canola oil, soybean oil, and the products of epoxidation using ASTM method D5554 (ASTM, 2001). The iodine value of canola oil and soybean oil was also estimated from the fatty acid composition using equation 1 from AOCS recommended practice Cd 1c-85 (AOCS, 1998):

$$IV = (\% \text{ palmitoleic} \times 0.950) + (\% \text{ oleic} \times 0.899) + (\% \text{ linoleic} \times 1.810) + (\% \text{ linolenic} \times 2.735) + (\% \text{ gadoleic} \times 0.818) + (\% \text{ erucic} \times 0.749) \quad (1)$$

The hydroxyl value and the oxirane oxygen content were determined on the products of epoxidation with AOCS methods Tx 1a-66 and Cd 9-57 (AOCS, 1980, 1989), respectively. The conversion of unsaturation to epoxy groups was calculated with the equation 2:

$$\% \text{ conversion} = \frac{OO_e}{OO_p} \quad (2)$$

where  $OO_e$  is the oxirane oxygen content experimentally determined, and  $OO_p$  is the maximum predicted oxirane content, which was calculated with equation 3 (Goud et al., 2006):

$$OO_p = \left[ \frac{\frac{IV_0}{2A_i}}{100 + \left(\frac{IV_0}{2A_i}\right)A_o} \right] \times A_o \times 100 \quad (3)$$

where  $A_i$  and  $A_o$  are the atomic weights of iodine (126.9) and oxygen (16.0), respectively; and  $IV_0$  is the initial iodine value of the vegetable oil determined by ASTM method D5554 (ASTM, 2001).

The selectivity for oxirane oxygen can be calculated by equation 4 (Campanella et al., 2008):

$$\text{Selectivity} = \frac{OO_e}{OO_p} \times \frac{IV_0}{IV_0 - IV} \quad (4)$$

where  $IV$  is the iodine value of the epoxidized sample determined by ASTM method D5554 (ASTM, 2001).

**FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY ANALYSIS**

The formation of epoxy groups and consumption of unsaturation were characterized on the products of epoxidation by FTIR spectroscopy (epoxy ring deformation: 823.3  $\text{cm}^{-1}$ ; CH stretching of =CH: 3007  $\text{cm}^{-1}$ ). FTIR spectra were collected from epoxy resins using a Nicolet 6700 FTIR spectrometer (ThermoFisher Scientific, Madison, Wisc.) operating with 32 scans and a resolution of 4  $\text{cm}^{-1}$ . The spectrometer was equipped with a deuterated triglycine sulfate (DTGS) detector, and spectra were collected with the Smart ARK multiple reflection ATR accessory (ThermoFisher Scientific, Madison, Wisc.) equipped with a 45° ZnSe crystal. Peak identities were determined with OMNIC software version 7.0 (ThermoFisher Scientific, Madison, Wisc.).

**VISCOSITY**

Viscosity measures of the products of epoxidation were carried out in a VT500 viscometer (Haake, Saddle Brook, N.J.) using the PK cone and plate sensor system (cone angle 0.5°). Epoxidized canola oil tended to crystallize at room temperature; therefore, the analysis was carried out at 40°C. A 0.1  $\text{cm}^3$  sample was placed on the plate, covering the complete surface, and then the plate and sample were positioned

**Table 2. Reaction conditions for comparison of epoxidized canola oil (ECO) and epoxidized soybean oil (ESO) prepared with and without solvent.**

Vegetable Oil	Molar Ratio (U/AA/HP)	AA (mL)	HP (g)	HP (% wt)	Catalyst (g)	Solvent (mL)	T (°C)
Canola oil	1/0.5/2	37.9	180.4	50	54.6	--	60
Canola oil	1/0.5/2	37.9	180.4	50	54.6	150	60
Soybean oil	1/0.5/2	47.7	226.9	50	68.7	--	60
Soybean oil	1/0.5/2	47.7	226.9	50	68.7	150	60

in contact with the cone for 5 min to equilibrate sample temperature before sample shearing was initiated. The viscosity (mPa·s) and shear stress were measured at four shear rates: 5994, 3596, 2155, and 1294 s<sup>-1</sup>. Torque values were within the range of 0.2 to 0.5 N·cm. Shear rate was held constant for 20 s before the viscosity reading was recorded. The tests were carried out in triplicate, using fresh sample for each replicate. The resins were observed to be shear-thinning. Therefore, shear stresses at the different shear rates (s<sup>-1</sup>) for each sample were fitted to the power law model (eq. 5):

$$\sigma = K\gamma^n \quad (5)$$

where  $\sigma$  is the shear stress (Pa),  $\gamma$  is the shear rate (s<sup>-1</sup>),  $K$  is the flow consistency index (Pa·s<sup>n</sup>), and  $n$  is the flow behavior index (dimensionless) (Singh and Heldman, 2001). The fit of data to the power law model was used to find  $K$  and  $n$ .

#### MODULATED DIFFERENTIAL SCANNING CALORIMETRY (MDSC) ANALYSIS

Onset and maximum crystalline melting temperatures, enthalpy of melting, and liquid heat capacity were determined on the products of epoxidation by MDSC analysis with a Q1000 DSC (TA Instruments, New Castle, Del.). Indium was used as a temperature and enthalpy calibration, and sapphire was used for heat capacity calibration. Dry nitrogen gas with a flow rate of 50 mLmin<sup>-1</sup> purged the cell. Runs were carried out using an empty cell as a reference. Samples (8 to 15 mg) were placed in aluminum hermetic cells. The analyses were carried out from -90 °C to 75 °C, with a ramp of 3 °C min<sup>-1</sup>. A period of 40 s and amplitude of 0.6 °C were used to produce the sinusoidal modulation. The data were analyzed by TA Instruments' Universal Analysis 2000 software to separate total heat flow into the reversing and non-reversing components. Enthalpy of melting was obtained by integration of the melting peak using the reverse heat flow signal.

#### STATISTICAL ANALYSIS

The analysis of variance (ANOVA) was generated to identify the significant factors using the oxirane oxygen content as the response variable (SAS 9.1 software). The significance of the factors of the F-value was evaluated at a probability level (p) of 0.05.

#### SOLVENT-FREE EPOXIDATION VERSUS SOLVENT EPOXIDATION

One of the set of conditions from table 1 that resulted in high conversion to epoxy groups was selected to epoxidize canola oil and soybean oil with and without solvent (toluene) and scaled up from 50 g to 300 g of vegetable oil per batch. The epoxidation reactions were carried out as described earlier, but with 300 g of oil and with two additional steps when incorporating toluene: (1) 150 mL of toluene were added to the reaction mix, and (2) after the epoxidized sample was dried with anhydrous magnesium sulfate, toluene was re-

moved by heating under vacuum. When soybean oil was epoxidized, the amount of the reagents was adjusted to the molar content of unsaturation of soybean oil (1.668 mole of unsaturation per 300 g of soybean oil). The reaction conditions are shown in table 2. Oxirane oxygen content, iodine value, hydroxyl value, conversion, selectivity, yield, viscosity, crystalline melting properties, and liquid heat capacity were analyzed in the products of epoxidation. The yield of epoxidized vegetable oils in the presence and absence of solvent was evaluated with equation 6:

$$\% \text{ yield of epoxidation} = \frac{\text{mass epoxidized vegetable oil}}{\text{mass initial vegetable oil}} \times 100 \quad (6)$$

## RESULTS

#### FATTY ACID PROFILES OF CANOLA OIL AND SOYBEAN OIL

The fatty acid profiles of canola oil and soybean oil used in this study are shown in table 3. The content of saturated fatty acids (16:0, 18:0, and 20:0) in canola oil (7%) was lower than in soybean oil (15%). Saturated fatty acids cannot be epoxidized; thus, they cannot participate in crosslinking during the preparation of polymers. This characteristic of the fatty acid profile of canola oil makes it well suited to the development of new epoxy resins. The fatty acid composition of vegetable oils varies with climate, and can be genetically manipulated. The content of oleic acid found in the canola oil used in this study (64%) was slightly higher than the range of 60% to 63% reported in the literature (Ackman, 1990; Mungru et al., 2008; Campanella et al., 2009). This was not unexpected due to the genetic manipulation efforts to increase the content of this fatty acid. Based on these fatty acid profiles, the content of unsaturation per mole of triglyceride was 3.7 for canola oil and 4.4 for soybean oil. The predicted iodine value of canola oil from the fatty acid profile using equation 1 was 111.2, while the determined iodine value (ASTM, 2001) was 112.2 ± 0.3.

**Table 3. Fatty acid profiles of canola oil and soybean oil used to prepare epoxy resins.**

Common Name	C:U (P) <sup>[a]</sup>	Fatty Acid (%)	
		Canola Oil	Soybean Oil
Palmitic	16:0	4.3	10.7
Stearic	18:0	2.0	4.4
Oleic	18:1 (9)	64.0	22.5
Linoleic	18:2 (9,12)	18.4	52.4
Linolenic	18:3 (9,12,15)	7.2	6.7
Arachidic	20:0	0.6	0.3
Gadoleic	20:1 (9)	1.1	0.2

<sup>[a]</sup> C = number of carbons of the fatty acid chain.

U = number of unsaturation.

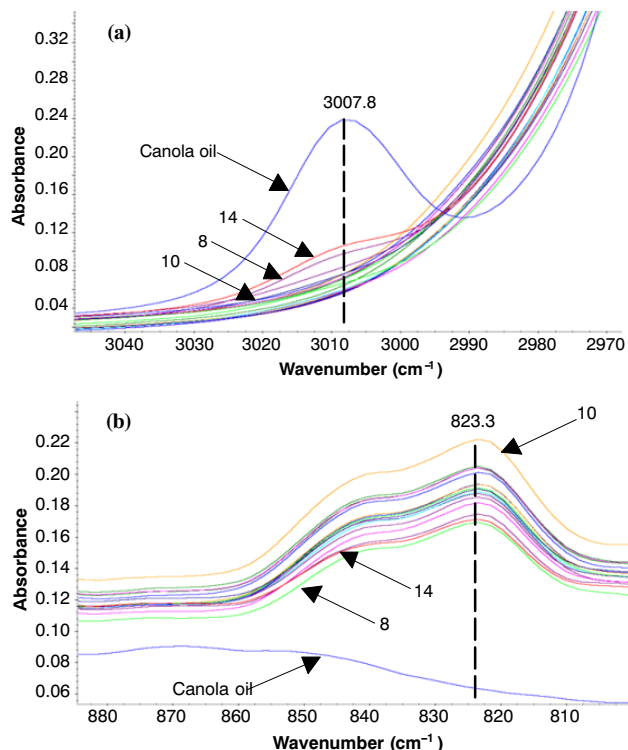
P = position of carbon after which the unsaturation is located.

## CHARACTERIZATION OF THE SOLVENT-FREE EPOXIDIZED CANOLA OIL

The iodine value and the oxirane oxygen content are especially important properties in the characterization of epoxidized vegetable oils. While the iodine value indicates the remaining unsaturation after the epoxidation reaction, the oxirane oxygen content indicates the epoxy groups present in the products (table 4). In the preparation of polymers, epoxy resins with a lower iodine value and higher oxirane oxygen content are desired. The iodine values of the 16 treatments were reduced 93% to 99.7% relative to the initial iodine value of canola oil. The reductions in iodine values indicated the consumption of the unsaturation during the epoxidation, but they did not represent solely conversion to epoxy groups because epoxy ring degradation generates side products.

The predicted oxirane oxygen content for canola oil using equation 3 and the determined iodine value was 6.6%. Oxirane oxygen values varied from 4.7 to 6.5, which represents 71% to 98.5% conversion of unsaturation to epoxy groups (table 4). Recently, Campanella et al. (2009) reported a 95% conversion in the epoxidation of canola oil in the presence of performic acid and benzene. Mungroo et al. (2008) reported a 90% conversion in the epoxidation of small (23 g) samples of canola oil, under conditions similar to this study, but with magnetic stirring and taking a series of samples at intervals of time from the reactor. Their lower conversion in comparison with the highest conversion (98.5%) in this study could be due to the different mixing conditions. In addition, the sampling of the reactor may have altered the relative amounts of the three-phase reaction system (organic phase, aqueous phase, and solid catalyst phase). Selectivity was correspondingly high (>0.96) in most of the treatments, except treatments 8 and 14 with selectivities of 0.76 and 0.78, respectively (table 4).

The unsaturation and epoxy groups can also be monitored by Fourier transform infrared (FTIR) spectroscopy. FTIR spectroscopy is a rapid, nondestructive technique that has been widely applied in the characterization of lipids because lipids have functional groups with characteristic absorption bands in the infrared region of the electromagnetic spectrum (Hendl et al., 2001; Flatten et al., 2005). Figure 1a shows the



**Figure 1.** FTIR spectra of canola oil and canola epoxy resins, showing (a) unsaturation present at 3007 cm<sup>-1</sup> and (b) epoxy groups present at 823.3 cm<sup>-1</sup>. Treatment numbers correspond to those in tables 1 and 4.

presence of unsaturation in canola oil at 3007.8 cm<sup>-1</sup> (Chen et al., 2002); among the canola epoxy resins, only treatments 8 and 14 with the lowest oxirane oxygen contents and highest iodine values showed absorbance in this region of the spectrum. Figure 1b shows the presence of epoxy groups in the canola epoxy resins at 823.8 cm<sup>-1</sup> (Vicek and Petrovic, 2006), while canola oil did not show any peak in this region. Thus, the FTIR spectra confirmed the results from the analytical oxirane oxygen content and iodine value determinations for the 16 treatments.

### Statistical Analysis

Because oxirane oxygen content is a direct measure of the degree of epoxidation, this parameter was used to evaluate the impact of the following reaction conditions in the conversion of unsaturation from canola oil to epoxy groups: (A) acetic acid:unsaturation molar ratio, (B) hydrogen peroxide:unsaturation molar ratio, (C) concentration of the aqueous solution of hydrogen peroxide, (D) concentration of the catalyst, and (E) temperature. The analysis of variance (ANOVA) identified factors A, C, and E, and their interactions (AC, AE, and CE) as statistically significant ( $p < 0.05$ ) for the levels in this study.

Oxirane oxygen content (OO%) can be predicted with the regression model (eq. 7) based on the significant factors:

$$OO\% = 6.0938 + 0.2188x_1 + 0.2188x_2 + 0.2313x_3 - 0.2313x_1x_2 - 0.1438x_1x_3 - 0.1938x_2x_3 \quad (7)$$

where  $x_1$ ,  $x_2$ , and  $x_3$  are the coded variables on the interval (-1, +1) that represent factors A, C, and E, respectively.

Initially, two levels for each factor were selected in order to screen their effect in the conversion to epoxy groups. Fur-

**Table 4.** Chemical properties, percent conversion, and selectivity of the solvent-free epoxidized canola oil (means  $\pm$ SD).

Treatment	Iodine Value (g I <sub>2</sub> /100 g)	Oxirane Oxygen Content (%)	Percent Conversion	Selectivity
1	0.3 $\pm$ 0.4	6.3 $\pm$ 0.3	95.5	0.96
2	1.7 $\pm$ 2.0	6.4 $\pm$ 0.3	97.0	0.98
3	1.8 $\pm$ 0.8	6.3 $\pm$ 0.2	95.5	0.97
4	1.2 $\pm$ 0.3	6.3 $\pm$ 0.3	95.5	0.96
5	6.9 $\pm$ 0.2	6.2 $\pm$ 0.5	94.0	1.00
6	6.3 $\pm$ 1.0	6.2 $\pm$ 0.6	94.0	1.00
7	1.9 $\pm$ 0.1	6.5 $\pm$ 0.7	98.5	1.00
8	7.1 $\pm$ 0.3	4.7 $\pm$ 0.2	71.2	0.76
9	0.6 $\pm$ 0.8	6.3 $\pm$ 0.1	95.5	0.96
10	0.8 $\pm$ 0.1	6.5 $\pm$ 0.0	98.5	0.99
11	0.4 $\pm$ 0.5	6.3 $\pm$ 0.1	95.5	0.96
12	6.9 $\pm$ 0.2	6.1 $\pm$ 0.3	92.4	0.98
13	2.8 $\pm$ 2.1	6.5 $\pm$ 0.1	98.5	1.01
14	7.0 $\pm$ 0.5	4.8 $\pm$ 0.2	73.0	0.78
15	6.5 $\pm$ 0.9	6.1 $\pm$ 0.3	92.4	0.98
16	6.5 $\pm$ 0.7	6.0 $\pm$ 0.3	91.0	0.96

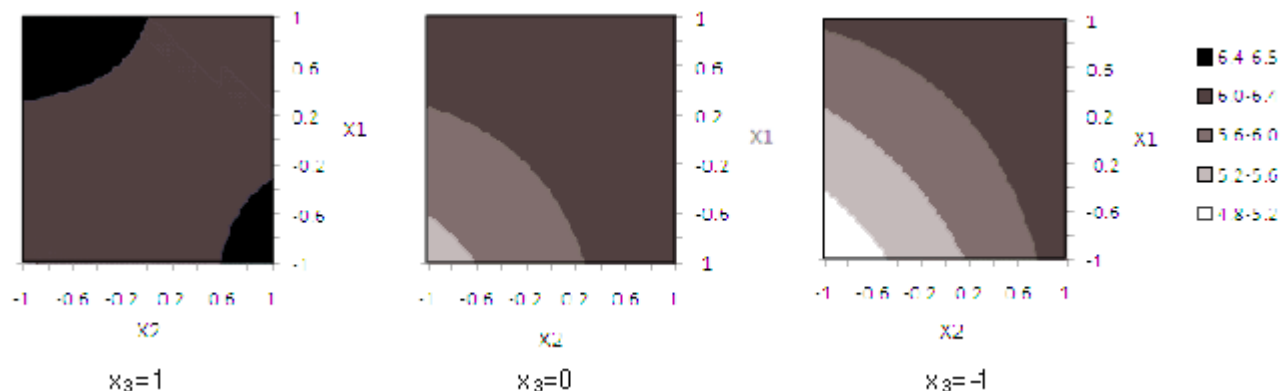


Figure 2. Oxirane oxygen content variation as a function of significant factors: A( $x_1$ ) = acetic acid:unsaturation molar ratio; C( $x_2$ ) = concentration of hydrogen peroxide solution; and E( $x_3$ ) = temperature.

ther optimization was deemed not necessary because of the high degree of epoxidation obtained with the initial array of conditions. The selection of only two levels for each factor limited the accuracy of the obtained mathematical model. A two-level factorial design intrinsically assumes a linear relationship between each of the factors and the response variable, but such linear relationships are often not valid for the entire region of the design space.

Studies of epoxidation of vegetable oils generally define the optimal conditions of the process by analyzing one or two factors at a time (Rangarajan et al., 1995; Goud et al., 2006; Goud et al., 2007; Mungroo, et al., 2008). However, a fractional factorial design allows evaluation of the effects of several factors simultaneously.

Acetic acid participates as the oxygen carrier and is regenerated after the formation of epoxy groups; therefore, it can also participate in the degradation of epoxy groups. If the aqueous solution of hydrogen peroxide is more dilute, then more water is added to the system, increasing the possibility of epoxy group degradation. Therefore, to optimize the concentration of these reagents, it is relevant not only to achieve a high concentration of epoxy groups but also low degradation. Studies of epoxidation of different vegetable oils reported that increasing the reaction temperature increased both the rate of conversion and the rate of degradation of epoxy groups. (Sinadinovik-Fiser et al., 2001; Rangarajan et al., 1995; Viecek and Petrovic, 2006; Goud et al., 2006; Goud et al., 2007; Mungroo, et al., 2008). Figure 2 shows the expected results of oxirane oxygen content in the defined design space for the significant factors (A) acetic acid:unsaturation molar ratio, (C) concentration of the aqueous solution of hydrogen peroxide, and (E) temperature. At the highest temperature ( $x_3 = 1$ ), the best conversion to epoxy groups was achieved when the molar ratio of acetic acid to unsaturation and hydrogen peroxide concentration were at different ends of the spectrum (+1,-1 or -1, +1), which corresponded to treatments 7, 10, and 13 (table 4). These results showed that, although treatments 7 and 13 were prepared with the lower concentration of hydrogen peroxide solution, the elevated temperature (60°C) had a larger effect in increasing the conversion to epoxy groups.

In contrast, the combination of the lower levels of these significant factors, corresponding to treatments 8 and 14, achieved lower conversion to epoxy groups and higher degradation, as indicated by their selectivities (table 4). The more dilute hydrogen peroxide leads to the addition of more water,

which promotes the hydrolysis of the epoxy groups, as noted above. Therefore, as temperature decreases, it is important to have both the other significant factors at the highest levels. In summary, at the highest temperature, the response is generally more robust, with lessened impact of the other factors. As temperature drops, the other factors become more significant.

Factors B (hydrogen peroxide:unsaturation molar ratio) and D (% catalyst) were not significant in the defined experimental design, but those factors are important in the epoxidation process. Hydrogen peroxide participates as the oxidant in epoxidation and is usually added in excess to ensure completion of the reaction. As a consequence, it can also participate in the degradation of the epoxy groups (Goud et al., 2007). In this study, the levels of factor B (hydrogen peroxide:unsaturation) of 1.5:1 and 2:1 were not significant. This result implied that the delimited design space of factor B did not include the area where this factor had an impact in the conversion to epoxy groups. An ion exchange resin was used as the catalyst in the epoxidation reaction. This catalyst reduces the degradation of the epoxy groups because large molecules from the organic phase cannot go into the resin where the peracetic acid is produced (Campanella and Baltanás, 2005). For this reason, it was expected that increasing the amount of catalyst would increase formation and decrease the degradation of the epoxy groups. However, the effect of catalyst concentration (factor D) was not significant at the given levels (25% and 35%), indicating that the analyzed levels were in excess. Other studies reported an effect of the catalyst concentration on conversion using lower catalyst concentrations (Sinadinovik-Fiser et al., 2001; Mungroo et al., 2008).

#### CHARACTERIZATION OF THE SOLVENT-FREE AND SOLVENT EPOXIDATION PRODUCTS

Treatment 10 (table 1) was scaled up to 300 g to epoxidize canola and soybean oil in the presence and absence of solvent (toluene) to compare the chemical properties, conversion, yield (table 5), and physical properties (tables 6 and 7) of the products. As shown in table 5, treatments 7, 10, and 13 had similar, high values of oxirane oxygen content; treatment 10 was selected because it also had the lowest standard deviation and lower iodine value, which implies a lower content of unsaturation. The scale up from 50 g to 300 g of vegetable oil batch was successful because scale up did not decrease the yield of epoxidation and the conversion to epoxy groups. This

**Table 5. Chemical characteristics, conversion, yield, and selectivity of solvent-free and solvent epoxidized canola oil (ECO) and epoxidized soybean oil (ESO) (means  $\pm$ SD).**

Epoxidized Vegetable Oil	Iodine Value (g I <sub>2</sub> /100 g)	Hydroxyl Value (mg KOH/g)	Oxirane Oxygen Content (%)	Conversion (%)	Selectivity	Yield of Epoxidation (%)
ECO (solvent-free)	0.3 $\pm$ 0.05	4.5 $\pm$ 0.6	6.5 $\pm$ 0.02	98.5	0.99	80.8 $\pm$ 0.4
ECO (solvent)	0.3 $\pm$ 0.02	2.9 $\pm$ 0.04	6.5 $\pm$ 0.04	98.5	0.99	90.3 $\pm$ 0.2
ESO (solvent-free)	0.3 $\pm$ 0.05	4.3 $\pm$ 0.9	7.1 $\pm$ 0.3	91.0	0.91	79.5 $\pm$ 0.5
ESO (solvent)	0.3 $\pm$ 0.00	3.4 $\pm$ 0.7	7.1 $\pm$ 0.04	91.0	0.91	90.2 $\pm$ 0.4

outcome could not be assumed, given the three-phase reaction system. Mass transfer could easily become limiting and result in a less successful outcome upon scale up.

The iodine value of soybean oil predicted from the fatty acid profile using equation 1 was 133.5, while the iodine value determined by ASTM method D5554 (ASTM, 2001) was 134.2  $\pm$ 0.2. The predicted oxirane oxygen content for soybean oil, using equation 3 and the determined iodine value, was 7.8%. Canola oil has less unsaturation than soybean oil, but is more readily epoxidized with high conversion and high selectivity.

Epoxidation with solvent facilitated sample handling, thereby minimizing filtration losses and providing higher sample recoveries. The theoretical epoxidized product weights of 100 g of initial oil based on the predicted oxirane content ( $OO_p$ ) are 106.4 g for canola oil and 109.6 g for soybean oil. The solvent-free process showed 10% lower yields than the solvent process because some product adhered to the surface of the catalyst. The solvent-free process showed the same conversion to epoxy groups as the solvent process. Similar results were found by Sinadinovic-Fiser et al. (2001), who studied the epoxidation of soybean oil and found that the presence of benzene did not have a significant effect in the conversion of unsaturation to epoxy groups. Other studies of epoxidation of vegetable oils evaluated the effect of the solvent in the conversion to epoxy groups; however, information about final product yields was not usually provided. Some studies found that diluting the organic phase with a solvent decreases the rate of side reactions that open the epoxy ring. For example, because hydrogen peroxide has a higher solubility in organic solvent than in water, the production of carboxylic acids, one type of side reaction product, decreases (Vicek and Petrovic, 2006; Goud et al., 2007). In the presence of solvent, the epoxidized canola and soybean oils showed lower hydroxyl values than in the solvent-free epoxidations, indicating lower presence of hydroxyl side products. However, since iodine values and oxirane oxygen content remained the same, selectivity did not decrease in the absence of solvent. Rheological properties at 40 °C were characterized in the products of epoxidation of canola and soybean oil in the presence and absence of solvent (table 6).

**Table 6. Rheological properties (at 40 °C) of solvent-free and solvent epoxidized canola oil (ECO) and epoxidized soybean oil (ESO) (means  $\pm$ SD).**

Epoxidized Vegetable Oil	Apparent Viscosity <sup>[a]</sup> (mPa·s)	Flow Behavior Index ( <i>n</i> )	Flow Consistency Index ( <i>K</i> , Pa·s <sup>n</sup> )
ECO (solvent-free)	152.0 $\pm$ 0.5	0.60	4.64
ECO (solvent)	140.0 $\pm$ 0.5	0.71	0.60
ESO (solvent-free)	160.5 $\pm$ 0.6	0.82	0.70
ESO (solvent)	155.0 $\pm$ 0.5	0.81	0.23

<sup>[a]</sup> Determined by cone-and-plate viscometer at shear rate = 5994 s<sup>-1</sup>.

The epoxidized canola samples showed a lower apparent viscosity than the samples from epoxidized soybean oil. The addition of the epoxy rings in the fatty acids chains increases the polarity of the modified vegetable oils; this in turn increases the intermolecular interactions among molecules, increasing the viscosity (Samuelsson and Johansson, 2001; La Scala and Wool, 2005). Epoxidized soybean oil has a higher content of epoxy groups; consequently, it was expected that its viscosity would be higher than the samples of epoxidized canola oil. Recently, Campanella et al. (2009) evaluated the viscosity of epoxidized canola oil (prepared with performic acid in the presence of benzene) and epoxidized soybean oil in the range of 25 °C to 100 °C at a shear rate of 1 s<sup>-1</sup>. Their results also showed a higher viscosity for epoxidized soybean oil.

Vegetable oils are Newtonian fluids, but the chemical differences in polarity of their epoxidation products are thought to induce shear-thinning behavior (La Scala and Wool, 2005). Shear-thinning fluids show a non-linear relationship between shear stress and shear rate; the apparent viscosity decreases as the shear rate increases. However, reports of shear-thinning behavior in epoxidized vegetable oils were not found. The prepared epoxy resins in this study were observed to be shear-thinning, as indicated by flow behavior indices <1. The flow consistency index (*K*) and flow behavior index (*n*) were calculated by the method of least squares, with  $r^2 = 0.99$  in all cases (table 6).

Information on the thermal behavior of the products of epoxidation is relevant for the control and design of the process where they will be applied. Crystalline melting temperature, enthalpy, and liquid heat capacity provide information on the physical appearance of the epoxides and the energy required for their processing. The level of epoxidation impacted the crystalline melting temperatures of the epoxidized vegetable oils. The presence of the epoxy rings inhibits the close packing of the fatty acid chains, preventing the transition of the liquid state to the grease state (Wool and Sun, 2005). Therefore, as the level of epoxidation increases, the crystalline melting temperature decreases. This behavior was confirmed with the results of the MDSC analysis. Table 7 shows the onset temperature, i.e., the temperature at which the melting process begins (Sathivel et al., 2008). All treatments showed one melting peak with multiple crests. Vegetable oils and their derivatives generally do not show a single crystalline melting point because they are mixtures of compounds (triglycerides) and the oil crystals have several polymorphic modifications (Fasina et al., 2008).

Comparing epoxidized soybean oil with epoxidized canola oil, higher oxirane oxygen content corresponded to a lower crystalline melting temperature with a higher enthalpy. Whereas epoxidized soybean oil remained liquid at room temperature, epoxidized canola oil tended to crystallize at room temperature. The crystallization was gradual, and started with the formation of seed crystals in the bottom of the

**Table 7. Crystalline melting properties and liquid heat capacity of solvent-free and solvent epoxidized canola oil (ECO) and epoxidized soybean oil (ESO) (means  $\pm$ SD).**

Epoxidized Vegetable Oil	Onset Temperature (melting point °C)	Crystalline Melting Temperature (°C)		Enthalpy (J g <sup>-1</sup> )	Heat Capacity at 40°C (J g <sup>-1</sup> K <sup>-1</sup> )
		Maximum crest	Secondary crest		
ECO (solvent-free)	8.7 $\pm$ 0.1	15.5 $\pm$ 0.2	25.4 $\pm$ 0.2	9.6 $\pm$ 0.0	1.9 $\pm$ 0.6
ECO (solvent)	8.2 $\pm$ 0.7	15.3 $\pm$ 0.1	25.0 $\pm$ 0.6	8.3 $\pm$ 0.9	1.5 $\pm$ 0.7
ESO (solvent-free)	-27.3 $\pm$ 0.1	-5.7 $\pm$ 0.1	-12.0 $\pm$ 0.0, -17.8 $\pm$ 0.0	12.8 $\pm$ 0.1	1.7 $\pm$ 0.4
ESO (solvent)	-27.3 $\pm$ 0.1	-6.5 $\pm$ 0.1	-12.2 $\pm$ 0.3, -17.8 $\pm$ 0.0	15.3 $\pm$ 1.6	2.0 $\pm$ 0.0

container to the walls, turning from a clear appearance to a turbid and milky appearance, and finally to the grease state. Liquid heat capacities of the products of epoxidation were comparable with those of the unmodified vegetable oils. Santos et al. (2005) reported heat capacities of 2.3 and 1.8 J g<sup>-1</sup> K<sup>-1</sup> at 40 °C for soybean and canola oil respectively.

## CONCLUSION

An epoxy resin was prepared from canola oil using a solvent-free process in the presence of a heterogeneous catalyst and process factors selected through fraction factorial design for high conversion. This process provides a greener alternative to the production of petroleum-based resins. The prepared epoxidized canola oil had a high content of epoxy groups, which makes it suitable for application in composite materials. The process was scaled up from 50 g to 300 g without a reduction in conversion and yield. Rheological and crystalline melting properties of the products were determined; the literature seldom, if ever, reports these properties for epoxidized vegetable oils. Statistical analysis showed the potential to reduce the amounts of catalyst and hydrogen peroxide. Further optimization of those factors is desirable to reduce waste streams and production costs. Finally, the elimination of solvent from the epoxidation process did not reduce the conversion to epoxy groups, and it helps to establish this process as a more environmentally benign alternative to traditional epoxidation processes.

## ACKNOWLEDGEMENTS

The authors are thankful for research support from the North Dakota Agricultural Experiment Station and USDA-CSREES (under Agreement No. 2007-38624-18602), the National Canola Research Program, the Northern Canola Growers Association, and the North Central Canola Research Program. Kristi Tostenson, Curt Doetkott, Leonard Cook, Heidi Docktor, Jorge Ortega, Mukesh Kumar, and Rachel Brudvik are acknowledged for their valuable assistance in the analyses and experiments.

## REFERENCES

Ackman, R. G. 1990. Chapter 6: Canola fatty acids: An ideal mixture for health, nutrition, and food use. In *Canola and Rapeseed: Production, Chemistry, Nutrition, and Processing Technology*. F. Shahidi, ed. New York, N.Y.: Van Nostrand Reinhold.

AOCS. 1980. Method Tx 1a-66: Hydroxyl value. Champaign, Ill.: AOCS.

AOCS. 1989. Method Cd 9-57: Oxirane oxygen. Champaign, Ill.: AOCS.

AOCS. 1998. Recommended practice Cd 1c-85: Calculated iodine value. Champaign, Ill.: AOCS.

ASTM. 2001. D5554-95: Standard test method for determination of the iodine value of fats and oils. West Conshohocken, Pa.: ASTM.

Boquillon, N. 2006. Use of an epoxidized oil-based resin as matrix in vegetable fibers-reinforced composites. *J. Applied Polymer Sci.* 101(6): 4037-4043.

Campanella, A., and M. A. Baltanás. 2005. Degradation of the oxirane ring of epoxidized vegetable oils with hydrogen peroxide using an ion exchange resin. *Catal. Today* 107-108: 208-214.

Campanella, A., C. Fontanini., and M. A. Baltanás. 2008. High-yield epoxidation of fatty acid methyl esters with performic acid generated in situ. *Chem. Eng. J.* 144(3): 466-475.

Campanella A., M. Fahimian, R. P. Wool, and J. Raghavan. 2009. Synthesis and rheology of chemically modified canola oil. *J. Biobased Materials and Bioenergy* 3(1): 91-99.

Chen, J., M. D. Soucek, W. J. Simonsick, and R. W. Celikay. 2002. Epoxidation of partially nonborylnized linseed oil. *Macrol. Chem. Phys.* 203(14): 2042-2057.

Fasina, O. O., M. C. Schmidt, Z. Colley, and H. Hallman. 2008. Predicting melting characteristics of vegetable oils from fatty acid composition. *LWT - Food Sci. and Tech.* 41(8): 1501-1505.

Flatten, A., E. A. Bryhni, A. Kohler, B. Egelandsdal, and T. Isaksson. 2005. Determination of C22:5 and C22:6 marine fatty acids in pork fat with Fourier transform mid-infrared spectroscopy. *Meat Sci.* 69(3): 433-440.

Goud, V. V., A. V. Patwardhan, and N. C. Pradhan. 2006. Studies on the epoxidation of mahua oil (*Modhumica indica*) by hydrogen peroxide. *Bioresour. Tech.* 97(12): 1365-1371.

Goud, V. V., A. V. Patwardhan, S. Dinda, and N. C. Pradhan. 2007. Kinetics of the epoxidation of jatropha oil with peroxyacetic and performic acid catalyzed by acidic ion exchange resin. *Chem. Eng. Sci.* 62(15): 4065-4076.

Güner, F. S., Y. Yağci, and T. Erciyes. 2006. Polymers from triglycerides oils. *Prog. Polymer Sci.* 31(7): 633-670.

Gunstone, F. D. 1997. Chapter 29: Epoxidized oils. In *Lipid Technologies and Applications*. F. D. Gunstone and F. B. Padley, eds. Boca Raton, Fla.: CRC Press.

Hang, X., and H. Yang. 1999. Model for a cascade continuous epoxidation process. *JAOCs* 76(1): 89-92.

Hendl, O., J. A. Howell, J. Lowery, and W. Jones. 2001. A rapid and simple method for the determination of iodine values using derivative Fourier transform infrared measurements. *Anal. Chim. Acta.* 427(1): 75-81.

La Scala, J., and R. P. Wool. 2005. Rheology of chemically modified triglycerides. *J. Applied Polymer Sci.* 95(3): 774-783.

Liang, G., A. Gark, K. Chandrashekhara, V. Flanigan, and S. Kapila. 2005. Cure characterization of pultruded soy-based composites. *J. Reinf. Plast. Compos.* 24(14): 1509-1520.

Liu, Z., and S. Z. Erhan, 2005. Development of soy composites by direct deposition. In *Industrial Uses of Vegetable Oils*, 131-142. Champaign, Ill.: AOCS Press.

Mungroo, R., N. C. Pradhan, V. V. Goud, and A. K. Dalai. 2008. Epoxidation of canola oil with hydrogen peroxide catalyzed by acidic ion exchange resin. *JAOCs* 85(9): 887-896.

Myers, R. H., and D. C. Montgomery. 2002. *Response Surface Methodology: Process and Product Optimization Using Designed Experiments*. New York, N.Y.: John Wiley and Sons.

- Parreira, T. F., M. M. C. Ferreira, H. J. S. Sales, and W. B. de Almeida. 2002. Quantitative determination of epoxidized soybean oil using near-infrared spectroscopy and multivariate calibration. *Appl. Spec.* 56(12): 1607-1614.
- Rangarajan, B., A. Havey, E. A. Grulke, and P. D. Culnan. 1995. Kinetics of the parameters of a two-phase model for in situ epoxidation of soybean oil. *JAOCS* 72(10): 1161-1169.
- Samuelsson, J., and M. Johansson. 2001. A study of fatty acid methyl esters with epoxy or alkyne functionalities. *JAOCS* 78(12): 1191-1196.
- Santos, J. C. O., M. G. O. Santos, J. P. Dantas, M. M. Conceição, P. F. Athaide-Filho, and A. G. Souza. 2005. Comparative study of specific heat capacities of some vegetable oils obtained by DSC and microwave oven. *J. Thermal Analysis and Calorimetry* 79(2): 283-287.
- Sathivel, S., W. Prinyawiwatkul, I. I. Negulescu, and J. M. King. 2008. Determination of melting points, specific heat capacity, and enthalpy of catfish visceral oil during the purification process. *JAOCS* 85(3): 291-296.
- Sinadinovik-Fiser, S., M. Jankovic, and Z. S. Petrovic. 2001. Kinetics of in situ epoxidation of soybean oil in bulk catalyzed by ion exchange resin. *JAOCS* 78(7): 725-731.
- Singh, R. P., and D. R. Heldman. 2001. *Introduction to Food Engineering*. 3rd ed. San Diego, Cal.: Academic Press.
- Vicek, T., and Z. S. Petrovic. 2006. Optimization of the chemoenzymatic epoxidation of soybean oil. *JAOCS* 83(3): 247-252.
- Wool, R. P., and X. S. Sun. 2005. Chapter 7: Properties of triglyceride-based thermosets. In *Biobased Polymers and Composites*. San Diego, Cal.: Academic Press.
- Zheljazkov, V. D., B. A. Vick, M. W. Ebelhar, N. Buehring, B. S. Baldwin, T. Astatkie, and J. F. Miller. 2008. Yield, oil content, and composition of sunflower grown at multiple locations in Mississippi. *Agron. J.* 100(3): 635-642.

