

EPOXIDATION AND DI-HYDROXYLATION OF CAMELINA SATIVA OIL

by

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Abstract

Plant oil-based raw materials have become more attractive alternatives in polymer industry as fossil resources depletion and environmental concerns continue to arise. Camelina (*camelina sativa* L.) seed contains about 45% of oil and about 90% of the oil is unsaturated fatty acids such as linoleic acid, α -linolenic acid, and erucic acids. It also provides the advantages of low cost and low fertilizer demand. Functionalized oils such as epoxidized camelina oil (ECO) and di-hydroxyl camelina oil (DCO) can be used for resins, adhesives, coatings, etc. The objectives of this work were to synthesize and characterize ECO and DCO from 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 from camelina oil using excess hydrogen peroxide and a molar ratio of formic acid of less than 1 for 5 hours in 50 °C. Camelina oil yields higher epoxy content (7.52 wt%) than soybean oil (6.53 wt%); however, soybean oil had a higher conversion rate of 80.16% compared to camelina oil because of uniform fatty acids distribution. In this study, we found that epoxidation efficiency is significantly affected by fatty acids composition, structure, and distribution.

DCO was synthesized from ECO with different reaction parameters. The ring opening of ECO was performed with water, perchloric acid, and THF as proton donor, catalyst, and solvent respectively. Hydroxyl value of DCO was measured, and the maximal hydroxyl value was 369.24 mg KOH/g. physical properties of DCO were characterized by acid value and moisture content; thermal properties of DCO were obtained using differential scanning calorimeter (DSC), thermogravimetric analysis (TGA). Amount of solvent and acid catalyst addition affected the hydroxyl value and residual acid in DCO. Heat capacity, phase transition temperatures, and

thermal stability of DCO were obtained and showed higher values than ECO's. The DCO showed higher peel adhesion when it was formulated with epoxidized soybean oils through UV curing because camelina oil allows higher epoxy content, which results in higher hydroxyl values.

Table of Contents

List of Figures	vii
List of Tables	ix
Acknowledgements.....	x
Chapter 1 - Introduction.....	1
1.1. Overview.....	1
1.2. Objective.....	3
1.3. Literature review.....	4
1.3.1. Structure of plant oils.....	4
1.3.2. Functionalization of plant oils	5
1.3.1.1. Autoxidation	5
1.3.1.2. Epoxidation.....	6
1.3.1.3. Hydroxylation	7
1.3.3. Plant oil-based polymers.....	8
1.3.3.1. Soybean oil polymers.....	8
1.3.3.2. Tung oil polymers.....	9
1.3.3.3. Linseed oil polymers.....	10
1.3.3.4. Castor oil polymers	10
1.3.4. Camelina oil	11
Chapter 2 - Epoxidation of <i>Camelina sativa</i> oil	18
2.1. Abstract.....	18
2.2. Introduction.....	18

2.3. Materials and methods	21
2.3.1. Materials	21
2.3.2. Fatty acid distribution and iodine value of CO and SO	21
2.3.3. Epoxidation reaction	22
2.3.4. Epoxy content and conversion rate	22
2.3.5. Fourier Transform Infrared (FTIR) analysis	23
2.3.6. Adhesive applications of epoxidized camelina oil.....	23
2.4. Results and Discussion	24
2.4.1. Fatty acid composition, molecular weight, and iodine value of CO and SO	24
2.4.2. Effects of formic acid on epoxy content	24
2.4.3. Effects of hydrogen peroxide on epoxy content	25
2.4.4. Effects of reaction time and temperature on epoxy content	25
2.4.5. Conversion rate of epoxidation	26
2.4.6. Epoxidation of methyl oleate (MO), methyl linoleate (MLO), and methyl linolenate (MLON)	27
2.4.7. Potential applications of epoxidized camelina oils for adhesives.....	28
2.5. Conclusions.....	29
Chapter 3 - Hydroxylation of epoxidized <i>camelina sativa</i> oil.....	41
3.1. Abstract.....	41
3.2. Introduction.....	41
3.3. Materials and Methods.....	43
3.3.1. Materials	43
3.3.2. Di-hydroxylation of ECO.....	43

3.3.3. Hydroxyl value of DCO	44
3.3.4. Physical properties of DCO	44
Acid value of DCO	44
Moisture content of DCO.....	45
3.3.5. Thermal properties of DCO	45
Differential Scanning Calorimetry (DSC) analysis of DCO.....	45
Thermogravimetric analysis (TGA) of DCO	45
3.4. Results and discussion	46
3.4.1. Hydroxyl value of DCO	46
3.4.2. Physical properties of DCO	46
3.4.3. Thermal properties of DCO	47
DSC analysis	47
TGA	48
3.5. Conclusion	49
Chapter 4 - Conclusions and future work	57

List of Figures

Scheme 1.1. A typical triglyceride molecule and its functionalities.....	13
Figure 2.1. (a) Epoxy content of camelina oil with varying formic acid ratio to the number of C=C from 0.66 to 1.2 at fixed rest parameters. (b) FTIR spectra for four ECO samples with different formic acid ratio enclosed the wavenumber range between 3100 and 3700.....	31
Figure 2.2. (a) Epoxy contents of camelina oil and soybean oil with varying hydrogen peroxide ratios from 0.5 to 1.7 for camelina oil and from 0.85 to 1.7 for soybean oil. (b) FTIR spectra for six ECO samples with different hydrogen peroxide ratio enclosed the wavenumber range between 750 and 900 cm^{-1}	32
Figure 2.3. (a) Epoxy contents of camelina oil and soybean oil with varying reaction time from 3 to 11 hours for camelina oil and from 5 to 10 hours for soybean oil. (b) FTIR spectra for six ECO samples with different reaction time enclosed the wavenumber range between 3700 and 3100 cm^{-1}	33
Figure 2.4. (a) Epoxy contents of camelina oil and soybean oil with different reaction temperature from 40 to 65 $^{\circ}\text{C}$ for camelina oil and from 50 to 70 $^{\circ}\text{C}$ for soybean oil. (b) FTIR spectra for three ECO samples with different reaction temperature enclosed the wavenumber range between 3700 and 3100 cm^{-1}	34
Figure 2.5. FTIR spectra between camelina oil (solid line) vs. epoxidized camelina oil (dashed line); reaction condition of 0.66 formic acid and 1.7 hydrogen peroxide molar ratio to the number of C=C, 5 hrs reaction, and reaction temperature of 50 $^{\circ}\text{C}$	35
Figure 3.1. Hydroxyl values of DCO with different THF addition amount.	51
Figure 3.2. Hydroxyl values of DCO with different acid addition amount.	52
Figure 3.3. DSC thermograms of DCO and ECO with heating rate of 10 $^{\circ}\text{C}$ /min.	53

Figure 3.4. TGA thermograms of DCO and ECO with heating rate of 20 °C /min and about 10mg sample loading. 54

List of Tables

Table 1.1. Most common fatty acids and their double bonds	14
Table 1.2. Fatty acids distribution in different plant oils. (Wool and Sun 2005; Abaramovič and Abram 2004)	15
Table 1.3. Physical properties of some plant oils.	16
Table 1.4. Camelina oil fatty acids composition in different countries. (Abramovič and Abam 2005; Budin et al. 1995; Eidhin et al. 2003; Zubr et al. 1997)	17
Table 2.1. Epoxidation reaction parameters of camelina oil and soybean oil.	36
Table 2.2. Epoxidation reaction parameters of methyl esters: methyl oleate, methyl linoleate, and methyl linolenate, and its corresponding epoxy content, epoxy number in TG, and conversion rate.	37
Table 2.3. Adhesion properties of camelina oils derived adhesives.	38
Table 2.4. Fatty acid composition (w/w) of camelina oil (CO) and soybean oil (SO).	39
Table 2.5. Epoxidation results of camelina and soybean oils using reference parameters and optimized parameters.	40
Table 3.1. Reaction conditions and its corresponding physical results of di-hydroxylation reaction using ECO.	55
Table 3.2. Thermal properties of DCO and ECO from DSC and TGA.	56

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Chapter 1 - Introduction

1.1. Overview

Sustainable development is a trending topic globally in many industries, including both the private and public sectors. The concept of sustainable development and the most widely used definition resulted from the release of the Brundtland Commission Report (UNWCED 1987). The Brundtland Commission was established by the United Nations, in efforts to gather nations together to engage in sustainable development.

The Brundtland Commission Report defines sustainable development as “development that meets the needs of the present without compromising the ability of future generations to meet their own needs”. In this particular definition, ‘needs’ refers to promoting economic and social development needs, more specifically for those with lower standards of living, while concurrently protecting natural resources and the environment. Sustainable development incorporates the concepts of economic growth, environmental protection, and social equality.

The Brundtland Commission Report and other literature released in recent decades increased public awareness of the damaging effects of harmful chemicals on humans’ health and the environment. As a result, the concept of “green chemistry” and its 12 principles originated in 1998 (Anastas & Warner, 1998). Green chemistry is defined as “the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances” (Anastas & Warner, 1998). This concept introduced the use of plant-based chemistry in order to help protect the environment.

The 12 principles of green chemistry ignited a modification in how the Environmental Protection Agency approaches environmental issues. Furthermore, plant-based chemistry and green chemistry principles applied to industrial processes not only resulted in benefits to the environment, but to companies as well. The 12 principles of green chemistry introduced a new concept stating “it is better to prevent waste than to treat or clean up waste after it is formed” (Anastas & Warner, 1998). In the past, the Environmental Protection Agency created strategies aimed towards treatment of toxic waste, rather than prevention.

Anastas & Warner define the 12 principles as the following: (1) Prevention, (2) Atom Economy, (3) Less hazardous chemical syntheses, (4) Designing Safer Chemicals, (5) Safer Solvents and Auxiliaries, (6) Design for Energy Efficiency, (7) Use of Renewable Feedstocks, (8) Reduce Derivatives, (9) Catalysis, (10) Design for Degradation, (11) Real-time analysis for Pollution Prevention, and (12) Inherently Safer Chemistry for Accident Prevention.

The specific techniques used in green chemistry which reflect the 12 principles include non-polluting synthetic pathways; using alternative reaction conditions; designing less toxic chemicals; using renewable sources, such as plant-based materials instead of diminishing fossil fuels; and incorporating recycling techniques rather than discarding in chemical processes. These 12 principles establish the foundation of green chemistry and specific examples of application in industrial situations proved to benefit the environment, industry, and human health as well.

Green chemistry is a concept that will continue to be used widely within the chemistry community, educational facets, as well as in technological development. Under the umbrella of green chemistry principles, chemists will place more focus on developing plant-based chemistry applications, an essential component in the advancement of green chemistry. The results of green

chemistry produce cost effective techniques and processes, improve the safety of the environment and human health, and contribute to the world's sustainable development progress.

As a response to the increasing fossil fuel prices, depleting oil reserves, increasing green house gas emission, and other environmental concerns, development of alternative resources to petrochemical-based industry is essential. Fats and oils derived from plants possess a large potential for current petrochemical-based polymer industry because they are biodegradable and sustainable, and they can be converted into various industrial polymers (Meier, 2007). *Camelina sativa* 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 due to its high content of ω -3 fatty acids (Eidhin et al., 2003) and distribution of highly unsaturated fatty acids. 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 a high potential to be functionalized through epoxidation process. 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., 2011b).

1.2. Objective

The objective of this study is to design and identify the potential of camelina oil as a starting material for bio-polymer industry. The specific objectives are listed below:

1. to develop method of epoxidation reaction of camelina oil with peroxy acid using formic acid and hydrogen peroxide and characterize the properties of epoxidized camelina oil (ECO).

2. to develop method of di-hydroxylation reaction of ECO with perchloric acid and water with an organic solvent (Tetrahydrofuran) and characterize properties of di-hydroxyl camelina oil (DCO).

1.3. Literature review

1.3.1. Structure of plant oils

Plant oils are composed of triglycerides, which are the consequence of the reaction of a molecule of glycerol and three molecules of fatty acids as known as esterification. During the esterification reaction, alcohol groups of glycerol and carboxylic acid from each of the three fatty acids are removed. A fatty acid consists of a carboxylic acid and an aliphatic chain of either saturated or unsaturated. The most common fatty acids and their double bonds are shown in **Table 1.1** (Verhe 2004). Most fatty acids possess even number of carbons, and most of the unsaturated fatty acids show *cis*-configuration in the double bonds. Some fatty acids, such as ricinoleic and vernolic acids contain functional groups, hydroxyl and epoxy groups, respectively.

Plant oils have different fatty acids distribution (**Table 1.2**). The chemical and physical properties of plant oils vary with their fatty acid distribution; the aliphatic chain length, number of double bonds, and double bond position in the aliphatic chain affect the physical properties such as viscosity, specific gravity, melting point, etc., as shown in **Table 1.3**. The distribution of

fatty acids in plant oils differs in varieties as well as growing conditions, and most plant oils are liquid in form in at ambient temperatures.

1.3.2. Functionalization of plant oils

Triglycerides of plant oils contain active sites (**Scheme 1.1**) that can be functionalized and used to be polymerized with appropriate treatments. Triglycerides of some plant oils, such as linseed oil can be polymerized by autoxidation, and others can be modified by chemical reactions using its intrinsic active sites. The inherent double bonds in triglyceride enable to functionalize the triglyceride (plant oils) by epoxidation, hydroxylation, acrylation, maleinization, hydrogenation, halogenations, ozonolysis, demerization, and metathesis (Khot et al. 2001; Pelletier & Gandini 2006; Mol 2002); and their derivatives have different physical properties depending on the aliphatic chain length and distribution of unsaturated sites (Behr et al. 2008). Among the above functionalization methods, epoxidation and hydroxylation are the most common reactions using intrinsic double bonds in triglyceride of plant oils.

1.3.1.1. Autoxidation

Plant oils can be divided into three categories depending on its iodine value (IV) – non-drying, semi-drying, and drying oils. Iodine value indicates mass of iodine consumed by 100g of oils and fats, and is often used for determination of amount of unsaturation in fatty acids. Oils can be classified as non-drying oils if iodine value is less than 90, semi-drying oils if iodine value is between 90 and 130, and drying oils when iodine value is higher than 130 (Belgacem and Gandini 2008). The presence of double bonds increases as the iodine value increases. Drying oils, which have more double bonds (i.e., linolenic acid) in their fatty acids, have higher

reactivity to be polymerized by air oxidation or UV radiation. For example, Linseed oil is in the drying oil category with highly polyunsaturated fatty acids; however, drying rate of linseed oil is too slow, thus addition of drying agent is required to accelerate process (Mallégol et al. 2000).

Autoxidation is the oxidative deterioration of unsaturated fatty acids via an autocatalytic process consisting of a free radical chain mechanism. The overall mechanism of autoxidation consists of three phases: (1) initiation, (2) propagation, and (3) termination (Kumarathasan 1992).

1.3.1.2. Epoxidation

Epoxidation of plant oils have been conducted by many researchers to improve the epoxy yield as well as to optimize the epoxidation reaction. Epoxidized plant oils can be used as monomers for functional polymeric materials, such as polyols (Kiatsimkul et al., 2006), lubricants (Hwang and Erhan, 2006), plasticizers (Petrović et al. 2013), and so on. Epoxidation of vegetable oils can be implemented by several methods: conventional method (Prileshajev-epoxidation) (Dinda et al. 2008), catalytic epoxidation using acidic ion exchange resin (AIER) (Petrović 2002), chemo-enzymatic epoxidation (Klass and Warwel 1999), and metal-catalyzed epoxidation (Gerbase et al. 2002).

The conventional method (Prileshajev-epoxidation) is the most commonly used method for epoxidation (Saurabh et al. 2011). This process is achieved by reacting a carboxylic acid with concentrated hydrogen peroxide to form peracids (Knothe & Derksen 1999). The epoxidation reaction of plant oils can be performed with its C-C double bonds in the unsaturated sites of triglyceride with peracids.

The next method is catalytic epoxidation using acidic ion exchange resin (AIER), via a gel type catalyst composed of polymer beads (Piazza et al. 2003). Peroxy acid results in a

reaction between hydrogen peroxide and carboxylic acid, and then enters the pores of the catalyst. This method uses less harsh catalyst such as concentrated sulfuric acid compared with the conventional method, decreases side reactions, improves selectivity, and offers an environmental friendly method for vegetable oil epoxidation.

Another environmental friendly method is the chemo-enzymatic epoxidation method. This method utilizes an immobilized lipase as catalyst . This method is an alternative to using strong acid catalysts and does not produce any by-products. One drawback of this method is the sensitivity and lower stability of the lipase catalyst in reaction conditions (Saurabh et al., 2011). Another trending method is the metal-catalyzed epoxidation method, using metals such as molybdenum, titanium, tungsten, or rhenium as catalysts (Cai et al 2009).

1.3.1.3. Hydroxylation

Biopolyol, a resultant of hydroxylation of plant oil, has typically been studied for polyurethane (PU) applications which in the field of elastomers, plasticizers, and coatings. Many researchers have studied hydroxylation of plant oils; Guo et al. prepared soybean oil-based polyols by catalytic hydrogenation for rigid polyurethane foams(Guo et al. 2000a), and synthesized four different hydroxylated soybean oils for PU application with hydrochloric acid, hydrobromic acid, methanol, and hydrogen (Guo et al. 2000b); Okieimen et al. reported both hydroxylation and epoxidation of rubber seed oil by one-pot multi-step reactions (Okieimen et al. 2005); Ahn et al. investigated chemical pathways of epoxidized and hydroxylated fatty acid methyl esters and triglycerides with phosphoric acid (Ahn et al. 2011a) and reported peel adhesion strength for pressure sensitive adhesives (PSAs) application using formulation from soybean-based polyol, ESO, and rosin ester (Ahn et al, 2011b).

1.3.3. Plant oil-based polymers

1.3.3.1. Soybean oil polymers

Soybean oils are biodegradable and readily available in bulk. Highly unsaturated triglyceride of soybean oil and modified soybean oil can be polymerized and used as a polymeric material. Soybean oil-based polymers studied intensively by Li and Larock (Li & Larock 2000a; Li & Larock 2001a; Li & Larock 2001b; Li & Larock 2002a; Li & Larock 2002b). Li and Larock investigated thermal and mechanical properties of copolymers by cationic copolymerization of regular, low saturated, or conjugated low saturated soybean oils (Li & Larock 2001a). Li & Larock found that the conjugated soybean oil polymers have the highest glass transition temperature and thermal stability among the different soybean oils. Can, Kuseflogu, & Wool prepared monoglycerides from soybean oil, and soybean oil-based rigid thermoset polymer by radical polymerization were prepared (Can et al. 2001). In 2002, Liu, Erhan, Xu, & Calvert reported synthesis of soybean oil-based composites by the solid free forming fabrication method (Liu et al. 2002). Liu et al. found that the type of fiber and fiber alignments degree affect the property of the product. Using epoxidized allyl soyate, soybean oil-based epoxy resin was synthesized by Shabeer et al., and mechanical properties such as storage modulus and loss tangent were studied (Shabeer et al., 2005). Shabeer et al. concluded that soy-based epoxy resin has a great potential as a replacement of petrochemicals in noise and vibration attenuation applications. Bonnaillie et al. produced polymeric foams from a thermosetting polymer and a pressurized gas with a free-radical initiator using acrylated epoxidized soybean oil (Bonnailli et al. 2007). Soybean oil-based resin by transesterification and epoxidation of soybean oil was prepared by Shabeer et al. (Shabeer et al. 2007); Shabeer et al. reported that the addition of

soybean-based epoxy diluents can produce a less glassy and more rubbery material. Ahn et al. prepared PSA by mixing epoxidized soybean oil and di-hydroxyl soybean oil, as di-hydroxyl soybean oil used for a tackifier (Ahn et al. 2011a; Ahn et al. 2011b). The peel strength of epoxidized soybean oil-based PSA was comparable with commercial adhesives such as scotch magic tape and post-it notes. Ahn et al. also investigated the thermal properties such as glass transition, melting point, and coefficient of thermal expansion of PSA from epoxidized soybean oil and di-hydroxyl soybean oil (Ahn et al. 2011b). Li and Sun synthesized di-hydroxyl soybean oil with different hydroxyl values (157.2, 238.7, and 284.2 mg KOH/g) and studied thermal properties of di-hydroxyl soybean oil and peel adhesion strength (Li & Sun 2014). The epoxidized soybean oil and di-hydroxyl soybean oil formulations with different ratio were tested, and the highest peel strength was 4.6 N/in.

1.3.3.2. Tung oil polymers

Tung oil, also known as China wood oil is one of the oldest drying oils. Tung oil is highly unsaturated, thus tung oil can rapidly undergo polymerization. Li & Larock conducted cationic polymerization of tung oil with divinylbenzene in the presence of boron trifluoride diethyl etherate was studied and produced promising plastics (Li & Larock 2000b). Also, thermal polymerizations in the temperature range of 85 – 160 °C with styrene and divinylbenzene of tung oil was performed and fully cured thermosets were obtained after post-curing at 160 °C (Li & Larock 2003). Trumbo and Mote reported the synthesis of tung oil and diacrylate copolymer and studied the resulting films; the films showed good solvent resistance, gloss, and a reasonable hardness-flexibility balance (Trumbo & Mote 2001).

1.3.3.3. Linseed oil polymers

Linseed oil contains a very high rate of linolenic acid composition (about 55%). Linseed oil and tung oil have been used in the paint and varnishes industries as well as used in organic coatings either as resins or as a raw material for the preparation of resins. Linseed oil was epoxidized and then copolymerized with styrene by Motawie et al. for pipeline coatings applicability (Motawie et al. 1995). Tuman et al. studied the autooxidative curing of linseed oil using differential scanning calorimetry (Tuman 1996). Heat of reaction of the differential scanning calorimetry was quantified, and effect of metal catalyst to the differential scanning calorimetry thermogram was found. Cationic, thermal, free radical, and oxidative polymerizations of linseed oil, as a model for oxidative alkyd paint system were studied by Meneghetti et al. (Meneghetti et al. 1998). Lead and zirconium were used as catalysts for polymerization step, and zirconium performed better reaction efficiency than lead. Meneghetti et al. suggested using the zirconium salts as a substitute for lead compounds in industrial applications.

1.3.3.4. Castor oil polymers

Castor oil has a unique triglyceride composition. About 90% of the fatty acids are ricinoleic acid, which contain intrinsic hydroxyl functional group on its fatty acid carbon chain (Karleskind 1996). Cassidy & Schwank reported the copolymerization of dehydrated castor oil with styrene (Cassidy & Schwank 1974). The dehydrated castor oil was polymerized in benzene, and the product was isolated for characterization. Dehydrated castor oil was used to determine reactivity ratio, and it was found that the dehydrated castor oil have a high chain transfer constant and a low reactivity ratio (0.086) compared to styrene (11.6). Ashraf et al. found that the

copolymerization was difficult when the dehydrated castor oil concentration is more than 20%. Then, Ashraf and coworkers prepared blends of dehydrated castor oil with epoxy resin and dehydrated castor oil with poly (methyl methacrylate), and studied miscibility; The results showed that dehydrated castor oil epoxy was immiscible with poly (methyl methacrylate) (Ashraf et al. 2005; Ashraf et al. 2006).

1.3.4. Camelina oil

Camelina sativa (L.) Crantz, commonly known as gold of pleasure or false flax, is a cruciferous oilseed plant. From the earlier records, *Camelina sativa* (L.) Crantz, *Camelina microcarpa*, and *Camelina Linicola* were already known in the Bronze and the Iron Ages in Europe. During the Iron Ages, camelina was a substantial part of the human diet (Hatt 1937; Hjelmquist 1979). Then during The Middle Ages, camelina crops gradually disappeared and sporadically distributed in parts of Europe (Knorzer 1978). The cultivation of camelina sativa peaked in the early 20th century, slowly declined, and by 1947 only a small amount of camelina was grown in some countries: Holland, Belgium, and Russia (Plesser et al. 1962).

Recently, interest in camelina is increasing. As an oilseed crop, properties of camelina oil were investigated (Budin et al. 1995; Abramovic and Abram 2005). Due to lower production costs of camelina oil, studies of camelina oil as a feedstock for biodiesel production have been conducted (Fröhlich and Rice 2003). In addition, camelina oil contains about 50% polyunsaturated fatty acid content with rich omega-3 fatty acids. Omega-3s are considered essential fatty acids, thus consumption of camelina sativa oil is anticipated to improve general health of the population.

The unsaturation of camelina sativa oil is high compared to other oil crops (Abramovic and Abram 2005). Camelina sativa oil contains about 35% of α -linolenic acid in its triglyceride (**Table 1.4**). Among other oils crops, only linseed oil contains about 55% of α -linolenic acid. Camelina sativa oil also contains gondoic acid (20:1) which is commonly absent in most plant oils. The C-C double bond number of triglyceride in camelina sativa oil is 5.5 – 5.8 which is comparably higher than other oils as listed in **Table 1.2**.

Cultivation of camelina sativa is also beneficial. Camelina sativa oil can be grown as an annual summer crop or biannual winter crop (Zubr 1997), and fertilizer demand is moderate to low. In addition, the crop can grow in arid region, and the period of growth in summer varieties is about 120 days.

Scheme 1.1. A typical triglyceride molecule and its functionalities.

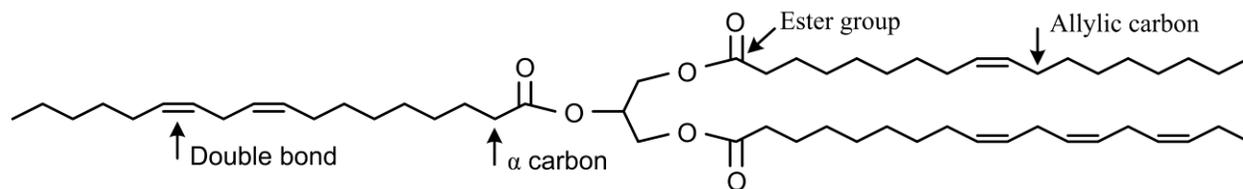


Table 1.1. Most common fatty acids and their double bonds

Fatty acid	Formula	DB
Caprylic	$C_8H_{16}O_2$	0
Capric	$C_{10}H_{20}O_2$	0
Lauric	$C_{12}H_{24}O_2$	0
Myristic	$C_{14}H_{28}O_2$	0
Palmitic	$C_{16}H_{32}O_2$	0
Palmitoleic	$C_{16}H_{30}O_2$	1
Stearic	$C_{18}H_{36}O_2$	0
Oleic	$C_{18}H_{34}O_2$	1
Linoleic	$C_{18}H_{32}O_2$	2
γ -linolenic	$C_{18}H_{30}O_2$	3
α -linolenic	$C_{18}H_{30}O_2$	3
α -Eleostearic	$C_{18}H_{30}O_2$	3
Ricinoleic	$C_{18}H_{34}O_3$	1
Vernolic	$C_{18}H_{32}O_3$	1
Arachidic	$C_{20}H_{40}O_2$	0
eicosaenoic	$C_{20}H_{38}O_2$	1
Arachidonic	$C_{20}H_{32}O_2$	4
Eicosapentaenoic	$C_{20}H_{30}O_2$	5
Behenic	$C_{22}H_{44}O_2$	0
Erucic	$C_{22}H_{42}O_2$	1
Docosapentanoic	$C_{22}H_{34}O_2$	5
Docosahexanoic	$C_{22}H_{32}O_2$	6

Table 1.2. Fatty acids distribution in different plant oils. (Wool and Sun 2005; Abaramovič and Abram 2004)

Fatty Acid	#C:#DB ¹	Canola	Corn	Linseed	Olive	Rapeseed	Soybean	Camelina
Myristic	14:0	0.1	0.1	0	0	0.1	0.1	0
Myristoleic	14:1	0	0	0	0	0	0	0
Palmitic	16:0	4.1	10.9	5.5	13.7	3	11	6.43
Palmitoleic	16:1	0.3	0.2	0	1.2	0.2	0.1	0
Margaric	17:0	0.1	0.1	0	0	0	0	0
Margaroleic	17:1	0	0	0	0	0	0	0
Stearic	18:0	1.8	2	3.5	2.5	1	4	2.57
Oleic	18:1	60.9	25.4	19.1	71.1	13.2	23.4	17.4
Linoleic	18:2	21	59.6	15.3	10	13.2	53.2	16.9
Linolenic	18:3	8.8	1.2	56.6	0.6	9	7.8	35.2
Arachidic	20:0	0.7	0.4	0	0.9	0.5	0.3	1.24
Gadoleic	20:1	1	0	0	0	9	0	14.9
Eicosadienoic	20:2	0	0	0	0	0.7	0	2.12
Eicosatrienoic	20:3	0	0	0	0	0	0	1.61
Behenic	22:0	0.3	0.1	0	0	0.5	0.1	0
Erucic	22:1	0.7	0	0	0	49.2	0	1.62
Lignoceric	24:0	0.2	0	0	0	1.2	0	0
#DB/#TG ²		3.9	5.5	6.6	2.8	3.8	4.6	5.5

¹ #C, number of carbon atom in the fatty acid; #DB, number of double bonds in the fatty acid;

TG, triglyceride; ² TG, stands for triglyceride.

Table 1.3. Physical properties of some plant oils.

Name	Viscosity at 37.8°C (mPa·s)	Specific gravity at 20°C	Refractive index at 20°C	Melting point (°C)
Castor oil	293.4	0.951	1.473 – 1.480	–18
Linseed oil	29.6	0.925	1.480 – 1.483	–24
Palm oil	30.92	0.890	1.453 – 1.456	35
Soybean oil	28.49	0.917	1.473 – 1.477	–16
Sunflower oil	33.31	0.916	1.473 – 1.477	–17

Table 1.4. Camelina oil fatty acids composition in different countries. (Abramovič and Abam 2005; Budin et al. 1995; Eidhin et al. 2003; Zubr et al. 1997)

Fatty Acid	Slovenia	Minnesota	Ireland	Central and Northern Europe
Palmitic	6.43	5.7 - 8.4	5.5	5.3 - 5.6
Stearic	2.57	1.4 - 3.5	2.3	2.3 - 2.7
Oleic	17.4	14.2 - 19.4	14.9	14.0 - 16.9
Linoleic	16.9	19.0 - 24.0	15.8	13.5 - 16.5
Linolenic	35.2	27.1 - 34.7	38.9	34.9 - 39.7
Arachidic	1.24	/	0.4	1.2 - 1.5
Gadoleic	14.9	12.3 - 14.7	16.2	15.1 - 15.8
Eicosadienoic	2.12	/	2.1	1.7 - 2.0
Eicosatrienoic	1.61	/	1.3	1.3 - 1.7
Erucic	1.62	0 - 4.0	2.4	2.6 - 3.0

Chapter 2 - Epoxidation of *Camelina sativa* oil

2.1. 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 hours at 50 °C. Camelina oil yields higher epoxy content (7.52 wt%) than soybean oil (6.53 wt%); however, soybean oil had a conversion rate of 80.16% because of uniform fatty acids distribution. In this study, we 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 through UV curing because camelina oil allows higher epoxy content, which results in higher hydroxyl values. Epoxidized camelina oil has potential industrial applications in the field of pressure-sensitive adhesives, coatings, and resins.

2.2. 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 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 due to its high content of ω -3 fatty acids (Eidhin et al., 2003) and distribution of highly unsaturated fatty acids. 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., 2011b).

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) (Petrović 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. 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 hours; 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 hours 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.

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 2.1**).

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.

2.3. Materials and methods

2.3.1. 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 (0.1N) 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).

2.3.2. Fatty acid distribution and iodine value of CO and SO

Fatty acid analysis of the oils was performed with a 6890N 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 (IV) of oils was determined through titration methods following ASTM D5768: 1g 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 hour. Afterward, 20 ml of KI solution and 100 ml of water were added followed by titrated by 0.1N sodium thiosulfate. The iodine value was used during further calculations of conversion rate.

2.3.3. 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.

2.3.4. Epoxy content and conversion rate

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

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

where N, V, B, and W are normality of the HBr in acetic acid, HBr solution used for titration of the sample (mL), HBr solution used for titration of the blank (mL), and sample weight (g), respectively. Because oil triglyceride double-bond number and molecular weight could be obtained from GC-FID analysis and epoxy content of epoxidized oil was measured, the conversion rate of epoxidation could be easily estimated.

2.3.5. Fourier Transform Infrared (FTIR) analysis

FTIR was used to examine the changes in functional groups before and after the epoxidation reaction. FTIR spectra were collected using a PerkinElmer spectrum 400 FT-IR spectrometer with scan range of 400 to 4000 cm^{-1} and 32 scans co-added.

2.3.6. Adhesive applications of epoxidized camelina oil

After obtaining epoxidized oils under optimized conditions, we further di-hydroxylized ECO into di-hydroxyl camelina oil polyol (DCO, hydroxyl value 295 mg KOH/g), following our previous work on soybean oils, and formulated adhesives with the oils through UV polymerization (Li and Sun, 2014). UV curing was carried out with a Fusion 300S 6-in. UV system (300 W/inch power, D bulb, UV radiation dose 215-231 mJ/cm^2 per pass at 7 ft/min conveyor speed) equipped with an LC6B bench-top conveyor. Peel adhesion of the adhesive tapes on a stainless steel panel was measured following ASTM D3330/D3330M-04. Experimental design and adhesion data were summarized in Table 3.

2.4. Results and Discussion

2.4.1. Fatty acid composition, molecular weight, and iodine value of CO and SO

Fatty acid compositions of camelina oil and soybean oil are similar to those reported in the literature (**Table 2.4**) (Zubr, 1997). Soybean oil mainly contains oleic acid (C18:1, 22.0%), linoleic acid (C18:2, 54.9%), and linolenic acid (C18:3, 7.0%), whereas camelina oil contains much less oleic acid (14.8%) and linoleic acid (18.6%) but more linolenic acid (37.4%) as well as 13.2% gondoic acid (C20:1). The average number of C=C double bonds in CO and SO triglycerides were calculated to be 5.8 and 4.6, respectively, based on their fatty acid compositions. Molecular weights of CO and SO were also calculated to be 892 and 872 g/mol, respectively. Iodine values of CO and SO were measured to be 172.02 ± 0.92 and 141.36 ± 2.40 . The average numbers of C=C in camelina oil and soybean oil, based on iodine values and triglyceride molecular weights, were estimated to be 6.0 and 4.86, respectively, which are close to the values obtained from GC-FID analysis.

2.4.2. Effects of formic acid on epoxy content

Formic acid could act either as an active oxygen carrier and catalyst in the formation of the oxirane ring or as a reactant to hydrolyze the newly formed oxirane in generating formates and hydroxyl groups, depending on its concentration and other conditions (Zaher and El-Shami, 1990). To attain maximal epoxy content, the optimal level of acid should be used to balance both effects. For the epoxidation reaction, use of less than one molar ratio of formic acid is recommended to minimize the side reaction of epoxy ring opening (Strukul, 1993). Epoxy content of ECO decreased significantly from 7.52% to 4.35% as the formic acid molar ratio

increased from 0.66 to 1.2 (**Figure 1a**). A similar trend of decreasing epoxy content was also observed for ESO. A certain amount of formic acid was required to generate enough peracid in-situ to promote the epoxidation reaction, but once the concentration of formic acid became too high, epoxy ring-opening with formic acid was accelerated, which was evidenced by the increased intensity of OH groups at 3463 cm^{-1} (**Figure 1b**).

2.4.3. Effects of hydrogen peroxide on epoxy content

Hydrogen peroxide acts as an oxygen donor during epoxidation. Theoretically, one molar ratio of hydrogen peroxide to the C=C of the oils would be needed to complete the reaction, but we found that with the increase of hydrogen peroxide molar ratio from 0.5 to 1.5, the epoxy content of both CO and SO increased progressively (**Figure 2a**). When the molar ratio increased further to 1.7, only minor differences in the final epoxy content were noticed. A similar optimal hydrogen peroxide molar ratio of 1.5 was also reported in the literature when epoxidizing canola oil (Mungroo et al., 2008). Overall, the maximal epoxy content of ECO is still much higher than that of ESO because of the higher iodine value of camelina oil. The successful epoxidation and formation of an oxirane ring was further confirmed by the peak at 822 cm^{-1} in the FTIR spectra (**Figure 2b**). Because of the higher epoxy content of ECO, we observed stronger peak intensity at the corresponding position.

2.4.4. Effects of reaction time and temperature on epoxy content

The epoxy content of ECO first increased and then decreased with increased reaction time (**Figure 3a**). When the reaction time was too short, conversion of double bonds to oxirane was incomplete, resulting in lower epoxy content; however, when the reaction time was too long,

the ring-opening reaction of the newly formed oxiranes with formic acid was dominated in the system, leading to lower epoxy content as well. The formation of hydroxyl groups through hydroxylation at longer reaction times was evident in the FTIR spectra (**Figure 3b**). ECO's highest epoxy content was achieved with a reaction time of 5 hours.

The effects of temperature on epoxidation were studied at temperatures of 40, 50, and 65 °C with 5 hours of reaction time (**Figure 4a**). As expected, at a lower reaction temperature (40 °C), the reaction was not completed within 5 hours, and the epoxy content of ECO was low (5.8%). At a higher temperature (65 °C) with 5 hours of reaction, both epoxidation and ring-opening reaction occurred, and ECO was partially hydroxylized through oxirane cleavage, resulting in lower epoxy content and stronger hydroxyl peaks in FTIR spectra (**Figure 4b**). A moderate reaction temperature of 50 °C for 5 hours led to maximal epoxy content of 6.25% with a lower degree of oxirane cleavage, which is more acceptable for the reaction.

2.4.5. Conversion rate of epoxidation

Based on number of C=C in TG and epoxy content, the conversion rate was calculated according to equation (2):

$$\text{Conversion rate (\%)} = \text{No. of epoxy} / \text{No. of C} = C \times 100 \quad (2)$$

The number of epoxy groups in a TG was calculated using epoxy content and molecular weight (MW) of the epoxidized oils according to the following equation (3):

$$\text{No. of epoxy} = \text{epoxy content} \times \text{MW} / 16 \quad (3)$$

The highest epoxidation conversion rate of camelina oil was 76.34% under the optimum reaction conditions obtained in this study, with a 0.66 formic acid molar ratio and a 1.7 hydrogen peroxide molar ratio reacted at 50 °C for 5 hours (**Table 5**). However, the highest conversion rate

for soybean oil in this study was 80.16%, with a 0.66 formic acid molar ratio and a 1.5 hydrogen peroxide molar ratio at 50 °C for 5 hours, which is slightly lower than the published result (83.4%) by Meyer et al. (Meyer 2008). Although camelina oil allows higher epoxy content, it contains 5.8 double bonds, whereas soybean oil contains 4.6.

The epoxidation of camelina oil was evidenced by the peaks of C-C double bond and epoxy groups before and after the reaction (**Figure 5**). The peak at 3020 cm^{-1} was attributed to the C-C double bond, which disappeared after the epoxidation reaction (**Figure 5a**), whereas the epoxy group peak at 840 cm^{-1} appeared after epoxidation (**Figure 5b**). The peak around 1750 cm^{-1} is attributed to the carbonyl (C=O) of the triglyceride ester group, which remained unchanged before and after epoxidation, indicating the triglyceride structure was stable and unaffected during this reaction.

2.4.6. Epoxidation of methyl oleate (MO), methyl linoleate (MLO), and methyl linolenate (MLON)

To confirm whether or not the epoxidation efficiency of camelina oil could be improved, we conducted further experiments to study how the conversion of unsaturated fatty acid esters was related to the number of double bonds, as well as reaction conditions. Three methyl esters (MO, MLO, and MLON) that contain 1, 2, and 3 C-C double bonds in their fatty acid backbones, were epoxidized at a fixed reaction time and temperature. Epoxidation of MO yielded a 79.12% conversion rate (**Table 2**) from its double bonds to epoxides with a 0.66 molar ratio of formic acid and a 1.15 molar ratio of hydrogen peroxide. Under exactly the same conditions, epoxidized MLO had a conversion rate of 73.28%, whereas epoxidized MLON had a conversion rate of only 6.37%. Epoxidation parameters obviously need to be tailored and optimized for different oils

with specific fatty acid double bond compositions and distributions. For example, with a 3.93 molar ratio of hydroxyl peroxide, the conversion rate of epoxidized MO reached 93.75% (**Table 2.2**). Using meta-chloroperoxybenzoic acid (m-CPBA) as a peroxycarboxylic acid catalyst and dichloromethane (DCM) as a solvent achieved a conversion rate of 97.4% for epoxidized MO. With the same molar ratio of m-CPBA to the number of double bonds, the conversion rate of epoxidized MLO was 90%, which is slightly lower than that of epoxidized MO. Scala (Scala 2002) also reported that higher epoxidation efficiency was obtained under varied epoxidation conditions for fatty acids with single, two, and three double bonds, respectively.

In this study, camelina oil contained 14.8% oleic acid (C18:1), 18.6% linoleic acid (C18:2), 37.4% linolenic acid (C20:3), and 13.2% gondoic acid (C20:1), each of which has its own optimum epoxidation conditions. Finding an optimum condition for every unsaturated fatty acid would be difficult, and we did not conduct thorough experiments to identify optimum conditions for linolenic and gondoic fatty acids in this study due to limited funding. Potential to further improve camelina epoxidation efficiency remains.

2.4.7. Potential applications of epoxidized camelina oils for adhesives

We prepared four adhesive formulations based on ESO, ECO, and DCO and synthesized adhesives via UV-cationic polymerization (**Table 2.3**). The oxirane of epoxidized oils (ESO or ECO) could be either homopolymerized into the polymer network or copolymerized with hydroxyl groups of DCO into polymers (Li and Sun, 2014). A1 containing ECO and DCO had a peel adhesion strength of 2.1 N/in. Combining ESO and DCO (A2-A4) yielded better peel adhesion performance; for example, A4 had a peel adhesion strength of 7.0 N/in. With a higher amount of DCO in the formulation, the peel adhesive either exhibited some cohesive failure

(e.g., A3) or could not be cured (e.g., A2) under the experimental conditions because of the excessive amount of hydroxyl groups relative to the oxirane groups in the resin. The peel adhesion results demonstrate that epoxidized camelina oil has great potential to be further formulated for high-performance adhesive applications, but this was beyond the scope of this study.

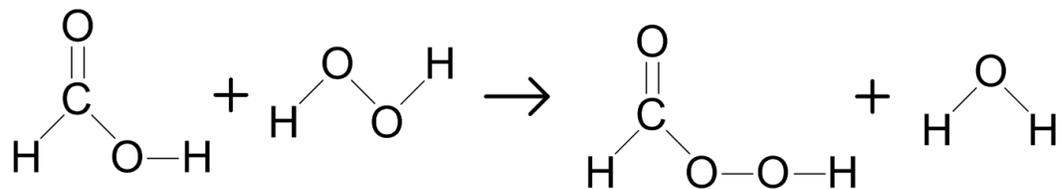
2.5. Conclusions

Epoxidation parameters of camelina oil, including formic acid ratios, hydrogen peroxide ratios, reaction time, and temperature, were optimized. A maximal conversion rate of 76.34% was obtained for camelina oil at a 0.66 molar ratio of formic acid and a 1.7 molar ratio of hydrogen peroxide for 5 hours of reaction time at 50°C. Soybean oil had a higher maximal conversion rate of 80.16% at a 0.66 molar ratio of formic acid and a 1.5 molar ratio of hydrogen peroxide for 5 hours of reaction time at 50°C because of its uniform fatty acids distribution. The highest epoxy contents obtained from camelina oil and soybean oil were 7.52 wt% and 6.53 wt%, respectively. Based on the results of the epoxidation experiments of model compounds (MO, MLO, and MLON), we concluded that epoxidation parameters must be tailored to and optimized for different oils according to their specific fatty acid composition, structure, and distribution. Peel adhesion results showed that epoxidized camelina oil has great potential to be further formulated for high-performance adhesive applications. In conclusion, epoxidized camelina oil is a promising raw material for bio-polymer industrial applications because its epoxy content is comparable to soybean oil and because it can be further converted into various derivatives.

Tables and Figures

Scheme 2.1. Epoxidation reaction of C=C with formic acid and hydrogen peroxide.

Step 1



Step 2

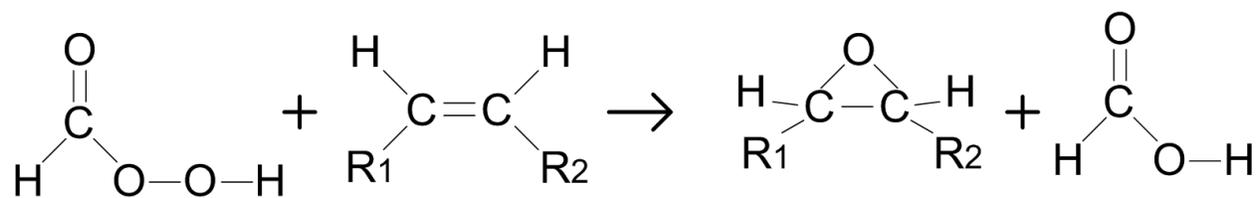
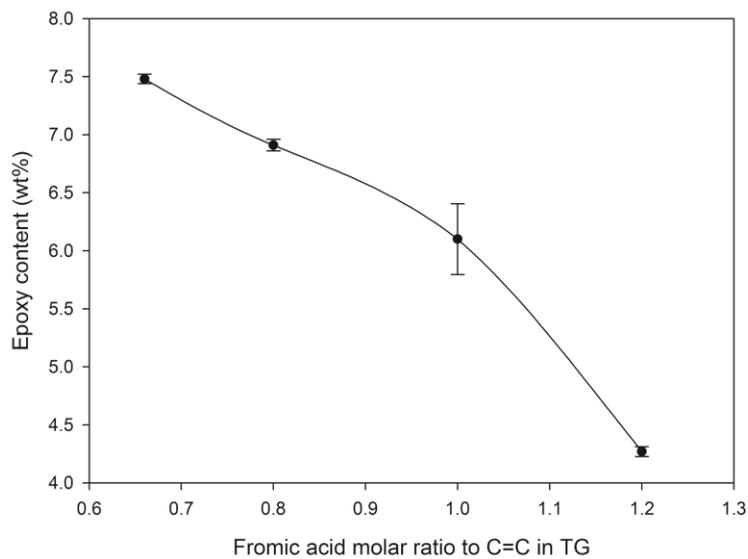


Figure 2.1. (a) Epoxy content of camelina oil with varying formic acid ratio to the number of C=C from 0.66 to 1.2 at fixed rest parameters. (b) FTIR spectra for four ECO samples with different formic acid ratio enclosed the wavenumber range between 3100 and 3700.

(a)



(b)

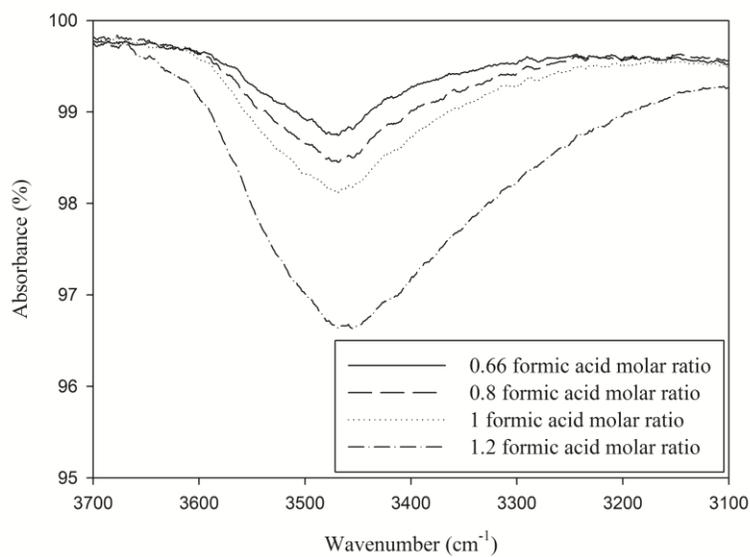
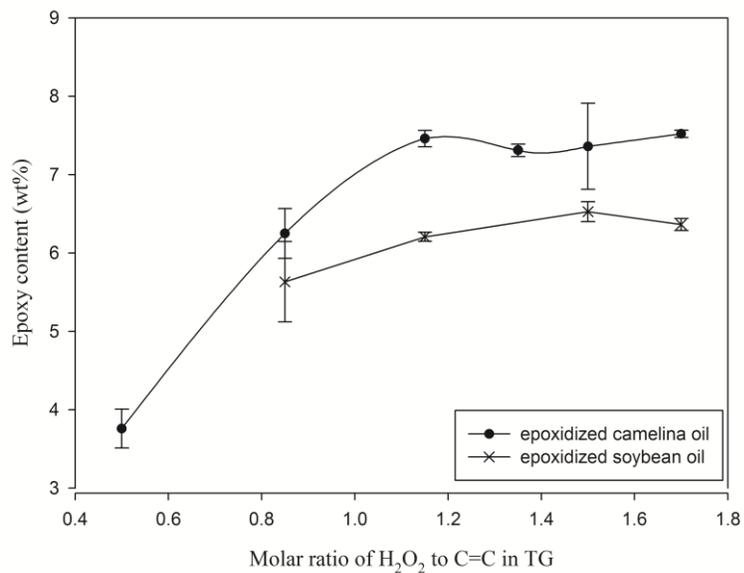


Figure 2.2. (a) Epoxy contents of camelina oil and soybean oil with varying hydrogen peroxide ratios from 0.5 to 1.7 for camelina oil and from 0.85 to 1.7 for soybean oil. (b) FTIR spectra for six ECO samples with different hydrogen peroxide ratio enclosed the wavenumber range between 750 and 900 cm^{-1} .

(a)



(b)

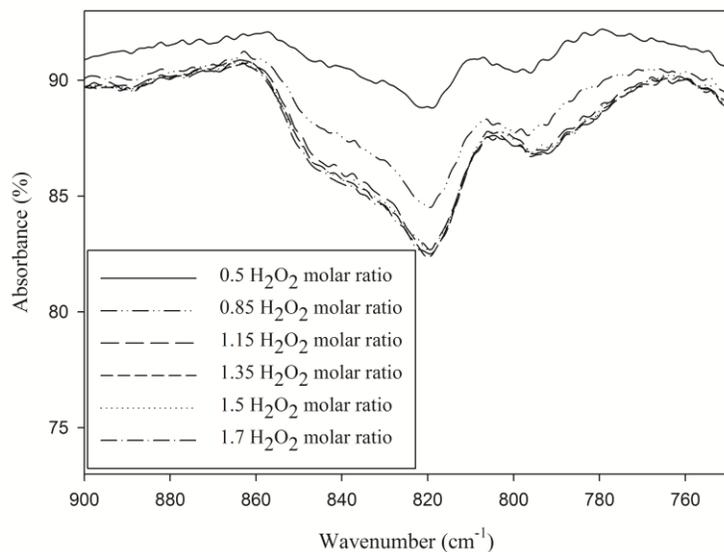
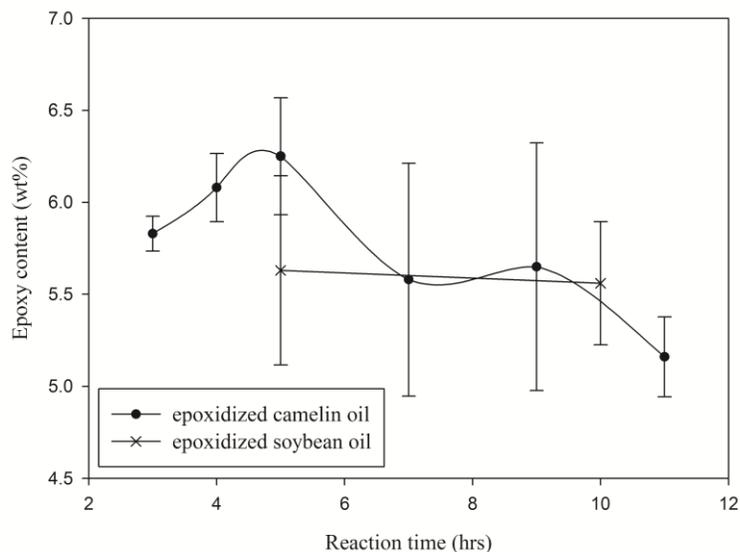


Figure 2.3. (a) Epoxy contents of camelina oil and soybean oil with varying reaction time from 3 to 11 hours for camelina oil and from 5 to 10 hours for soybean oil. (b) FTIR spectra for six ECO samples with different reaction time enclosed the wavenumber range between 3700 and 3100 cm^{-1} .

(a)



(b)

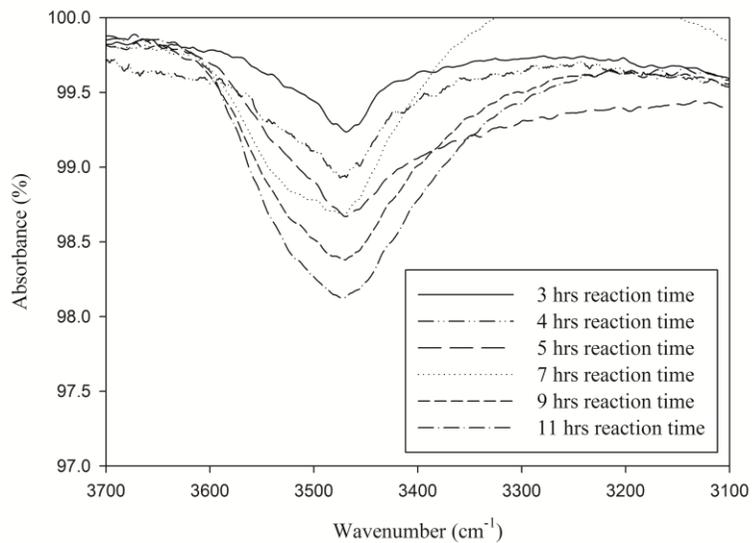
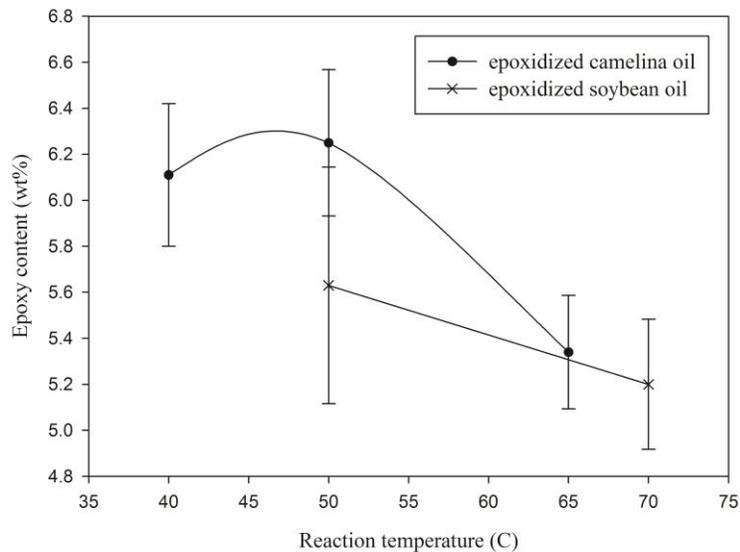


Figure 2.4. (a) Epoxy contents of camelina oil and soybean oil with different reaction temperature from 40 to 65 °C for camelina oil and from 50 to 70 °C for soybean oil. (b) FTIR spectra for three ECO samples with different reaction temperature enclosed the wavenumber range between 3700 and 3100 cm⁻¹.

(a)



(b)

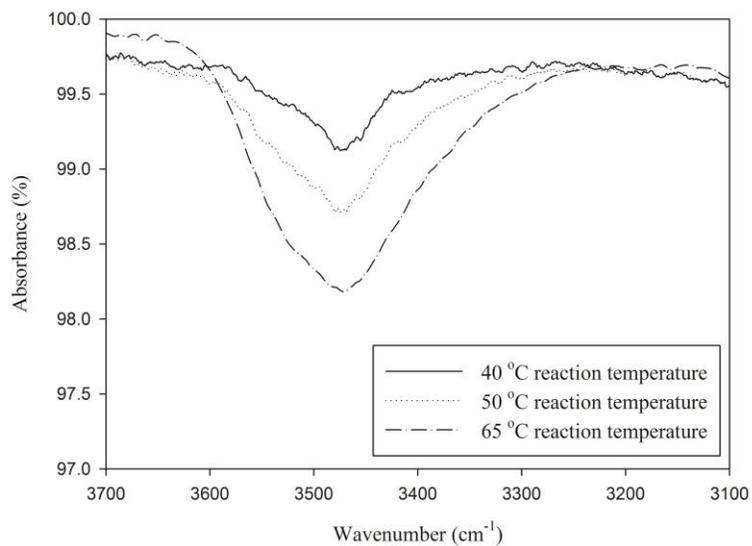
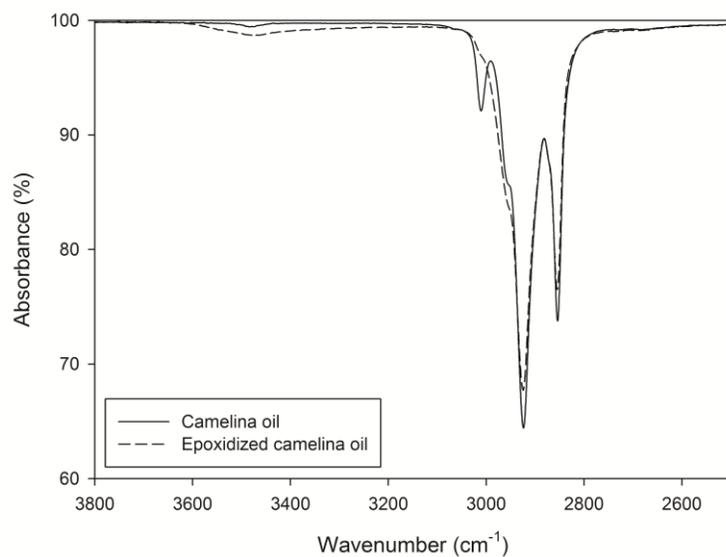


Figure 2.5. FTIR spectra between camelina oil (solid line) vs. epoxidized camelina oil (dashed line); reaction condition of 0.66 formic acid and 1.7 hydrogen peroxide molar ratio to the number of C=C, 5 hrs reaction, and reaction temperature of 50 °C.

(a)



(b)

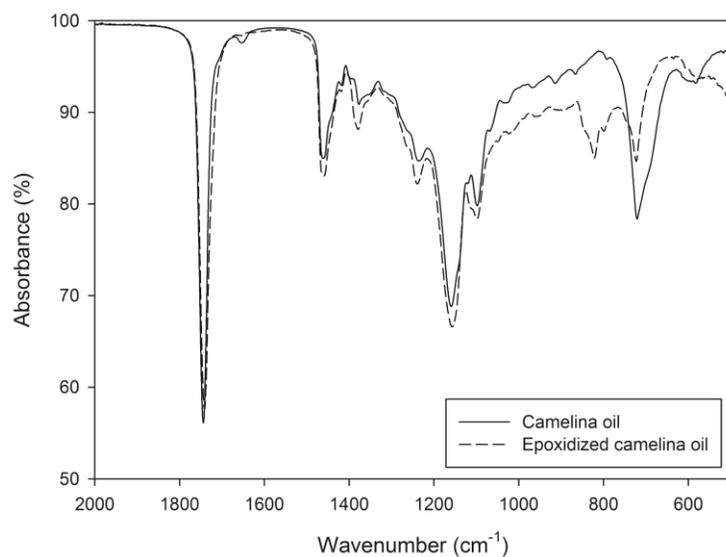


Table 2.1. Epoxidation reaction parameters of camelina oil and soybean oil.

Sample	Acid ratio	H2O2 ratio	Reaction time (hrs.)	Reaction temp. (°C)
CO	0.66 - 1.2	1.7	5	50
	0.66	0.85 - 1.7	5	50
	0.66	0.85	3 - 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	5 - 10	50
	0.66	0.85	5	50 - 70

Table 2.2. Epoxidation reaction parameters of methyl esters: methyl oleate, methyl linoleate, and methyl linolenate, and its corresponding epoxy content, epoxy number in TG, and conversion rate.

Sample ¹	Acid ratio	H2O2 ratio	Epoxy content (wt%)	Epoxy No.	Conversion rate (%)
MO		0.85	3.15 ± 0.09	0.61	61.46
	0.66	1.15	4.05 ± 0.12	0.79	79.12
		3.93	4.8 ± 0.05	0.94	93.75
MO ²	2.23	1.15	2.55 ± 0.01	0.5	49.84
		3.93	4.18 ± 0.11	0.82	81.69
MO ²	/	/	4.97 ± 0.03	0.97	97.4
MLO	0.33		5.95 ± 0.07	1.21	60.72
	0.44	1.15	6.85 ± 0.15	1.4	69.86
	0.66		7.18 ± 0.04	1.47	73.28
MLO ²	/	/	12.74 ± 0.05	1.81	90.23
MLON	0.44		5.35 ± 0.09	1.14	37.97
	0.66	1.15	0.9 ± 0.08	0.19	6.37

¹ Reaction time and temperature for epoxidation with formic acid/ H2O2 were fixed at 5 hours and 50 °C; ² MO and MLO were epoxidized with meta-chloroperoxybenzoic acid (m-CPBA) (1 to 1 molar ratio of m-CPBA to double bond) in dichloromethane (DCM) at 25 °C for 18 hours.

Table 2.3. Adhesion properties of camelina oils derived adhesives.

Formulation ID ¹	ESO (g)	ECO (g)	DCO (g)	UV passes	Adhesion strength, N/in
A1	0	1	0.7	3	2.1 ± 0.5
A2	1	0	0.7	6	²
A3	1	0	0.6	4	5.2 ± 1.7 ³
A4	1	0	0.5	3	7.0 ± 3.1

¹ All the formulations contained 0.5 g rosin ester as tackifier and 0.03 g diaryliodonium hexafluoroantimonate as photo-initiator; ² Adhesive was not cured; ³ Half cohesive failure was observed.

Table 2.4. Fatty acid composition (w/w) of camelina oil (CO) and soybean oil (SO).

Oil	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C20:2	C20:3	C20:4	C24:0	C24:1	Ave. #DB ¹	Ave. MW ²
SO	0.1	11.6	0.1	4.4	22	54.9	7	0	0	0	0	0	0	0	4.6	872
CO	0.1	5.7	0.1	2.6	14.8	18.6	37.4	1.3	13.2	1.8	1.4	2.3	0.2	0.5	5.8	892

¹ Ave. #DB, average number of double bonds in the oil; ² Ave. MW, average molecular weight of the oil.

Table 2.5. Epoxidation results of camelina and soybean oils using reference parameters and optimized parameters.

Sample	H ₂ O ₂ /DB molar ratio	Formic acid/DB molar ratio	Time, hours	Temp., °C	Epoxy content, wt%	Conversion rate, %
SO ¹	1.7	0.84	10	50	6.13	83.3
SO	1.7	0.88	10	50	6.2	76.2
CO	1.7	0.88	10	50	7.14	72.5
SO	1.5	0.66	5	50	6.53	80.16
CO	1.7	0.66	5	50	7.52	76.34

¹ Reaction parameters and results by Meyer (Meyer 2008).

Chapter 3 - Hydroxylation of epoxidized *camelina sativa* oil

3.1. Abstract

Di-hydroxyl camelina oil (DCO) was synthesized from epoxidized camelina oil with different reaction parameters. The ring opening of epoxidized camelina oil was performed with water, perchloric acid, and THF as proton donor, catalyst, and solvent respectively. Hydroxyl value of DCO was measured, and the maximal hydroxyl value was 369.24 mg KOH/g. physical properties of DCO were characterized by acid value and moisture content; thermal properties of DCO were obtained using differential scanning calorimeter (DSC), thermogravimetric analysis (TGA). Amount of solvent and acid catalyst addition affected the hydroxyl value and residual acid in DCO. Heat capacity, phase transition temperatures, thermal stability of DCO were obtained and showed higher value than ECO.

3.2. Introduction

Due to petroleum oil depletion, global warming and other environmental concerns, the transition of petroleum feedstock to renewable resources is crucial to a sustainable development in the future. Fats and oils derived from plants have a large potential for current petrochemical-based polymer industry because they are biodegradable, sustainable, and can be converted into various industrial polymers (Meier, 2007).

Biopolyol, a resultant of hydroxylation of plant oil, has typically been studied for polyurethane (PU) applications which in the field of elastomers, plasticizers, and coatings. Di-hydroxylated plant oils are used for cross-linking agents in the PU industry (Lligadas et al. 2006). Many researchers have studied hydroxylation of plant oils. Guo et al. prepared soybean oil-based polyols by catalytic hydrogenation for rigid polyurethane foams (Guo et al. 2000a), and

synthesized four different hydroxylated soybean oils for PU application with hydrochloric acid, hydrobromic acid, methanol, and hydrogen (Guo et al. 2000b); Okieimen et al. reported both hydroxylation and epoxidation of rubber seed oil by one-pot multi-step reactions (Okieimen et al. 2005); Ahn et al. prepared PSAs by mixing ESO and DSO, as DSO used as a tackifier (Ahn et al. 2011a; Ahn et al. 2011b). The peel strength of ESO-based PSA was comparable with commercial adhesives such as scotch magic tape and post-it notes. Ahn et al. also investigated the thermal properties such as glass transition, melting point, and coefficient of thermal expansion of PSAs from ESO and DSO (Ahn et al. 2011b). Li and Sun synthesized DSO with different hydroxyl values (157.2, 238.7, and 284.2 mg KOH/g) and studied thermal properties of DSO and peel adhesion strength (Li & Sun 2014). The ESO and DSO formulations with different ratio were tested, and the highest peel strength was 4.6 N/in.

Camelina oil contains significantly high polyunsaturated fatty acids content, and its growing condition is cost-efficient (Zubr 1997; Abramovic and Abram 2005). As a reaction site, the number of carbon-carbon double bond in the triglyceride of camelina oil was determined by iodine number measurement and gas chromatography method (5.8 – 6.0) which is higher than the other common plant oils used in polymer industry such as soybean oil (4.6) and canola oil (3.9). Regarding the C-C double bond in triglycerides as reactive sites, the more double bonds present anticipates the higher reactivity.

Hydroxylation reaction can be completed by ring opening of the epoxidized plant oils with proton donors. Ahn et al. prepared di-hydroxyl soybean oil from commercial epoxidized soybean oil using water as proton donor, perchloric acid as catalyst, and THF as solvent (Ahn et al. 2011b). In this study, epoxidized camelina oil was di-hydroxylated with different reaction parameters: perchloric acid and THF. Perchloric acid, water, and THF were used as catalyst,

proton donor, and solvent, respectively. Chemical pathway of the reaction is shown in **Scheme 2**. Di-hydroxylated camelina oil was then characterized its physical and thermal properties employing titration methods, DSC, and TGA. Functionalized camelina oil-based polyol is anticipated to be used in bio-polymer industries.

3.3. Materials and Methods

3.3.1. Materials

Camelina oil was obtained from Montana Gluten Free Processors (Montana, USA). perchloric acid (70%, ACS grade), acetic anhydride (ACS grade), Tetrahydrofuran (certified, contains about 0.025% butylated hydroxytoluene as a preservative), pyridine (ACS grade), sodium hydroxide (ACS grade), potassium hydroxide (ACS grade), isopropyl alcohol (reagent grade), and toluene (laboratory grade) were purchased from Fisher Scientific (Pittsburgh, PA, USA).

3.3.2. Di-hydroxylation of ECO

Epoxidized camelina oil prepared using formic acid and hydrogen peroxide described in previous chapter. The optimal epoxidation reaction was found at reaction parameters with 0.66 formic acid molar ratio, 1.7 hydrogen peroxide molar ratio, 5 hours reaction time, and 50°C reaction temperature. Epoxy content of 7.56 wt% was obtained from the epoxidation reaction. Epoxides from ECO were converted to di-hydroxyl groups using water, perchloric acid, and THF. For the di-hydroxylation reaction, ECO (about 30g) was added in a 250ml Erlenmeyer flask equipped with a magnetic stir bar. Predetermined amounts of THF and water were added to the flask, and placed on a magnetic stirrer. While stirring, calculated amount of perchloric acid was gradually added to the flask drop by drop. After 5 hours of reaction, the product was extracted in

a separatory funnel with ethyl acetate, washed with distilled water, and neutralized using saturated sodium bicarbonate solution. The residuary solvent and water in the product were eliminated using rotary evaporator connected to a vacuum pump.

To study the effect of the reaction parameters, we changed the amount of acid catalyst ratio and solvent ratio based on the mass of ECO with fixed water ratio (50% v/w ECO), reaction time (5 hours), and temperature (RT). Di-hydroxylation reaction parameters varied with each experiment and the experimental design is shown in **Table 3.1**.

3.3.3. Hydroxyl value of DCO

Hydroxyl value of the DCO was measured according to ASTM D4274-11, test method A. The DCO sample was diluted in the acetylation reagent (mixture of acetic anhydride and pyridine), and placed in a hot water bath (about $98 \pm 2^\circ\text{C}$) with blank samples for 2 hours. After 2 hours, the DCO samples were rinsed with water and titrated with 0.5N sodium hydroxide solution. The hydroxyl value was calculated following Equation (4) below:

$$\text{Hydroxyl value} = [(B - A)N \times 56.1] / W \quad (4)$$

where A, B, N, and W are NaOH required for titration of the blank, mL, NaOH required for titration of the sample, mL, normality of the NaOH, and sample used, g, respectively. The calculated hydroxyl value is expressed as a unit of mg KOH/g.

3.3.4. Physical properties of DCO

Acid value of DCO

Acid value of DCO was measured according to ASTM D1639 – 90 method. Camelina oil, ECO, and Synthesized DCO sample were weighed in a 250mL Erlenmeyer flask and diluted with 100mL of neutral solvent (toluene and isopropyl alcohol). Once the DCO sample dissolved

in the neutral solvent, titration with 0.1N KOH solution began. The acid value was calculated using the following Equation (5) below:

$$\text{Acid value} = V \times K / (S \times N) \quad (5)$$

where V, K, S, and N are volume of KOH solution required for titration of the sample, mL, weight of KOH per mg of KOH solution, mg, DCO weight, g, and nonvolatile content of the material expressed as a decimal fraction, respectively.

Moisture content of DCO

The moisture content of DCO was measured employing Karl Fischer titration using a mettler-Toledo C20 KF-titrator.

3.3.5. Thermal properties of DCO

Differential Scanning Calorimetry (DSC) analysis of DCO

DSC was used to investigate its thermal transition with a TA DSC Q200 instrument. About 8 mg of sample was measured and used for DSC measurement. Heating rate of 10 °C/min was used for the temperature range between –80°C and 200°C. Empty pan was used for reference, and nitrogen gas flow rate was 50 ml/min during the measurement. A flow of nitrogen gas was maintained over the samples to create a reproducible and dry atmosphere. The nitrogen atmosphere also eliminated air oxidation of the samples at high temperatures. ECO was used for measurement as a comparison.

Thermogravimetric analysis (TGA) of DCO

TGA was used for thermal stability measurement. Perkin Elmer Pyris1 TGA instrument was used, and the temperature range was from 50 to 600 °C. About 10mg of the sample was used at the heating rate of 20 °C/min. ECO also was used as a comparison.

3.4. Results and discussion

3.4.1. Hydroxyl value of DCO

Di-hydroxyl camelina oils with different reaction condition were prepared, and hydroxyl values were measured. Hydroxyl value is the number of KOH (in mg) required to neutralize any acid when combined with acrylation in 1g of the sample. The highest hydroxyl value of DCO found was 369.24 mg KOH/g. As shown in **Figure 3.1** and **Figure 3.2**, the reaction condition for optimal hydroxyl value was obtained by using 200% (v/w of ECO) of THF and 1.5% (v/w of ECO) of perchloric acid.

Based on the number of epoxides in the ECO which obtained as 4.6, the maximum hydroxyl value is about 530 mg KOH/g. From our maximal hydroxyl value, conversion rate of hydroxylation from ECO is about 70%. However, there might some side reactions such as ring opening reaction of newly formed epoxide with residual acids during epoxidation of camelina oil (Zaher and El-Shami, 1990) and/or oligomerization of ECO and DCO during the hydroxylation reaction (Caillol et al. 2012). Thus, ECO could contain hydroxyl groups already, and there might some oligomerized molecules. The overall conversion from C-C double bonds from CO to hydroxyl number from DCO is about 55%. However, the hydroxyl value we gained from DCO is higher compared to the soybean-based polyol which was reported as 290 mg KOH/g (Li & Sun 2014).

3.4.2. Physical properties of DCO

Acid value is an important indicator of plant oil quality. Acid value is expressed as the amount of KOH (in mg) required neutralizing free fatty acids in 1g of oil. A high amount of free fatty acid indicates hydrolysis of triglyceride caused by the action of lipase enzyme and results

inadequate processing and storage conditions. From this study, acid value range obtained was 2.77 – 6.97 mg KOH/g for DCO (**Table 3.1**). Acid values of CO and ECO were also measured and were similar, 3.11 and 3.02 mg KOH/g, respectively. In addition, acid values of DCO with different reaction parameters showed tendencies that, (1) as the amount of THF increased, acid value of DCO decreased; (2) as the amount of acid increased, acid value was also increased. From the results, it is expected that the residual acid could be washed out with enough amount of solvent. Considering the reaction conversion, however, i.e., decrement of hydroxyl value with higher THF addition, amounts of acid catalyst and solvent have to be examined for optimal conversion.

Moisture content of the DCO measured less than 0.5% for all the DCO samples.

3.4.3. Thermal properties of DCO

DSC analysis

Differential Scanning Calorimetry (DSC) measures the temperatures and heat flows associated with transitions in materials as a function of time and temperature. These measurements provide quantitative and qualitative information about physical and chemical changes that involve endothermic or exothermic processes or changes in heat capacity. DSC monitors heat effects associated with phase transitions and chemical reactions as a function of temperature. In DSC, the difference in heat flow to the sample and a reference at the same temperature is recorded as a function of temperature. The reference is an inert material such as alumina, or just an empty aluminum pan. The temperature of both the sample and reference are increased at a constant rate. From the DSC analysis, glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) were obtained and are shown in **Table 3.2**, as well as heat capacity and heat changes (C_p , ΔH_m , and ΔH_c). Thermal phase

transition temperatures of ECO were also obtained for comparison. The transition temperatures of DCO (T_g , -19.17 °C; T_c , -0.45 °C, T_m , 12.04 °C) were higher than ECO's (T_g , -57.87 °C; T_c , -35.71 °C, T_m , -8.1 °C). The higher transition temperatures of DCO than ECO can be explained by the higher molecular weight of DCO than ECO.

TGA

TGA measures the amount and rate of change in the mass of a sample as a function of time and temperature in the nitrogen atmosphere. The data from TGA can be used to determine the thermal stabilities of materials and also their compositional properties. From TGA data, we can see the materials' mass loss or gain due to denaturation (decomposition), oxidation or volatiles loss. TGA is a very useful instrument that provides valuable information that can be used to select materials for certain end-use applications, predict product performance, and improve product quality (Kawakami, 2007).

The TGA data of DCO from heating rate of 20 °C/min and sample size of about 10mg was obtained as shown in **figure 3.4**; ECO was also used for comparison at the same heating rate and sample size. Temperature at 10% of weight loss, $T_{d, 10\%}$ and temperature at maximum decomposition rate, $T_{d, max}$ were obtained as listed in **table 3.2**.

Both the $T_{d, 10\%}$ and $T_{d, max}$ of DCO with heating rate of 20 °C/min and 10mg sample size were obtained as 372.67 °C and 418.33 °C, respectively. TGA data of ECO were also obtained with 10mg sample loading and heating rate of 20 °C/min. Compared with ECO, DCO shows stronger thermal stability. The weight % vs temperature data of DCO was compared with ECO's data as shown and listed in **figure 3.4** and **table 3.2**. Similar values of $T_{d, 10\%}$ and $T_{d, max}$ were obtained for each of the samples, but the decomposition rate of the DCO was higher than ECO.

3.5. Conclusion

Epoxidized camelina oil with epoxy content of 7.45 wt% was di-hydroxylated with perchloric acid, water, and THF. The highest hydroxyl value of DCO, 369.24 mg KOH/g was found when the reaction condition of 50% of water (v/w ECO), 200% of THF (v/w ECO), 1.5% of perchloric acid (v/w ECO), 5hours reaction time in room temperature. Acid catalyst (perchloric acid) and solvent (THF) amounts affected conversion from ECO to DCO. Effect of acid and solvent addition amount to the residual acid in DCO also confirmed by acid value; as the amount of THF increased, acid value of DCO decreased, and as the amount of acid increased, acid value was also increased. Moisture content of DCO was under 0.5%. Thermal properties such as heat capacity, phase transition temperature, and thermal stability of DCO and ECO were also studied; compared to ECO, DCO showed higher heat capacity, phase transition temperatures, and thermal stability temperature ($T_{d 10\%}$). DCO is anticipated to be used in applications such as PSAs, coatings, polyurethane, and etc.

Scheme 3.1. Chemical pathwat of di-hydroxylation of epoxidized camelina oil.

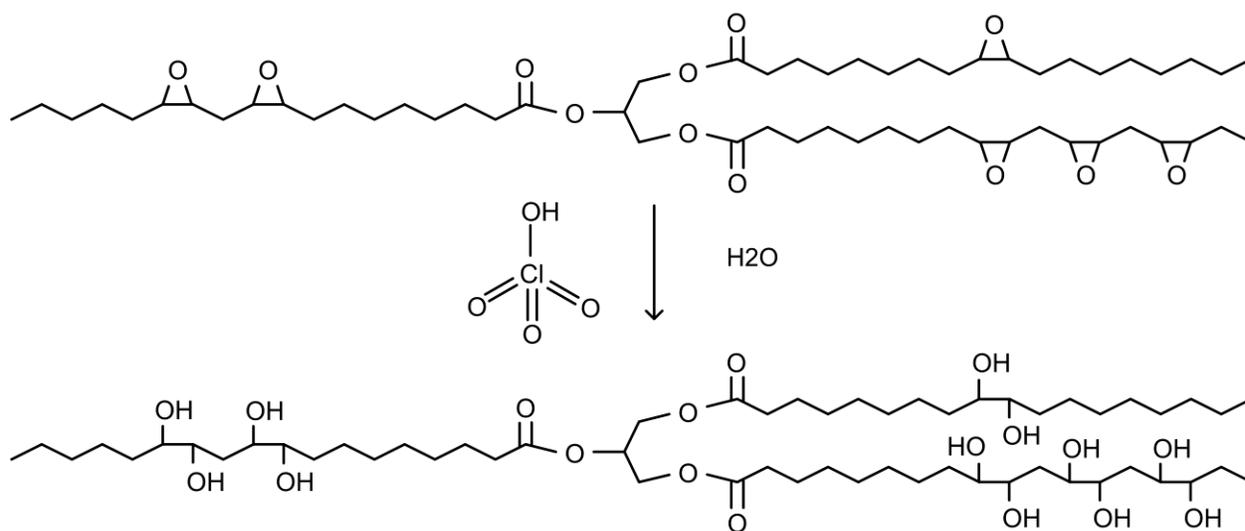


Figure 3.1. Hydroxyl values of DCO with different THF addition amount.

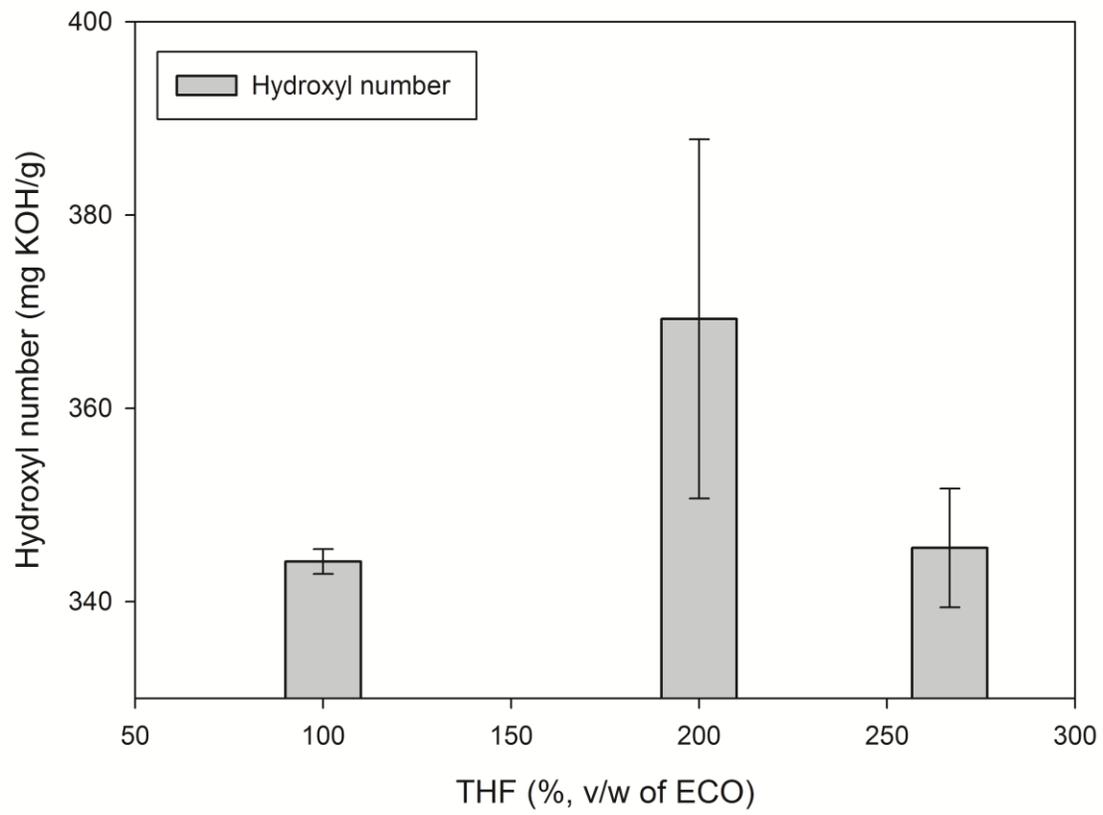


Figure 3.2. Hydroxyl values of DCO with different acid addition amount.

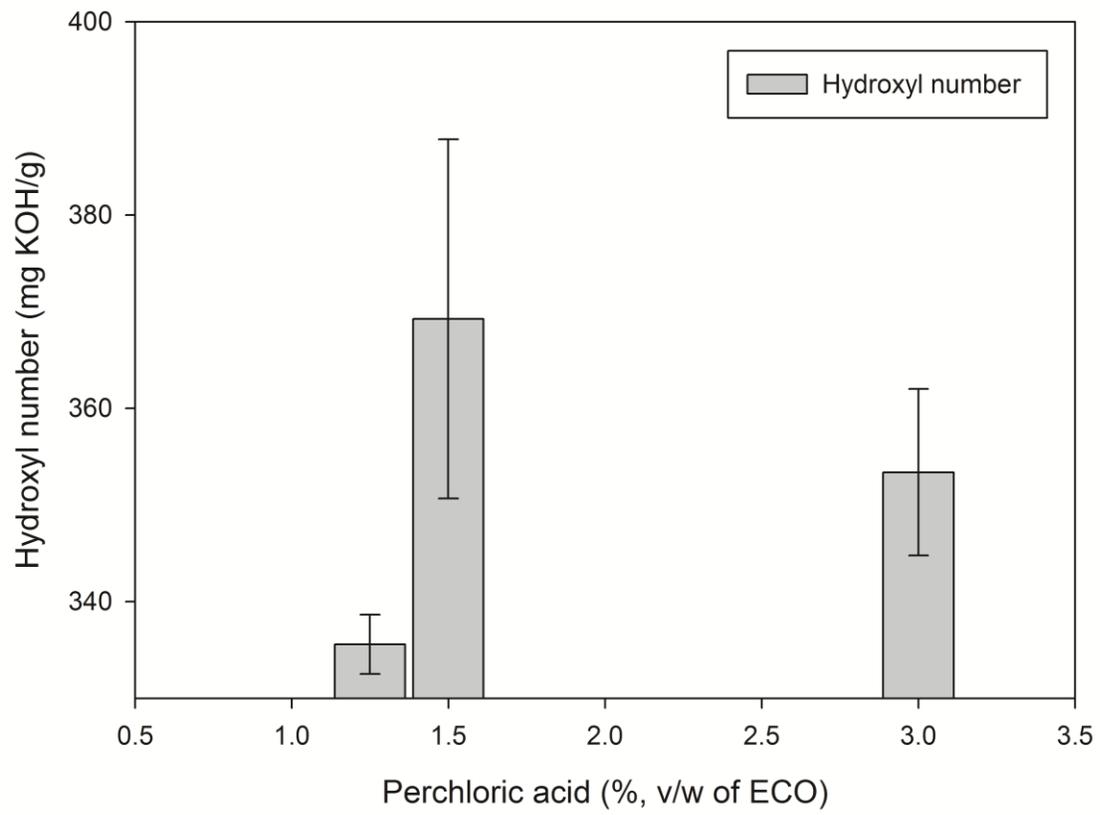


Figure 3.3. DSC thermograms of DCO and ECO with heating rate of 10 °C /min.

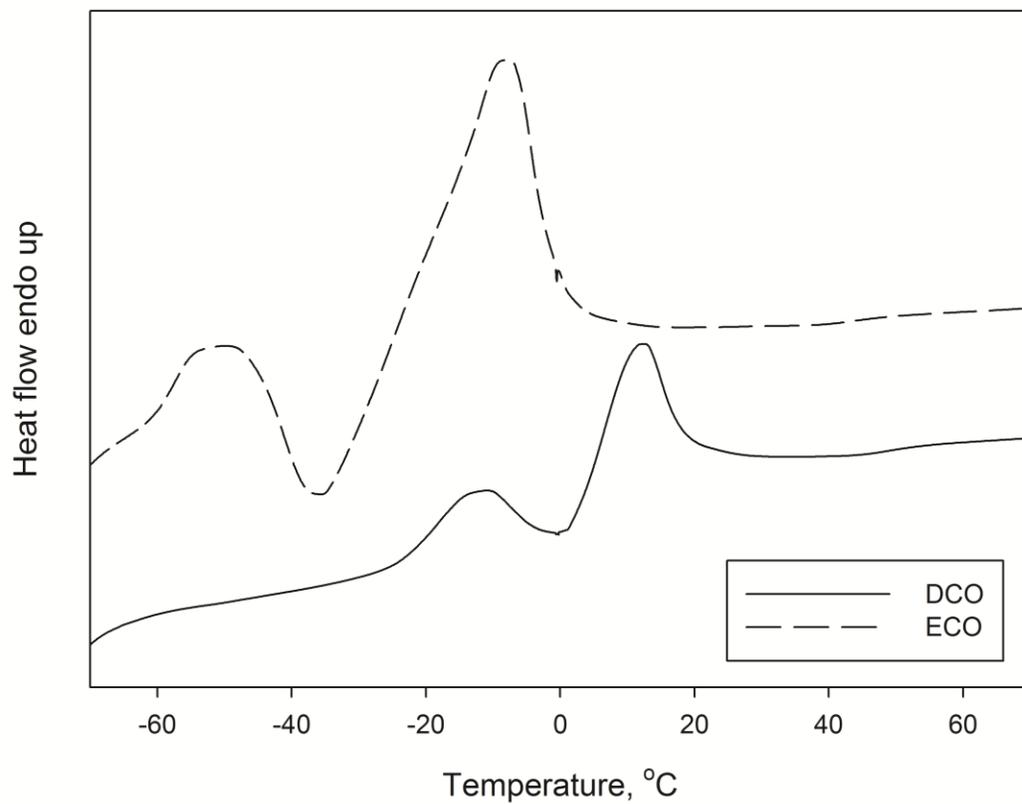


Figure 3.4. TGA thermograms of DCO and ECO with heating rate of 20 °C /min and about 10mg sample loading.

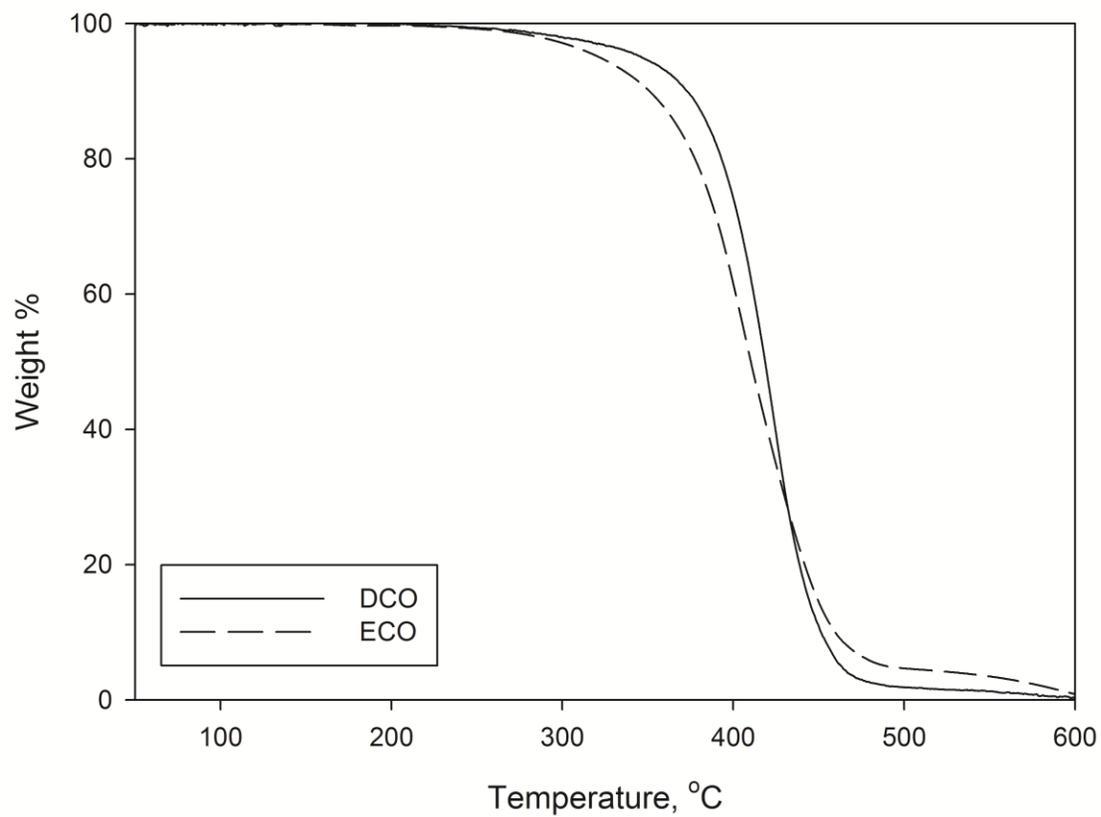


Table 3.1. Reaction conditions and its corresponding physical results of di-hydroxylation reaction using ECO.

sample	ECO (g)	water (%) ¹	THF (%) ¹	Perchloric acid (%) ¹	Reaction time (hrs.)	Reaction temp. (°C)	Hydroxyl value (mg KOH/g)	Acid value (mg KOH/g)	MC (%)
			100				344.16	4.29	0.47
			200	1.5			369.24	3.63	0.40
ECO	30	50	266.67		5	RT	345.55	3.14	0.19
				1.25			335.59	2.77	0.18
			200	1.5			369.24	3.63	0.40
				3			353.39	6.97	0.46

¹ Percentages of water, THF, and perchloric acid denote % volumes based on weight of ECO (v/w).

Table 3.2. Thermal properties of DCO and ECO from DSC and TGA.

sample	C_p (J/g/°C)	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_c (J/g)	ΔH_m (J/g)	$T_{d, 10\%}$ (°C)	$T_{d, \max}$ (°C)
DCO	0.42	-19.17	-0.45	12.04	3.26	8.15	372.67	418.33
ECO	0.39	-57.87	-35.71	-8.1	12.45	25.63	350.67	406

Chapter 4 - Conclusions and future work

Epoxidation parameters of camelina oil, including formic acid ratios, hydrogen peroxide ratios, reaction time, and temperature were optimized. Maximal conversion rate of 76.34% was obtained for camelina oil at 0.66 molar ratio of formic acid and 1.7 molar ratio of hydrogen peroxide for 5 hours reaction in 50°C. Soybean oil showed a higher maximal conversion rate of 80.16% at 0.66 molar ratio of formic acid and 1.5 molar ratio of hydrogen peroxide for 5 hours reaction at 50°C, because of more uniform fatty acids distribution of soybean oil. However, camelina oil has the higher epoxy contents (7.52 wt%) than soybean oil (6.53 wt%) because camelina oil contains higher unsaturation degree than soybean oil.

Based on the results of the epoxidation experiments of model compounds (MO, MLO, and MLON), we concluded that epoxidation parameters always need to be tailored and optimized for respective oils with specific fatty acid composition, structure, and distribution. Peel adhesion results showed great potential that the epoxidized camelina oil can be further formulated for high performance adhesive applications.

Epoxidized camelina oil with epoxy content of 7.45 wt% was di-hydroxylated with perchloric acid, water, and THF. The highest hydroxyl value of DCO, 369.24 mg KOH/g was found when the reaction condition of 50% of water (v/w ECO), 200% of THF (v/w ECO), 1.5% of perchloric acid (v/w ECO), 5hours reaction time in room temperature. Acid catalyst (perchloric acid) and solvent (THF) amounts affected conversion from ECO to DCO. Effect of acid and solvent addition amount to the residual acid in DCO also confirmed by acid value; as the amount of THF increased, acid value of DCO decreased, and as the amount of acid increased, acid value was also increased. Moisture content of DCO was under 0.5%. Compared to ECO, DCO showed higher heat capacity, phase transition temperatures, and thermal stability

temperature ($T_{d 10\%}$). DCO is anticipated to be used in applications such as PSAs, coatings, polyurethane, and etc. In conclusion, epoxidized camelina oil is expected to be a promising raw material for bio-polymer industrial applications with its comparable epoxy content as soybean oil and its further conversion to various derivatives.

For better hydroxyl functionality of di-hydroxylated camelina oil, identification of effects of reaction time, reaction temperature, and water addition need to be investigated. In addition, for adhesive and coating applications of modified camelina oil, the higher hydroxyl value of DCO and ECO should be formulated to examine adhesion performance. Also, the shelf lives of modified camelina oils need to be evaluated.

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