



Epoxidation of *Camelina sativa* oil and peel adhesion properties



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ABSTRACT

Camelina oil is a promising material for the biopolymer industry due to its high unsaturated fatty acid content of 90%. The aim of this study was to optimize the epoxidation parameters of camelina oil. The epoxidation reaction of camelina oil was completed with formic acid and hydrogen peroxide. Catalyst ratio, reaction time, and temperature effects on the epoxidation reaction were studied. The optimum epoxy content of 7.52 wt% with a conversion rate of 76.34% was obtained for camelina oil using excess hydrogen peroxide and a molar ratio of formic acid of less than 1 for 5 h at 50 °C. We also found that epoxidation efficiency is significantly affected by fatty acids composition, structure, and distribution. The di-hydroxylized epoxidized camelina oil showed higher peel adhesion when it was formulated with epoxidized soybean oils. Epoxidized camelina oil has potential industrial applications in the field of pressure sensitive adhesives, coatings, and resins.

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1. Introduction

Making the transition from petroleum to renewable resources is crucial to sustainable development because of depleting oil reserves, global warming, and other environmental concerns. Fats and oils derived from plants have high potential for use in the currently petrochemical-based polymer industry because they are biodegradable and sustainable and can be converted into various industrial polymers (Meier, 2007).

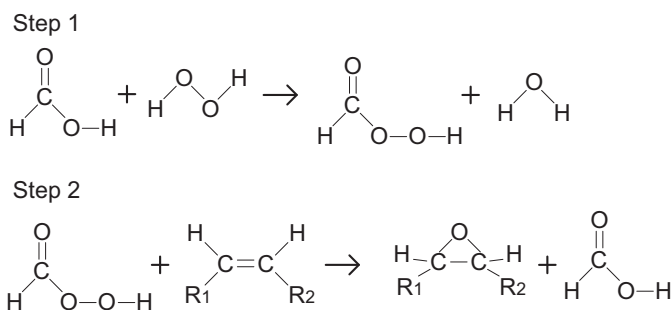
Camelina sativa (camelina) is a cruciferous plant that is also known as false flax or gold-of-pleasure (Zubr, 1997). Although cultivation and use of camelina disappeared during the Middle Ages, interest in camelina has increased in recent years (Eidhin et al., 2003). Camelina has several agronomic advantages comparing with some other traditional commodity oilseed crops (e.g., rapeseed, canola, soybean, sunflower), including low requirement for water and fertilizer, adaptability to adverse environmental conditions (e.g., cold weather, semiarid area), capacity to grow in marginal lands, and resistance to common cruciferous pests and pathogens (Francis and Warwick, 2009; McCann et al., 2014; Razeq et al., 2014). Besides, camelina is a non-food oilseed crop that would not compete with food productions. Camelina seed contains up to 50% oil (Abramovic and Abram, 2005), and about 90% of camelina oil

is unsaturated fatty acids, such as linoleic acid, α -linolenic acid, and erucic acid. Unsaturated fatty acids have high potential to be functionalized through epoxidation. Epoxidized vegetable oils have been applied in many industrial applications as plasticizers (Petrović et al., 2013), lubricants (Hwang and Erhan, 2006), polyols (Kiatsimkul et al., 2006), resins (Tan and Chow, 2011), composites (Liu et al., 2006), coatings (Yildirim et al., 2013), elastomers (Boonkerd et al., 2013), and adhesives (Ahn et al., 2011).

Epoxidation of vegetable oils can be implemented through several methods: the conventional method (Prileshajev-epoxidation) (Dinda et al., 2008), catalytic epoxidation using acidic ion exchange resin (AIER) (Petrovic et al., 2002), chemo-enzymatic epoxidation (Klass and Warwel, 1999), and metal-catalyzed epoxidation (Gerbase et al., 2002). The conventional method is the most widely used and cost-effective method for epoxidation; in it, hydrogen peroxide is used as an oxygen donor, and carboxylic acid (e.g., formic acid, acetic acid) is used as active oxygen carrier as well as a catalyst. The process is considered relatively environmental-friendly. Sometimes, a small amount of inorganic acid (e.g., HCl, H₂SO₄, HNO₃, H₃PO₄) is also added to further catalyze the reaction (Goud et al., 2006; Dinda et al., 2008). Soybean oil and jatropha oil were epoxidized (Meyer et al., 2008) using formic acid and hydrogen peroxide for 10 h; the maximum epoxy conversion rates were 83.3% and 87.4% for soybean oil and jatropha oil, respectively. In another study, the epoxy conversion rate of soybean oil reached 97% using formic acid and hydrogen peroxide after 16 h of reaction time. We applied the optimized epoxidation conditions of soybean oil from Meyer's study to camelina oil and obtained a 72.5% conversion rate.

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Scheme 1. Epoxidation reaction of C=C with formic acid and hydrogen peroxide.

Camelina and soybean oils have different fatty acids compositions and distributions; for example, soybean oil contains about 80% total of oleate and linoleate fatty acids with one and two double bonds, whereas camelina oil contains more distributed fatty acids, such as 37% linolenate fatty acids with three double bonds. Therefore, in this study, the main objective was to optimize the epoxidation reaction of camelina oil with conventional process methods using with peroxy acids. Chemical pathways of the epoxidation reaction involve two steps: first, the reaction of formic acid and hydrogen peroxide results in the formation of peroxy acid and water; second, peroxy acid donates an oxygen atom to C=C in fatty acid. During the second step, the double bonds were opened and an epoxy ring was formed (Scheme 1).

The specific objectives of this study were to optimize the epoxidation parameters of camelina oil and characterize the properties of epoxidized camelina oil (ECO). The epoxidation parameters included formic acid content, hydrogen peroxide content, reaction time, and temperature. Soybean oil was also epoxidized for comparison purposes when necessary. Epoxy content represents net epoxy rings in the reaction, so it was used to evaluate the conversion efficiency of the optimization process. Then the conversion rate was calculated from the epoxy content based on the total number of double bonds.

2. Materials and methods

2.1. Materials

Camelina oil was obtained from Montana Gluten Free Processors (Belgrade, MT, USA). Soybean oil, formic acid (88%), hydrogen peroxide (50%), chlorobenzene (99.8%), 0.1 N hydrogen bromide, iso-octane (ACS grade), potassium iodide (ACS grade), and sodium thiosulfate (0.1 N) were purchased from Fisher Scientific (Pittsburgh, PA, USA). 0.1 M Wijs' solution (iodine solution) and Methyl linolenate (99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Methyl oleate (96%) was purchased from Alfa Aesar (Ward Hill, MA, USA). Methyl linoleate (95%) was purchased from TCI America (Portland, OR, USA).

Table 1
Epoxidation reaction parameters of camelina oil (CO) and soybean oil (SO).

Sample	Acid ratio	H ₂ O ₂ ratio	Reaction time (h)	Reaction temp. (°C)
CO	0.66–1.2	1.7	5	50
	0.66	0.85–1.7	5	50
	0.66	0.85	03–11	50
	0.66	0.85	5	40–65
SO	0.66–1.1	0.85	5	50
	0.66	0.85–1.7	5	50
	0.66	0.85	05–10	50
	0.66	0.85	5	50–70

2.2. Fatty acid distribution and iodine value of camelina oil and soybean oil

Fatty acid analysis of the oils was performed with a 6890 N gas chromatograph coupled to a flame ionization detector (GC-FID, Agilent Technologies, Santa Clara, CA, USA). Oils were converted into fatty acid methyl esters (FAMES) through reaction with methanolic hydrochloric acid. FAMES were extracted using hexane:chloroform (4:1), then analyzed in duplicate. Pentadecanoic acid (C15:0) was used as an internal standard.

Iodine value of oils was determined through titration methods following ASTM D5768: 1 g of sample was dissolved with 20 ml of iso-octane and 25 ml of the Wijs solution, and kept in a dark storage for 1 h. Afterward, 20 ml of KI solution and 100 ml of water were added followed by titrated by 0.1 N sodium thiosulfate. The iodine value was used during further calculations of conversion rate.

2.3. Epoxidation reaction

The calculated amounts of the molar ratio of formic acid, based on the number of C=C in triglycerides of camelina oil and soybean oil, were added in a 250-ml Erlenmeyer flask. Hydrogen peroxide was added one drop at a time while stirring for about half of the reaction time at a set temperature. The reaction time was measured from the initial hydrogen peroxide addition and lasted for a predetermined amount of time. After the reaction, the epoxidized product was extracted with ethyl acetate and washed with distilled water and saturated sodium bicarbonate solution until natural. The solvent and residue water were eliminated using a rotary evaporator connected with a vacuum pump, and epoxidized oil was collected.

We studied the effect of four epoxidation reaction parameters on conversion rate of camelina oil and soybean oil: the molar ratio of formic acid to the number of C=C in TG, the molar ratio of hydrogen peroxide to the number of C=C in TG, reaction time, and reaction temperature. The experimental design is shown in Table 1. To better understand the relationship between triglyceride fatty acid profiles and epoxidation conversion rate, we further epoxidized fatty acid methyl ester model compounds under varied formic acid and hydrogen peroxide ratios. Methyl oleate, methyl linoleate, and methyl linolenate, which contain one, two, and three C=C double bonds, respectively, were used. The experimental design is shown in Table 2.

2.4. Epoxy content and conversion rate

Epoxy contents of camelina oil and soybean oil were obtained following ASTM D1652. About 0.5 g of the epoxidized sample was measured in a 125-ml Erlenmeyer flask and dissolved with 10 ml of chlorobenzene, then titrated with 0.1 N hydrogen bromide. Epoxy content was calculated following Eq. (1):

$$\text{Epoxy content (wt\%)} = 1.6 \times N \times \frac{V - B}{W} \quad (1)$$

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