Industrial Crops and Products 77 (2015) 133–138

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Influence of oil extraction method on properties of canola biodiesel, epoxies, and protein-based plastics

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ARTICLE INFO

Article history:
Received 12 March 2015
Received in revised form 16 August 2015
Accepted 22 August 2015
Available online 7 September 2015

Keywords:
Canola
Oil extraction
Biobased plastic
Epoxy
Biodiesel

ABSTRACT

Canola oil was extracted using a liquid carbon dioxide extraction process (LCE), laboratory screw-pressing, and industrial solvent extraction. Oilseed meal generated from these methods was used to extract proteins for protein-based plastics, and the oil was used to produce both epoxy resins and biodiesel. Protein isolates obtained from the LCE-generated meal produced plastics with higher toughness and elongation, but lower tensile strength and modulus, than those using meal obtained from screw pressing and solvent extraction. The oils extracted using the LCE process produced cured epoxy resins with higher flexural modulus than those produced from solvent-extracted oil. However, dynamic mechanical properties such as storage and loss modulus showed no significant differences with respect to oil extraction method. Oils obtained from extraction methods had similar fatty acid profiles and produced biodiesel with no significant differences in properties.

1. Introduction

Efficient use of renewable resources to produce higher value products in advanced biorefineries will help reduce global dependence on petroleum. Oilseeds such as canola (*Brassica napus* L.) can be used to produce a diverse range of bioproducts. Biopolymers and biofuels can be produced from its oil and oilseed meals are rich in protein which can be used in the production of bioplastics.

Bioproduct markets are expected to grow at an annual rate of 20–37% and the biobased plastics industry is predicted to reach $7.02 billion by 2018 (Lucintel, 2014). Biobased materials such as epoxidized vegetable oils are already used as plasticizers to provide flexibility and durability in PVC and other materials. A major proportion (more than 90%) of the epoxy-based plasticizers and neat plastics are produced using soy oil. However, competing products such as canola oil-based plastics not only have room for growth, but also will make the industry more vibrant with new products having a variety of properties. Finding efficient ways to extract canola oil with minimum use of petrochemical solvents while preserving quality of the by-products will benefit the canola industry as well as other oilseed processors.

Current biodiesel biorefineries are focused on fuel yield and quality with coproduct quality considered of secondary importance. Optimized production of both biofuels and coproducts may strengthen biofuel industries and reduce fossil fuel use. Oilseed meals produced in biodiesel production are rich in protein, and can be used for a variety of applications ranging from low-value animal feed to higher-value food additives and industrial applications such as plastics, biocomposites, and adhesives. Given the fact that oilseed meals are produced in large volumes, finding higher value uses would have a particularly large impact on biofuel producers during periods of high feedstock prices.

The standard technology for extracting oil from oilseeds such as canola includes screw-pressing and solvent extraction with hexane. Oilseed meal quality can be negatively affected from high temperatures generated during screw-pressing and from exposure to solvents (Camire, 1991; Sun et al., 1999; L'Hocine et al., 2006). Proteins processed in this manner become partially denatured altering their functionality and reducing flexibility and value for use in food or industrial processes. Protein quality is typically given little consideration in oil extraction processes but developing higher value uses for proteins could change that. Also, adopting less severe processing conditions including lower temperatures will provide the required flexibility to use the by-products in a wider variety of high-value applications.

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http://dx.doi.org/10.1016/j.indcrop.2015.08.050
0926-6690/

Another approach for oilseed extraction uses a subcritical liquid carbon dioxide extraction method (LCE) (Ferreira et al., 1993; Stahl et al., 1980). Compared to supercritical carbon dioxide extraction it is carried out at lower pressures (<72.9 atm) and temperatures (<31.3 °C) in the liquid phase (Mangold, 1983). The process can use chemical adjuncts such as ethanol to replace hexane, which is a known carcinogen and can be very difficult and dangerous to work with. Also, industries utilizing oilseed coproducts are beginning to request or specify non-hexane processing for marketing, safety, and regulatory reasons.

The goal of this research was to explore how oil extraction technology influences the ability to develop more diverse oilseed biorefineries with increased coproduct options. The specific objective was to compare the effects of canola oil extraction using LCE, screw-pressing, and hexane extraction on the properties of plastics, epoxies, and biodiesel produced from the resulting meal and oil.

2. Materials and methods

2.1. Materials

Raw canola seed and processed canola meal were obtained from Archer Daniels Midland (ADM) Company's crushing plant at Velva, ND, USA. Seeds were cleaned according to USDA–GIPSA recommendations for canola (USDA, 2004). Hexane, acetone, ethanol, and isopropanol were purchased from EMD Chemicals (Gibbstown, NJ, USA). A biodegradable aliphatic co-polyester (PBI 001®) (Natureplast Inc., Caen, France) was blended with proteins in the extrusion process; it had a density of 1.26 g cm^{-3}, a melt-mass flow rate of 0.45 g min^{-1}, and a melt temperature of 115 °C. Glycerol, polyvinylpyrrolidone (PVP), and zinc sulfate ($ZnSO_4$) were used without further treatment as plasticizer, compatibilizer, and cross-linker, respectively, in plastic preparation.

A petroleum-based epoxy resin (Resinfusion 8603) was purchased from Huntsman Corp. (The Woodlands, TX, USA). The catalyst, Amberlite IR120H resin, was obtained from Acros Organics (Morris Plains, NJ, USA), and anhydrous magnesium sulfate was purchased from Mallinckrodt Baker, Inc. (Phillipsburg, NJ, USA). The amine curing agent used for epoxy testing was PACM-20 [Bis(*p*-aminocyclohexyl methane)] (TCI America, Portland, OR, USA). The mold release agent Frekote 770-NC was obtained from Henkel Corp. (Rocky Hill, CT, USA). An aqueous solution of hydrogen peroxide (50%), anhydrous sodium carbonate, and other chemicals (NaOH, KOH, methanol, acetic acid, and HCl) were purchased from EMD Chemicals (Gibbstown, NJ, USA).

2.2. Preparation of canola oil and meal flour

Canola oil and meal were prepared using three oil extraction methods: (1) liquid carbon dioxide extraction (LCE) process at Cool Clean Technologies, Inc. (Eagan, MN, USA), (2) screw pressing followed by hexane extraction (SPE) process at North Dakota State University (Fargo, ND, USA), and, (3) industrial solvent extraction process (ISE) at ADM (Velva, ND, USA). The ISE method was a conventional hexane extraction process using the extraction parameters that are quite similar throughout the industry. Also, ground canola meal and oil obtained from ADM were used as industry standards to prepare protein isolates/protein-based plastics and biodiesel/epoxy resins, respectively.

LCE oil and meal were prepared by grinding canola seed for at least 1 min using a coffee grinder and then drying for 24 h at 50 °C until moisture content was less than 1% (measured using a Mettler Toledo LJ16 moisture analyzer, Mettler Toledo Inc., Columbus, OH, USA). Ground seed was stored in an air-tight container until further processing. Before oil extraction, the ground seed was placed in a convection oven at 50 °C for at least 1 h. A 50-g batch of ground seed was measured into a 500-mL beaker and mixed immediately with 250 mL of co-solvent (acetone, ethanol, or isopropanol). The mixture was then blended for 10 min using an Oster model BPST02-B (Jarden Corp., Boca Raton, FL, USA) professional series blender. The mixture was then transferred again to a 500-mL beaker and seed oil bodies were further ruptured and homogenized for 20 min using a Hielscher ultrasonic homogenizer. The mixture was immediately transferred to a 1-L LCE unit, filled with liquid CO_2 (approximately 700 mL) and agitated for 5 min. Reactor pressure was approximately 6.2 MPa with a corresponding saturation temperature of 23 °C. After soaking, liquid CO_2 was drained from the material through a 1-μm filter. The pressure in the separation vessel was slowly lowered causing the CO_2 to evaporate leaving the extractables for collection. Canola oil and meal extracted using ethanol were used further to prepare biodiesel, epoxies, and protein-based plastics based on higher oil extraction efficiency, and higher protein content in the resultant protein isolates.

SPE process of meal preparation used screw-pressing of seeds followed by solvent extraction. The moisture content of canola seeds was determined gravimetrically using a Mettler Toledo LJ16 moisture analyzer. Seed moisture content was adjusted to 7% by addition of distilled water followed by overnight equilibration. Seeds were then fed at 80 g min^{-1} to a model S87G Komet screw press (Monchengladbach, Germany) with a press head temperature of 70 °C. A compression screw and a restriction die with a 6-mm (diameter) die opening were used. Screw rotation speed was maintained at 24 rpm. The resulting canola meal was immediately pressed again using the same conditions (except for moisture adjustment) to further remove oil. The meal was then ground using a Retsch ZM1 mill (Brinkmann Instruments Inc., Westbury, NY) and passed through a 25-mesh screen. The residual oil in the resulting canola flour was removed by solvent extraction with hexane for 24 h using a Soxhlet extraction unit. The defatted flour was desolventized in a fume hood at room temperature for 2 d.

2.3. Preparation of protein isolates

Protein isolates were prepared as described previously (Manamperi et al., 2011). Canola meal flour (100 g) was dispersed in 400 mL of distilled water. The pH of the suspension was adjusted to 11 using NaOH (6 mol L^{-1}) and stirred for 1 h to solubilize the proteins. The suspension was centrifuged at 5000 × *g* for 30 min to remove fiber and other suspended solids. The protein-rich supernatant was further filtered through cheese cloth and through a Whatman 41 filter paper. In the case of LCE isolate, supernatant was centrifuged again at 5000 × *g* for 30 min and carefully filtered using cheese cloth and Whatman 41 filter paper to remove the top fat layer (due to high fat content in meal) from the protein rich bottom layer. Protein in the supernatant was then precipitated by drop-wise addition of HCl (6 mol L^{-1}) to lower the pH to 5.5. The precipitated proteins were recovered by centrifugation at 5000 × *g* for 30 min and freeze-dried at a freezing temperature of −25 °C and a drying shelf temperature of 25 °C. Lyophilized protein isolates were used for preparation of plastic specimens. The protein content in both isolates and meals were determined by Kjeldahl analysis (AOAC, 1995).

2.4. Preparation of protein-based plastics

Canola protein-based plastic specimens were prepared according to the method described by Mungara et al. (2002) with modifications. Canola protein isolate (35% by weight), plasticizer (15%), synthetic co-polyester (40%), compatibilizer (2%), water (7%), and cross-linker (1%) were mixed mechanically until a homoge-