Development Of Biobased Plasticizers From Vegetable Oils For Poly(Vinyl Chloride), PVC

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Abstract

Phthalate plasticizers have long been used in poly(vinyl chloride), PVC formulations until recent studies have shown they can cause adverse health effects when ingested. Alternative plasticizers are available but they do not match the cost and performance of phthalates. Vegetable oils are ubiquitous, nontoxic, low cost materials that can be chemically modified to function as plasticizers in PVC. To be compatible, vegetable oils must be modified to reduce molecular weight, balance of polarity, and introduce branching along the fatty acid backbone. Readily available soybean oil was used as the primary starting material to meet these structural requirements. The oil was transesterified with different alcohols to reduce molecular weight and change its overall polarity. To increase polarity and add branching, estolides were introduced onto the fatty acid ester backbone at the site of unsaturation by two synthetic methods. The perchloric acid method provided estolides with low estolide number and higher crosslinking products, while the epoxy method resulted in higher estolide numbers which imparted better compatibility with PVC. Separation and characterization of the components of the epoxy method found they contained cyclic tetrahydrofuran ether estolides in significant quantities. These were formed by the ring opening reaction of diepoxy linoleate by acetic acid. To reduce the formation of these cyclic ether estolides castor oil epoxy fatty acid alkyl ester estolides were synthesized and evaluated as plasticizers. These epoxy fatty acid alkyl ester estolides from castor oil had excellent plasticizing properties but the higher cost and limited availability of castor oil would make them prohibitive. Considering the better performance of castor oil based epoxy fatty acid ester estolides, soybean oil derived epoxy fatty acid alkyl ester estolides with reduced cyclic ether content were prepared. These compounds with medium molecular weight head group

(butyl and pentyl) provided good functionality in PVC. Based on their performance, these epoxy fatty acid ester estolides would be useful replacements for phthalates in low water contact applications such as wire and cable coatings or wall coverings.

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Abbreviations:

DEHP: diethyl hexyl phthalate

DINCH/Elatur CH: 1,2-cyclohexane dicarboxylic acid diisononyl ester

DINP: diisononyl phthalate

DOP: dioctyl phthalate

DMA: Dynamic Mechanical Analysis

DSC: Differential Scanning Calorimetry

ESBO: epoxy soybean oil

FABE: fatty acid *iso*-butyl ester

FAB/ME: fatty acid *iso*-butyl/methyl ester

FAEHE: fatty acid ethyl hexyl ester

FAME: fatty acid methyl ester

FTIR: Fourier Transform Infrared Spectroscopy

GC: Gas Chromatography

phr: parts per hundred resin

PVC: poly(vinyl chloride)

SnS: Soft-N-Safe

SBO: soybean oil

S.D.: standard deviation

TGA: Thermogravimetric Analysis

Tg: glass transition temperature.

Chapter 1: Introduction and Literature Review

1.1.Introduction

Plasticizers are non-volatile organic liquid compounds that impart flexibility to polymers and increase the range of end applications. The majority of plasticizers are used in the utilization of polyvinylchloride (PVC). PVC, due to its unique combination of price, performance, and versatile use, is one of the oldest and widely used high volume plastics. The PVC products formulated with various additives, range from very rigid pipes and siding to flexible flooring, sheeting, and adhesives [1,2]. PVC formulation includes multi-functional additives that modify and/or enhance the properties of the PVC. In general the formulations contain the polymer (resin), thermal stabilizers, fillers, plasticizers, and other specific property enhancers such as fire resistance materials. Rigid PVC may contain low levels of plasticizer usually less than 20 phr (parts per hundred parts resin) and is primarily used for pipe work, ducts, and similar applications where structural rigidity and chemical resistance is required. Flexible PVC contains high concentrations of plasticizer (up to 100+ phr) and is useful for numerous applications such as films, sheeting, cable coverings, moldings, stationary products, toys, hoses, leather goods, clothing and various furnishings.

PVC is produced from vinyl chloride (CH_2=CHCl) by free radical polymerization and has the following structure:

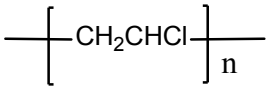


Figure 1 Structure of PVC

The repeat units, n, depend on the degree of polymerization and ranges from 500 to 3500, with an approximate molecular weight of 30K to more than 200K Daltons. Having chlorine more than 50% of the weight of the polymer makes it one of the most cost effective fire retardant materials.

PVC contains two structural domains, ordered crystalline structures distributed in the amorphous matrix as shown in Figure 2. The plasticizer, upon addition and compounding embeds in the polymer matrices, reduces the glass transition temperature (Tg) thus rendering the polymer more flexible. The small molecular size of the plasticizer allows it to incorporate into the amorphous regions of the polymer matrix and alters the inter and intra molecular interactions thereby increasing the polymer chains mobility and overall flexibility. Thus the plasticizer increases the flexibility, softness, workability, pliability, and distensability of the polymer resulting in materials useful for a variety of applications. As a result the plasticized PVC compound has reduced tensile strength and elastic modulus with increased elongation at tensile failure at ambient temperatures. Plasticizers are only adsorbed into the matrix of the polymer but do not covalently bind to the polymer chains [2].

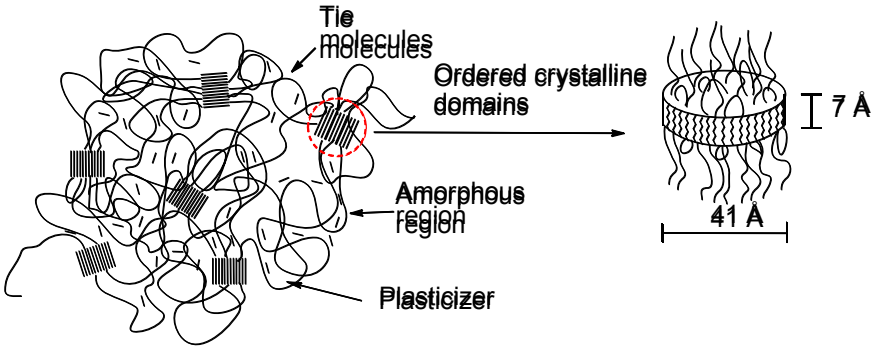


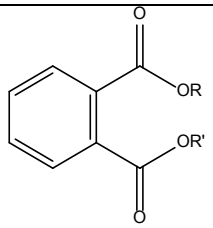
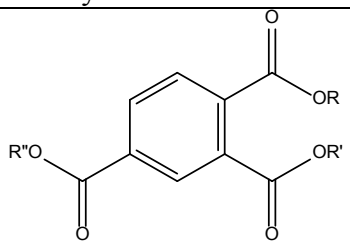
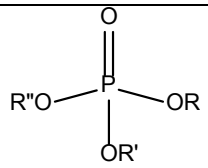
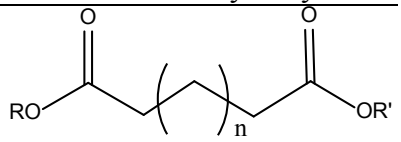
Figure 2 PVC compounded with plasticizer

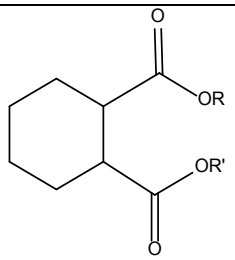
Plasticizers are the largest category of plastics additives, accounting for 54% of total volume. The global plasticizer market is a $20 billion industry, with 90% of production consumed in vinyl based formulations [3].

Currently there are many different types of plasticizers on the market. The end application and the cost dictate the type of plasticizer used. Of these different types, the dominant class of plasticizers used in the vinyl industry today is the petroleum derived phthalates. These compounds are produced by reacting phthalic anhydride with two equivalents of alcohol to form a diester. The largest produced phthalate for the vinyl industry is the versatile diethyl hexyl phthalate (DEHP), aka dioctyl phthalate (DOP) which has been used since the 1930s [4]. Recently the use of phthalates in products such as medical plastics, food contact materials, and children's toys has come under scrutiny [5]. In 2008 congress passed the Consumer Product Safety Modernization Act, which banned certain phthalates from being used in children's toys [6]. Some of the phthalates are in California's Proposition 65, which specifies a list of chemicals known to cause cancer, birth defects, or other reproductive harm [7]. Recently the Chronic Hazard Advisory Panel on Phthalates and Phthalate Alternatives submitted an extensive report to the U.S. Consumer Products Safety Committee on the harmful effects of individual phthalates [8]. Studies have indicated that leaching of plasticizers from these products enter the body of consumers and can cause hormonal disruptions [9]. A recent C&E News cover story article (A Reckoning For Phthalates) emphasizes the health issues associated with phthalates and the search for alternatives [10]. This has resulted in the plastics industry and end users searching for safer alternatives to phthalates.

The chemical structure information of various phthalates and non-phthalates are shown in Table 1.

Table 1 Common petroleum derived plasticizers.

Plasticizer	Abbreviation	Structure
Phthalates:		
di(2-ethylhexyl)	DOP or DEHP	R=R'= 2-ethylhexyl
diisononyl	DINP	R=R'= isononyl
diisooctyl	DIOP	R=R'= isooctyl
butylbenzyl	BBP	R= butyl R'= benzyl
linear C7,C11	711 Phthalate	R= n-heptyl R'= n-undecyl
Trimellitates:		
tris(2-ethylhexyl)	TOTM	R=R'=R"= 2-ethylhexyl
triisooctyl	TIOTM	R=R'=R"= isooctyl
Phosphates:		
trioctyl	TOP	R=R'=R"= octyl
tricresyl	TCP	R=R'=R"= cresyl
tri(2-ethylhexyl)	TEHP	R=R'=R"= 2-ethylhexyl
Aliphatic Esters:		
di(2-ethylhexyl) adipate	DOA	R=R'= 2-ethylhexyl n= 2
di(2-ethylhexyl) azelate		R=R'= 2-ethylhexyl n= 5
di(2-ethylhexyl) sebacate		R=R'= 2-ethylhexyl n= 6

Non-Aromatic Cyclic Esters:		
1,2-cyclohexane dicarboxylic acid diisononyl ester	DINCH/Elatur CH	R=R'= isononyl

The use of materials derived from natural/renewable resources is an attractive and safer solution to replace phthalate plasticizers. Generally it is believed that the materials derived from natural products and their degradation compounds are bio-compatible and non-toxic, and can be used in sensitive applications such as medical products and toys. With the recent price fluctuations of petroleum products, production of natural materials can be more dependable and cost competitive. Additionally, with the comparable performance, the new materials will gain market share at the expense of the petroleum derivatives.

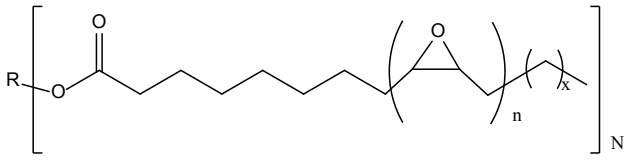
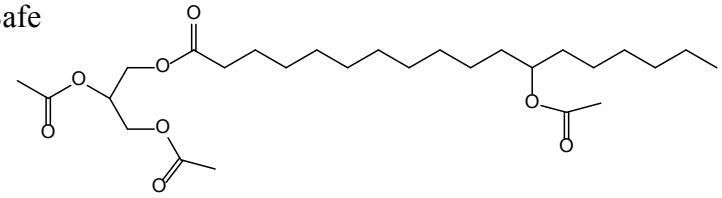
1.2.Bioplasticizers:

Considerable research efforts have been made by various commercial organizations such as Danisco, Battelle, PolyOne, ADM, Evonik, Arkeema, and Dow Inc. to develop plasticizers from renewable materials that are as effective as dioctyl phthalate (DOP). One example, shown in Table 2, is Grindsted® Soft-N-Safe or SnS (Danisco, Patent Nos: US 6,734,241 B1; US 6,949,597 B2); a fully acylated monoglyceride ester derived from hydrogenated castor oil. Other bio-based products are epoxidized fatty acid esters derived from epoxidized oils, such as linseed and soybean, trans-esterified with various polyols (Battelle, Patent No: US 6,797,753). SnS is purported to be a 1:1 replacement for DOP. To our understanding, SnS has limited production volume due to

starting material availability (hydrogenated castor oil) and is approximately two times more expensive than phthalate esters.

Historically, epoxidized vegetable oils, in particular epoxidized soybean oil (ESBO), have been utilized as cost effective plasticizers in PVC. Due to its high molecular weight, ESBO has limited compatibility with PVC and exudes out of the polymer at high concentrations. Therefore ESBO is used as a secondary plasticizer and stabilizer at lower concentrations (<5%) in many PVC applications. The technology developed at Battelle Labs has been licensed to PolyOne Corporation and ADM is based on the epoxy fatty acid esters having lower molecular weight[3]. The structures of the epoxy fatty acid esters, ReFlex - 100 and ReFlex – 300 that are commercially available are shown in Table 2. Galata Chemicals announced their Drapex Alpha series product line that is purported to be a sustainable alternative to phthalates and is derived from vegetable oils. The structure of these materials is currently not disclosed. In 2014 Dow chemical launched its Ecolibrium line of plasticizers for replacement of phthalates in wire and cable coatings. This plasticizer is purported to be made from 100% biorenewable feed stock. Ecolibrium's structure is currently not disclosed either.

Table 2 Commercial bio-based plasticizers

Plasticizer	Name	Structure
Epoxides:		
Soybean Oil	ESBO	R= glyceryl n=1-3 x=1-6 N=3 oxirane oxygen %= 7.0
Linseed Oil		R= glyceryl n=1-3 x=1-6 N=3 oxirane oxygen %= 9.0
Epoxy fatty acid esters PolyOne/ADM	ReFlex® 100. 300	R= alkyl n=1-3 x=1-6 N≥2 oxirane oxygen %= 6-8
Grindsted®/Dupont	Soft-N-Safe (SnS)	
Galata Chemicals	Drapex Alpha	??
Dow Inc.	Ecolibrium	??

A list of prior art published as patents and patent applications on bioplasticizers is presented in Appendix A.

In spite of continued effort by researchers and industry to replace phthalates with more benign plasticizers, none of the currently available products perform at the level of phthalates at comparable cost. The goal of this research is to develop new plasticizers for PVC that are compatible, non-toxic, and cost competitive with current phthalate plasticizers. Vegetable oils are benign, readily available raw materials that can be modified using a variety of chemistries which can change their properties and make them

useful in different applications. Our strategy was to synthesize vegetable oil derived compounds having the structural features necessary to plasticize PVC. These features include optimal polarity by balancing hydrophobic and hydrophilic groups, molecular weight lower than triacylglycerols, and introduction of branching on the acyl chains. The chlorine groups in PVC make the polymer polar thus plasticizers having higher polarity can more effectively interact with the polymer making them more compatible. The overall polarity of the molecule is the hydrophobic and hydrophilic balance contributed by the nature and size of the ester head group and the presence of epoxy and estolide functions on the acyl chain. Molecular weight plays an important role in compatibility and volatility of plasticizers. Based on various plasticizers currently used, the ideal molecular weight range is between 300-500 g/mol. Plasticizers with higher molecular weight will have reduced compatibility whereas plasticizers with lower molecular weight are too volatile at PVC compounding temperatures. Transesterification of vegetable oils with alcohols can effectively reduce their molecular weight to the desired molecular weight range. Depending upon the alcohol used for transesterification, they can also increase or reduce the overall polarity, size, and nature of the molecule based on the carbon chain length or functional groups of the alcohol. Branching can be accomplished by introducing epoxy and/or estolide groups onto the backbone of the fatty acid esters. The epoxy and estolide functions can also increase polarity and compatibility of the molecule.

In the present research study we synthesized and characterized vegetable oil derived compounds with the above described structural features. These experimental

materials were compounded with PVC and their performance as plasticizers were evaluated and compared with the commercial plasticizers.

Chapter 2: Materials and Methods

2.1.Materials

The detailed lists of chemicals used for the synthesis and characterization of each set of compounds are listed in each publication and are given in chapters 4-7 in the materials and methods sections. In general soybean oil and soy fatty acid methyl esters were obtained from Cargill and used without further purification for the synthesis of the biobased plasticizers. Epoxy soybean oil was obtained from Galata Chemicals. Castor oil, several of the alcohols, and PVC resin without stabilizers were obtained from Sigma-Aldrich. Formulated PVC resin with stabilizers and processing aids used in chapters 4 and 5 was obtained from Aspen Research. Plastisol formulations in chapters 6 and 7 were developed by our collaborators at Evonik Performance Materials.

2.2.Instrumentation and Methods

The detailed instrumentation and methods used in the study are described in each publication and provided in chapters 4-7 in the materials and methods sections. In general the synthetic products and intermediates were characterized using ^{1}H NMR and FTIR spectroscopies, and gas chromatography. The physical properties of the experimental plasticizers such as acid value, saponification value, and hydroxyl value were determined by the Official Methods and Recommended Practices of the American Oil Chemists' Society (AOCS). The APHA color and epoxy content were determined using the standard methods of ASTM International. The viscosities of the experimental plasticizers were determined based on the Brookfield viscometer manual or by ASTM International.

PVC was compounded with the experimental and commercial plasticizers using different methods that are detailed in chapters 4-7 in the materials and methods sections.

In general two methods were employed, dry blending and plastisol formulation. In the dry blending method the PVC and plasticizers were blended together in either a Brabender mixing bowl or using a screw extruder to form sheets or strips respectively. In the plastisol formulations the PVC, stabilizers, and plasticizers were mixed into a paste and heated in an oven to form the films. The evaluations of the plasticized PVC sheets/films are detailed in chapters 4-7 in the results and discussion sections.

Chapter 3: Results and Discussion

3.1. Synthesis and Characterization

Vegetable oils are triacylglycerol esters having various fatty acids esterified to glycerol. Two different vegetable oils, soybean oil and castor oil have been used as raw materials in this study. The fatty acid compositions of these two oils are provided below in Figure 3.

Fatty Acid (%)	Soybean oil	Castor oil
Sat. FA (C16:0 + 18:0)	16.0	1.5
Oleic (C18:1)	22.0	4.0
Linoleic C18:2)	55.0	3.0
Linolenic (C18:3)	7.0	0.75
Ricinoleic (C18:1, OH)	0.0	90.0

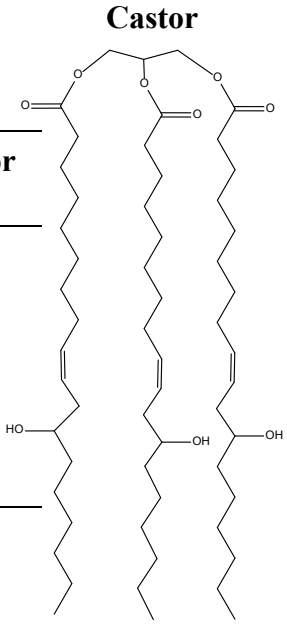
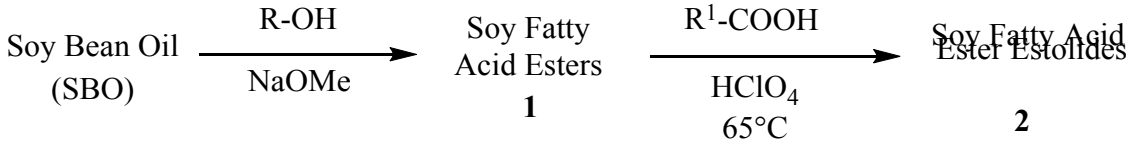


Figure 3 Generalized structures and fatty acid compositions of soybean oil and castor oil.

In an effort to synthesize potential plasticizers from vegetable oils we went through several chemical modifications to create structural features that would improve compatibility and functionality with PVC. Estolide esters of soybean oil were initially targeted due to their straight forward synthesis and the structural variability that can be imparted by using different fatty acids for the estolide linkages. These included long chain, lauric acid, and short chain, acetic acid, as the estolide esters. The headgroup was

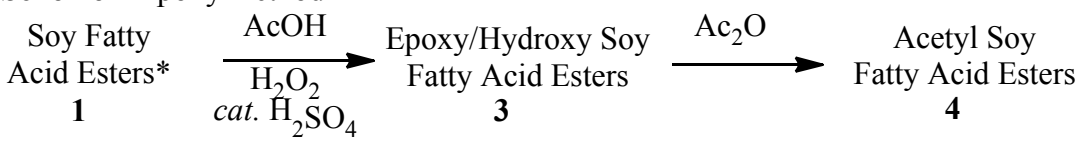
also modified by transesterification with different alcohols such as methanol, *iso*-butanol, 2-ethyl hexanol, and glycerol. In Chapter 4: Soybean oil fatty acid ester estolides as potential plasticizers, we synthesized fatty acid ester estolides using two different synthetic methods. These included a perchloric acid method and an epoxy method (see Scheme 1 and Scheme 2 below).

Scheme 1 Perchloric acid method



R= methyl, 2-ethylhexyl, or glyceryl R^1= methyl or undecyl

Scheme 2 Epoxy method



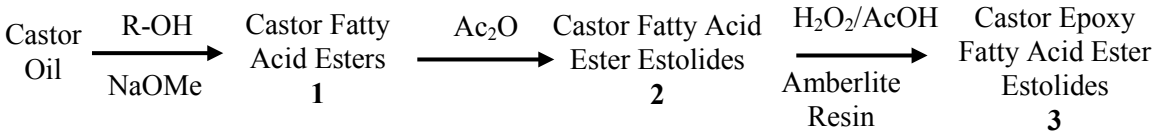
*methyl or *iso*-butyl

The estolides were prepared with varied estolide ester chain lengths by reacting with lauric or acetic acid. The ester headgroups incorporated alcohols of various size and polarity such as methyl, *iso*-butyl, 2-ethylhexyl, and glyceryl. The mineral acid method resulted in estolides with much lower estolide numbers than the estolides synthesized by the epoxy ring opening method. It was found that the best plasticizer candidate was the fatty acid methyl ester acetate estolides prepared by the epoxy ring opening method. The higher polarity of these materials was thought to contribute to better compatibility with PVC.

Based on these findings in Chapter 5: Synthesis and evaluation of soy fatty acid ester estolides as bioplasticizers in poly(vinyl chloride), we further evaluated the composition and plasticizer properties of the fatty acid ester estolides prepared from the epoxy ring opening method and compared their functionality with commercial phthalate plasticizers. By separating the components and characterizing their structures it was found that the ring opening of diepoxy linoleate esters with acetic acid resulted in formation of cyclic ether estolides. These compounds were present in significant quantities due to the presence of over 55% linoleic acid in soybean oil. The effect of this moiety to plasticize PVC is currently unknown. In an effort to reduce the presence of this component and reduce the heterogeneity of the bioplasticizer, we prepared similar compounds from castor oil.

Castor oil contains >90% ricinoleic acid, which can be functionalized on the fatty acid backbone at both the double bond and the hydroxyl group to form a bifunctional fatty acid ester estolide. The literature describes how the epoxy group provides stability in PVC formulations by scavenging free HCl that is liberated during compounding. Due to this property we prepared epoxy castor fatty acid ester estolides by transesterifying castor oil with alkyl alcohols, acetylating the hydroxyl group, and epoxidizing the double bond as shown in Scheme 3. We evaluated these compounds in Chapter 6: Castor epoxy fatty acid alkyl ester estolides as bioplasticizers.

Scheme 3 Castor oil epoxy fatty acid ester estolides



Compound	R =
a	methyl
b	*n*-butyl

In this study it was found that the linear epoxy fatty acid ester estolides from castor oil provided excellent thermal stability and overall good plasticizer properties. Castor oil is more expensive than soybean oil thus plasticizes prepared from this starting material would be significantly higher in cost than the commercial phthalate plasticizers.

Soybean oil is considerably less expensive than castor oil. A significantly less expensive plasticizer than those from castor oil could be synthesized if we could partially open the epoxy rings in soy epoxy fatty acid alkyl esters. This would reduce the formation of the cyclic ether estolides and retain the epoxy function. By reducing the amount of acetic anhydride used in the epoxy ring opening reaction we successfully accomplished having both epoxy and estolide functionalities. A series of epoxy soy fatty acid ester estolides were prepared and evaluated for their plasticizer properties in Chapter 7: Soy epoxy fatty acid alkyl ester estolides as bioplasticizers for poly (vinyl chloride). In this study we found the lower molecular weight epoxy fatty acid ester estolide with methyl head group had higher volatility with fast fusing properties, a desirable characteristic useful in PVC formulations. The higher molecular weight epoxy fatty acid ester estolides had lower volatility but poor compatibility with PVC. Whereas the

medium molecular weight epoxy fatty acid ester estolides (butyl and pentyl esters) have the optimal plasticizer performance and are suitable to replace phthalates.

Further details on the synthesis, characterization, and functional evaluations of these compounds in PVC can be found in chapters 4-7.

Chapter 4: Soybean oil fatty acid ester estolides as potential plasticizers

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4.1. Synopsis

Fatty acid ester estolides were synthesized from soybean oil and evaluated for plasticizer functionality in poly(vinyl chloride) (PVC). The plasticization ability of the fatty acid ester estolides depends upon the molecular features such as polarity, molecular weight, and branching. The structure of the fatty acid derivatives were modified at the ester head group with various alcohols and the estolide branch was created at the site of unsaturation. Soy fatty acid esters of methanol, *iso*-butanol, 2-ethylhexanol, and glycerol were prepared to vary the size and polarity at the ester head group. Estolides of these fatty acid esters were prepared using two synthetic routes. In the first, the fatty acid ester was condensed with an aliphatic acid at the site of unsaturation in the presence of a strong mineral acid. In the second, the fatty acid ester double bonds were converted to epoxy groups which were ring opened and acetylated to form acetate estolides. The first synthetic route resulted in low average estolide content per fatty acid chain while the second route had higher estolide content per fatty acid chain. The fatty acid ester estolides compounded with PVC showed good plasticizer properties as evidenced by the rheological properties and reduction in glass transition temperature. The fatty acid ester estolides with higher estolide content had better plasticizer functionality, comparable to commercial controls.

4.2.Introduction

Plasticizers are non-volatile organic liquid compounds that impart flexibility to polymers and increase the range of end uses. The majority of plasticizers are used in poly(vinyl chloride) (PVC) formulations. Due to its unique combination of price, performance, and versatile use, PVC is one of the oldest and widely used high volume plastics. PVC products formulated with various additives, range from very rigid pipes and siding to flexible flooring, sheeting, and adhesives. The plasticizer, upon addition and mixing embeds in the polymer matrices, reduces glass transition temperature (Tg) and renders the polymer more flexible [11]. Thus the primary functions of a plasticizer are to increase the flexibility, softness, workability, pliability, and distensibility of the polymer.

While there are many different types of plasticizers on the market, the end application dictates the type of plasticizer used. Of these different types, the dominant class of plasticizers used in the vinyl industry today is the petroleum derived phthalates. The largest used phthalate in the vinyl industry is the versatile diethyl hexyl phthalate (DEHP), aka dioctyl phthalate (DOP) which has been used since the 1930s [4]. Recently the use of phthalates in products such as medical plastics, food contact materials, and children's toys has come under scrutiny. Over the time of use, plasticizers migrate to the surface and leach out from these plastic products and can enter the body of consumers. It has been documented that exposure to certain phthalates can result in a number of health problems such as hormonal disruptions [9] and disruption of male reproductive development [8]. Due to the health implications of phthalates, both the industry and consumers are searching for new types of plasticizers that are more environmentally and physiologically benign.

The use of materials derived from natural/renewable resources is an attractive and safer alternative to petroleum derived products. Usually the materials derived from natural products and their degradation compounds are bio-compatible and non-toxic, and can be used in sensitive applications. Vegetable oils in particular are readily available and can be easily modified into functional materials that can be useful as plasticizers. During the mid-20th century numerous studies were conducted to utilize vegetable oil derivatives for use as plasticizers in PVC [12–20]. Of the various plasticizers developed, only epoxidized oils, particularly epoxy soybean oil (ESBO) was used in PVC applications. However, ESBO has limited compatibility with PVC and would exude at higher concentrations. Thus the use of ESBO has been limited to a secondary plasticizer/stabilizer in PVC formulations [21]. With increasing concerns raised regarding the safety of phthalate plasticizers in the early 2000s, interest was renewed in development of safer alternatives, many of which were developed from vegetable oil sources [22–28]. This resulted in several companies such as Dow-DuPont and Battelle that have developed and commercialized plasticizers from vegetable oils.

This study is a part of a continued effort that focuses on the development of estolide esters derived from soybean oil as potential new plasticizers for PVC that are cost effective and functionally comparable to DOP. Fatty acid ester estolides, the general structure shown in Figure 4, have aliphatic acids esterified on the backbone of a fatty acid at the sight of unsaturation [29]. Structural modifications of the soybean oil fatty acids in this study included variation of size and polarity of the ester headgroup as well as the chain length of the estolide fatty acid. Fatty acid ester estolides with various modifications were synthesized and tested for their plasticizer functionality. Fatty acid

esters of lower alcohols containing acetate estolides performed well as plasticizers in PVC.

4.3.Materials and Methods

4.3.1. Materials

PVC was procured from two sources for this study. Unstabilized PVC (Mn ~ 55,000) from Sigma Aldrich was used for preliminary plasticizer Tg reduction. Stabilized PVC (here-in referred to as "PVC") containing thermal stabilizers and lubricants (mercapto-tin 1.0 phr (parts per hundred parts resin), calcium stearate 1.5 phr, and amide wax 2.0 phr) was obtained from Aspen Research Corporation (Whitebear Lake, MN). Glacial acetic acid was purchased from Alfa Aesar (Ward Hill, MA). Soybean oil and soy Fatty Acid Methyl Ester (FAME) or soy biodiesel was obtained from Cargill Inc. (Minneapolis, MN). Perchloric acid (70%), anhydrous methanol (99.8%), 2-ethyl-1-hexanol (≥99.6%), sodium methoxide (reagent grade), anhydrous *iso*-butanol (99.5%), hydrogen peroxide (50% w/w H_2O), dioctyl phthalate, DOP (99%) and activated charcoal (untreated 100-400 mesh) were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, WI). Potassium hydroxide was purchased from EM Science (Gibbstwon, NJ). Lauric acid (>98 %) was purchased from TCI America (Portland, OR). Hexanes (technical grade-for extractions), toluene (ACS), p-toluene sulfonic acid (certified), and sulfuric acid (ACS+) were purchased from Fischer Scientific (Pittsburg, PA). Grindsted ® Soft-N-Safe, SnS a commercial biobased plasticizer derived from castor oil was obtained from Danisco (Copenhagen, Denmark). Magnesol® R60, a magnesium silicate adsorbent was obtained from The Dallas Group of America Inc. (Whitehouse, NJ). Pure-Flo® B80, a bleaching agent was obtained from Oil-Dri Corporation of America (Chicago, IL) TLC was

performed on Analtech (Newark, DE) Unisil GF 250μm silica plates, charred on a hot plate after spraying with 50% sulfuric acid. Low Range Oil Quality Test Strips, used to estimate the acidity of the products were obtained from 3M Company (Maplewood, MN).

Table 3 Compounding formulation

Component	Concentration (phr)
PVC Suspension Resin	100.0
Heat stabilizer (mercapto-tin)	1.5
Lubricants: calcium stearate	1.0
amide wax	2.0
Plasticizer	10, 20, 40, or 60

4.3.2. Instrumentation and Methods:

^{1}H NMR spectra were recorded on a Varian Unity 200, 200 MHz spectrophotometer with a 4-nucleous probe and auto-sampler. All experiments were run using CDCl3 as a solvent. The integration of the proton chemical shifts to determine the number of protons for the compounds were based on the terminal methyl peak at 0.88 ppm as internal standard for all compounds except the *iso*-buyl esters. For these compounds the α-carbonyl protons at 2.29 ppm were used as internal standard.

FTIR spectra were obtained on a MIDAC Corp. M-Series FTIR neat using NaCl disks. The regions of each spectrum monitored were: C=O stretches of acids (1705-1720) and esters (1735-1750), =C-H stretches of alkenes (3000-3100), and the O-H stretches of acids (2500-3300).

Thermo Gravimetric Analysis (TGA) was performed on a TA Instruments Q250 thermogravimetric analyzer with aluminum pans. Pre-weighed samples were heated at

10°C/min from ambient temperature to 500°C. The weight loss was recorded with increase in temperature once for each sample.

Viscosity measurements were made using a Newport Scientific RVA-Super4 rapid visco analyzer with a built in variable temperature controller or a Brookfield model DV-E viscometer. Twenty-eight grams of product were placed in the RVA-Super4 viscometer in the aluminum sample holder and stirred with a poly(ethylene terephthalate) paddle. The material was allowed to equilibrate at a given temperature before the viscosity measurement was recorded once for each sample. Viscosity measurements were performed on the Brookfield model DV-E with a small sample adapter using spindle number 18. The adapter was attached to a circulating water bath and maintained at constant temperature. The plasticizer was added to the sample chamber and allowed to equilibrate with the water bath for 10 minutes. Viscosity of each sample was measured once at 100 RPM after the 5th revolution of the spindle.

Differential Scanning Calorimetry (DSC) measurements were performed on a TA Instruments DSC 2920 modulated differential scanning calorimeter using two methods. For the first method, a solvent casting method modified from Drexler was employed [30]: A quantity of plasticizer was weighed and added to PVC and suspended with cyclohexane. The suspension was stirred at 40°C for 24hrs until the solvent was removed from the PVC/plasticizer mixture. 5-10 mg of the samples were weighed and non-hermetically sealed in aluminum pans for DSC measurements. The measurements were made once for each sample. The pans were loaded into the DSC manually at ambient temperature, heated to 100°C at 15°C/min; held at 100°C for 10 min to equilibrate above the PVC Tg;

cooled at 10°C/min to 0°C. Scans to measure the Tg of the samples were taken by a final heating of the sample from 0°C to 120°C at 10°C/min.

For the second method, compounded PVC with plasticizers previously ground to <40 mesh was added to the DSC pans without solvent casting and analyzed with the same DSC procedure as above.

Tensile testing was performed on an Instron tensile tester following the procedures of ASTM D638 (ASTM International 2008). Low plasticizer concentration samples were machined into Type I tensile bars while higher plasticizer concentration samples were frozen with liquid nitrogen, ground into powder, and molded into Type V tensile bars. Three tensile bars were prepared for each sample for Type I tensile bars and five tensile bars were prepared for each sample for Type V tensile bars. The samples were conditioned at 25°C and 50% relative humidity for >3 days and the tensile tests conducted between 21-25 °C. The bars were extended at strain rate of 1.3 cm/min until the specimen ruptured. Stress and strain data were collected using Bluehill® materials testing software (Instron).

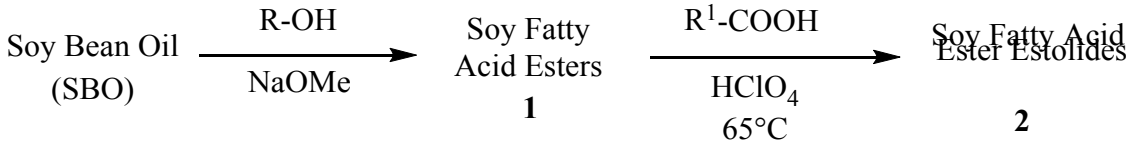
Dynamic Mechanical Analysis (DMA) was performed on the compounded materials using a Rheometrics RDA II dynamic mechanical analyzer. Samples were cut to size (2.54 cm diameter) using a hammer and die. Sample thickness varied, but was measured and used in the calculations of the outputs. All samples were strained 5%, with frequencies from 0.1 to 75 s-1. Frequency sweeps were made at 200, 210, 220, 230, 240 and 250°C. Time-temperature superposition, done by hand (not by software) was used to generate master curves.

Acid Content of the products was determined using two methods. Oil quality test strips by 3M Company were used to approximate the acid values from 0.5-2.5% free fatty acid. Most of the samples had less than 0.5% free fatty acids which was an acceptable level for plasticizer applications. Samples beyond the range of the test strips (2.5% free fatty acid) were measured in triplicate according to AOCS Official Method Cd 3d-63 (AOCS 2009).

4.3.3. Synthetic Procedures

The synthetic steps involved to synthesize soy fatty acid ester estolides by the perchloric acid method are shown in Scheme 4. The detailed reaction conditions employed in each step of the synthesis for different compounds are described below.

Scheme 4 Perchloric acid method



R= methyl, 2-ethylhexyl, or glyceryl R^1= methyl or undecyl

Fatty Acid Methyl Ester (FAME), aka soy biodiesel is commercially available and used as starting material for estolide preparation. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.32 (m, 3.02H), 3.65 (s, 2.91H), 2.75 (t, 1.35H), 2.29 (t, 2.01H), 2.02 (m, 3.34H), 1.60 (m, 2.13H), 1.24 (d, 16.70H), 0.86 (t, 3.00H).

Fatty Acid 2-EthylHexyl Ester (FAEHE): To a flask was added 100 g of FAME and 2 equivalents of 2-ethyl-1-hexanol and heated to 80ºC under vacuum for 1 hr to remove moisture. Sodium methoxide (0.2% w/w) was added under an inert atmosphere. The flask was returned to slight vacuum and the temperature was increased to 120ºC and monitored by TLC for the disappearance of the FAME spot in a 90/10 hexanes/diethyl ether solvent

system. The reaction mixture was cooled to 60-70°C and Magnesol® R60 (2% w/w FAME) was added with stirring. After cooling to room temperature the contents were filtered under vacuum. Excess alcohol was removed by vacuum distillation. After the distillation, the reaction product was cooled to 60-70°C, activated charcoal and Magnesol® R60 (2% w/w of each) were added. The contents were cooled to room temperature and vacuum filtered to give *Fatty Acid Ethyl Hexyl Ester (FAEHE)* in quantitative yield. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.32 (m, 3.02H), 3.95 (d, 2.03H), 2.74 (t, 1.36H), 2.26 (t, 2.01H), 2.05 (m, 3.35H), 1.57 (m, 3.21H), 1.28 (m, 25.09H), 0.86 (t, 9.00H).

Fatty Acid Ester Acetate Estolides: Estolides were prepared by slight modification of the method of Cermak and Isbell [31]. To a flask containing 100 g FAME was added 1.54 equivalents of glacial acetic acid and heated to 65ºC under a slight vacuum and stirring. While under an inert atmosphere, 0.1 equivalent of 70% $HClO_4$ was added to the flask then returned to partial vacuum. The solution was reacted for 48 hrs then cooled to room temperature. The reaction mixture was diluted with 30 mL hexanes extracted with 3x100 mL H_2O, 1x100 mL brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resulting acidic product (acid value ≈ 124 mg KOH/g) was re-esterified with methanol or 2-ethylhexanol as described below.

Methyl Fatty Acid Ester Acetate Estolides **(2-a)**: To the reaction product obtained above was added 4 equivalents methanol and a catalytic amount *p*-toluene sulfonic acid (0.2% w/w, based on acetate estolide). The mixture was azeotropically distilled with toluene (equal v/v methanol) for 17 hrs into a Dean & Stark apparatus containing 3A molecular sieves. After cooling to 60-70°C, Magnesol® R60 (2% w/w) was added and cooled to

room temperature. The contents were vacuum filtered and concentrated *in vacuo* to quantitatively yield dark brown oil with an acid content of <0.5% free fatty acid estimated with oil quality test strips. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.37 (m, 0.38H), 4.85 (m, 0.19H), 3.65 (s, 2.43H), 2.29 (t, 2.70H), 1.94 (m, 2.06H), 1.57 (m, 4.46H), 1.25 (s, 18.43H), 0.88 (t, 3.00H).

2-Ethylhexyl Fatty Acid Ester Acetate Estolides **(2-b)**: To the product obtained from the acetate estolides reaction was added 3 equivalents 2-ethylhexanol and a catalytic amount of sulfuric acid (0.4% w/w acetate estolide). The mixture was azeotropically distilled with toluene (1/2 v/v 2-ethyhexanol) into a Dean & Stark apparatus for 3 hrs. After cooling to 60-70°C, Magnesol® R60 (2% w/w) was added and cooled to room temperature. The contents were vacuum filtered and excess alcohol was removed by vacuum distillation to quantitatively yield dark brown oil with an acid content of <0.5% free fatty acid estimated with oil quality test strips. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.37 (m, 0.92H), 4.85 (m, 0.26H), 3.95 (d, 1.96H), 2.29 (t, 2.42H), 1.94 (m, 2.81H), 1.57 (m, 5.15H), 1.25 (s, 27.66H), 0.88 (t, 9.00H).

The resulting fatty acid acetate estolides were dark brown and the color of the products were reduced by heating with Pure-Flo® B80 bleaching earth at 80°C for 24 hrs under vacuum. The products were cooled to 60-70°C and filtered to yield light brown oils.

1,2 or (1,3)-diacetyl 1- (or 2-) glyceryl Fatty Acid Ester Acetate Estolides **(2-c)**: To a flask containing 100g soybean oil at 65ºC was added dropwise a mixture of 4.62 equivalents glacial acetic acid and 0.1 equivalent 70% $HClO_4$, while stirring. The solution was stirred under a partial vacuum for 32 hr then cooled to room temperature.

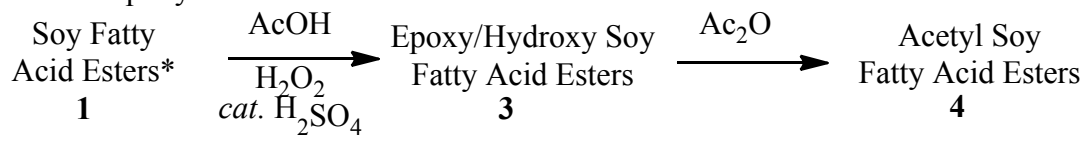
The reaction mixture was diluted with 50 mL hexanes and extracted with 3x150 mL H_2O, 1x150 mL brine, dried (Na_2SO_4), and concentrated *in vacuo*. The resulting acidic product (acid value ≈ 97) was esterified with methanol by adapting a similar procedure previously described (methyl acetate estolides, **2-a**). After cooling to 60-70°C, Magnesol® R60 (2% w/w) was added and cooled to room temperature. The product was filtered and concentrated *in vacuo*. The product was added to a flask containing 2 equivalents triacetin and heated to 110°C under vacuum for an hour to remove moisture. Sodium methoxide (7% w/w) was added under an inert atmosphere and returned to vacuum. After 5 hrs Magnesol® R60 (2% w/w) was added and cooled to room temperature. The mixture was diluted with hexanes (50% v/v), vacuum filtered, and concentrated *in vacuo* to yield a brown oil with an acid content of <0.5% free fatty acid estimated with oil quality test strips. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.35 (m, 0.37 H), 5.23 (m, 0.84 H), 4.82 (m, 0.39 H), 4.32-4.07 (dd, 4.56 H), 2.29 (t, 1.97 H), 2.05 (s, 6.65 H), 2.01 (s, 1.37 H), 1.93 (m, 1.20 H), 1.73-1.46 (m, 4.40 H), 1.26 (s, 15.27 H), 0.85 (t, 3.00 H)

*Methyl or 2-ethylhexyl Fatty Acid Ester Laurate Estolides (**2-d** or **2-e**):* A flask containing 200 g FAEHE or FAME and 1.69 equivalent of lauric acid was heated to 65ºC under vacuum with stirring. Under an inert atmosphere, 0.1 equivalent 70% $HClO_4$ was added and returned to vacuum. The solution was reacted for 24 hours then cooled to room temperature. The reaction mixture was neutralized by adding 3 M KOH in 95% ethanol/water, as indicated by a phenolphthalein end point. Water was added to the reaction mixture until separation of phases was observed. The solution was extracted with 3x200 mL hexanes. The organic layers were combined, extracted with 2x500 mL H_2O, 1x500 mL brine, dried (Na_2SO_4), filtered, and concentrated *in vacou* to yield 50-64%

methyl fatty acid ester laurate estolides (**2-d**) or *ethylhexyl fatty acid ester laurate estolides* (**2-e**) as a light yellow oils with acid contents of <0.5% free fatty acid estimated with oil quality test strips. *methyl fatty acid ester laurate estolides* (**2-d**): ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.37 (m, 0.49H), 4.85 (m, 0.20H), 3.65 (s, 2.34H), 2.29 (t, 1.92H), 1.94 (m, 0.97H), 1.57 (m, 2.87H), 1.25 (s, 14.93H), 0.88 (t, 3H). *ethylhexyl fatty acid ester laurate estolides* (**2-e**): ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.37 (m, 0.18H), 4.85 (m, 0.09H), 3.95 (s, 1.91H), 2.29 (t, 2.16H), 1.94 (m, 0.69H), 1.57 (m, 3.97H), 1.25 (s, 25.80H), 0.88 (t, 9.00H).

The synthetic steps involved to synthesize soy fatty acid ester estolides by the epoxy method are shown in Scheme 5. The detailed reaction conditions adopted for each step of the synthesis for different compounds are described below.

Scheme 5 Epoxy method



*methyl or *iso*-butyl

Fatty Acid iso-Butyl Ester (FABE): A flask containing 500 g soybean oil was heated to 120°C under vacuum for 2 hours to remove moisture. The flask was cooled to 100°C and 6 equivalents of 2-methyl-1-propanol (*iso*-butanol) and 0.2% sodium methoxide were added and heated to reflux. The reaction was monitored by TLC for the disappearance of the triacylglycerol spot in a 60/40 hexanes/diisopropyl ether solvent system. The reaction mixture was cooled to room temperature and transferred to a separatory funnel. The glycerol phase was removed and the oil phase was washed 3x500 mL H_2O, 1x500 mL

brine, and dried on Na_2SO_4. Excess alcohol was removed by vacuum distillation to yield *Fatty Acid iso-Butyl Ester (FABE)* quantitatively as a light yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.32 (m, 3.22H), 3.83 (d, 2.06H), 2.76 (t, 1.41H), 2.29 (t, 2.11H), 2.02 (m, 3.43H), 1.91 (m, 1.04H), 1.61 (m, 2..21H), 1.26 (d, 17.41H), 1.00-0.86 (6.00H, overlapped 3.00H).

Fatty Acid iso-Butyl/Methyl Ester (FAB/ME): A flask containing 500 g FAME was heated in a 120°C oil bath under vacuum for 2hrs. The flask was cooled to 100°C and 2 equivalents of 2-methyl-1-propanol (*iso*-butanol) and 0.2% (w/w FAME) sodium methoxide were added and heated to gentle reflux.. *Iso*-butanol and methanol were removed at 64°C by azeotropic distillation. The reaction was monitored by TLC (60/40 hexanes/diisopropyl ether solvent system) and stopped after four hours. The reaction product was cooled to 80°C and 2% Magnesol R60 was added and allowed to cool further to room temperature before being vacuum filtered. The excess alcohol was removed by vacuum distillation to quantitatively yield *Fatty Acid iso-butyl/Methyl Ester (FAB/ME)* as a mixture of 94/6 *iso*-butyl/methyl ester. The ratio was adjusted to 70/30 *iso*-butyl/methyl ester by the addition of excess FAME. The 70/30 *iso*-butyl/methyl ester ratio was also obtained by mixing FABE and FAME products from above. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.33 (m, 3.05H), 3.83 (d, 1.31H), 3.65 (s, 0.96H), 2.76 (t, 1.35H), 2.29 (t, 2.00H), 2.02-1.85 (m, 4.01H), 1.64 (m, 2.14H), 1.27 (d, 16.52H), 1.00-0.86 (overlapped, 6.90H).

General Epoxidation/Hydroxylation of Fatty Acid Esters ***(3-a** to **3-c**)**: Epoxy/hydroxy fatty acid esters were prepared by modification of the method of Swern [32]. To a flask was added 250 g soy fatty acid esters (FAME, FABE, or FAB/ME) and a mixture of 0.25

equivalents glacial acetic acid and 2% concentrated sulfuric acid while mechanically stirring (104 RPM for FAME and 208 RPM for FABE and FAB/ME). To the flask was slowly added 3 equivalents per double bond of hydrogen peroxide (50% w/w H_2O) over the course of one hour to maintain the exothermic reaction below 45°C. The reaction endpoint was monitored by the complete disappearance of the unsaturation, which takes 18 hours for FAME (16 hours for FABE and FAB/ME). The resulting products were then transferred to a separatory funnel where the aqueous layer was removed. The organic layer was dried on Na_2SO_4 and vacuum filtered to quantitatively yield *Epoxy/Hydroxy Fatty Acid Methyl Ester* ***(3-a),*** *Epoxy/Hydroxy Fatty Acid iso-butyl Ester* ***(3-b)****, or Epoxy/Hydroxy Fatty Acid iso-butyl/Methyl Ester* ***(3-c)*** as light yellow oils. *Epoxy/Hydroxy Fatty Acid Methyl Ester* (**3-a**)**:** ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.21 (m, 0.09H), 4.00 (d, 0.16H), 3.62 (s, 3.58H), 3.33 (m, 0.26H), 3.07 (m, 0.83H), 2.96 (m, 0.74H), 2.86, (m, 0.62H), 2.26 (t, 2.33H), 1.69 (m, 0.89H), 1.58 (m, 2.73H), 1.47 (m, 5.71H), 1.25 (d, 15.28), 0.84 (m, 3.00H). *Epoxy/Hydroxy Fatty Acid iso-butyl Ester* ***(3-b):*** ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.23 (m, 0.07H), 3.92 (d, 0.16H), 3.83 (d, 1.97H), 3.33 (m, 0.21H), 3.10 (m, 0.74H), 2.97 (m, 0.73H), 2.89, (m, 0.37H), 2.26 (t, 2.00H), 1.90 (m, 1.35H), 1.71 (m, 0.85H), 1.60 (m, 2.21H), 1.49 (m, 4.46H), 1.27 (d, 13.13), 0.92 (overlapped, 8.13H). *Epoxy/Hydroxy Fatty Acid iso-butyl/Methyl Ester* ***(3-c):*** ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.23 (m, 0.40H), 4.01 (d, 0.80H), 3.81 (d, 1.25H), 3.65 (s, 0.91H), 3.45 (m, 0.37H), 3.36 (m, 0.38H), 2.27 (t, 2.00H), 1.91 (m, 1.20H), 1.59 (m, 2.20H), 1.27 (d, 17.14), 0.89 (overlapped, 5.55H).

General Acetylation of Epoxy/Hydroxy Fatty Acid Esters ***(4-a*** *to* ***4-c)****:* To a flask was added *Epoxy/Hydroxy Fatty Acid Ester* (**3-a, 3-b,** or **3-c**), sodium acetate (1% w/w), and

acetic anhydride (2 equivalents per double bond based on original unsaturations) while magnetically stirring. The contents of the flask were reacted for three hours at 130°C. The reaction was cooled to room temperature; 200 mL hexanes were added and the contents transferred to a separatory funnel. The oil phase was extracted 3x500 mL H_2O, 1x500 mL 5% $NaHCO_3$, 1x500 mL Brine, dried (Na_2SO_4), and concentrated *in vacuo* to quantitatively yield *Acetyl Fatty Acid Methyl Ester* ***(4-a)*** *, Acetyl Fatty Acid iso-Butyl Ester* ***(4-b)*** *, or Acetyl Fatty Acid iso-butyl/Methyl Ester* **(4-c)** as brown oils (Gardner Color 12-16). All three of the final compounds had an acid content of <0.5% free fatty acid estimated with oil quality test strips. *Acetyl Fatty Acid Methyl Ester* ***(4-a)*** **:** ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.25 (m, 0.29H), 5.21 (m, 0.19H), 4.97 (t, 0.97H), 4.85 (m, 0.31H), 4.15 (m, 0.24H), 3.85 (m, 0.42H),3.65 (t, 3.80H), 2.26 (t, 2.33H), 2.07 (s, 5.82H), 1.59 (m, 3.89H), 1.49 (m, 2.91H), 1.25 (d, 19.07H), 0.86 (t, 3.05H). *Acetyl Fatty Acid iso-Butyl Ester* ***(4-b):*** ^{1}H NMR ($CDCl_3$, 200 MHz δ 5.26 (m, 0.11H), 5.22 (m, 0.13H), 4.97 (t, 0.46H), 4.84 (m, 0.16H), 4.25 (m, 0.07H), 4.12 (m, 0.17H), 3.83 (m, 1.91H), 2.26 (t, 2.00H), 2.05 (s, 3.32H), 1.92 (m, 1.14H), 1.59 (m, 2.86H), 1.46 (m, 1.08H), 1.25 (d, 13.70H), 0.91 (overlapped, 8.13H). *Acetyl Fatty Acid iso-Butyl/Methyl Ester* **(4-c)*:*** ^{1}H NMR ($CDCl_3$, 200 MHz): ^{1}H NMR ($CDCl_3$, 200 MHz δ 5.25 (m, 0.14H), 5.20 (m, 0.11H), 4.96 (t, 0.43H), 4.84 (m, 0.20H), 4.12 (m, 0.14H), 3.83 (m, 1.43H), 3.65 (s, 1.02H), 2.52 (m, 0.21H), 2.32 (0.25H), 2.27 (m, 2.00H), 2.05 (s, 3.58H), 1.89 (m, 0.96H), 1.58 (m, 3.57H), 1.46 (m, 1.32H), 1.25 (d, 14.23H), 0.84 (overlapped, 6.40H).

4.3.4. PVC-Plasticizer Compounding

The compounding of commercial and experimental plasticizers with PVC was conducted at Aspen Research Corporation (Whitebear Lake, MN). The stabilized PVC

from Aspen (see Table 3) was used to make low plasticizer compositions (10-20 phr), PVC was mixed in a Brabender fusion bowl at 175°C for 6 minutes, plasticizer was added and mixed for an additional 19 minutes. At the end of the blending the plasticized PVC mass was removed from the Brabender, placed in a hydraulic press, and pressed into a 3.18 mm thick sheet at 190°C. After pressing for 2 minutes the sheets were removed and cooled to room temperature. The sheets were machined into Type I tensile bars (three per sample) according to ASTM D638 for tensile testing and cut into 2.54 cm diameter circles with a die and hammer for dynamic materials analysis testing.

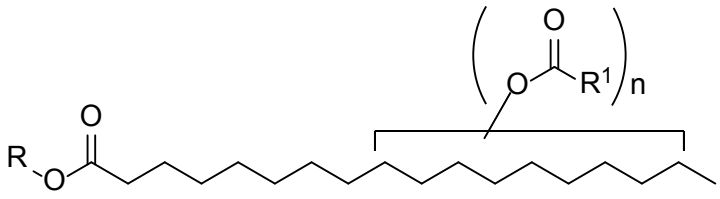
The higher plasticizer compositions (20,40,60 phr), after compounding in the Brabender fusion bowl, the plasticized PVC was pressed into 3.18 mm thick sheets and held under pressure while the platens cooled to room temperature. The sheet was cut into 2.54 cm diameter circles with a die and hammer for dynamic materials analysis. The remainder of the plastic sheet was cut into approximately 2.5x2.5 cm pieces, cooled with liquid nitrogen and ground to a powder of < 40 mesh (0.4 mm) using an analytical mill. The powder was pressed into Type V tensile bars (five per sample) according to ASTM D638 for tensile testing using a mold and Carver press.

4.4. Results and Discussion

Important characteristics of a plasticizer are: the ability to reduce the Tg of PVC that increases the flexibility; low volatility that reduces the weight loss at processing temperatures; low viscosity that helps mixing and processing; low Gardner color that reduces the color contribution to the PVC; and low exudation from the PVC matrix that slows the plasticizer migration and loss which increases compatibility and retains flexibility for long life. Some molecular features that allow for these properties are

molecular weight, polarity, and number and size of branching. Molecular weight and polarity play an important role in PVC processing and in retention of the plasticizer in the PVC matrix. Lower branching increases efficiency of the plasticizers and further lowers the Tg of PVC [2]. The aim of this study was to synthesize plasticizers by modifying fatty acid esters of soybean oil containing variations of these molecular features. Using acetic and lauric acids as the estolide fatty acids provided the contrast in the relative polarity and chain length of the estolides. The fatty acid ester headgroup was esterified with methanol, *iso*-butanol, glycerol, and 2-ethyl-1-hexanol varied the molecular weight and relative polarity of the compounds.

Two synthetic routes were utilized to introduce estolide branches at the site of unsaturation of the fatty acid which had structural modifications at the fatty acid ester headgroup. In the first route soybean oil was transesterified with methanol, 2-ethylhexanol, or interesterified with triacetin to vary the relative polarity and size of the compounds at the ester head group. The estolides were synthesized by adapting methods of Cermak and Isbell [31,33,34] with different reaction conditions. Perchloric acid was used as catalyst to synthesize estolide branches having short or long chains by reacting soy fatty acid esters with acetic and lauric acid, respectively. However, this method had side reactions such as crosslinking to form oligomers that resulted in less than one estolide per double bond. The perchloric acid method produced compounds that had very dark color and the color was difficult to remove even after bleaching with hydrogen peroxide. The synthetic steps employed to make the estolides by this method are shown in Scheme 1 and the typical structures of the compounds, acetate estolides(**2-a**, **2-b**, **2-c**) and laurate estolides (**2-d**, **2-e**) shown in Figure 4.



Compound	R	R^1	n
2-a	methyl	methyl	0-3
2-b	2-ethylhexyl	methyl	0-3
2-c	diacetylglyceryl	methyl	0-3
2-d	methyl	undecyl	0-3
2-e	2-ethylhexyl	undecyl	0-3
4-a	methyl	methyl	0-6
4-b	iso-butyl	methyl	0-6
4-c	isobutyl/methyl (70/30)	methyl	0-6

Figure 4 Soy fatty acid ester estolides synthesized by perchloric acid route (**2-a** to **2-e**) and by epoxy route (**4-a** to **4-c**)

Reacting the aliphatic acids with soy fatty acid esters in the presence of a catalytic amount of perchloric acid at 65°C resulted in quantitative yield of estolides. The estolide formation reduced the unsaturation of soy fatty acid esters >90% as evidenced by the reduction of unsaturation peaks in ^{1}H NMR at 5.37 ppm, as shown in Figure 5. Estolide formation is evidenced from the appearance of estolide methine proton at 4.8 ppm. The number of estolides per fatty acid chain was determined by the integration of the peak at 4.8 ppm divided by the average number of double bonds per fatty acid in soybean oil (1.54/chain) and is listed in Table 4. The amount of estolide formed from this synthesis was only about 25 % of what was expected if all the double bonds were converted into estolides. In the reaction mechanism of the estolide formation the strong acid protonates the double bond to form a carbocation. This cation can react with either a fatty acid to form an estolide or with another double bond on another fatty acid ester to form a higher

molecular weight oligomer. Each crosslink involves two unsaturation sites thereby reducing the estolide content per chain. The thermogravimetric analysis (Figure 6) shows both a lower molecular weight estolide fraction as well as the higher molecular weight fraction from the oligomers. The oligomer formation was reduced by decreasing the reaction temperature but it could not be entirely eliminated. Under the reaction conditions with perchloric acid, soy fatty acid esters undergo hydrolysis of the ester function to form free fatty acids which are undesirable for plasticizer applications. Irrespective of the ester headgroup size or variation of reaction conditions; hydrolysis could not be avoided. In order to decrease the free fatty acid content the resulting fatty acid estolides had to be re-esterified.

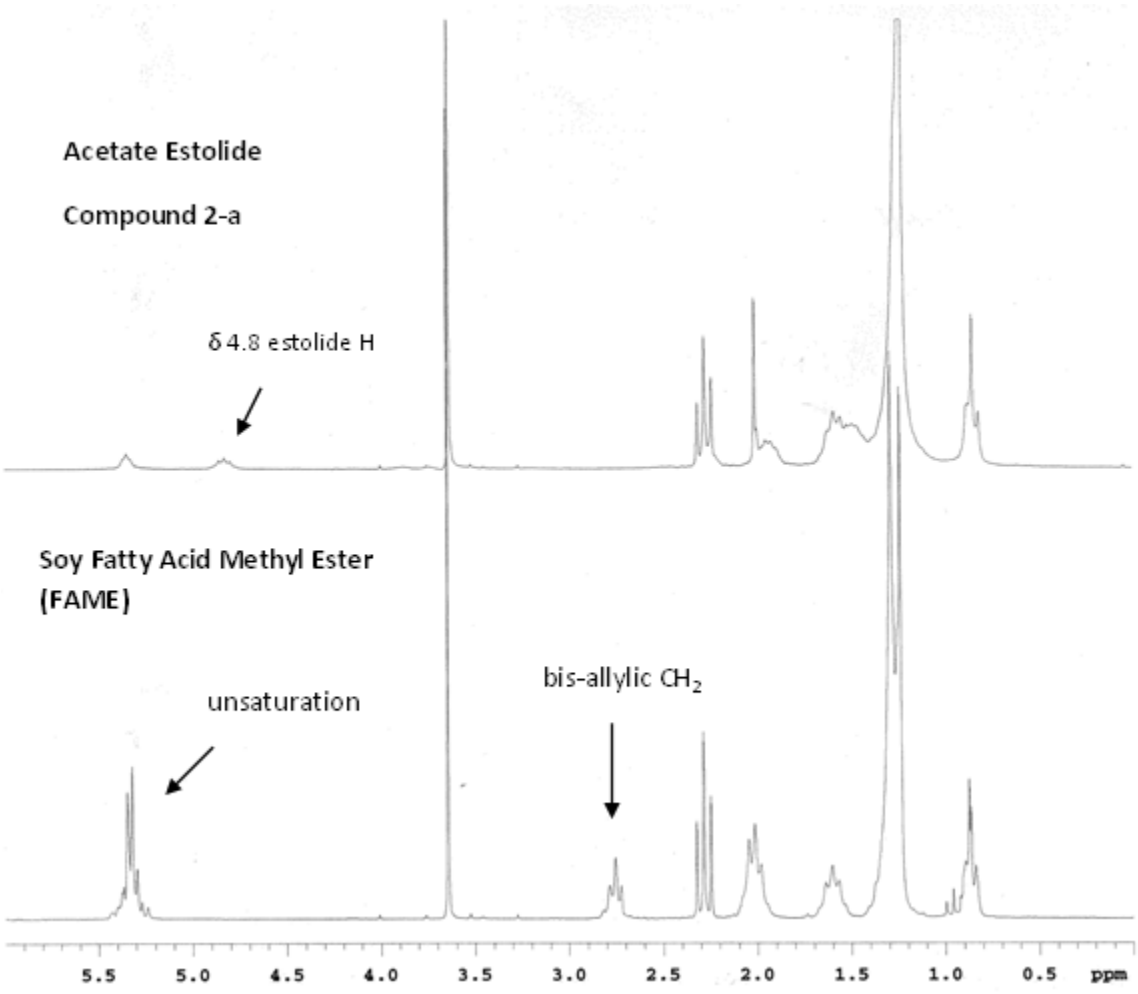


Figure 5 ^{1}H NMR spectra of Fatty Acid Methyl Ester (FAME) and its Acetate Estolide, **2-a**

Table 4 Properties of experimental and commercial plasticizers

Plasticizer	Estolide/chain [a]	Onset of weight loss (°C)	Viscosity at 25°C (cP)
DOP	na	225	82 [b] (67) [c]
SnS	na	249	120 [b] (119) [c]
2-a	0.20	196	46 [b]
2-b	0.26	254	46 [b]
2-c	0.25	-	-
2-d	0.13	140	42 [b]
2-e	0.10	203	37 [b]
4-a	0.79	207	113 [c]
4-b	0.56	210	109 [c]
4-c	0.57	230	87 [c]

[a] Estolide conversion = x/1.54, x = estolide methine peak integration at 4.8 ppm, 1.54 = ave number of double bonds per fatty acid in SBO
[b] Viscosity measured with Newport Scientific RVA-Super4 rapid visco analyzer
[c] Viscosity measured with Brookfield model DV-E viscometer

In order to increase the estolide content and to keep the ester headgroup intact without hydrolysis, an alternate method for producing estolides was developed. In this method the double bonds of fatty acid ester were converted into epoxides which can be ring opened under acidic conditions to produce dihydroxyls [32]. By applying this method the hydroxyls can be esterified with anhydrides to produce two estolide groups per double bond. The processing steps of this method are shown in Scheme 5, and the structures are shown in Figure 4. The products made by this method (**4-a, 4-b** and **4-c**) resulted in higher estolide content with minimal ester hydrolysis and lower color. However, the chain crosslinking still occurred in this method as well albeit to a lower extent, as evidenced from the thermogravimetric analysis shown in Figure 6.

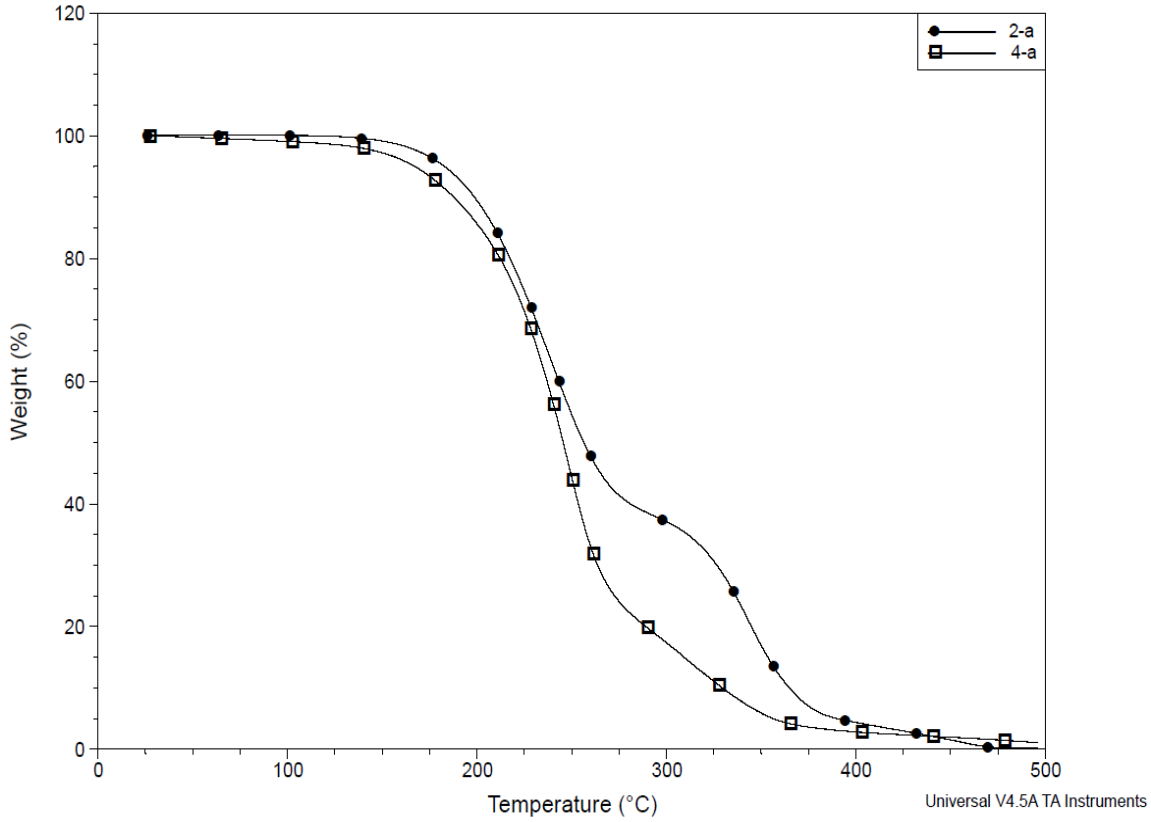


Figure 6 Thermogravimetric analysis of experimental plasticizers **2-a** and **4-a**

Plasticizers with low volatility are desirable due to lower weight loss at the high temperatures involved in PVC compounding (up to 180°C). The volatility of the plasticizers was determined from the temperature where the onset of the weight loss occurs in TGA (Table 4). Most of the experimental plasticizers in this study have an onset of weight loss temperature near 200 °C or above. All the experimental plasticizers had volatilities that were very similar to the volatility of the commercial plasticizers DOP and SnS, with the exception of compound **2-d** which was more volatile.

Lower viscosity plasticizers compound and absorb better into PVC resin than higher viscosity materials [2]. Listed in Table 4 are the viscosities of the experimental soy plasticizers along with commercial plasticizers DOP and SnS. The estolides from the

perchloric acid route showed lower viscosity than the commercial controls whereas the estolides produced from the epoxy route were higher but comparable to the two commercial controls.

4.5.Plasticizer Evaluation

The plasticization ability of the experimental compounds from the perchloric acid method were evaluated by adapting a DSC method to test the Tg reduction of non-stabilized PVC [30]. The reduction of Tg by the experimental plasticizers at various plasticizer loading concentrations was compared to commercial plasticizers DOP and SnS in Table 5. The PVC Tg (83.1 °C) is lowered by all of the experimental and commercial plasticizers at all three loading levels. At low loading levels the experimental plasticizers showed similar reduction in Tg as the commercial controls. Compounds **2-a**, **2-c**, and **2-d** showed significant Tg reduction at higher plasticizer concentration as compared to the other experimental plasticizers. Compounds **2-b** and **2-e** both having 2-ethylhexyl ester headgroups showed little to no Tg reduction with increased plasticizer concentration. The higher polarity of the methyl and glyceryl ester function contribute to better adsorption and gelation properties and Tg reduction as shown by compounds **2-a**, **2-c**, and **2-d** (Table 5). Even though compounds **2-c** and **2-d** were also effective plasticizers they were difficult to synthesize in larger quantities. Only compound **2-a** was available in sufficient quantities to be compounded with PVC to make tensile bars and evaluated for plasticizer functionality.

Table 5 Change in PVC Tg at different plasticizer concentrations[1]

Conc. (phr)	Tg (°C)							
	PVC[2]	DOP	SnS	2-a	2-b	2-c	2-d	2-e
0	83.1	-	-	-	-	-	-	
5	-	68.9	69.8	69.6	72.8	74.8	69.4	69.0
10	-	57.0	59.1	60.9	70.1	67.4	59.8	68.2
20	-	36.4	40.3	54.9	69.2	50.5	42.1	68.1

[1] Solvent casting
[2] Non-stabilized PVC from Sigma-Aldrich

Table 6 Change in PVC Tg at different plasticizer concentrations[1]

Conc. (phr)	Tg (°C)					
	PVC[2]	DOP	SnS	4-a	4-b	4-c
0	81.8	-	-	-	-	-
20	-	23.0	14.1	20.3	25.4	24.0
40	-	-38.6	-41.7	-31.0	-36.9	-35.4
60	-	-61.8	-54.3	-47.8	-51.2	-51.6

[1] Mechanically compounded
[2] Stabilized PVC from Aspen Research

The experimental plasticizers synthesized from the epoxy route were compounded with PVC and the Tg reduction was measured by DSC (Table 6). At 20 and 40 phr plasticizer concentration, the experimental plasticizers reduced the Tg of PVC to a similar extent to the commercial controls. At the highest plasticizer concentration (60 phr) the experimental plasticizers **4-b** and **4-c** had similar glass transition reduction to SnS but were higher than DOP.

Compounding of PVC and PVC with plasticizers was conducted in a Brabender mixer. The torque was recorded as a function of mixing time for each of the formulations. For example a few of the curves are shown in Figure 7. When fusion of the PVC occurs there is an increase in the torque of the mixer. In the case of PVC without plasticizer, the fusion doesn't occur until about 16 minutes into the mixing. With the addition of

plasticizer, fusion occurs shortly after plasticizer addition as can be seen after 5 minutes. The experimental and commercial plasticizers showed a significant increase in torque as can be seen in Figure 7. All the experimental plasticizers at different plasticizer concentration showed this fusion/gelation of the PVC between 3 to 8 minutes during the compounding.

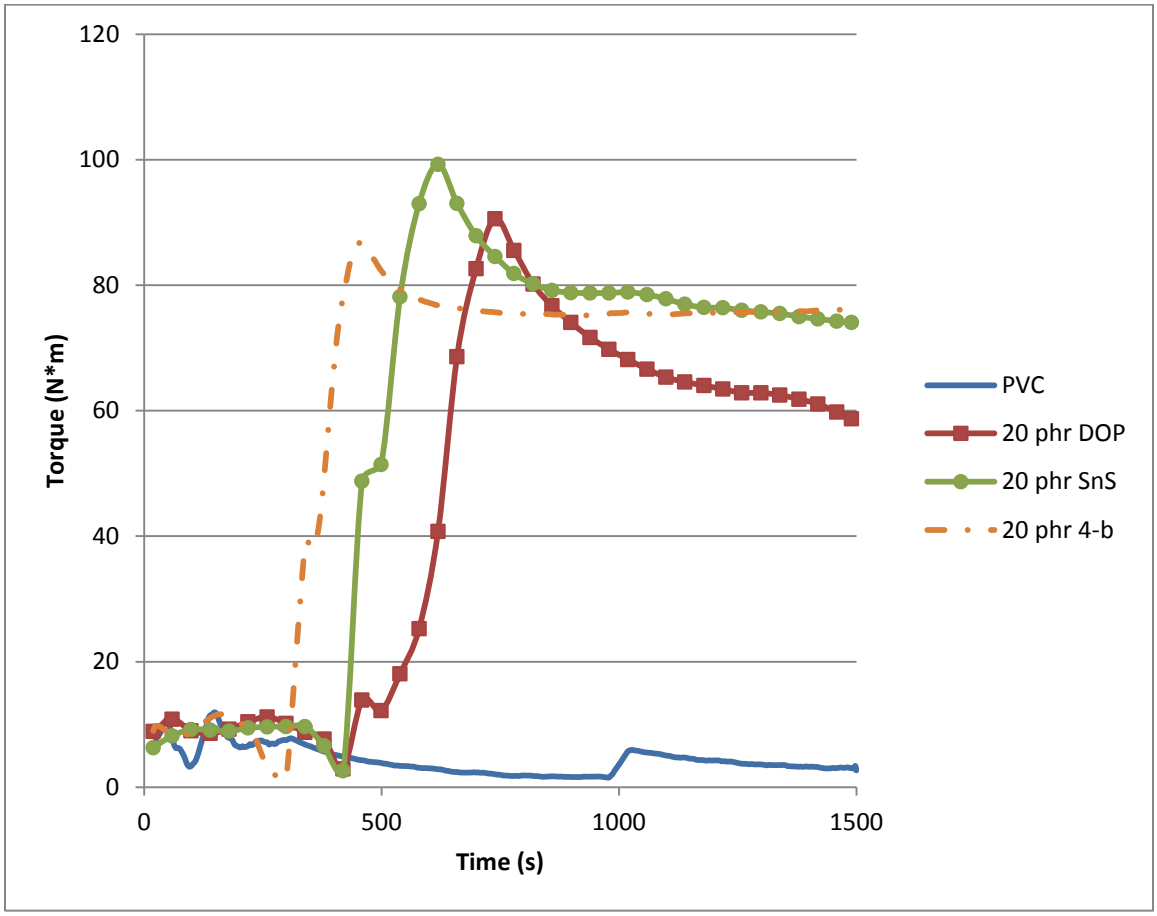


Figure 7 Brabender torque curves for PVC and PVC compounded with commercial and experimental plasticizers at 20 phr

Tensile bars were cut from the compounded sheets containing 10 and 20 phr of DOP, SnS, and **2-a**. The tensile properties of these compounds were measured and are listed in Table 7. A second set of compounded sheets was prepared with 20, 40, and 60 phr of DOP, SnS, **4-a**, **4-b**, and **4-c.** These sheets were ground into a powder and tensile

bars were formed by molding in a hot press. The tensile properties of these materials were measured and are listed in

Table 8. The entries for the commercial plasticizers are slightly different in Table 6 than in Table 7 due to differences in compounding and tensile bar formation procedures. With increased plasticizer concentration, the tensile strength of PVC decreased with all the plasticizers evaluated. At 10 phr plasticizer concentrations both the control plasticizers, DOP and SnS, had little tensile strength reduction, increased modulus and decreased elongation. Experimental plasticizer, **2-a**, showed much lower tensile strength and slightly reduced modulus and elongation at 10 phr concentration. At 20 phr plasticizer concentration, the commercial controls significantly reduced the tensile strength and modulus for DOP and SnS. Elongation was also significantly increased for DOP but only slightly for SnS. At 20 phr concentration, **2-a** reduced the tensile strength more than DOP and SnS but the elongation was significantly lower than the DOP indicating lower plasticization of the PVC. The tensile properties of the experimental plasticizers **4-a**, **4-b**, and **4-c** performed similar to commercial controls at all plasticizer concentrations tested. The only significant difference was observed in the elongation at 60 phr. At this concentration the elongation of compounds **4-a** and **4-c** were slightly lower than the commercial controls. This may be due to a decreased plasticization effectiveness of the experimental plasticizers at the higher concentrations. Compound **2-a,** which had lower estolide content than **4-a**, **4-b**, and **4-c,** showed lower tensile strength and elongation properties indicating poor plasticization, albeit at lower concentrations than the later experimental samples.

Table 7 Tensile properties of PVC and PVC compounded with commercial or experimental plasticizer **2-a**.

Plasticizer	Conc. (phr)	Tensile Strength (MPa)	S.D.	Modulus (MPa)	S.D.	Elongation (%)	S.D.
PVC	0	49.1	1.1	2757.9	78.6	10	0.7
DOP		46.7	1.0	2856.5	66.9	3.2	0.3
SnS	10	48.6	1.3	2904.1	52.4	5.3	1.8
2-a		26.1	1.6	2620.7	157.9	8.1	5.2
DOP		26.9	3.8	1167.3	996.3	150.8	137.7
SnS[1]	20	18.1	-	940.4	-	16.9	-
2-a		13.1	2.6	1477.5	133.8	1.9	0.8

[1]Only one defect free tensile bar was obtained from the compounded sheet.

Table 8 Tensile testing results of PVC compounded with commercial and experimental plasticizers 4-a to 4-c.

Plasticizer	Conc. (phr)	Tensile Strength (MPa)	S.D.	100% Modulus (MPa)	S.D.	Elongation (%)	S.D.
DOP		28.6	1.5	26.0	0.6	139.0	12.0
SnS		26.0	2.3	22.5	0.7	153.3	28.7
4-a	20	26.5	1.3	25.3	1.2	113.9	14.0
4-b		27.0	-	26.9	-	104.7	-
4-c		29.1	1.5	26.6	0.5	146.1	10.1
DOP		12.2	0.2	5.0	0.1	381.9	10.6
SnS		14.1	0.5	5.2	0.1	449.9	23.7
4-a	40	12.9	1.0	5.2	0.1	393.8	44.6
4-b		13.4	0.7	6.6	0.1	311.0	22.1
4-c		14.5	0.5	6.5	0.1	342.5	10.4
DOP		3.6	0.4	1.5	0.0	358.3	40.7
SnS		5.0	0.3	1.9	0.0	405.2	39.8
4-a	60	3.9	0.2	1.9	0.0	279.6	3.7
4-b		5.1	0.2	2.0	0.0	367.3	20.2
4-c		3.0	0.4	2.0	0.0	182.7	27.3

The storage modulus master curves, obtained by DMA, of PVC compounded with commercial and experimental plasticizers **4-a** and **4-b** are shown in Figure 8. As expected, the storage modulus decreases with increased plasticizer concentration for all of the compounds as they become more elastic. The PVC compounded with **4-a** showed a

similar trend to those compounded with DOP while the PVC compounded with **4-b** showed a similar trend to those of SnS.

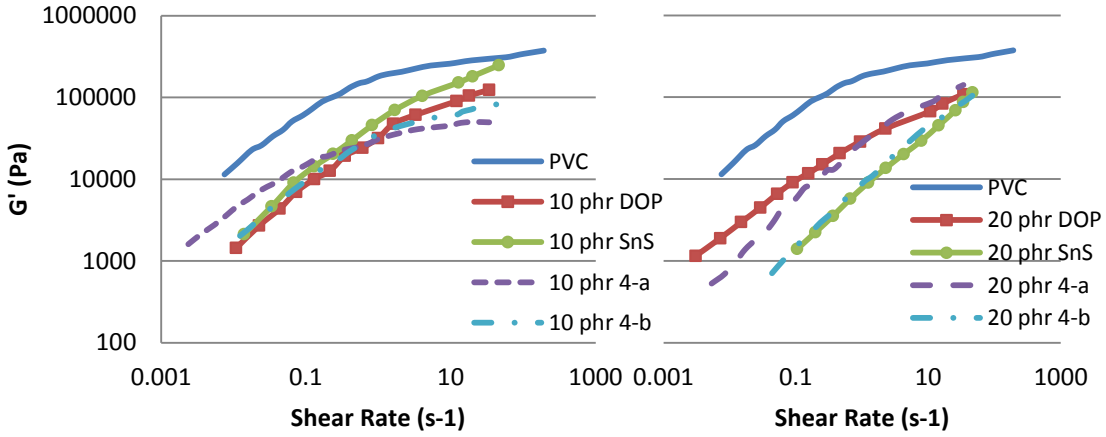


Figure 8 Storage modulus master curves of PVC and PVC compounded with commercial and experimental plasticizers at 10 and 20 phr at different shear rates

4.5. Conclusions

The fatty acid ester estolides were synthesized from two different routes, in the presence of strong acid catalyst and through epoxidation, ring opening, and acetylation. The strong acid catalyzed estolides gave low average estolide content per chain due to higher crosslinking. The epoxy route gave higher average estolide content per chain. Some of the estolides synthesized in this study showed good plasticizer properties, comparable to commercial controls DOP and SnS. The plasticizers with higher estolide content per chain synthesized by the epoxy route had better plasticizer properties and lower color than the lower estolide content plasticizers from the perchloric acid route.

Chapter 5: Synthesis and evaluation of soy fatty acid ester estolides as bioplasticizers in poly(vinyl chloride)

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5.1.Synopsis

Plasticizers are non-volatile organic liquids that impart flexibility to polymers. Due to environmental, health and safety reasons the industry is looking for bioplasticizers to replace petroleum derived phthalates. To fulfill this need, soy fatty acid ester estolides were synthesized, characterized and evaluated as phthalate replacements. Soybean oil was transesterified with methanol or glycerol to form lower molecular weight fatty acid esters that were epoxidized and ring opened with acetic acid and acetylated to give the final products. Ring opening and acetylation of the epoxidized oleic acid esters gave acyclic acetate fatty acid ester estolides, whereas the polyunsaturated fatty acid esters, linoleate and linolenate gave cyclic tetrahydrofuran derivatives and cross linked higher molecular weight materials. The cyclization mechanism to form the tetrahydrofuran derivatives was postulated. Soy fatty acid ester estolides were compounded with formulated poly(vinyl chloride), (PVC) and tested for their functional properties. The physical and functional properties of the new bioplasticizers were compared with commercial plasticizers. The elasticity of PVC compounded with experimental plasticizers and commercial phthalates were comparable. PVC compounded with fatty acid methyl ester estolide showed lower glass transition temperature and similar tensile properties compared to PVC compounded with the commercial phthalate. PVC compounded with the glyceryl fatty acid ester estolide showed a higher glass transition

temperature, higher tensile properties compared to PVC compounded with the commercial phthalate.

5.2.Introduction

Poly(vinyl chloride), (PVC) is the third largest commodity plastic and is extensively used in a variety of applications such as rigid piping, wire and cable coatings, vinyl flooring, children's toys, and many others. The versatility of PVC in various applications is due to the flexibility imparted by the plasticizers in PVC formulations. Plasticizers are high boiling organic liquids used primarily to impart elasticity and softness to polymeric materials. Plasticizers are incorporated into the polymer matrix either mechanically or thermally to lower the glass transition temperature (Tg) of the polymer thereby rendering it more flexible.

The dominant class of plasticizers used in PVC applications is phthalates, phthalic acid esters of aliphatic alcohols. Due to their low production costs and functionality they have been used in PVC formulations for several decades [35]. Plasticizers are incorporated into the PVC matrix but are not covalently bound, and over time can migrate out of the polymer matrix to the surface and release into the environment. The exudation of plasticizer from the polymer matrix can be problematic as some of the phthalate plasticizers have been shown to have adverse health effects such as hormonal disruptions and other ailments, and have been banned in certain applications such as children's toys [9,36–38]. Due to these health concerns, consumer and regulatory pressure have been increasing on the industry to limit or replace phthalates from certain applications [39]. The exudation of plasticizer from the polymer matrix over a period of time also results in the gradual loss of functionality.

Previously we reported the synthesis and evaluation of fatty acid ester estolides derived from soybean oil as alternative plasticizers in PVC [40]. In that investigation we found the compounds which had the best plasticizer performance were acetate estolides with higher estolide content synthesized from epoxidized fatty acid esters. In continuation, the first objective of the current study is to optimize the synthesis of fatty acid ester estolides with higher estolide content and determine the composition. The second objective is to evaluate the functional properties of the new plasticizers after compounding with PVC.

5.3.Materials and Methods

5.3.1. Materials

Soybean oil (SBO) and soy fatty acid methyl esters (FAME) or soy biodiesel were obtained from Cargill Inc. (Minneapolis, MN). Hydrogen peroxide (50% w/w H2O), sodium methoxide (reagent grade), acetic acid (ACS reagent >99.7%), acetic anhydride (99.5%), diisononyl phthalate (DINP, industrial grade), peracetic acid (39% w/w acetic acid), Amberlite® IR120 (H+ form), and glycerol (ACS reagent ≥99.5%) were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, WI). Stabilized PVC with thermal stabilizers and lubricants (see Table 9) herein referred to as "PVC" was obtained from Aspen Research Corporation (Whitebear Lake, MN). Diisopropyl ether (certified), sulfuric acid (ACS+), and basic alumina (60-325 mesh) were purchased from Fischer Scientific (Pittsburg, PA). Magnesol® R60, a magnesium silicate adsorbent, was obtained from The Dallas Group of America Inc. (Whitehouse, NJ). TLC was performed on Analtech (Newark, DE) Unisil GF 250μm silica plates developed with an appropriate solvent and visualized by charring on the hot plate after spraying with 50% sulfuric acid.

5.3.2. Instrumentation and Methods

GC analysis was performed on a Shimadzu GC 2010 Plus gas chromatograph equipped with a programmed temperature vaporizer injector and a flame ionization detector. The analysis utilized a high-temperature column (RTX Biodiesel TG; 15 m, 0.32 mm [inner diameter], 0.10- μm df; Restek, Bellefonte, PA). Sample (1 μl) was introduced into the injector at 60 °C. Both the injector and column utilized a temperature heating profile of 60°C for 1 min, with a 10°C/min temperature ramp to 360°C where they were held for 15 min. The carrier gas (helium) was used at a linear velocity of 20 cm/s and the FID was maintained at a constant temperature of 370 °C.

^{1}H NMR spectra were recorded on a Varian Unity 300 (300 MHz) spectrophotometer with a 4-nucleous probe and autosampler for routine reaction characterization and on a Varian Inova 500 (500 MHz) spectrophotometer for isolated reaction components. All experiments were run using $CDCl_3$ with trimethylsilane as internal reference standard.

FTIR spectra were obtained on a MIDAC Corp. M-Series FTIR neat using NaCl disks. The regions of each spectrum monitored were: C=O stretches of acids (1705-1720) and esters (1735-1750), =C-H stretches of alkenes (3000-3100), and the O-H stretches of acids (2500-3300) and hydroxyls (3200-3550).

Physical Properties of plasticizers listed in table 3 (acid value, saponification value, and hydroxyl value) were determined by titration in triplicate according to the Official Methods and Recommended Practices of the AOCS (Cd 3d-63, Cd 3-25 and Cd 13-60 respectively). Color of the materials was measured visually according to ASTM International method D1544-04 and compared to a standard Gardner color scale samples supplied by BYK.

Thermo Gravimetric Analysis (TGA) was performed on a TA Instruments Q250 thermogravimetric analyzer with aluminum pans. Pre-weighed samples were heated at 10°C/min from ambient temperature to 500°C in a nitrogen atmosphere. The weight loss was recorded with increase in temperature once for each sample.

Viscosity measurements were made on a Brookfield model DV-E viscometer equipped with a small sample adapter using spindle number 18. The adapter was attached to a circulating water bath and maintained at constant temperature. Viscosity tests were performed according to the Brookfield model DV-E manual. The plasticizer was added to the sample chamber and allowed to equilibrate with the water bath for 10 minutes. The viscosity was measured at 100 RPM after the 5^{th} revolution of the spindle once for each sample.

Compounding of plasticizers and PVC was conducted at Aspen Research Co (Whitebear Lake, MN) using stabilized PVC with the formulation listed in Table 9. Each of the formulations contained 10 parts per hundred parts resin (phr) TiO_2 and various concentrations of plasticizer. The experimental plasticizers were compared to a commercial control, diisononyl phthalate or DINP. The PVC was added to a Littleford Blender at 2000 RPM and allowed to heat up to 49°C before TiO_2 and plasticizer were added and further mixed until reaching a temperature of 90°C. The mass was discharged from the blender and allowed to cool to room temperature.

Table 9 Compounded PVC Formulation

Type	**phr**
Resin (Oxyvinyl 216)	100.0
Calcium Stearate	1.5
Amide Wax	2.5
Mercapto-Tin	1.0
Titanium dioxide	10
Plasticizer	10, 20, 30, or 40

The blended mass was fed into either a C.W. Brabender PL 2000 or Shanghai Shen Wei Da Machinery. Both were equipped with a four-chambered single screw extruder (screw length: diameter, 60.96:2.54 cm) rotating at 40 or 30 RPM respectively. The extruders were each equipped with a 7.62 x 0.64 cm die. The chamber temperatures were 170, 170, 175, and 175°C with a die temperature of 180°C. The compounded material was cut into ~0.3 m sections using a paper cutter and characterized based on the methods of Ward and Nielsen [41,42].

Differential Scanning Calorimetry (DSC) measurements were performed on a TA Instruments DSC Q1000 modulated differential scanning calorimeter. Measurements were taken on approximately 10 mg of sample sealed in non-hermetic aluminum pans. The pans were loaded into the DSC at ambient temperature and heated to 100°C at 15°C/min; held at 100°C for 10 min to equilibrate above the PVC glass transition temperature; cooled at 10°C/min to -150°C. The glass transition temperatures were measured by a second heating cycle from -150°C to 120°C carried out at 10°C/min. The scans were performed once for each sample and the glass transition temperature was calculated using Thermal Advantage software.

Tensile testing was performed on an Instron equipped with a 5 kN load cell with a gauge length of 40 mm. Samples were cut into rectangular strips with dimensions of 15 to 17

mm x 76 mm x 1.0 to 1.5 mm. Six specimens per sample were extended at strain rate of 40 mm/min (100%/min) until the specimen ruptured. Strain and stress data were collected using Bluehill® materials testing software (Instron).

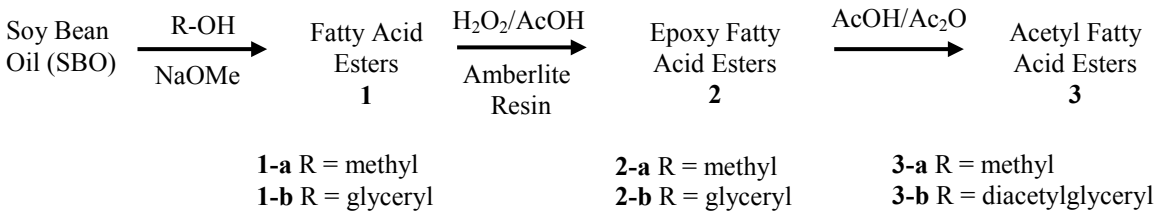
Mechanical hysteresis measurements were carried out on the tensile tester using the following protocol. The sample was deformed at 100%/min based on initial length to 50% elongation and returned to the initial starting point; this loading / unloading procedure was repeated to 150% and then 300% elongations. The area under the loading / unloading curve was calculated using the software provided by Instron Corporation. Two specimens were used for each material tested.

Thermomechanical Analysis (TMA) behavior of the materials was evaluated using TA Instruments TMA operating in the tensile mode. The sample width was 2.69 mm and a heating rate of 3ºC/min was used.

5.3.3. Synthetic Procedures

The synthetic steps adopted to synthesize fatty acid esters estolides are shown in Scheme 6 and the detailed synthetic procedures described below. The compounds were characterized by ^{1}H NMR and FTIR and the spectra are provided in the supplementary information.

Scheme 6 Synthetic scheme for synthesis of soy fatty acid ester estolides



Soy Fatty Acid Methyl Esters (FAME, **1-a***):* aka, soy biodiesel was available commercially and used as starting material without further purification. The ^{1}H NMR of FAME and Soybean Oil are provided in the supplementary information. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.32 (m, 2 H, -C**H**=C**H-**), 3.65 (s, 3 H, -OC**H**$_3$), 2.75 (t, 2 H, =CH-C**H**$_2$-CH=), 2.29 (t, 2 H, -C(O)C**H**$_2$-), 2.02 (m, 2 H, =CHC**H**$_2$-), 1.60 (m, 2 H, -C(O)CH$_2$C**H**$_2$-), 1.24 (d, 18 H, -C**H**$_2$-), 0.86 (t, 3 H, -C**H**$_3$).

Fatty Acid Glycerol Esters (FAGE, **1-b***):* A flask containing 1000 g Soybean Oil (SBO) and 211.2 g (2 mol eq.) glycerol were heated to 210°C under vacuum to remove moisture. Under an inert atmosphere, 2.00 g (0.2% w/w SBO) of sodium methoxide was added and the flask returned to vacuum. The temperature was increased to 220°C and the reaction was run until the disappearance of the SBO spot on TLC (20/80 hexanes/isopropyl ether) was observed (approximately 2 hours). At this stage the glycerol was consumed to convert the triacylglycerol into mostly monoacylglycerol along with a minor amount of diacylglycerol. The reaction mixture was cooled to 180°C and 20 g (2% w/w SBO) Magnesol R60 was added and returned to vacuum. Magnesol was removed by vacuum filtration after the reaction temperature reached 150°C. The reaction resulted in the quantitative yield of *Fatty Acid Glycerol Esters (FAGE*, **1-b**) as a light yellow semisolid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.33 (m, 2 H, -C**H**=C**H-**), 4.13 (d, 1 H, glyceryl-C**H**), 3.89 (m, 2 H, glyceryl C**H**$_2$-), 3.61 (dd, 2 H, glyceryl C**H**$_2$-), 3.28 (s, 1 H, **H**O-), 2.75 (m, 2 H, =CH-C**H**$_2$-CH=), 2.32 (t, 2 H, -C(O)C**H**2-), 2.01 (m, 2 H, =CHC**H**$_2$-), 1.60 (m, 2 H, -C(O)CH$_2$C**H**$_2$-), 1.27 (d, 18 H, -C**H**$_2$-), 0.90 (t, 3 H, -C**H**$_3$). FTIR (neat)

3443 cm^{-1} (O-H stretching), 3009 cm^{-1}(=C-H stretching), 2863 cm^{-1} (C-H stretching), 1732 cm^{-1} (C=O stretching).

*General Procedure for Epoxidation of Fatty Acid Esters (***2-a** *and* **2-b***):* The epoxidation reaction utilized was an adaptation of the method by Sinadinovic-Fiser [43] with some modifications. A flask containing 100 g of esters (FAME, **1-a** or FAGE, **1-b**), 0.5 mol per double bond glacial acetic acid and 5% (w/w soy fatty acid esters) Amberlite IR 120 (H+ form) were added and heated to 60°C in a flask equipped with a reflux condenser. While mechanically stirring at 800 RPM H_2O_2 (1.1 mol per double bond) (50% w/w H_2O) was added and the flask removed from the heating source. The exothermic reaction was allowed to further heat the reaction mixture to 75°C. The temperature was maintained at 75°C by cooling with a water bath for the first hour. After the exotherm subsided the flask was heated to maintain 75°C for an additional 6 hours. While still hot, the reaction mixture was filtered to remove the Amberlite resin. Unreacted acetic acid, H_2O, and H_2O_2 were removed from the filtrate by vacuum distillation. The reaction products *Epoxidized Fatty Acid Methyl Esters (EFAME*, **2-a**) and *Epoxidized Fatty Acid Glycerol Esters (EFAGE*, **2-b**) were obtained in quantitative yield as pale yellow oils. (*EFAME*, **2-a**) ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.60 (s, 3 H, -OC**H**$_3$), 3.05 (m, 1 H, epoxy C**H**), 2.92 (m, 1 H, epoxy C**H**), 2.84 (m, 1 H, epoxy C**H**), 2.24 (t, 2 H, -C(O)C**H**$_2$-), 1.67 (m, 2 H, bis-epoxy C**H**$_2$), 1.56 (m, 2 H, -C(O)CH$_2$C**H**$_2$-), 1.44 (m, 2 H, alpha to epoxy C**H**$_2$), 1.24 (d, 18 H, -C**H**$_2$-), 0.83 (t, 3 H, -C**H**$_3$); FTIR (neat) 3481 cm^{-1} (O-H stretching), 2927 cm^{-1} (C-H stretching), 1740 cm^{-1} (C=O stretching), 842 cm^{-1} (epoxy C-O deformation); (*EFAGE*, **2-b**) ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.10 (d, 2 H, glyceryl-C**H**$_2$), 3.88 (m, 1 H, glyceryl-C**H**), 3.59 (dd, 2 H, glyceryl-C**H**$_2$), 3.34 (s, 1 H, **H**O-), 3.08 (m, 1 H, epoxy C**H**), 2.95

(m, 1 H, epoxy C**H**), 2.88 (m, 1 H, epoxy C**H**), 2.29 (t, 2 H, -C(O)C**H**2-), 2.01 (m, 3 H, -OC(O)C$\mathbf{H}_3$ trace amount), 1.71 (m, 2 H, bis-epoxy C$\mathbf{H}_2$), 1.58 (m, 2 H, -C(O)CH_2C$\mathbf{H}_2$-), 1.47 (m, 2 H, alpha to epoxy C$\mathbf{H}_2$), 1.24 (d, 18 H, -C$\mathbf{H}_2$-), 0.85 (t, 3 H, -C$\mathbf{H}_3$); FTIR (neat) 3450 cm^{-1} (O-H stretching), 2856 cm^{-1} (C-H stretching), 1740 cm^{-1} (C=O stretching), 1461 cm^{-1}, 1170 cm^{-1}, 825 cm^{-1} (epoxy C-O deformation).

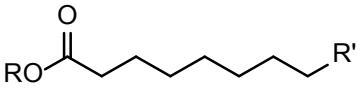
*General Procedure for Ring Opening and Acetylation of Epoxy Fatty Acid Esters (***3-a** *and* **3-b**): To a flask equipped with a reflux condenser containing 100 g Epoxidized Fatty Acid Esters (**2-a** or **2-b**), was added glacial acetic acid (1.2 mol per original double bond), and acetic anhydride (1.15 per mol for **2-a** or 3.15 per mol for **2-b**). The reaction mixture was heated and maintained at 130°C for five hours. The contents of the flask were cooled to room temperature where 3% peracetic acid (w/w epoxidized soy fatty acid esters) was added and allowed to bleach the reaction mixture for 2 hours. The crude reaction mixture was heated up to 100°C under high vacuum to removed acetic acid and trace amounts of acetic anhydride and peracetic acid. While the reaction mixture was hot, basic alumina (8% w/w Epoxidized Fatty Acid Esters) was added, stirred for 20 minutes under vacuum, and vacuum filtered to give the final products *Acetylated Fatty Acid Methyl Esters (AFAME*, **3-a**) and *Acetylated Fatty Acid Glycerol Esters (AFAGE*, **3-b**) in quantitative yield. *(AFAME*, **3-a**) ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.21 (m, 1 H, estolide C**H**), 5.16 (m, 1 H, estolide C**H**), 4.93 (m, 1 H, estolide C**H**), 4.80 (m, 1 H , estolide C**H**), 4.08 (m, 2 H, THF ring C$\mathbf{H}_2$), 3.82 (m, 2 H, THF ring C$\mathbf{H}_2$), 3.59 (s, 3 H, -OC$\mathbf{H}_3$), 2.23 (t, 2 H, -C(O)C$\mathbf{H}_2$-), 2.10 (s, 3 H, -OC(O)C$\mathbf{H}_3$), 1.54 (m, 2 H, -C(O)CH_2C$\mathbf{H}_2$-), 1.45 (m, 2 H, alpha to estolide C$\mathbf{H}_2$), 1.21 (d, 18 H, -C$\mathbf{H}_2$-), 0.81 (t, 3 H, -C$\mathbf{H}_3$); FTIR (neat) 3465 cm^{-1} (O-H stretching), 2931 cm^{-1} (C-H stretching), 1739 cm^{-1} (C=O stretching); *(AFAGE*,

3-b) ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.16 (m, 1 H, glyceryl C**H**), 4.91 (m, 1 H, estolide C**H**), 4.78 (m, 1 H, estolide C**H**), 4.15 (dd, 4 H, glyceryl C**H**$_2$), 3.81 (m, 2 H, THF ring C**H**$_2$), 3.60 (m, 2 H, THF ring C**H**$_2$), 2.24 (t, 2 H, -C(O)C**H**$_2$-), 1.99 (s, 3 H, -OC(O)C**H**$_3$), 1.51 (m, 2 H, -C(O)CH$_2$C**H**$_2$-), 1.42 (m, 2 H, alpha to estolide C**H**$_2$), 1.19 (d, 18 H, -C**H**$_2$-), 0.80 (t, 3 H, -C**H**$_3$); FTIR (neat) 3471 cm^{-1} (O-H stretching), 2926 cm^{-1} (C-H stretching), 1739 cm^{-1} (C=O stretching).

5.4.Results and Discussion

The reaction sequence used to prepare the fatty acid ester estolides of this study is shown in Scheme 6. Previously we reported the synthesis of soy fatty acid ester estolides by two different routes (Stolp et al. 2019). In the first method the unsaturation sites of the fatty acid esters were converted to estolides in the presence of a strong mineral acid, perchloric acid, and in the second method the double bonds were converted to epoxy groups and then ring opened with acetic acid/anhydride to form estolides. Theoretically, the first method would result in one estolide per double bond whereas in the second method, two estolides per double bond would form. Both methods resulted in lower estolide content than expected due to crosslinking reactions. In the second method, the fatty acid ester unsaturation sites were converted to epoxy groups with *in situ* generated peracetic acid. Peracetic acid was generated by the reaction of hydrogen peroxide with acetic acid using sulfuric acid as catalyst. The sulfuric acid also catalyzed two side reactions: ring opening of the epoxy groups to free hydroxyls and hydrolysis of the fatty acid ester headgroup to free fatty acids. To minimize these side reactions we modified the method of Sinadinovic-Fiser et al. and replaced the mineral acid with an ion exchange resin (Amberlite IR 120 H+ form) to catalyze the formation of peracetic acid [43]. This

method minimized the ester hydrolysis and the ring opening of epoxy groups during epoxidation and was successfully utilized for scale-up of the reaction.



3-a and **3-b**

Compound	**R =**
3-a	methyl
3-b	diacetylglyceryl

R' for both compounds =

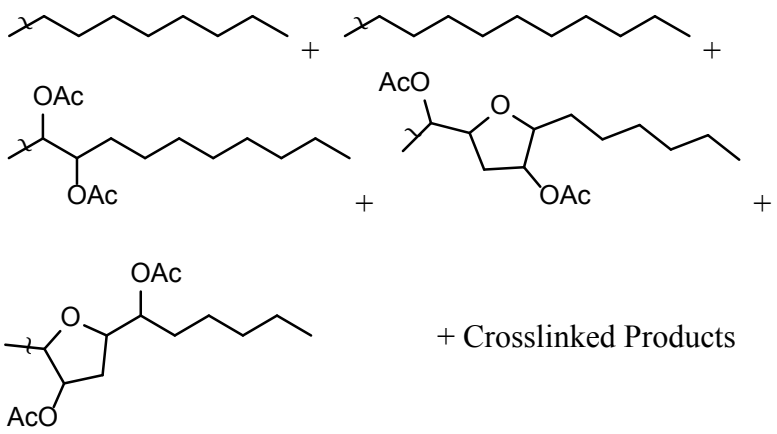


Figure 9 Typical structure of soy fatty acid ester estolides

The epoxy groups in the epoxidized fatty acid esters were ring opened using acetic acid and the resulting hydroxyl functions were acetylated with acetic anhydride to form acetate estolides at the site of unsaturation. The compounds thus synthesized had the typical structures shown in Figure 9. Theoretically each epoxy group should result in two estolides at the site of unsaturation on the fatty acid chain. Based on the soybean oil fatty acid composition, the conversion of the double bonds to epoxy groups and the ring opening of the epoxy groups to form estolides would result in an average of 3.08 estolide groups per fatty acid. However, the ^{1}H NMR spectral data showed only 1.85 estolides or

60% of theoretical. We further investigated the composition of reaction product **3-a** and separated the components using column chromatography and vacuum distillation. Characterization of the components by ^{1}H NMR and the GC elution profile revealed the formation of a new product, a five membered cyclic ether, during the epoxy ring opening with acetic acid. This predominant side reaction occurs mainly from the diepoxy fatty acid esters formed from linoleate, the major fatty acid present in soybean oil. The ring opening of diepoxy linoleate with acetic acid results in two different tetrahydrofuran acetyl-hydroxyl isomers depending upon the site of attack on the epoxy carbons as shown in Figure 10. The hydroxyl group generated during the epoxy ring opening of the intermediate compound attacks the adjacent epoxy group to form two different cyclic ether tetrahydrofuran compounds as shown by the mechanism in Figure 10. The ^{1}H NMR spectrum of the fraction separated from the reaction product by column chromatography containing two tetrahydrofuran derivatives is shown in Figure 11. The complete structures of acetylated tetrahydrofuran estolides A and B are shown in

Figure 12.

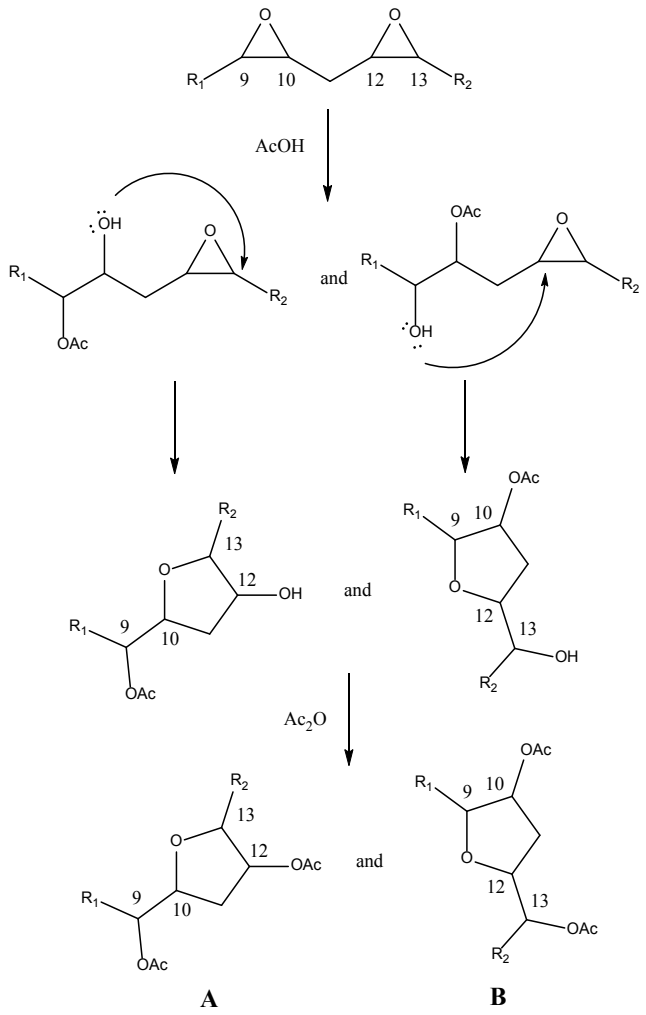


Figure 10 Cyclic ether formation mechanism during the ring opening and acetylation of diepoxy linoleate

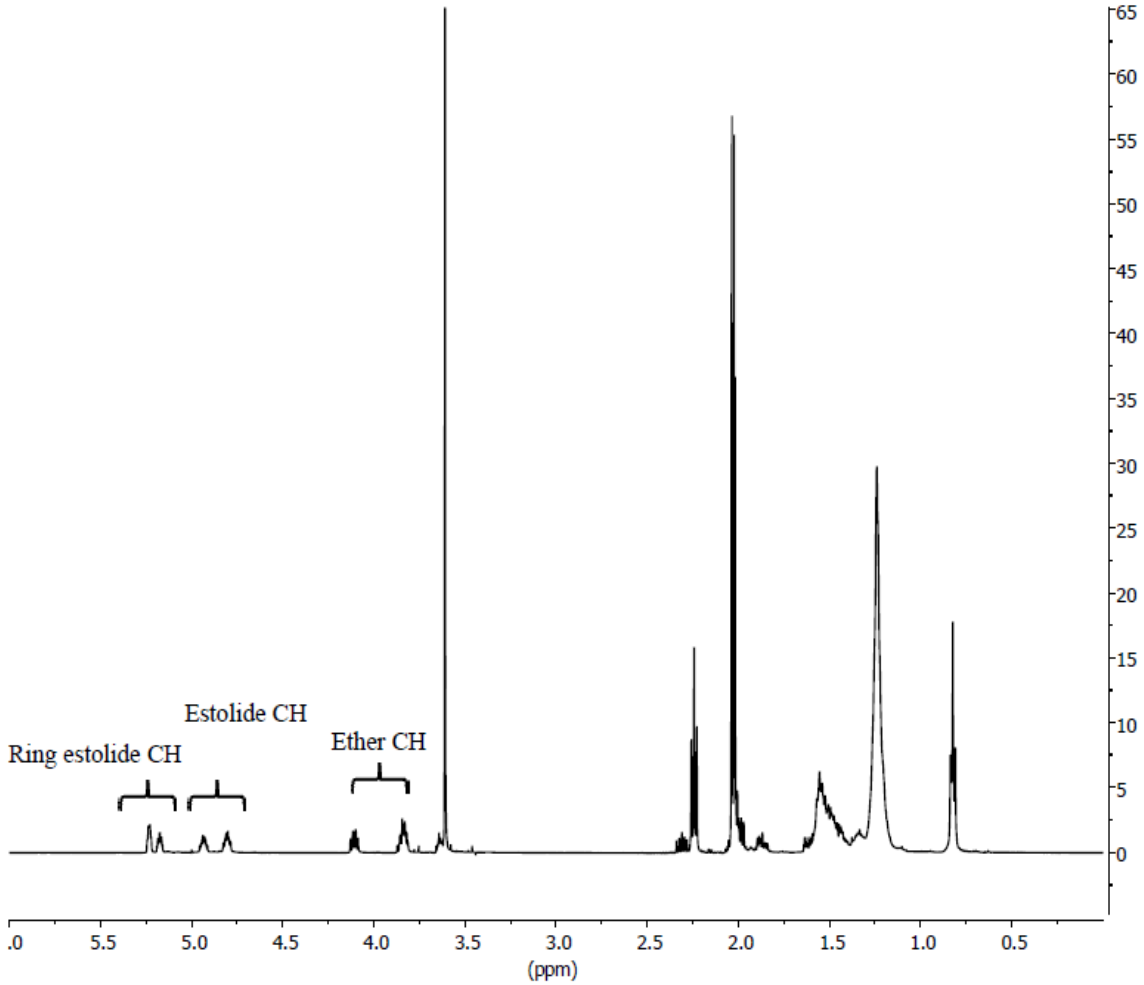
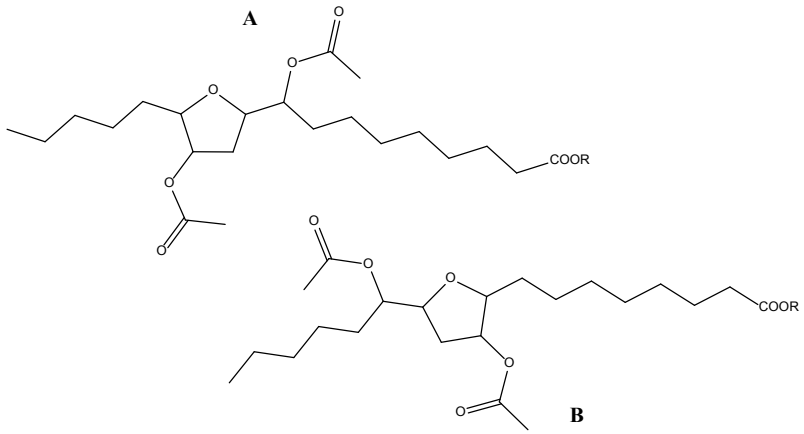


Figure 11 [1]HNMR spectrum of tetrahydrofuran compounds (A and B) isolated by column chromatography from fatty acid methyl ester estolide (**3-a**)



R = methyl or diacetylglyceryl

Figure 12 Tetrahydrofuran estolide structures, A and B formed from the ring opening and acetylation of epoxidized linoleic acid ester

Formation of cyclic ether compounds from the acid catalyzed ring opening of diepoxy fatty acids have been reported in the literature. We initially reported these cyclic ethers in a patent that described acetylated fatty acid ester estolides as biobased plasticizers. In another study Bantchev et al. found that reaction of diepoxy fatty acid ethylhexyl esters with acid ion exchange resin in 2-ethyhexanol resulted in furan ring formation [44]. The furan compounds showed characteristic peaks in ^{1}H NMR at 2.54 ppm and 5.81 ppm for furan hydrogens. These peaks were not present in our purified cyclic ether compounds as shown in Figure 11. Khuddus et al. reported on the difficulty of producing tetrahydroxy stearic acids due to the formation of cyclic ether products during the acid catalyzed ring opening of diepoxy linoleate [45]. Borhan et al. synthesized and fully characterized the stereochemistry of tetrahydrofuran diols formed by acid catalyzed ring opened diepoxy linoleate [46]. In their study they found four isomers were produced from the ring opening of diepoxy linoleate and the mechanism likely proceeded through an epoxy diol intermediate. In the current study the tetrahydrofuran isomers formed were not isolated and their stereochemistry was not determined as it was beyond the focus of the study. Since soybean oil contains ~55% linoleic acid, the tetrahydrofuran compounds formed were a significant portion (~38%) of the final product composition. The elution profile in the GC chromatogram (Figure 13) shows the saturated fatty acid methyl esters followed by acyclic fatty acid methyl ester acetate estolides derived from epoxidized oleic acid methyl ester. The acyclic acetate estolides were followed by the tetrahydrofuran estolides and higher molecular weight crosslinked fatty acid ester compounds formed by ring opening of epoxidized linoleate and linolenate esters. The TGA shown in Figure 14 also confirms the presence of a higher molecular weight

crosslinked fraction in the reaction product as evidenced by the weight loss at higher temperatures.

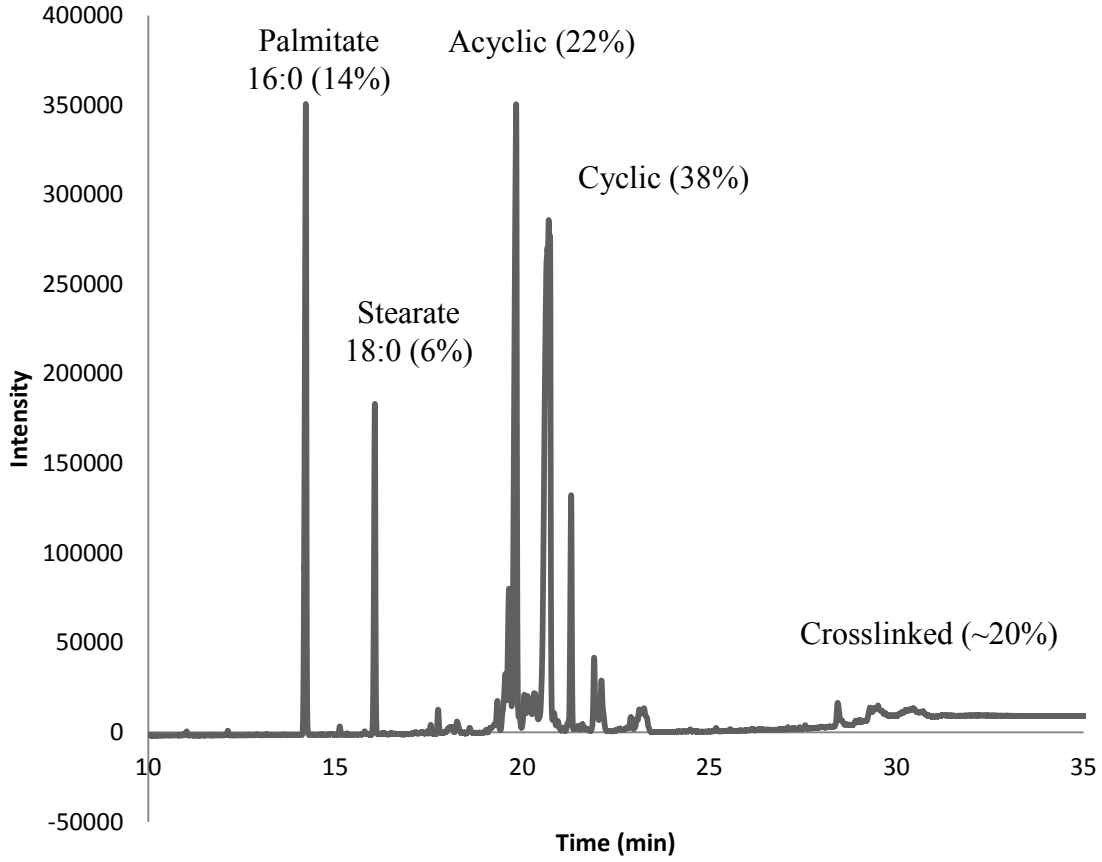


Figure 13 GC chromatogram of AFAME (**3-a**)

The physical properties of the plasticizers were determined according to standardized methods from the American Oil Chemists Society or ASTM International and are listed in Table 11. The weight loss or volatility of the sample at a given temperature for the experimental and commercial plasticizers was determined using TGA and is shown in Figure 14. The onset of weight loss for the plasticizers derived from TGA is listed in Table 10. The majority of weight loss for compound **3-a** occurred during the first onset but a second onset was observed above 300°C indicating higher molecular

weight materials were present. Compound **3-b** had three distinct regions of weight loss, initially 10% occurred around 100°C, the majority occurred around 285°C and the remaining 10% occurred around 400°C.

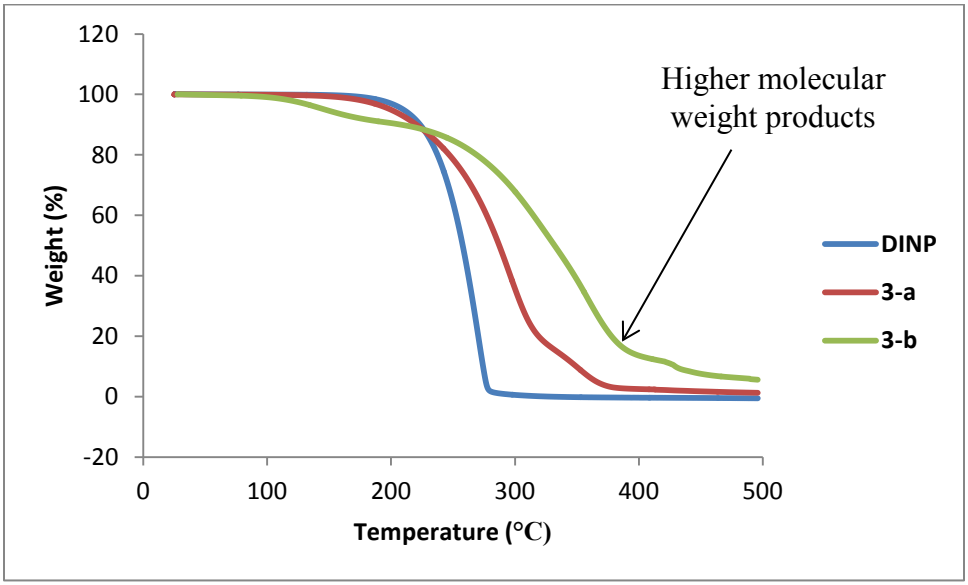


Figure 14 TGA of experimental and commercial plasticizers **3-a**, **3-b** and DINP

Table 10 Onset of weight loss of experimental and commercial plasticizers.

Plasticizer	Temperature (°C)
DINP	240
3-a	228
3-b	285*

* majority of weight loss

The physical properties of the experimental plasticizers are listed in Table 11. The acid value and color of the experimental compounds were higher than DINP but within an acceptable range for plasticizer applications. Reaction optimization and further bleaching of the experimental plasticizers would reduce the acid value and color to reach the same levels as DINP. The viscosity of **3-b** was much higher than DINP which might pose a problem in compounding the plasticizer with PVC.

Table 11 Physical properties of experimental and commercial plasticizers.

Property	Test Method	Plasticizer		
		DINP Exp. (Lit.)	**3-a**	**3-b**
Acid Value (mg KOH/g)	AOCS Cd 3d-63	0.03 [1]	3.09 (± 1.82)	3.35 (± 3.56)
Saponification Value (mg KOH/g)	AOCS Cd 3-25	NA	363.0 (± 9.5)	436.0 (± 33.7)
Hydroxyl Value (mg KOH/g)	AOCS Cd13-60	NA	13.2 (± 11.1)	3.8 (± 3.0)
Color (Gardner Number)	ASTM D1544-04	1 (25)[1, 2]	4	6
Viscosity (cP) @ 25°C (Brookfield)		80	116	1756

All AOCS tests were performed in triplicate. Color and viscosity were measured once.

[1] *Exxon Mobile* DINP Plasticizer technical data sheet

[2] The number in parentheses is Platinum-Cobalt scale

The glass transition temperature (Tg) measured by DSC of PVC and PVC compounded with plasticizers at various concentrations are listed in Table 12. As plasticizer concentration increased the Tg of the compounded PVC decreased for all compositions. Compound **3-a** showed a greater ability to lower the Tg of PVC than DINP and compound **3-b**. The higher glass transition temperature coupled with increased modulus and higher break strength indicates more effective inter-molecular interactions with the more polar glyceryl ester derivative with the polymer molecular structure. The blend of DINP and **3-a** produced a slightly lower Tg reduction of PVC compared to DINP.

Table 12 Glass transition temperature of PVC and PVC compounded with experimental and commercial plasticizers.

Plasticizer Concentration (phr)	**Tg (°C)**				
	PVC	DINP	**3-a**	**3-b**	50/50 DINP/**3-a**
0	80.3	-	-	-	-
10	-	-	-	52.9	-
20	-	19.8	9.3	24.2	-
30	-	14.4	9.4	-	12.8
40	-	-5.1	-33.7	-	-7.5

The tensile properties of the compounded PVC with plasticizers are given in Table 13. The tensile data showed that as DINP concentration increases there is a significant decrease in modulus of the compounded PVC. This is expected as the Tg of the compounded PVC decreases with the increased concentration of the plasticizer and the material becomes softer. Experimental compound **3-a** also showed a similar decrease in modulus but to a greater extent than DINP at 20 and 40 phr concentration and a lower extent at 30 phr concentration. The blend of DINP and **3-a** at 30 phr had a higher modulus than either of the individual plasticizers at 30 phr. At 40 phr the blend of DINP and **3-a** had a modulus between the two pure plasticizers. The modulus of the PVC compounded with experimental plasticizer **3-b** had a different trend. At 10 phr the modulus showed an increase of ~70 % over the control PVC. As the **3-b** content increased from 10 phr to 20 phr, there was a decrease in modulus as expected, but compared to DINP and **3-a** plasticizers at the same loadings, the **3-b** plasticized material had significantly higher modulus and tensile strength values without compromising elongation to break. One of the reasons for the difference in behavior of **3-b** could be the over an order of magnitude higher viscosity value compared to DINP and **3-a**. The reason for this may be due to molecular interactions of the polymer and plasticizer such as hydrogen bonding. At lower concentrations the plasticizer acts as a reinforcing agent with

the polymer but at higher concentrations it acts more as a plasticizer. In addition, the higher Tg value also explains the higher modulus value. This is a particularly interesting result when taking into account the strain to break values to be discussed later.

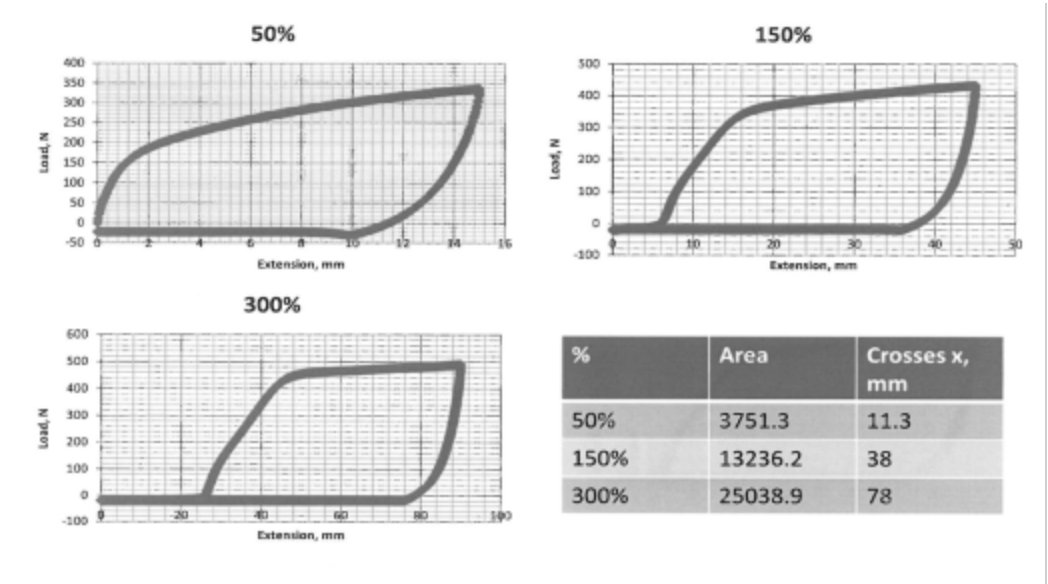
Table 13 Tensile properties of PVC and PVC compounded with experimental and commercial plasticizers at different concentrations.

Concentration (phr)	Plasticizer	Modulus (MPa)	Stress @ break (MPa)	Strain @ break (%)
Control	-	767.1 (±229.6)	38.83 (±3.33)	9.25 (±2.87)
10	**3-b**	1320.3 (±180.8)	55.48 (±7.16)	6.33 (±0.82)
20	DINP	149.9 (±37.2)	21.84 (±2.20)	380.33 (±49.11)
	3-a	131.1 (±17.5)	20.54 (±1.44)	410.00 (±40.23)
	3-b	653.2 (±47.9)	24.50 (±4.50)	366.29 (±33.66)
30	DINP	145.2 (±24.8)	20.28 (±1.39)	409.29 (±31.34)
	3-a	164.8 (±18.5)	6.85 (±2.17)	424.38 (±42.57)
40	DINP	39.0 (±4.2)	-	-
	3-a	15.5 (±6.3)	-	-
15/15	DINP/ **3-a**	234.4 (±23.5)	17.55 (±2.09)	411.00 (±59.09)
20/20	DINP/ **3-a**	24.3 (±2.9)	2.15 (±1.51)	433.71 (±49.99)

When PVC was plasticized with DINP or **3-a**, as plasticizer content was increased there was decrease in modulus values as expected up to 30 phr loadings. However, a 15 phr/15 phr blend of DINP and **3-a** plasticizers showed an increase in modulus values which was unique behavior for the blends. The blends of DINP and **3-a** had stress at break values close to those of the individual plasticizer values at the same plasticizer concentrations. The strain at break values of PVC compounded with **3-a** were close to those of DINP and the blends also had similar strain at break values for a given

plasticizer concentration. Of particular interest was the strain at break value of ~366 % for PVC plasticized with 20 phr **3-b** plasticizer which also had the highest stress at break value among all the plasticized compositions at 20 phr plasticizer content. This relatively higher strain to break and stress to break values combined with a high tensile modulus of ~653 MPa makes **3-b** plasticized PVC material useful for novel applications that are tough and have higher modulus.

An example of loading – unloading curves from a typical hysteresis experiment is given in Figure 15 for PVC plasticized with 20 phr **3-a** plasticizer. Hysteresis curves were prepared and represent deformations of 50, 150 and 300 % elongations. Two parameters were compared from these plots; (i) area under the loading – unloading curve which provides hysteresis (ii) extension where the load increases from zero during the second (150%) and third (300%) loading cycle which provides permanent set information of the material between the unloading cycle and subsequent loading cycle.



%	Area	Crosses x, mm
50%	3751.3	11.3
150%	13236.2	38
300%	25038.9	78

Figure 15 Cyclic loading – unloading curves at 50%, 150% and 300% elongations for PVC with 20 phr **3-a** plasticizer

A comparison of the area under the loading – unloading cycles is given in Figure 16 for PVC plasticized with different plasticizers at different concentrations. For all plasticized materials as the plasticizer content increased, there was a decrease in hysteresis implying that the "elastomeric" character increased. However as the elongation was increased 50% to 150% and 300%, there was a significant increase in hysteresis indicating more energy dissipating character. The data for 50% elongation showed that there was a decrease in hysteresis with the addition of DINP from 20 to 40 phr, with a step drop in the 30-40 phr range. When comparing **3-a** and **3-b** plasticizers at 20 phr, the **3-b** plasticizer has higher hysteresis value, indicating it was less elastomeric, again indicating that there is greater molecular interaction between the plasticizer and PVC which increases the stiffness of the compounded PVC. The PVC containing 20 phr **3-b** plasticizer had the highest hysteresis value among the materials evaluated. This is in line with the previous observations from tensile experiments (i.e. high modulus, yield stress) and shows that this material is more "plastic" than "elastomeric". However at 40 phr plasticizer, the hysteresis values show that **3-a** plasticizer had the lowest value and hence would show the best "elastomeric" behavior.

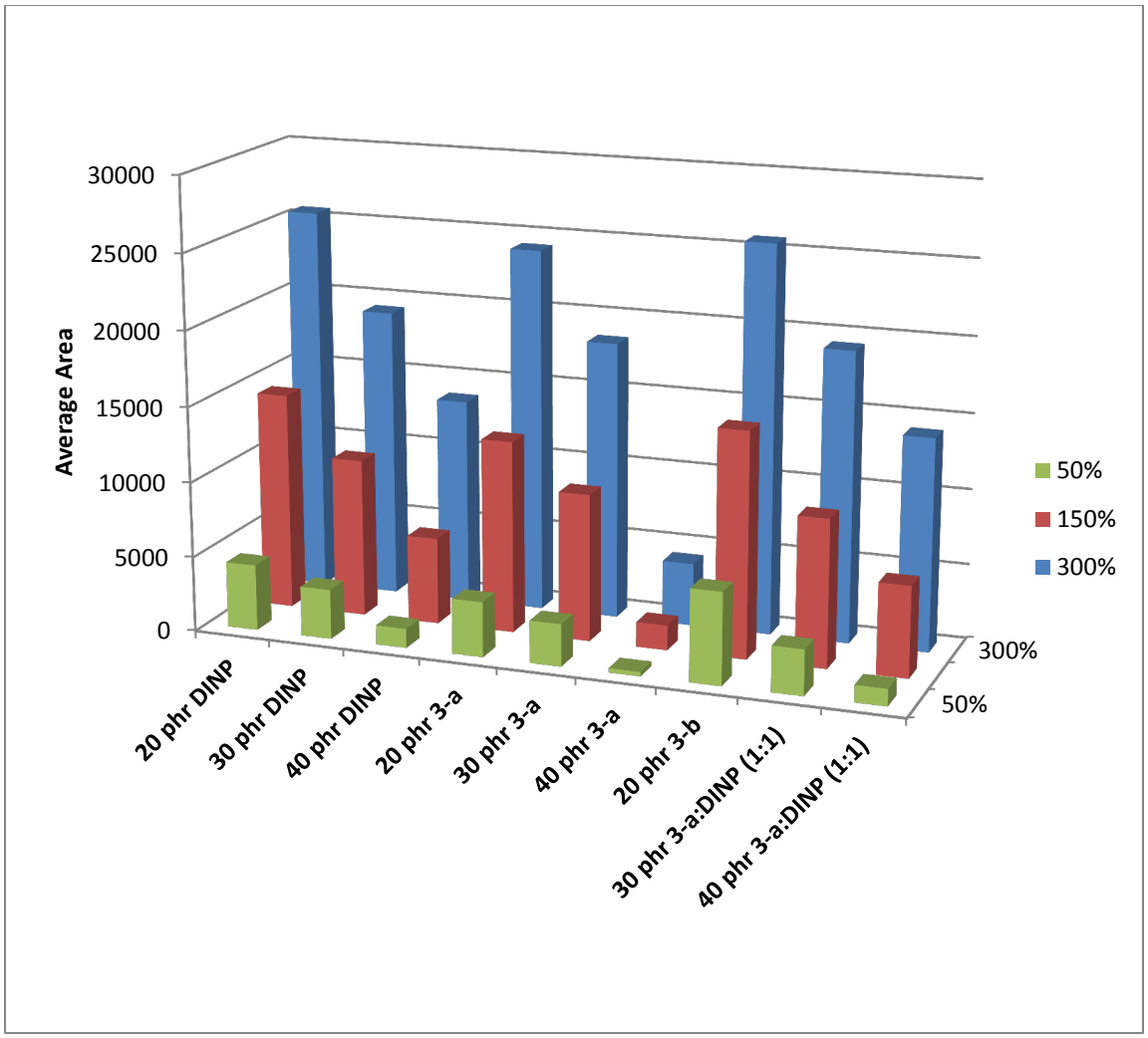


Figure 16 Cyclic loading-unloading, areas under the curve of PVC compounded with experimental and commercial plasticizers compared at 50, 150 and 300 % strain

When comparing the cyclic loading – unloading experiments at all three elongations (50, 150 and 300 %) the data show that the trends observed in the 50% loading – unloading experiment are also seen in the 150% and 300% loading – unloading hysteresis values. PVC with 40 phr **3-a** plasticizer had the least amount of hysteresis and was most "elastomeric." Comparing DINP, **3-a** and **3-b** plasticizers at 20 phr loading in

PVC, all materials appear to be similar; the **3-b** plasticized material had slightly higher hysteresis values.

The comparison of storage modulus (E') as a function of temperature for PVC with different plasticizers at 20 phr concentration is shown in Figure 17. The onset of decrease in modulus occurred initially for PVC plasticized with **3-a** followed by DINP, **3-b** and PVC with no plasticizer. This was in agreement with the room temperature mechanical property results and Tg depression by DSC discussed earlier. Specifically, the decrease in Tg with the addition of 20 phr **3-b** plasticizer was less than that for the DINP and **3-a** plasticizers, and as a consequence the room temperature modulus values are higher for the **3-b** plasticized PVC.

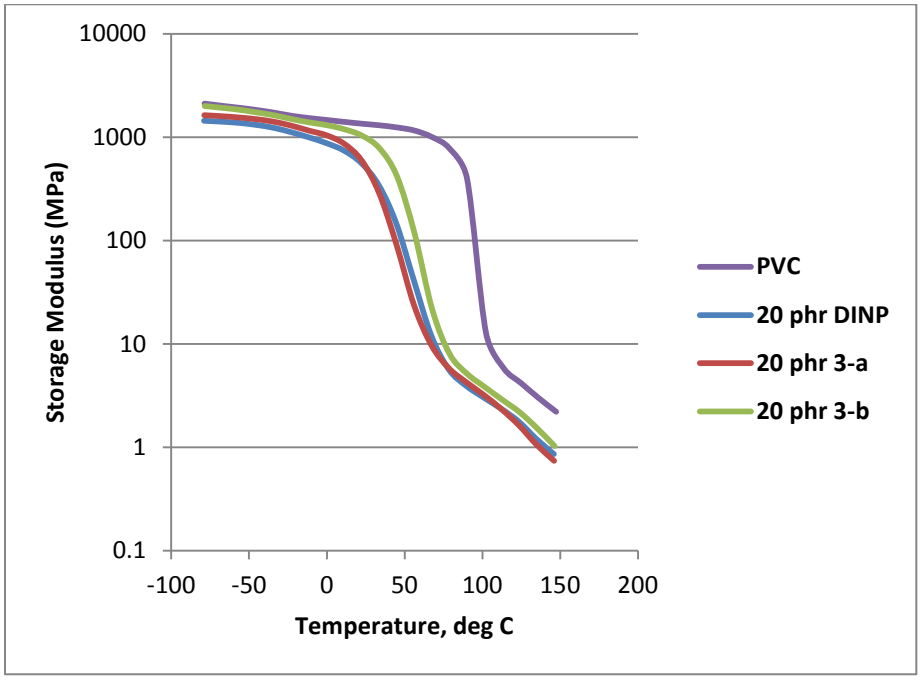


Figure 17 Storage modulus of PVC and PVC compounded with 20 phr commercial or experimental plasticizers

5.5.Conclusions

Soy fatty acid ester estolides were synthesized from soybean oil through transesterification, epoxidation, ring opening and acetylation. The analysis of the final product revealed that it contained acyclic and cyclic estolides along with some crosslinked material. The formation of cyclic tetrahydrofuran estolides resulted from the ring opening reaction of diepoxy linoleate, a predominant fatty acid present in soybean oil. A possible reaction mechanism for the formation of tetrahydrofuran estolides from diepoxy linoleate was proposed. The PVC compounded with fatty acid methyl ester estolide showed lower Tg values with increased plasticizer concentration compared to commercial phthalate, DINP. The PVC compounded with fatty acid methyl ester estolide had modulus and tensile properties that were similar to PVC compounded with DINP and would be useful as a replacement for most applications where DINP is used. However, PVC compounded with fatty acid glyceryl ester estolides showed higher Tg values and higher modulus compared to PVC compounded with DINP indicating higher polar-polar interaction of the glycerol head group and the polymer. The glycerol ester estolide would be useful for applications that require high strength materials at lower plasticizer concentration but would not be useful as a phthalate replacement at higher concentrations. PVC compounded with blends of DINP (15 phr) and **3-a** (15 phr) had higher modulus values compared to the corresponding pure components at 30 phr plasticizer levels and would find use in applications that would reduce the amount of phthalate plasticizers.

Chapter 6: Castor epoxy fatty acid alkyl ester estolides as bioplasticizers

Submitted to Journal of Industrial and Engineering Chemistry

6.1.Synopsis

Epoxy fatty acid alkyl ester estolides were synthesized from castor oil to be used as biobased plasticizers for poly (vinyl chloride), (PVC). In the first step of the synthesis castor oil was transesterified with methanol or *n*-butanol to quantitatively yield castor fatty acid alkyl esters. The hydroxyl function on the ricinoleic esters was acetylated with acetic anhydride to form estolide. The double bond was epoxidized to give a bifunctional epoxy fatty acid alkyl ester estolide. The experimental plasticizers were compounded with PVC in a plastisol formulation and were evaluated for their plasticizer functionality and compared with commercial phthalate plasticizers diisononyl phthalate (DINP, VESTINOL 9) and non-phthalate 1,2-cyclohexanoic acid diisononyl ester (DINCH, ELATUR CH). The experimental plasticizers showed excellent gelation, efficiency, and compatibility as well as plastisol viscosity and thermal properties, comparable to or better than the plastisols prepared with commercial controls DINP and ELATUR CH. The volatility of the methyl ester was inferior to the butyl ester. Both compounds showed low water resistance properties. Further evaluation of the butyl ester under tropical conditions of high temperature and humidity confirmed limited compatibility. This indicates that the castor epoxy fatty acid ester estolides would be better suited for non-water contact applications such as flooring, artificial leather, wiring or wall coverings.

6.2.Introduction

Poly(vinyl chloride) (PVC) is the third largest commodity plastic and finds use in a wide variety of applications from rigid pipes to flexible tubing and many things in-between. In and of itself PVC is a rigid polymer with limited applications. When compounded with certain additives PVC can become flexible, increasing the number of applications in which it can be used [2]. The additives that give PVC flexibility are a type of compound called plasticizers. Plasticizers are non-volatile organic liquids that imbed in the amorphous regions of the polymer matrix during compounding. This reduces the glass transition temperature (Tg) of the polymer making it more flexible.

There are numerous types of plasticizers on the market with the choice of plasticizer dependent on the polymer, cost, and end use application. Long chain esters of phthalic acid (phthalates) have been the dominate class of plasticizers used in PVC for many decades [35]. Up until recently the workhorse of the phthalate class has been diethylhexyl phthalate aka dioctyl phthalate (DOP). More recently due to its adverse health effects, DOP has been replaced in the US and EU with diisononyl phthalate (DINP) in many applications but still is the most dominant plasticizer in Asia. Not being permanently bound in the polymer, over time plasticizers migrate to the surface of plasticized materials where they can enter the environment and come in contact with consumers. Some phthalates, DOP in particular, have been found to cause adverse health effects, such as hormonal disruptions [9,36–38]. Due to these effects, the use of certain phthalates in sensitive applications such as children's toys has been banned [39]. These regulatory changes have been the driving force for the switch from DOP to DINP in many applications. Even though DINP has less health concerns than DOP consumers have become increasingly aware of and concerned with use of phthalates in many

products. This led us to find relatively safer alternatives that are biobased, nontoxic, and benign.

Biobased plasticizers have had limited use over the course of PVCs history. Epoxidized oils, such as soybean oil, have been used in PVC formulations as secondary plasticizers and stabilizers for many decades. Due to their high molecular weight the epoxy oils have limited compatibility and thereby restricted their use to small quantities [21]. Currently a biobased plasticizer, an acetylated fully hydrogenated fatty acid monoacylglyceride derived from castor oil (see Figure 18) is currently being sold under the trade name Soft-N-Safe® as a replacement to phthalate plasticizers by Dupont [47].

Our group has investigated fatty acid ester estolides derived from soybean oil as potential alternatives to phthalate plasticizers [40]. From these studies we found soy fatty acid ester estolides synthesized by ring opening of epoxy fatty acid esters provided compounds with similar plasticizer functionality in PVC as DOP. Further investigation of the composition of these soy fatty acid ester estolides found them to contain cyclic ether/tetrahydrofuran compounds in significant quantities [48]. The tetrahydrofuran derivatives were formed as the result of the ring opening of diepoxy linoleate using acetic acid. The objective of this current study is to improve upon the plasticizer properties of fatty acid ester estolides by using castor oil as starting material due to its more homogenous mixture of fatty acids (>90% ricinoleic acid). Experimental bioplasticizers were synthesized from castor oil in three steps: transesterification, acetylation, and epoxidation. The castor epoxy fatty acid ester estolides were evaluated for their plasticizer properties in PVC plastisol applications. The plasticizer properties were evaluated and compared with commercial plasticizers DINP and ELATUR CH (1,2-cyclohexanoic acid diisononyl ester, DINCH).

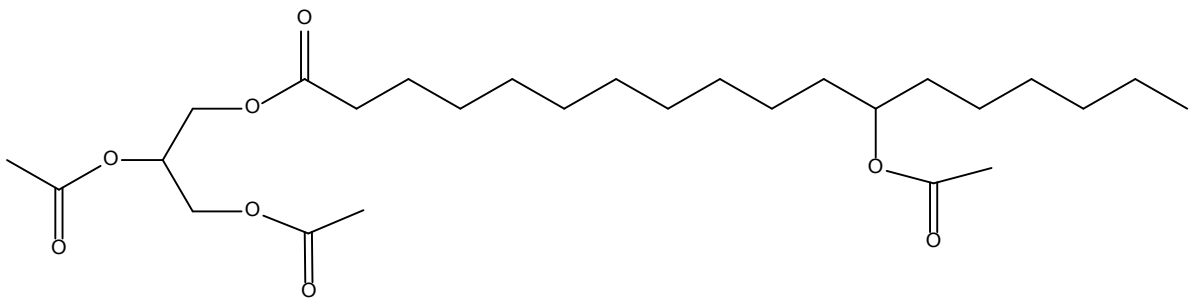


Figure 18 Structure of Soft-N-Safe® castor oil derived biobased plasticizer.

6.3.Materials and Methods

6.3.1. Materials

Castor Oil (refined), hydrogen peroxide (50% w/w H_2O), sodium methoxide (reagent grade), acetic anhydride (99.5%), Amberlite® IR120 (H+ form), and *n*-butanol (anhydrous, 99.8%) were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, WI). Diisopropyl ether (certified), hexanes (Certified ACS), sulfuric acid (ACS+), methanol (anhydrous), and basic alumina (60-325 mesh) were purchased from Fisher Scientific (Pittsburg, PA). DINP (VESTINOL 9) and ELATUR CH were obtained from Evonik Performance Materials (Marl, Germany).Magnesol® R60 (a magnesium silicate adsorbent) was obtained from The Dallas Group of America Inc. (Whitehouse, NJ). PVC (Vestolit B7021 ultra) was obtained from Mexichem (Tlalnepantla de Baz, Mexico). Epoxy soybean oil (Drapex 39) and stabilizer (Mark CZ 149) were obtained from Galata Chemicals (Southbury, CT). TLC was performed on Analtech (Newark, DE) Unisil GF 250μm silica plates developed with an appropriate solvent and visualized by charring on the hot plate after spraying with 50% sulfuric acid.

6.3.2. Instrumentation and Methods

^1H NMR spectra were recorded on either a Varian Unity 300 (300 MHz) spectrophotometer with a 4-nucleous probe and autosampler or a Varian Unity 400 (400 MHz) spectrophotometer. All experiments were run using $CDCl_3$ as a solvent with tetramethylsilane as internal standard.

Rheometric analysis was performed on Physica MCR 301 by Anton Paar (Graz, Austria) using PP25 plates. The resin, plasticizers, and stabilizers were mixed together into a paste and placed between the plates. The viscosity of the paste was measured as a function of temperature from room temperature to 180 °C and carried out with a frequency sweep between 0.1 and 120 Hz.

Shore A Hardness was measured using a Zwick Roell (Ulm, Germany) digital HPE II durometer on plastisol samples that were aged for 14 days.

Viscosity measurements on pure plasticizers were made on a Stabinger SVM 3000 Viscometer manufactured by Anton-Paar (Graz, Austria) according to ASTM International method D7042. Samples were introduced into the instrument and the dynamic viscosity was measured at 20 °C for each sample.

Tropical compatibility test was conducted to evaluate the plastisol films under high humidity and temperature conditions. The plastisol films were cut into 75 x 110 x 0.5 mm strips in duplicate and held over a sealed water bath at 70 °C for 1, 3, 7, 14, and 28 days. The films were removed from the bath at the given time, suspended freely in the air for one hour then the surfaces evaluated for sweating of plasticizer. The visual assessment graded according to the following: (0 = dry grip, smooth film; 1 = blunt grip, the film still dry, small amount of plasticizer is on the surface finger marks visible; 2 =

sticky handle, noticeable plasticizer on surface, finger marks clearly visible; 3 = weak, dry surface recognizable with naked eye; 4 = weak, liquid or greasy surface; 5 = strong dry surface; 6 = heavy greasy surface).

The films were wiped clean with an ethanol moistened paper towel and dried hanging freely in a 70 °C oven for 16 hours. After drying the films were hung at room temperature for one hour before the weight loss was measured. The weight loss was recorded as the arithmetic mean of the two samples.

Compounding of PVC with experimental and commercial plasticizers was conducted at Evonik Performance Materials GmbH (Marl, Germany). The experimental plasticizers were compared with commercial controls DINP (VESTINOL 9) and cyclohexane-1,2-dicarboxylic acid, diisononyl ester (ELATUR CH). Compounding was conducted using plastisol method. In the plastisol method PVC, plasticizers, and stabilizers (see formulation listed in Table 17) were mixed together into a paste. The paste was spread to a thickness of 1 mm then heated in a Werner Mathis oven at 200 °C for 2 minutes forming a thin plastic sheet.

Table 14 Formulation for plastisols

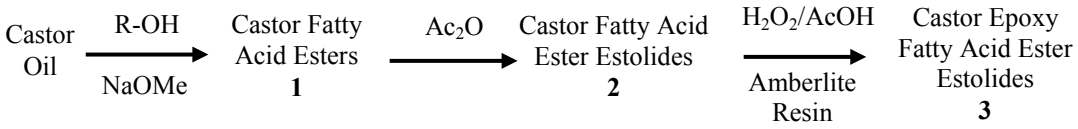
Formulation	Plastisol
PVC (Vestolit B7021 ultra)	100
Plasticizer	50
Epoxy Soybean Oil (Drapex 39)	3
Stabilizer (Mark CZ 149)	2

6.3.3. Synthetic Procedures

The sequence of reactions used to synthesize castor epoxy fatty acid ester estolides is shown in Scheme 1. In the first step, castor oil was transesterified with

methanol or *n*-butanol. The hydroxyl on the fatty acid backbone was acetylated and the double bond epoxidized.

Scheme 7 Reaction scheme to synthesize castor epoxy fatty acid ester estolides



Compound	R =
a	methyl
b	*n*-butyl

General Procedure for transesterification of Castor Oil with alcohol (**1a** and **1b**)*:* In a 2-L baffled reactor equipped with mechanical stirrer and a reflux condenser 1 kg Castor Oil was placed and heated to 110 °C under vacuum for 1 hour to remove moisture. After cooling under an inert atmosphere 4 mol eq. alcohol (methanol or *n*-butanol) and sodium methoxide (0.4% w/w Castor Oil) were added. The reactor was heated to slightly below the boiling point of the alcohol and allowed to react until the disappearance of the Castor Oil spot on TLC (10/90 hexanes/isopropyl ether) was observed (approximately 2-4 hours). The cloudy reaction mixture was phase separated and the bottom glycerol layer removed. Excess alcohol was removed by vacuum distillation. While still hot, 2% Magnesol was added and flask was placed under vacuum for 20 minutes. The Magnesol was removed by vacuum filtration to quantitatively yield light yellow oils of *Castor Fatty Alkyl Esters* (**1a** and **1b**). *Castor Fatty Acid Methyl Esters* (**1a**) ^{1}H NMR (300 MHz, Chloroform-d) δ 5.56 – 5.42 (m, 1H, =C**H-**), 5.42 – 5.26 (m, 1H, =C**H-**), 3.61 (s, 3H, -OC**H**$_3$), 3.60 – 3.47 (m, 1H, -C**H**OH), 2.25 (t, J = 7.5 Hz, 2H, -C(O)C**H**$_2$-), 2.15 (t, J =

6.6 Hz, 2H, =CHC**H**$_2$CHOH-), 2.08 – 1.89 (m, 2H, =CHC**H**$_2$CH$_2$-), 1.70 – 1.49 (m, 2H, -C(O)CH$_2$C**H**$_2$-), 1.41 (d, J = 6.5 Hz, 2H, -C**H**$_2$CHOH), 1.24 (d, J = 4.6 Hz, 15H, -C**H**$_2$-), 0.98 – 0.67 (m, 3H, -C**H**$_3$). *Castor Fatty Acid n-Butyl Esters* (**1b**) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.58 – 5.44 (m, 1H, =C**H-**), 5.44 – 5.26 (m, 1H, =C**H-**), 4.01 (t, J = 6.7 Hz, 2H, -OC**H**$_2$-), 3.67 – 3.49 (m, 1H, -C**H**OH), 2.25 (dt, J = 15.1, 7.7 Hz, 2H, -C(O)C**H**$_2$-), 2.20 – 2.09 (m, 2H, =CHC**H**$_2$CHOH-), 2.07 – 1.90 (m, 2H, =CHC**H**$_2$CH$_2$-), 1.65 – 1.48 (m, 4H, -C(O)CH$_2$C**H**$_2$-, -OCH$_2$C**H**$_2$-), 1.48 – 1.37 (m, 2H, -C**H**$_2$CHOH), 1.37 – 1.11 (m, 20H, -C**H**$_2$-), 1.02 – 0.78 (m, 6H, -C**H**$_3$).

*General Procedure for Acetylation of Castor Fatty Acid Alkyl Esters (***2a** and **2b**): To a flask equipped with a reflux condenser containing 1 kg Castor Fatty Acid Alkyl Esters (**1a** or **1b**) was added 1.5 mol of acetic anhydride. The flask was heated to 100 °C while mechanically stirring. After reacting for 8 hours excess acetic anhydride and acetic acid were removed by vacuum distillation. Magnesol (2% w/w Castor Fatty Acid Alkyl Ester) was added after cooling the distilled material to <100 °C and returned to vacuum for 1 hour. The Magnesol was removed by vacuum filtration to yield quantitatively *Castor Fatty Acid Alkyl Ester Estolides* (**2a** and **2b**) as orange/red oils. *Castor Fatty Acid Methyl Ester Estolides* (**2a**) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.40 (s, 1H, =C**H-**), 5.29 (s, 1H, =C**H-**), 4.91 – 4.72 (m, 1H, -C**H**OC(O)CH$_3$), 3.61 (s, 3H, -OC**H**$_3$), 2.25 (t, *J* = 7.6 Hz, 4H, -C(O)C**H**$_2$-, =CHC**H**$_2$CHOC(O)CH$_3$), 2.00 (d, *J* = 20.7 Hz, 5H, -C(O)C**H**$_3$, =CHC**H**$_2$CH$_2$-), 1.57 (s, 2H, -C(O)CH$_2$C**H**$_2$-), 1.47 (s, 2H, -C**H**$_2$CHOC(O)CH$_3$), 1.24 (d, *J* = 14.0 Hz, 17H, -C**H**$_2$-), 0.82 (d, *J* = 6.9 Hz, 3H, -C**H**$_3$). *Acetyl Castor Fatty Acid n-Butyl Ester Estolides* (**2b**) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.37 (s, 1H, =C**H-**), 5.26 (s, 1H, =C**H-**), 4.86 – 4.71 (m, 1H, -C**H**OC(O)CH$_3$), 3.99 (t, *J* = 6.7 Hz, 2H, -OC**H**$_2$-),

2.21 (t, *J* = 6.6 Hz, 4H, -C(O)C**H**$_2$-, =CHC**H**$_2$CHOC(O)CH$_3$), 2.07 – 1.85 (m, 6H, -C(O)C**H**$_2$-, =CHC**H**$_2$CHOC(O)CH$_3$), 1.63 – 1.39 (m, 6H, -C(O)CH$_2$C**H**$_2$-, -C**H**$_2$CHOC(O)CH$_3$, -OCH$_2$C**H**$_2$-), 1.39 – 1.06 (m, 21H, -C**H**$_2$-), 0.83 (dt, *J* = 22.1, 7.1 Hz, 6H, -C**H**$_3$).

*General Procedure for Epoxidation of Castor Fatty Acid Alkyl Ester Estolides (***3a** *and* **3b***):* The castor fatty acid alkyl ester estolides were epoxidized using a method adapted from Sinadinovic-Fiser [43]. To a flask equipped with a reflux condenser and stirrer was added 1 kg of one of the castor fatty acid alkyl ester estolides (**2a** or **2b**), 0.5 mol per double bond glacial acetic acid, and 5% (w/w Acetyl Castor Fatty Acid Alkyl Esters) Amberlite IR 120 (H+ form). The contents were heated to 60 °C while mechanically stirring at 800 RPM. To the reaction flask H_2O_2 (1.1 mol per double bond) (50% w/w H_2O) was added and the flask removed from the heating source. The exothermic reaction was allowed to further heat the reaction mixture to 75 °C. The reaction was maintained at 75°C with initial cooling (1 hour) followed by heating for an additional 6 hours. The crude reaction mixture was filtered while warm to remove the Amberlite resin and the aqueous layer was removed. The filtrate was vacuum distilled to remove unreacted acetic acid, H_2O, and H_2O_2. After the distillation, 2% Magnesol was added to the retentate and returned to vacuum for 20 minutes. While still warm the Magnesol was removed by vacuum filtration to quantitatively yield pale yellow oils of *Castor Epoxy Fatty Acid Alkyl Ester Estolides* (**3a** and **3b**). *Castor Epoxy Fatty Acid Methyl Ester Estolides* (**3a**) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.97 (s, 1H, -C**H**OC(O)CH$_3$), 3.56 (s, 3H, -OC**H**$_3$), 2.87 (s, 1H, epoxy-C**H**), 2.80 (s, 1H, epoxy-C**H**), 2.21 (s, 2H, -C(O)C**H**$_2$-), 2.06 – 1.89 (m, 3H, -C(O)C**H**$_3$), 1.74 (d, *J* = 15.2 Hz, 2H, epoxy-CHC**H**$_2$CHOC(O)CH$_3$), 1.63 (t, *J* =

7.3 Hz, 2H, epoxy-CHC**H**$_2$-), 1.52 (s, 2H, -C(O)CH$_2$C**H**$_2$-), 1.40 (s, 4H, -C**H**$_2$CHOC(O)CH$_3$), 1.21 (s, 15H, -C**H**$_2$-), 0.78 (s, 3H, -C**H**$_3$) or *Castor Epoxy Fatty Acid n-Butyl Ester Estolides* (**3b**) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.97 (s, 1H, -C**H**OC(O)CH$_3$), 4.02 – 3.92 (m, 2H, -OC**H**$_2$-), 2.87 (s, 1H, epoxy-C**H**), 2.80 (dt, *J* = 12.1, 6.0 Hz, 1H, epoxy-C**H**), 2.30 – 2.14 (m, 2H, -C(O)C**H**$_2$-), 2.08 – 1.90 (m, 3H, -C(O)C**H**$_3$), 1.73 (s, 2H, epoxy-CHC**H**$_2$CHOC(O)CH$_3$), 1.65 (s, 2H, epoxy-CHC**H**$_2$-), 1.60 – 1.46 (m, 4H, -C(O)CH$_2$C**H**$_2$-, -OCH$_2$C**H**$_2$-), 1.40 (s, 2H, -C**H**$_2$CHOC(O)CH$_3$), 1.33 – 1.11 (m, 15H, -C**H**$_2$-), 0.99 – 0.72 (m, 6H, -C**H**$_3$).

6.4.Results and Discussion

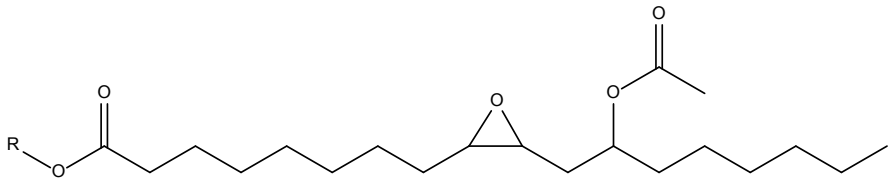
To be useful as a plasticizer a compound must contain molecular features that allow it to be compatible with PVC. One of the features is the appropriate hydrophobic/hydrophilic balance to provide compatibility with PVC. This balance can be obtained by increasing the carbon chain lengths or incorporation polar functional groups such as epoxy groups onto the compound. Ideally the molecular weight of the compound must be between 300-500 g/mol. This molecular weight range provides enough mobility for the compound to incorporate into the PVC matrix while also minimizing migration out of the polymer after compounding. Due to the high processing temperatures in PVC compounding, this weight range also minimizes volatility of the plasticizer during compounding.

Soy fatty acid ester estolides with high estolide content contained many of these structural features and showed promising plasticizer properties in PVC applications [40]. Further investigation of the composition of these soy fatty acid ester estolides found them

to contain cyclic ether/tetrahydrofuran derivatives formed during the epoxy ring opening reaction of diepoxy linoleate [48]. Soybean oil contains a high concentration of linoleic acid thus estolides prepared via ring opening of epoxy fatty acid esters from soybean oil would have a considerable amount of tetrahydrofuran derivatives. The effect of these structures on the plasticizing ability of soy fatty acid ester estolides is currently unknown.

The epoxy functional group has long been known to react with halogen acids to form halohydrins. Due to this reaction mechanism, epoxy oils are used in PVC formulations to prevent the degradation of the polymer by scavenging hydrochloric acid liberated during the high temperature compounding of PVC [2]. Due to its high molecular weight (~1000 g/mol) ESBO has limited compatibility with PVC and will exude at high concentrations. Reduction of the molecular weight of ESBO by transesterification with alkyl alcohols was shown to provide compounds with good plasticizing properties but higher volatility due to the molecular heterogeneity of the soybean oil [15,20].

Castor oil contains much lower heterogeneity due to its >90% ricinoleic acid content. The hydroxyl function and double bond of ricinoleic acid esters can be acetylated and epoxidized, respectively, to form an epoxy fatty acid ester estolide. This compound would not have the ability to cyclize to form tetrahydrofuran structures and would also retain the epoxy function that stabilizes PVC. Using this synthetic strategy, we synthesized the two castor epoxy fatty acid ester estolides (shown in Figure 28) and evaluated them as plasticizers in PVC.



Compound	R
3a	methyl
3b	*n*-butyl

Figure 19 Structure of castor epoxy fatty acid ester estolides of this study

The first step of the synthesis involved the transesterification of castor oil with either methanol or *n*-butanol which quantitatively yielded castor fatty acid alky esters **1a** and **1b**. The hydroxyl functionality of the castor fatty acid alkyl esters was acetylated using acetic anhydride in the second step of the reaction sequence giving castor fatty acid alkyl ester estolides **2a** and **2b**. In the final step of the reaction sequence, the double bond was epoxidized using *in-situ* generated peracetic acid.

The synthesized plasticizers were characterized and their physical properties are compared with DINP and ELATUR CH in Table 18. From the table it can be seen the experimental plasticizers have higher acid value than the commercial control plasticizers. This may be due to some ester hydrolysis occurring during the epoxidation reaction. Based on our experience the acid value can be further reduced by using 1-2% basic alumina to adsorb the free acids and reduce the acid value to less than 1 mg KOH/g. The hydroxyl values of the experimental plasticizers are also higher than the commercial materials. This may be due to some of the epoxy rings opening during the epoxidation reaction or cleavage of the estolide ester functionality. The viscosities of the experimental

plasticizers are in the same range as the commercial controls. The color of the experimental plasticizers are higher than the commercial controls but may be reduced by bleaching the materials after the final reaction step.

Table 15 Physical properties of experimental and commercial plasticizers

Plasticizer	Acid Value (mg KOH/g)	Hydroxyl Value (mg KOH/g)	Oxirane Oxygen (%)	Viscosity (cP @ 20°C)	Color (APHA)
DINP	0.04 [1]	-	-	75	4
ELATUR CH	0.05 [2]	-	-	50	2
3a	2.54	30.5	2.43	64	177
3b	4.91	20.9	3.21	80	144

Acid Value, AOCS Official Method Cd 3d-63 (Firestone 2009)
Hydroxyl Value, AOCS Official Method AOCS Cd13-60 (Firestone 2009)
Oxirane Oxygen, ASTM International Method D1652-04 (ASTM International 2004)
[1] From *Evonik* DINP (VESTINOL 9) Plasticizer technical data sheet
[2] From *Evonik* ELATUR CH Plasticizer technical data sheet

The volatility of the pure plasticizers after 10 minutes at 200 °C is shown in Figure 29. The volatility of experimental plasticizer **3a** is higher than both commercial controls whereas experimental plasticizer **3b** has a volatility that is in-between the control plasticizers. The higher volatility of **3a** is due to its lower molecular weight.

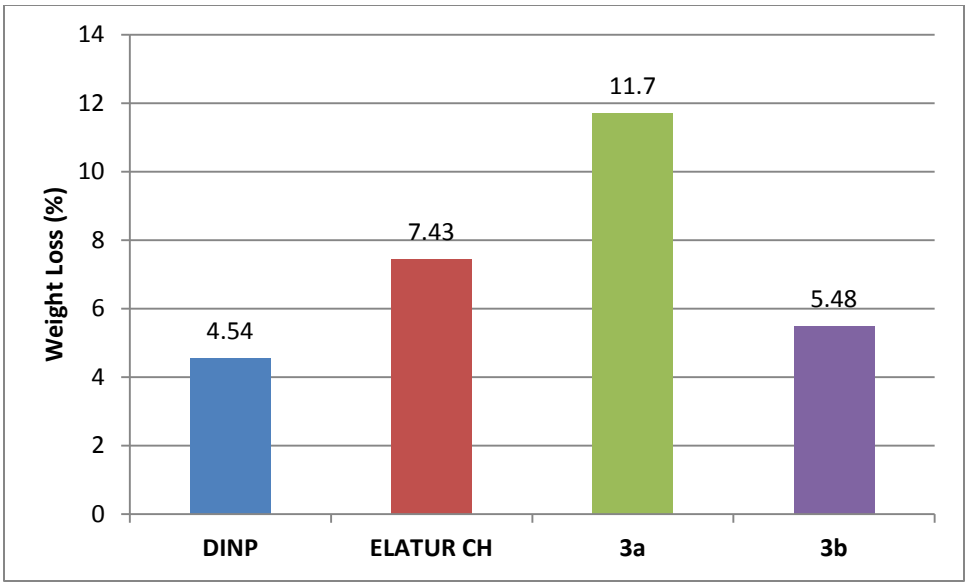


Figure 20 Volatility of commercial and experimental plasticizers at 200 °C after 10 minutes

The gelation curves of PVC plasticized with experimental and commercial plasticizers is shown in Figure 30. From the curve it can be seen that the experimental plasticizers reduce the PVC gelation temperature (indicated by the sharp increase in viscosity at a given temperature) more than the commercial controls. Lower gelation temperature is a desirable property for a plasticizer and also indicates they may be useful as fast fusing agents in plastisol applications.

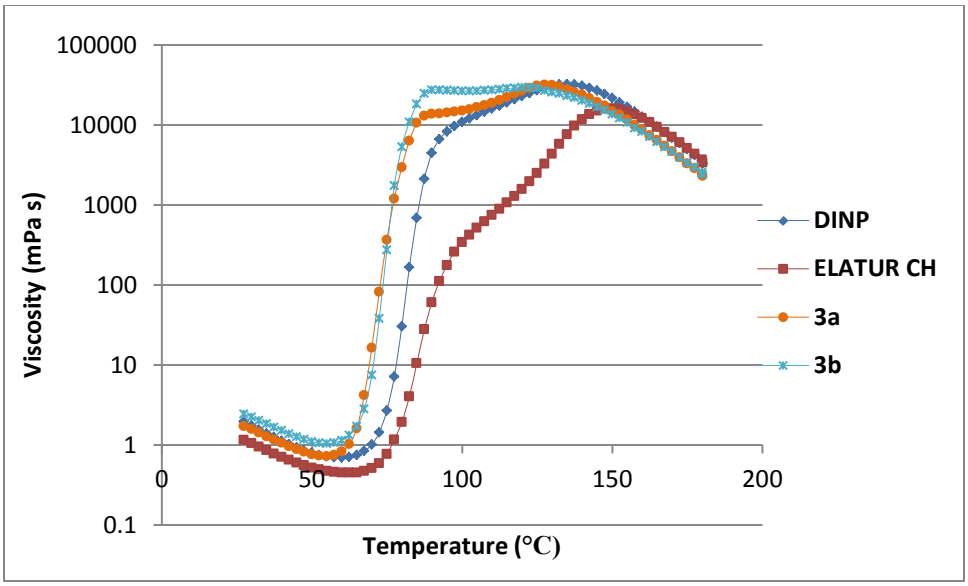


Figure 21 Gelation curves of PVC compounded with commercial and experimental plasticizers

The viscosity at different shear rates of plastisols compounded with experimental and commercial plasticizers is shown in Figure 22. The plastisol prepared with experimental plasticizer **3b** had the highest viscosity of all the plastisols tested but was still within an acceptable range. The plastisol prepared with **3a** had a viscosity profile that was very similar to the plastisol prepared with DINP.

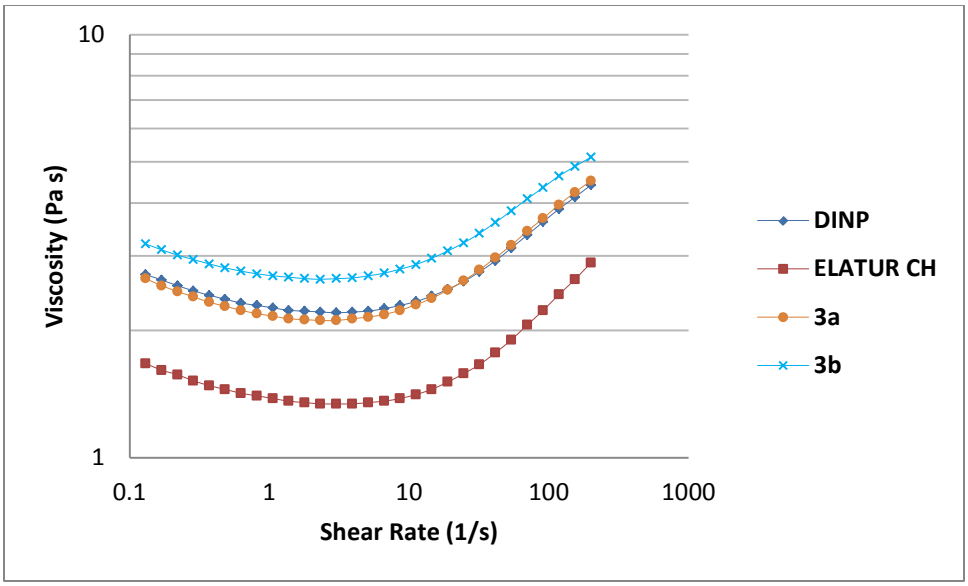


Figure 22 Plastisol viscosity of PVC compounded with commercial and experimental plasticizers.

The efficiency of the plasticizers was measured by Shore A Hardness and the results shown in Figure 31. Both experimental plasticizers had higher efficiency than the commercial controls. Experimental plasticizer **3b** had the highest efficiency thus would require less plasticizer addition to achieve a desired hardness which would save on cost.

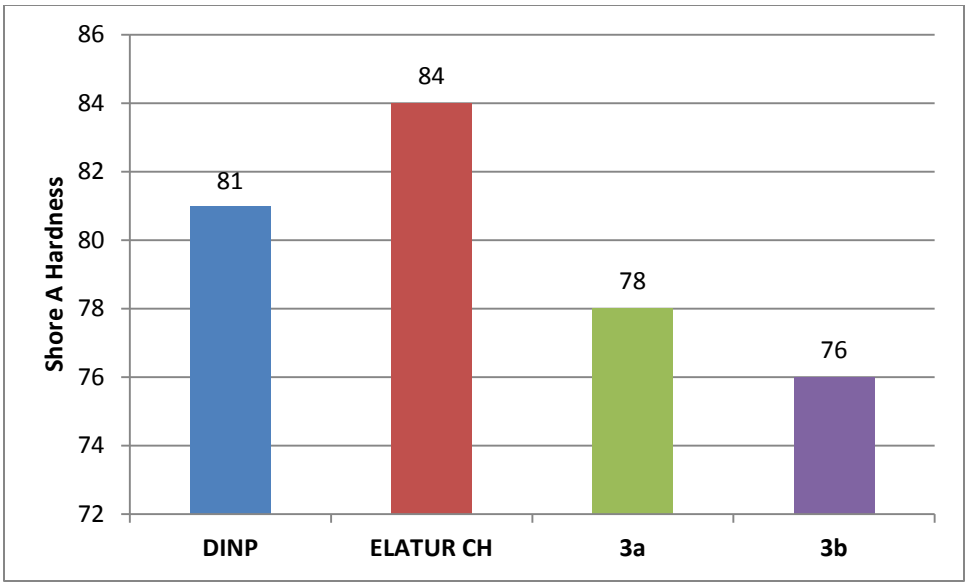


Figure 23 Shore A hardness of PVC compounded with commercial and experimental plasticizers

The water storage and extraction of plasticizers from plastisols was measured by immersion of the plastisols in a water bath and determining the weight change after one day, seven days, and after drying. The results of the water storage experiment are shown in Figure 32. The plastisols compounded with experimental plasticizers showed very little water uptake after one day but showed weight loss after seven days and also after drying indicating a loss of plasticizer from the plastisol with water contact. Plastisols prepared with experimental plasticizer **3a** showed greater loss than plastisols prepared with **3b**. The greater molecular weight and less polar *n*-butyl group may be contributing to the lower loss of plasticizer into water.

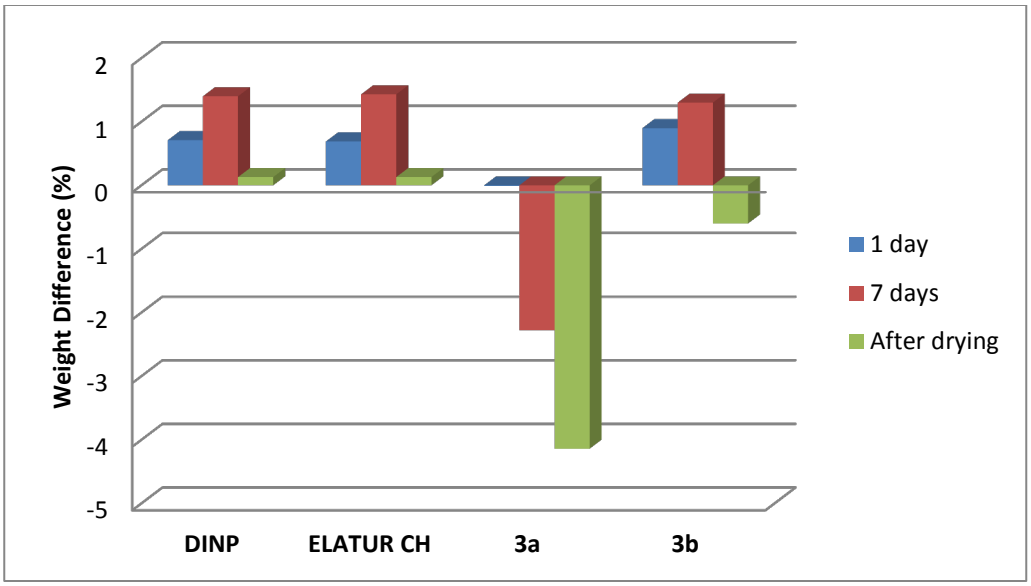


Figure 24 Water storage of PVC compounded with commercial and experimental plasticizers

Loop compression tests measure the exudation of plasticizer from plastisol sheet bent at 180° and given a rating of 0-3 with 0 being no exudation and 3 having high exudation. The tests were performed on the plastisols compounded with experimental and commercial plasticizers over the course of two weeks with the results listed in Table 16. As the table indicates, both experimental plasticizers showed no exudation over the course of two weeks.

Table 16 Plastisol loop exudation test[1]

Plastisol	1 day	7 days	14 days
DINP	0	0	0
ELATUR CH	0	0	0
3a	0	0	0
3b	0	0	0

[1] ASTM D 3291

0 = no exudation, 0.5 = very little, 1.0 = slight,
2.0 = medium, 3.0 = heavy, >3.0 = extreme

The glass transition temperature (Tg) of the plastisols compounded with experimental and commercial plasticizers was measured by DSC and is shown in Figure 33. Experimental plasticizer **3a** reduced the Tg of PVC slightly more than DINP but not as much as ELATUR CH. Experimental plasticizer **3b** reduced the Tg of PVC slightly less than DINP. The results of this test indicate the experimental plasticizers would be as useful as the controls in low temperature applications.

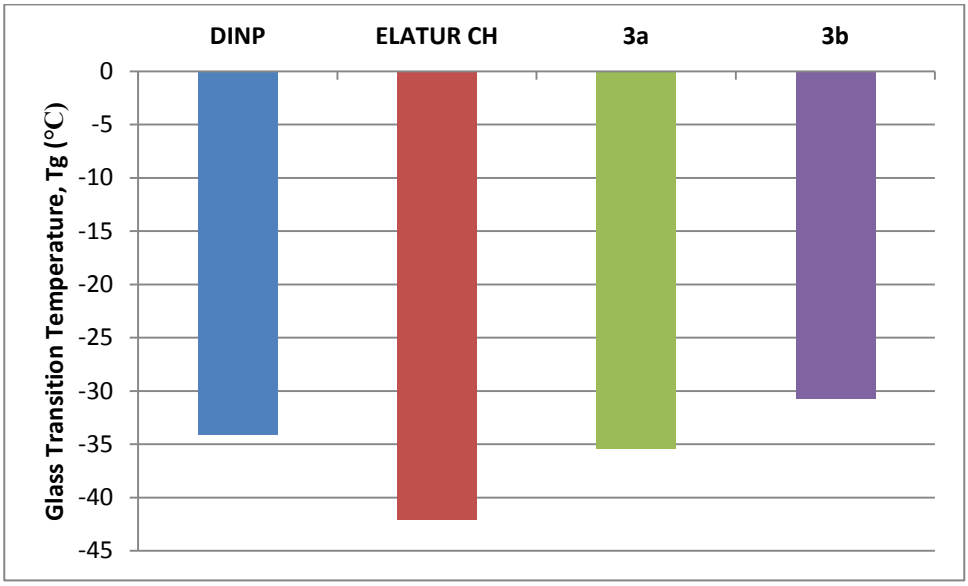


Figure 25 Glass transition temperature of PVC films compounded with commercial and experimental plasticizers.

The experimental plasticizer **3b** performed better than the commercial plasticizers in almost all functional evaluations. This prompted us to further evaluate **3b**'s compatibility by measuring the plasticizer exudation under tropical conditions of high humidity and temperature. The plastisols compounded with **3b** were stored over water in a sealed water bath at 70 °C for various lengths of time. The plastisol samples were

removed after 1, 3, 7, 14, and 28 days and visually assessed for plasticizer exudation, the results are shown in Figure 26. Under tropical conditions experimental plasticizer **3b** showed visible exudation after 1 and 3 days and heavy exudation after 14 and 28 days. After removal from the water bath conditions the films were wiped clean of exudate with an ethanol soaked paper towel and dried for 16 hours at 70 °C. The weight loss of the films was measured and the results shown in Figure 27. The films showed minor weight loss up to 14 days but after 28 days there was a significant loss.

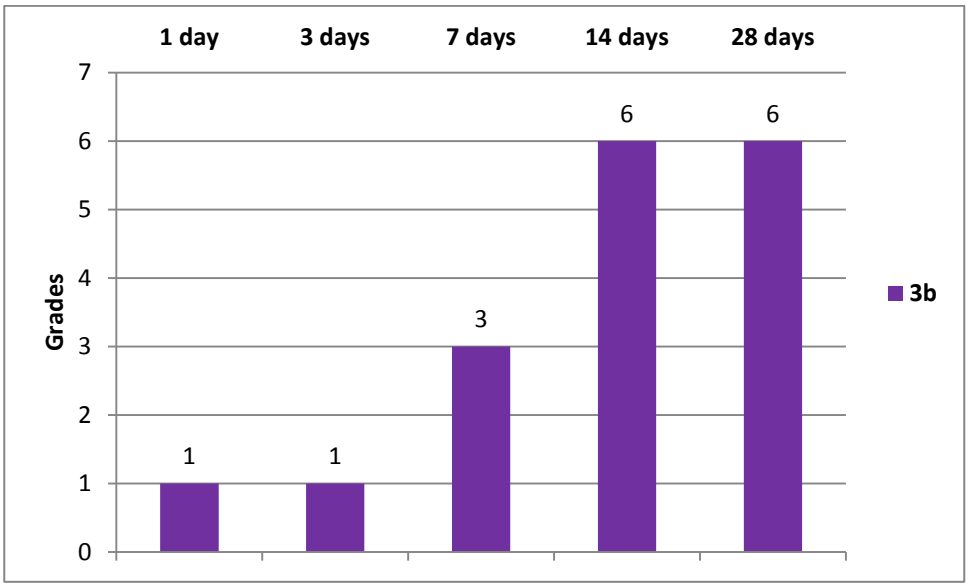


Figure 26 Optical properties of plastisols compounded with 3b after exposure to tropical conditions. (Key: 0 = dry grip, smooth film; 1 = blunt grip, the film still dry, small amount of plasticizer is on the surface finger marks visible; 2 = sticky handle, noticeable plasticizer on surface, finger marks clearly visible; 3 = weak, dry surface recognizable with naked eye; 4 = weak, liquid or greasy surface; 5 = strong dry surface; 6 = heavy greasy surface)

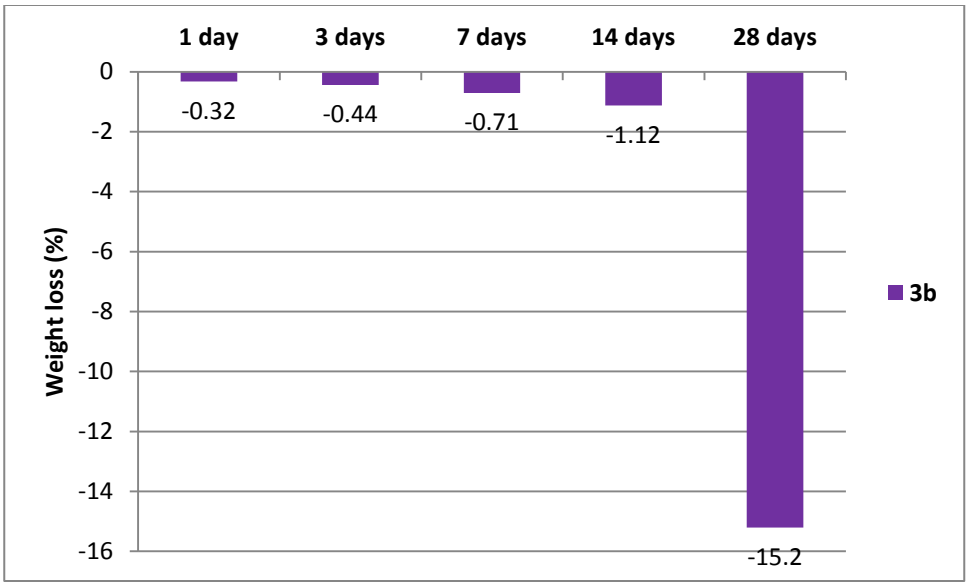


Figure 27 Weight loss of plastisols compounded with **3b** after exposure to tropical conditions.

6.5.Conclusions

Two experimental plasticizers were synthesized from castor oil with methyl and *n*-butyl fatty acid ester head group containing epoxy and estolide functionalities. The functional properties of the experimental plasticizers compounded with PVC showed excellent gelation, viscosity, efficiency, exudation, and thermal properties compared to commercial control plasticizers. Further testing of *n*-butyl ester under tropical conditions revealed limited compatibility. These plasticizers would be useful in dry applications such as wire and cable coatings or wall coverings but to be used in higher humidity/water contact applications further structural modifications of the plasticizer are necessary.

Chapter 7: Soy epoxy fatty acid alkyl ester estolides as bioplasticizers for poly (vinyl chloride)

To be communicated

7.1.Synopsis

A series of epoxy fatty acid ester estolides were synthesized from soybean oil and evaluated as alternative plasticizers to phthalates in poly(vinyl chloride)(PVC) applications. A number of soy fatty acid alkyl esters were prepared by transesterification with various aliphatic alcohols (methyl, *n*-butyl, *n*-pentyl, mixed pentyl, 2-ethyl hexyl, and isononyl). The double bonds of the fatty acid esters were epoxidized using *in situ* generated per acetic acid in the presence of solid acid catalyst, Amberlite IR120. The epoxy rings on the epoxy fatty acid esters were partially ring opened with acetic anhydride to yield the final products, epoxy fatty acid ester estolides. The experimental epoxy fatty acid ester estolides were compounded with PVC by a plastisol method and their plasticizer properties were evaluated and compared to commercial plasticizers diisononyl phthalate (DINP) and cyclohexane-1,2-dicarboxylic acid, diisononyl ester (DINCH, Elatur® CH). The lower molecular weight experimental plasticizer methyl ester showed better fast fusing properties but had high volatility compared to commercial plasticizers. The medium molecular weight butyl and pentyl esters showed comparable or better general purpose plasticizer properties, while the higher molecular weight experimental plasticizers 2-ethyl hexyl and isononyl) showed inferior properties compared to DINP and Elatur® CH.

7.2.Introduction

Poly(vinyl chloride), (PVC) is the third largest commodity plastic due to its price, performance and suitablity for a myriad of applications. These range from very rigid applications such as pipes and siding to flexible applications such as flooring and cable coatings. The versatility of PVC comes from its ability to be compounded with plasticizers that impart flexibility proportional to concentration. When compounded with PVC, plasticizers imbed in the amorphous regions of the polymer and reduce its intermolecular interactions. This lowers the glass transition temperature (Tg) of PVC which increases its flexibility. Due to the high processing temperatures of PVC compounding, plasticizers are typically high boiling, non-volatile organic liquids.

The most prevalent class of plasticizers on the market are phthalate esters. Of the various types of phthalates dioctyl phthalate (DOP) continues to be the most used in PVC. DOP has been used in PVC since the 1930's but has only recently come under scrutiny for its adverse health effects [8,9,36]. Plasticizers are noncovalently bound to the polymer and migrate out of the PVC where they can enter the environment and get ingested by consumers. This has resulted in numerous organizations banning different phthalates in sensitive applications such as children's toys. As a result the industry shifted away from the use of DOP in many applications and currently uses diisononyl phthalate (DINP) in its place. DINP has less health concerns than DOP but public awareness of the health and safety of phthalates has resulted in a shift away from the products that contain phthalates. This has prompted some retailers to remove products containing phthalates from their stores [49].

As a result consumers and industry are looking for alternatives that offer the same functionality as the phthalates without the harmful health effects. Plasticizers synthesized

form natural materials such as vegetable oils may offer a solution to this problem. Soy fatty acid ester estolides formed by the epoxy ring opening of epoxy fatty acid esters have been shown to successfully plasticize PVC [40]. These materials showed good compatibility with PVC but the ring opening reaction of diepoxy linoleate resulted in formation of tetrahydrofuran derivatives that had unknown plasticizing effect [48]. In order to prepare compounds which did not contain the tetrahydrofuran groups and retained the epoxy functionality, epoxy fatty acid ester estolides were prepared from castor oil [50]. It was successfully shown that the castor epoxy fatty acid ester estolides were very effective plasticizers and the epoxy functionality contributes to the stabilization of the PVC. This implies that the tetrahydrofuran ring system is neither beneficial nor essential. However, two hydroxyl groups are being used in the formation of the tetrahydrofuran ring system thereby limiting the potential formation of more estolides or retaining the epoxy function, both of which are beneficial for functionality. Soybean oil is more readily available and cost effective than castor oil. Our objective for the current work was to use soybean oil as the starting material to prepare epoxy fatty acid ester estolides to be used as plasticizers for PVC. To test the effect of polarity on the compounds the fatty acid ester headgroup would be esterified with different molecular weight alcohols from C1 to C9. The fatty acid ester estolides were compounded with PVC using a plastisol method and evaluated for their plasticizer functionality compared to commercial controls.

7.3.Materials and Methods

7.3.1. Materials

Soybean oil (SBO) and soy fatty acid methyl ester (FAME, or soy biodiesel) were obtained from Cargill Inc. (Minneapolis, MN). Hydrogen peroxide (50% w/w H_2O), sodium methoxide (reagent grade), acetic acid (ACS reagent >99.7%), acetic anhydride

(99.5%), Amberlite® IR120 (H+ form), *n*-butanol (anhydrous, 99.8%), ethyl acetate (ACS reagent >99%), and 2-ethylhexanol (>99.6%) were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, WI). Diisopropyl ether (certified), hexanes (Certified ACS), sulfuric acid (ACS+), and basic alumina (60-325 mesh) were purchased from Fisher Scientific (Pittsburg, PA). Mixed pentanol (65.7% *n*-pentanol, 32.1% 2-methyl-1-butanol, total C5 alcohols 99.35%) was obtained from BASF (Ludwigshafen, Germany). *n*-pentanol, isononanol, DINP (Vestinol 9), and Elatur® CH were obtained from Evonik Performance Materials (Marl, Germany). Magnesol® R60 (a magnesium silicate adsorbent) was obtained from The Dallas Group of America Inc. (Whitehouse, NJ). PVC (Vestolit B7021 ultra) was obtained from Mexichem (Tlalnepantla de Baz, Mexico). Epoxy soybean oil (Drapex 39) and stabilizer (Mark CZ 149) were obtained from Galata Chemicals (Southbury, CT). TLC was performed on Analtech (Newark, DE) Unisil GF 250μm silica plates developed with an appropriate solvent and visualized by charring on the hot plate after spraying with 50% sulfuric acid.

7.3.2. Instrumentation and Methods

^{1}H NMR spectra were recorded on a either a Varian Unity 300 (300 MHz) spectrophotometer with a 4-nucleous probe and autosampler or a Varian Unity 400 (400 MHz) spectrophotometer. All experiments were run using $CDCl_3$ as a solvent with tetramethylsilane as internal standard.

Viscosity measurements were made on a Stabinger SVM 3000 Viscometer manufactured by Anton-Paar (Graz, Austria) according to ASTM International method D7042. Samples were introduced into the instrument and the dynamic viscosity was measured at 20 °C for each sample.

Physical Properties of plasticizers listed in Table 18 (acid value and saponification value) were determined by titration in triplicate according to the Official Methods and Recommended Practices of the AOCS (Cd 3d-63, Cd 3-25 and Cd 13-60 respectively). Oxirane oxygen was measured in triplicate according to ASTM International method D1652-04. The color of the experimental plasticizers and controls was measured according to ASTM International method D1209-05.

Rheometric analysis was performed on Physica MCR 301 by Anton Paar (Graz, Austria) using PP25 plates. The resin, plasticizers, and stabilizers were mixed together into a paste and placed between the plates. The viscosity of the paste was measured as a function of temperature from room temperature to 180 °C and carried out with a frequency sweep between 0.1 and 120 Hz.

Shore A Hardness was measured using a Zwick Roell (Ulm, Germany) digital HPE II durometer on plastisol samples that were aged for 14 days.

Compounding of PVC with experimental and commercial plasticizers was conducted at Evonik Performance Materials GmbH (Marl, Germany). The experimental plasticizers were compared with commercial controls DINP and cyclohexane-1,2-dicarboxylic acid, diisononyl ester (Elatur CH). Compounding was conducted using the plastisol method. In the plastisol method PVC, plasticizers, and stabilizers (see formulation listed in Table 17) were mixed into a paste. The paste was spread to a thickness of 1 mm then heated in a Werner Mathis oven at 200 °C for 2 minutes forming a thin plastic sheet.

Table 17 Plastisol formulation

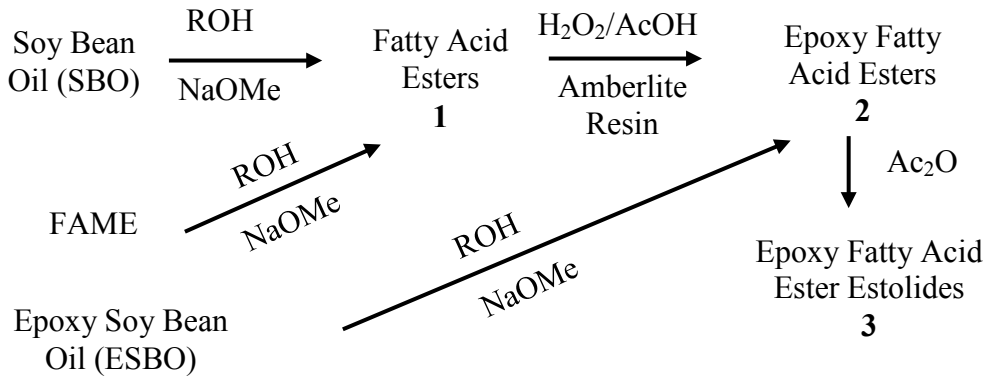
Formulation	phr [1]
PVC (Vestolit B7021 ultra)	100
Plasticizer	50
Epoxy Soybean Oil (Drapex 39)	3
Stabilizer (Mark CZ 149)	2

[1] phr = parts per hundred resin

7.4.Synthetic Procedures

The sequence of reactions used to synthesize epoxy fatty alkyl acid ester estolides is shown in Scheme 8. The triacylglycerols of soybean oil were transesterified with lower alcohol (methanol) and medium alcohol (*n*-butanol) into fatty acid alkyl esters in the first step of the reaction. Transesterification of soybean oil with higher alcohols (pentyl, ethyl hexyl, and isononyl) were more problematic as the glycerol did not cleanly separate from the fatty acid alkyl esters. In order to overcome this, commercially available soy FAME was used as starting material. The transesterification of FAME with these higher alcohols under slight vacuum to remove methanol resulted in cleaner products and higher yields. In the second step, the double bonds of the fatty acid esters were epoxidized with the *in situ* generated peracetic acid produced by the reaction of hydrogen peroxide and acetic acid in the presence of solid acid catalyst, Amberlite IR120. The epoxy groups were partially ring opened with acetic anhydride to form epoxy fatty acid ester estolides in the final reaction step. Alternatively epoxy soybean oil (ESBO) can be used as starting material to produce epoxy fatty acid alkyl esters that would reduce the number of steps in the reaction sequence. This method was used for the synthesis of the epoxy fatty acid isononyl esters (**2f**).

Scheme 8 Reaction scheme to synthesize fatty acid alkyl ester estolides



Compound	R =
a	methyl
b	*n*-butyl
c	*n*-pentyl
d	mixed pentyl
e	2-ethylhexyl
f	isononyl

Fatty Acid Methyl Esters (FAME)(**1a**)*:* aka, biodiesel is available commercially and was used without further purification as starting material for the higher molecular weight fatty acid ester synthesis. ^{1}HNMR of *Soy Fatty Acid Methyl Esters* (**1a**): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.32 (m, 2 H, =C**H-**), 3.65 (s, 3 H, -OC**H**$_3$), 2.75 (t, 2 H, =CH-C**H**$_2$-CH=), 2.29 (t, 2 H, -C(O)C**H**$_2$-), 2.02 (m, 2 H, =CHC**H**$_2$-), 1.60 (m, 2 H, -C(O)CH$_2$C**H**$_2$-), 1.24 (d, 18 H, -C**H**$_2$-), 0.86 (t, 3 H, -C**H**$_3$).

General procedure for transesterification of SBO with alkyl alcohols (**1b**)*:* A 5-L baffled reactor equipped with mechanical stirrer and a reflux condenser was charged with 2 kg SBO and heated to 110°C under vacuum for 1 hour to remove moisture. After cooling under an inert atmosphere 4 mol eq. *n*-butanol and sodium methoxide (0.4% w/w SBO) were added. The reactor was heated to slightly below the boiling point of the butanol (118 °C) and reacted until the disappearance of the SBO spot on TLC (20/80

hexanes/isopropyl ether) (approximately 2-4 hours). The cloudy reaction mixture was phase separated and the bottom glycerol layer was removed. Excess alcohol was removed by distillation. While still, hot 2% Magnesol was added and flask was placed under vacuum for 20 minutes. The Magnesol was removed by vacuum filtration to quantitatively yield *Fatty Acid n-Butyl Esters* (**1b**) as a light yellow oil. Transesterification of soybean oil using a similar procedure with the higher alcohols was performed but the separation of glycerol was not as clean as the with the lower alcohols (methanol and *n*-butanol). *Soy Fatty Acid n-Butyl Esters* (**1b**): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.48 – 5.20 (m, 3H, =C**H**-), 4.05 (t, *J* = 6.7 Hz, 2H, -OC**H**$_2$-), 2.76 (q, *J* = 5.8, 5.3 Hz, 2H, =CHC**H$_2$**CH=), 2.40 – 2.17 (m, 2H, -C(O)C**H**$_2$-), 2.02 (dt, *J* = 11.0, 5.7 Hz, 4H, =CHC**H**$_2$-), 1.73 – 1.49 (m, 4H, -C(O)CH$_2$C**H**$_2$-, -OCH$_2$C**H**$_2$-), 1.49 – 1.13 (m, 21H, -C**H**$_2$-), 1.02 – 0.78 (m, 6H, -C**H**$_3$).

General procedure for transesterification of soy FAME with alkyl alcohols (**1c-d**)*:* A 2-L round bottom reactor equipped with mechanical stirrer and a short path distillation condenser was charged with 1 kg soy FAME (**1a**) and heated to 110°C under vacuum for 1 hour to remove moisture. After cooling under an inert atmosphere 1.2 mol eq. alkyl alcohol (*n*-pentyl, mixed pentyl, or 2-ethylhexyl) and sodium methoxide (0.2% w/w SBO) were added. The reactor was heated slightly below the boiling point of the alcohol under a partial vacuum to collect the methanol formed during the reaction. The reaction was run until the disappearance of the soy FAME spot on TLC (20/80 hexanes/isopropyl ether) was observed (approximately 2-4 hours). Excess alkyl alcohol was removed by vacuum distillation. While still hot, 2% Magnesol was added and the flask was placed under vacuum for 20 minutes. The Magnesol was removed by vacuum filtration to

quantitatively yield light yellow oils *Fatty Acid n-Pentyl Esters* (**1c**), *Fatty Acid mixed Pentyl Esters* (**1d**), *Fatty Acid 2-Ethylhexyl Esters* (**1e**). *Soy Fatty Acid n-Pentyl Esters* (**1c**): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.44 – 5.18 (m, 3H, =C**H-**), 4.03 (t, *J* = 6.7 Hz, 2H, -OC**H**$_2$-), 2.74 (t, *J* = 5.7 Hz, 1H, =CHC**H$_2$**CH=), 2.36 – 2.14 (m, 2H, -C(O)C**H**$_2$-), 2.14 – 1.85 (m, 4H, =CHC**H**$_2$-), 1.73 – 1.49 (m, 4H, -C(O)CH$_2$C**H**$_2$-, -OCH$_2$C**H**$_2$-), 1.40 – 1.16 (m, 30H, -C**H**$_2$-), 1.02 – 0.76 (m, 6H, -C**H**$_3$). *Soy Fatty Acid mixed Pentyl Esters* (**1d**): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.36 – 5.20 (m, 3H, =C**H-**), 3.99 (t, *J* = 6.7 Hz, 2H, -OC**H**$_2$-), 3.94 – 3.74 (m, 1H, -OC**H**(CH$_3$)CH$_2$-), 2.70 (t, *J* = 6.6 Hz, 1H, =CHC**H$_2$**CH=), 2.30 – 2.14 (m, 2H, -C(O)C**H**$_2$-), 1.97 (p, *J* = 7.8, 7.4 Hz, 4H, =CHC**H**$_2$-), 1.63 – 1.52 (m, 5H, -C(O)CH$_2$C**H**$_2$-, -OCH$_2$C**H**$_2$-, -OCH(CH$_3$)C**H**$_2$-), 1.34 – 1.14 (m, 21H, -C**H**$_2$-), 0.90 – 0.77 (m, 6H, -C**H**$_3$). *Soy Fatty Acid 2-Ethylhexyl Esters* (**1e**): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.45 – 5.21 (m, 3H, =C**H-**), 3.96 (dd, *J* = 5.8, 1.4 Hz, 2H, -OC**H**$_2$-), 2.75 (t, *J* = 6.5 Hz, 1H, =CHC**H$_2$**CH=), 2.27 (t, *J* = 7.5 Hz, 2H, -C(O)C**H**$_2$-), 2.02 (dt, *J* = 14.9, 7.4 Hz, 4H, =CHC**H**$_2$-), 1.57 (dt, *J* = 20.7, 6.4 Hz, 3H, -C(O)CH$_2$C**H**$_2$-, -OCH$_2$C**H**), 1.42 – 1.18 (m, 36H, -C**H**$_2$-), 0.95 – 0.78 (m, 9H, -C**H**$_3$).

*General Procedure for Epoxidation of Soy Fatty Acid Esters (***2a-d***):* The following method was adapted from Sinadinovic-Fiser with slight modification [43]. A reactor containing 1 kg of one of the soy fatty acid alkyl esters (**1a-d**), 0.5 mol per double bond glacial acetic acid and 5% (w/w fatty acid esters) Amberlite IR 120 (H+ form) was heated to 60 °C while mechanically stirring at 800 RPM. To the reactor was added H_2O_2 (1.1 mol per double bond) (50% w/w H_2O) and the heating source removed from the reactor. The exothermic reaction heated the reaction mixture to 75 °C and was held at 75±5 °C with external cooling for approximately one hour. After the initial exothermic reaction

subsided, external heating was used to maintain 75 °C for an additional six hours. While still hot, the reaction mixture was filtered with vacuum to remove the Amberlite resin. The aqueous phase was removed and residual acetic acid and water in the organic phase were stripped under vacuum. After the stripping, 2% Magnesol was added to the retentate and returned to vacuum for 20 minutes. While still warm the Magnesol was removed by vacuum filtration to quantitatively yield pale yellow oils of e*poxy fatty acid esters* (**2a-d**). *Epoxy Soy Fatty Acid Methyl Esters* (**2a**): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.60 (s, 3 H, -OC**H**$_3$), 3.05 (m, 1 H, epoxy C**H**), 2.92 (m, 1 H, epoxy C**H**), 2.84 (m, 1 H, epoxy C**H**), 2.24 (t, 2 H, -C(O)C**H**$_2$-), 1.67 (m, 2 H, bis-epoxy C**H**$_2$), 1.56 (m, 2 H, -C(O)CH$_2$C**H**$_2$-), 1.44 (m, 2 H, alpha to epoxy C**H**$_2$), 1.24 (d, 18 H, -C**H**$_2$-), 0.83 (t, 3 H, -C**H**$_3$). *Epoxy Soy Fatty Acid n-Butyl Esters* (**2b**): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 3.99 (t, *J* = 6.7 Hz, 2H, -OC**H**$_2$-), 3.10 – 2.94 (m, 1H, epoxy-C**H**), 2.90 (d, *J* = 3.9 Hz, 1H, epoxy-C**H**), 2.32 – 2.15 (m, 2H, -C(O)C**H**$_2$-), 1.65 (t, *J* = 6.2 Hz, 2H, epoxy-CHC**H**$_2$-), 1.59 – 1.47 (m, 4H, -C(O)CH$_2$C**H**$_2$-, -OCH$_2$C**H**$_2$-), 1.44 (d, *J* = 6.2 Hz, 4H, epoxy-CHCH$_2$C**H**$_2$-), 1.40 – 1.15 (m, 18H, -C**H**$_2$-), 0.92 – 0.75 (m, 6H, -C**H**$_3$). *Epoxy Soy Fatty Acid n-Pentyl Esters* (**2c**): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.96 (t, *J* = 6.7 Hz, 2H, -OC**H**$_2$-), 3.12 – 2.95 (m, 1H, epoxy-C**H**), 2.88 (s, 1H, epoxy-C**H**), 2.80 (s, 1H, epoxy-C**H**), 2.19 (t, *J* = 7.5 Hz, 2H, -C(O)C**H**$_2$-), 1.63 (t, *J* = 6.3 Hz, 2H, epoxy-CHC**H**$_2$-), 1.58 – 1.49 (m, 6H, -C(O)CH$_2$C**H**$_2$-, -OCH$_2$C**H**$_2$-), 1.40 (s, 4H, epoxy-CHCH$_2$C**H**$_2$-), 1.31 – 1.13 (m, 19H, -C**H**$_2$-), 0.86 – 0.71 (m, 6H, -C**H**$_3$). *Epoxy Fatty Acid mixed Pentyl Esters* (**2d**): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.96 (t, *J* = 6.7 Hz, 2H, -OC**H**$_2$-), 3.82 (dd, *J* = 24.7, 6.4 Hz, 1H, -OC**H**(CH$_3$)CH$_2$-), 3.10 – 2.94 (m, 1H, epoxy-C**H**), 2.88 (s, 1H, epoxy-C**H**), 2.80 (s, 1H, epoxy-C**H**), 2.26 – 2.14 (m, 2H, -C(O)C**H**$_2$-), 1.70 – 1.58 (m, 1H, epoxy-CHC**H**$_2$-),

1.59 – 1.50 (m, 5H, -C(O)$CH_2C\mathbf{H}_2$-, -$OCH_2C\mathbf{H}_2$-), 1.40 (s, 5H, epoxy-$CHCH_2C\mathbf{H}_2$-), 1.32 – 1.10 (m, 19H, -$C\mathbf{H}_2$-), 0.87 – 0.74 (m, 6H, -$C\mathbf{H}_3$). *Epoxy Fatty Acid 2-Ethylhexyl Esters* (**2e**): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.02 – 3.86 (m, 2H, -$OC\mathbf{H}_2$-), 3.12 – 2.99 (m, 1H, epoxy-C**H**), 2.93 (s, 1H, epoxy-C**H**), 2.85 (s, 1H, epoxy-C**H**), 2.25 (t, *J* = 7.5 Hz, 2H, -C(O)$C\mathbf{H}_2$-), 1.77 – 1.64 (m, 1H, epoxy-$CHC\mathbf{H}_2$-), 1.58 (s, 1H, -C(O)$CH_2C\mathbf{H}_2$-), 1.48 (d, *J* = 27.7 Hz, 3H, epoxy-$CHCH_2C\mathbf{H}_2$-), 1.40 – 1.14 (m, 26H, -$C\mathbf{H}_2$-), 0.84 (t, *J* = 7.4 Hz, 9H, -$C\mathbf{H}_3$).

General procedure for transesterification of ESBO with isononanol (**2b**)*:* A 2-L reactor equipped with mechanical stirrer and a reflux condenser was charged with 1 kg ESBO and heated to 100°C under vacuum for 1 hour to remove moisture. Under an inert atmosphere 4 mol eq. isononanol and sodium methoxide (0.4% w/w SBO) were added and returned to vacuum for four hours. The cloudy reaction mixture was phase separated and the bottom glycerol layer was removed. Excess isononanol was removed by high vacuum distillation. While still, hot 2% Magnesol was added and flask was placed under vacuum for 20 minutes. The Magnesol was removed by vacuum filtration to quantitatively yield *Epoxy Fatty Acid isoNonly Esters* (**2f**) as a light yellow oil. This method would also be useful for the other alkyl alcohols to reduce the number of steps in the reaction sequence. *Epoxy Fatty Acid isoNonyl Esters* (**2f**): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.97 (dt, *J* = 11.8, 5.8 Hz, 2H, -$OC\mathbf{H}_2$-), 3.16 – 2.93 (m, 1H, epoxy-C**H**), 2.88 (s, 1H, epoxy-C**H**), 2.81 (s, 1H, epoxy-C**H**), 2.28 – 2.16 (m, 2H, -C(O)$C\mathbf{H}_2$-), 1.72 – 1.60 (m, 1H, epoxy-$CHC\mathbf{H}_2$-), 1.53 (s, 1H, bisepoxy-$CHC\mathbf{H}_2$-), 1.41 (s, 3H, -C(O)$CH_2C\mathbf{H}_2$-, epoxy-$CHCH_2C\mathbf{H}_2$-), 1.35 – 1.13 (m, 12H, -$C\mathbf{H}_2$-), 1.01 (d, *J* = 24.2 Hz, 1H, -$C\mathbf{H}(CH_3)CH_3$), 0.88 – 0.65 (m, 9H, -$C\mathbf{H}_3$).

*General procedure for partial ring opening and acetylation of epoxidized fatty acid esters (***3a-f**): In a 2-L reactor 1 kg of an epoxy fatty acid ester (**2a-f**) was added to a flask containing acetic anhydride (0.5 mol per original double bond of epoxy fatty acid esters). The flask was heated to 130 °C while mechanically stirring. After reacting for 8 hours the reaction mixture was cooled to room temperature. Upon reaching room temperature, H_2O_2 (4% w/w epoxidized alkyl esters) (50% w/w H_2O) was added to bleach the reaction mixture overnight at room temperature. The acetic acid, H_2O_2, and H_2O were stripped under vacuum. After stripping, basic alumina (2-8% w/w epoxidized fatty acid esters based on acid value of material) was added to neutralize the fatty acid and stirred at room temperature for 1 hour. The basic alumina was removed by vacuum filtration to quantitatively yield epoxy fatty acid ester estolides (**3a-f**) as pale yellow oils. *Epoxy Soy Fatty Acid Methyl Ester Estolides* (**3a**): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.92 (d, *J* = 6.8 Hz, 2H, -C**H**OC(O)CH_3), 3.60 (s, 3H, -OC**H**$_3$), 3.17 – 2.96 (m, 1H, epoxy-C**H**), 2.96 – 2.88 (m, 1H, epoxy-C**H**), 2.24 (t, *J* = 7.9 Hz, 2H, -C(O)C**H**$_2$-), 2.01 (d, *J* = 4.9 Hz, 3H, -C(O)C**H**$_3$), 1.80 – 1.62 (m, 2H, bis-epoxy C**H**$_2$), 1.56 (t, *J* = 7.9 Hz, 2H, -C(O)CH_2C**H**$_2$-), 1.44 (q, *J* = 7.3 Hz, 4Hepoxy-CHC**H**$_2$-), 1.35 – 1.05 (m, 14H, -C**H**$_2$-), 0.82 (t, *J* = 6.9 Hz, 3H, -C**H**$_3$).). *Epoxy Soy Fatty Acid n-Butyl Ester Estolides* (**3b**): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.78 (s, 1H, -C**H**OC(O)CH_3), 3.98 (t, *J* = 6.6 Hz, 2H, -OC**H**$_2$-), 3.02 (dt, *J* = 13.4, 6.6 Hz, 1H, epoxy-C**H**), 2.89 (s, 1H, epoxy-C**H**), 2.81 (s,1H, epoxy-C**H**), 2.21 (t, *J* = 7.4 Hz, 2H, -C(O)C**H**$_2$-), 2.00 (dd, *J* = 2.9, 1.8 Hz, 3H, -C(O)C**H**$_3$), 1.65 (s, 2H, bis-epoxy C**H**$_2$), 1.59 – 1.50 (m, 4H, -C(O)CH_2C**H**$_2$-, -OCH_2C**H**$_2$-), 1.43 (s, 2H, -C**H**$_2$CHOC(O)CH_3), 1.35 – 1.10 (m, 26H, -C**H**$_2$-), 0.93 – 0.74 (m, 6H, -C**H**$_3$). *Epoxy Fatty Acid n-Pentyl Ester Estolides* (**3c**): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.18 (s,

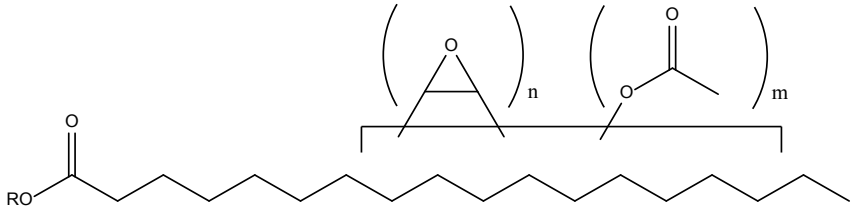
1H, -C**H**OC(O)CH_3), 4.89 (d, *J* = 4.9 Hz, 1H, -C**H**OC(O)CH_3), 3.95 (t, *J* = 6.7 Hz, 2H, -OC**H**$_2$-), 3.01 (d, *J* = 4.2 Hz, 1H, epoxy-C**H**), 2.87 (s, 1H, epoxy-C**H**), 2.79 (s, 1H, epoxy-C**H**), 2.26 – 2.11 (m, 2H, -C(O)C**H**$_2$-), 1.97 (dd, *J* = 4.6, 2.2 Hz, 3H, -C(O)C**H**$_3$), 1.62 (s, 2H, bis-epoxy C**H**$_2$), 1.51 (d, *J* = 6.9 Hz, 7H, -C(O)CH_2C**H**$_2$-, -OCH_2C**H**$_2$-), 1.39 (s, 1H, -C**H**$_2$CHOC(O)CH_3), 1.30 – 1.09 (m, 26H, -C**H**$_2$-), 0.87 – 0.72 (m, 6H, -C**H**$_3$). *Epoxy Fatty Acid mixed Pentyl Ester Estolides* (**3d**): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.84 (s, 1H, -C**H**OC(O)CH_3), 3.90 (t, *J* = 6.7 Hz, 2H, -OC**H**$_2$-), 3.76 (dd, *J* = 24.3, 6.4 Hz, 1H, -OC**H**(CH_3)CH_2-), 3.02 – 2.87 (m, 1H, epoxy-C**H**), 2.80 (s, 1H, epoxy-C**H**), 2.73 (s, 1H, epoxy-C**H**), 2.18 – 2.07 (m, 2H, -C(O)C**H**$_2$-), 2.00 – 1.87 (m, 3H, -C(O)C**H**$_3$), 1.69 – 1.53 (m, 1H, bis-epoxy C**H**$_2$), 1.46 (d, *J* = 6.8 Hz, 4H, -C(O)CH_2C**H**$_2$-, -OCH_2C**H**$_2$-), 1.35 (s, 2H, -C**H**$_2$CHOC(O)CH_3), 1.28 – 1.02 (m, 13H, -C**H**$_2$-), 0.86 – 0.65 (m, 6H, -C**H**$_3$). *Epoxy Fatty Acid 2-Ethylhexyl Ester Estolides* (**3e**): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.97 – 4.86 (m, 1H, -C**H**OC(O)CH_3), 3.91 (d, *J* = 5.5 Hz, 2H, -OC**H**$_2$-), 3.04 (s, 1H, epoxy-C**H**), 2.90 (s, 1H, epoxy-C**H**), 2.82 (s, 1H, epoxy-C**H**), 2.21 (d, *J* = 7.5 Hz, 2H, -C(O)C**H**$_2$-), 2.07 – 1.92 (m, 3H, -C(O)C**H**$_3$), 1.65 (s, 1H, bis-epoxy C**H**$_2$-), 1.61 – 1.37 (m, 2H, -C(O)CH_2C**H**$_2$-), 1.23 (dd, *J* = 29.2, 9.9 Hz, 26H, -C**H**$_2$-), 0.91 – 0.75 (m, 9H, -C**H**$_3$). *Epoxy Fatty Acid isoNonyl Ester Estolides* (**3f**): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.88 (s, 1H, -C**H**OC(O)CH_3), 3.94 (s, 2H, -OC**H**$_2$-), 3.00 (s, 1H, epoxy-C**H**), 2.85 (s, 1H, epoxy-C**H**), 2.77 (s, 1H, epoxy-C**H**), 2.17 (s, 2H, -C(O)C**H**$_2$-), 1.96 (d, *J* = 6.0 Hz, 3H, -C(O)C**H**$_3$), 1.61 (s, 1H, bis-epoxy C**H**$_2$-), 1.50 (s, 12H, -C(O)CH_2C**H**$_2$-, -OCH_2C**H**$_2$-), 1.38 (s, 8H, -C**H**$_2$CHOC(O)CH_3), 1.16 (d, *J* = 17.0 Hz, 43H, -C**H**$_2$-), 1.08 – 0.90 (m, 1H, -C**H**(CH_3)CH_3), 0.86 – 0.60 (m, 9H, -C**H**$_3$).

7.5.Results and Discussion

An ideal plasticizer contains structural features that make it compatible with PVC. These include optimal molecular weight, branching, and a balanced polarity. Vegetable oils provide an ideal starting material to incorporate these structural features as the fatty acid headgroups can be readily transesterified and the double bonds modified to incorporate polar groups and branching by various chemistries. The optimal molecular weight range for a plasticizer is ~300-500 g/mol. Plasticizers with lower molecular weight are too volatile during compounding and those with higher molecular weight have limited compatibility. Branching on the fatty acid ester backbone allows better intermolecular interactions which can improve compatibility. Due to the high polarity of PVC, plasticizers with higher polarity are more compatible with PVC than less polar fatty acid ester derivatives.

Using these structural features as guidance, we prepared a series of epoxy fatty acid ester estolides from soybean oil to evaluate as plasticizers in PVC formulations. The general structure of these compounds is shown in Figure 28. The fatty acid ester head group of soybean oil or soy fatty acid methyl esters were transesterified with either *n*-butyl, *n*-pentyl, mixed pentyl, 2-ethyl hexyl, or isononyl alcohols. These alcohols provided a range of ester headgroups with different polarities and molecular weights. The double bonds on the fatty acid esters were converted to epoxy groups to increase the polarity by *in situ* formed peracetic acid using an Amberlite acid ion exchange resin. This method was adapted from Sinadinovic-Fiser [43], with a slight modification of using higher concentration H_2O_2 and shorter reaction times. The plasticizers that contain epoxy function provide thermal stability during PVC compounding and enhance longevity of the product [2]. In our previous work we found that complete ring opening of the epoxy

groups using acetic acid, and capping the resulting free hydroxyls with acetic ahydride, increased the polarity of the fatty acid esters and improved their compatibility with PVC. In this study, we retained some epoxy functions in the final products to provide the thermal stability to PVC. To accomplish the partial ring opening of the epoxy groups, we reduced the amount of acetic anhydride in the epoxy ring opening reaction to 0.5 mol equivalent per mol of epoxy. By adopting this modification about half of the epoxy rings were opened and converted to estolides while retaining the rest of the epoxy functions on the fatty acid esters.



Compound	R	n = 0-3 m = 0-6
3a	methyl	
3b	*n*-butyl	
3c	*n*-pentyl	
3d	mixed pentyl	
3e	2-ethylhexyl	
3f	isononyl	

Figure 28 Structure of epoxy fatty acid ester estolides

The physical properties of the experimental epoxy fatty acid ester estolides are compared to commercial controls DINP and Elatur CH in Table 18. The acid values of some of the experimental plasticizers were higher than the commercial controls. One reason for this could be hydrolysis of the fatty acid ester during the epoxidation reaction. The higher acid values of these compounds can be effectively reduced by treating with

basic alumina to below 1.0 mg KOH/g sample. The viscosity of a plasticizer plays an important role in PVC processing with lower viscosity plasticizers being easier to transport and compound. The viscosity of the experimental plasticizers **3a** and **3d** were almost the same as Elatur CH and DINP respectively. The viscosities of the remaining experimental plasticizers were higher than the commercial controls but still within an acceptable range. To be useful in most applications plasticizers should be as colorless as possible. Higher plasticizer color will cause clear PVC products to look yellow and colored products may need additional additives to overcome any color distortions. The colors of all the experimental plasticizers were higher than the commercial controls but **3a** and **3f** had much lower color than the other experimental plasticizers. The plasticizers color can be further reduced using longer bleaching times or increasing the bleaching reaction temperature.

Table 18 Physical properties of experimental and commercial plasticizers

Plasticizer	Acid Value (mg KOH/g)	Saponification Value (mg KOH/g)	Oxirane Oxygen (%)	Viscosity (cP @ 20°C)	Color (APHA)
DINP	0.03 [1]	-	-	75	4
Elatur CH	0.05 [2]	-	-	50	2
3a	6.39	257.8	3.56	52	89
3b	1.48	274.6	3.61	90	276
3c	2.07	287.4	2.20	137	414
3d	0.97	257.2	2.96	76	174
3e	1.55	257.2	1.37	153	153
3f	0.83	233.7	2.23	173	43

[1] From *Evonik* DINP Plasticizer technical data sheet
[2] From *Evonik* Elatur® CH Plasticizer technical data sheet

Due to the high temperatures employed in PVC compounding (up to 200 °C) plasticizers must have minimal volatility at these temperatures. In Figure 29 the volatility of the experimental plasticizers and commercial controls is compared by measuring the

weight loss of the plasticizers after holding at 200 °C for 10 minutes. As the figure shows, **3a** has considerable weight loss compared to the commercial controls and other experimental plasticizers. The remaining experimental plasticizers have volatility comparable to commercial controls.

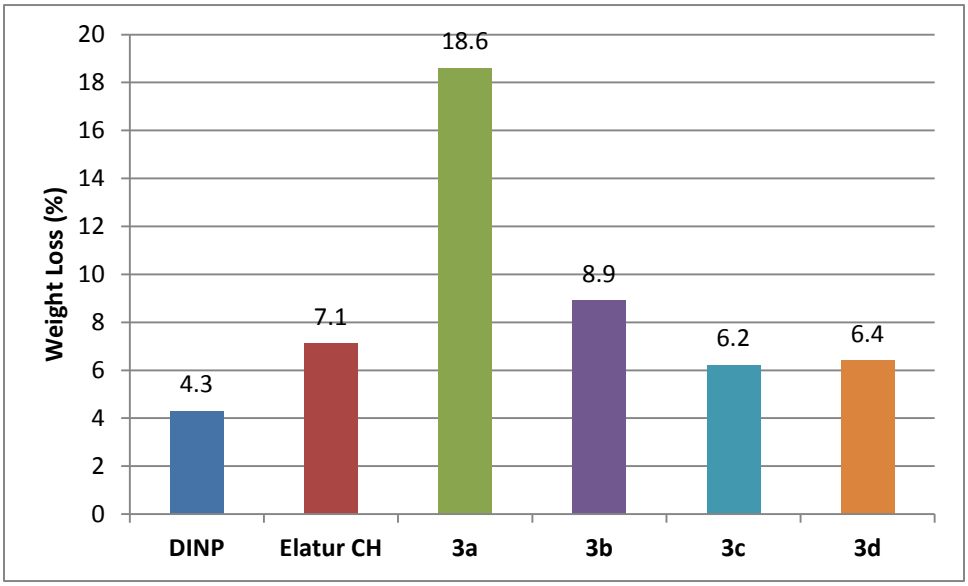


Figure 29 Volatility of commercial and experimental plasticizers at 200 °C after 10 minutes

The fusion characteristics of PVC resin and plasticizers were measured using a rheometer and the results shown in Figure 30. The gelation temperature of the plasticizers is shown by the sudden increase in viscosity at a given temperature. When gelation occurs at a lower temperature this can indicate a plasticizer acts as a fast fuser. From the figure it can be seen that experimental plasticizer **3a** shows fast fusing properties as the gelation temperature and time required are much lower than the commercial controls and other experimental plasticizers. The plasticizers having such gelation properties are used as additives in the PVC formulations as fast fusers. Experimental plasticizers **3b**, **3c**, and **3d** have similar gelation properties as DINP and much better than Elatur CH.

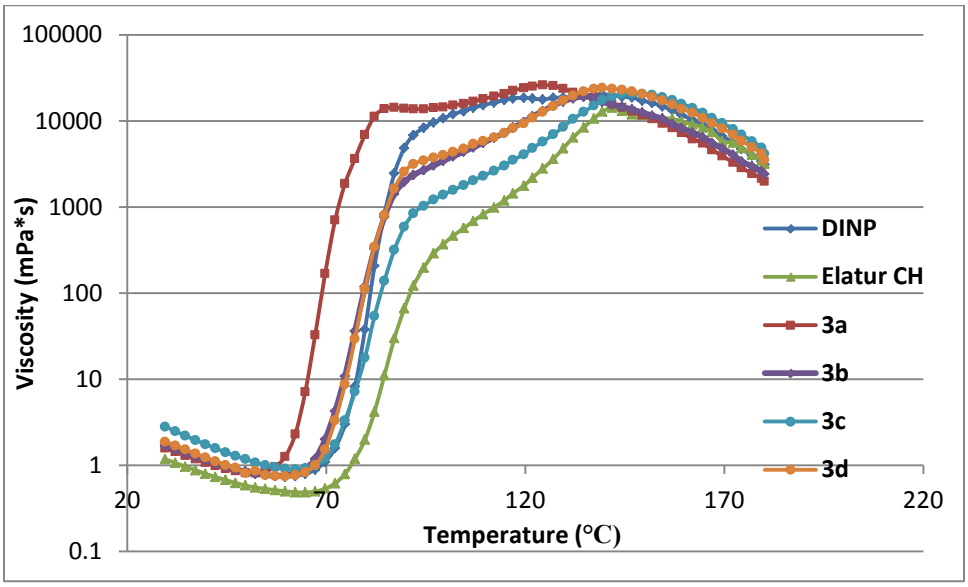


Figure 30 Gelation curves of PVC compounded with commercial and experimental plasticizers

The efficiency of the plasticizers determines the amount of plasticizer necessary to achieve the same amount of flexibility and is measured by Shore A hardness. The Shore hardness of plastisols made from experimental and commercial plasticizers are compared in Figure 31. Plasticizers with higher efficiency will produce a softer plastisol after compounding. In the figure it can be seen that experimental plasticizers **3a** and **3d** are more efficient than DINP and Elatur CH thus would require a lower amount in the formulation to produce the same amount of flexibility. Experimental plasticizers **3b** and **3c** have similar flexibilities to DINP and in between DINP and Elatur CH whereas experimental plasticizers **3e** and **3f** were much less efficient than the commercial controls and other experimental plasticizers.

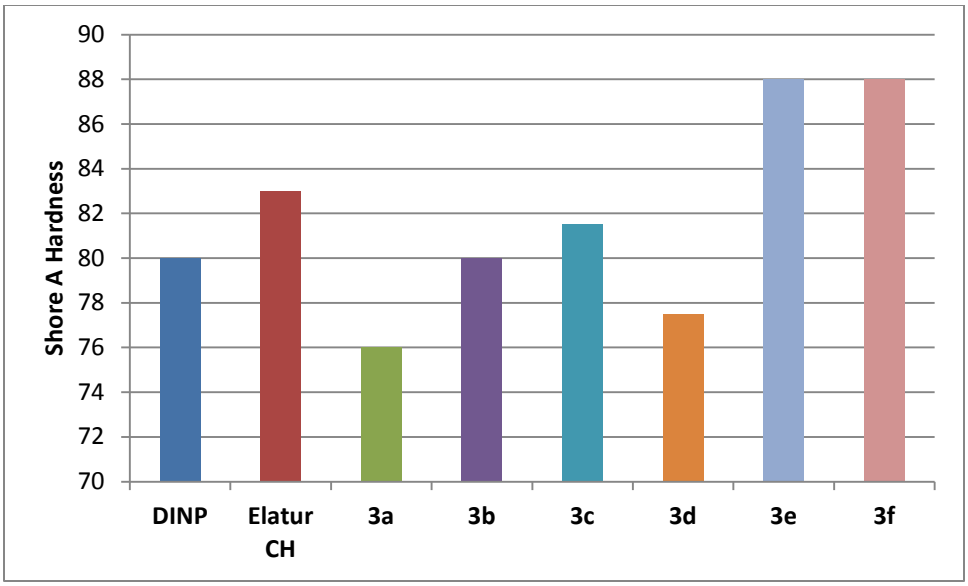


Figure 31 Shore A hardness of PVC compounded with commercial and experimental plasticizers

In applications where significant contact with water is expected, understanding the water storage properties of the plastisols indicates their expected performance in these applications. In Figure 32 plastisols compounded with experimental and commercial plasticizers were compared by measuring their weight change after submerging in water for one day, seven days, and after drying. In the figure it can be seen that all the plastisols except the one prepared with **3a** showed some weight increase as water was absorbed into the plastisol at 1 and 7 day intervals. The plastisol prepared with **3a** showed weight loss at all three measurement times indicating there was significant loss of the plasticizer into the water. The values of the remaining plastisols prepared from the experimental plasticizers showed comparable weight gain and plasticizer loss after drying with those of commercial controls and would be suitable for water contact applications.

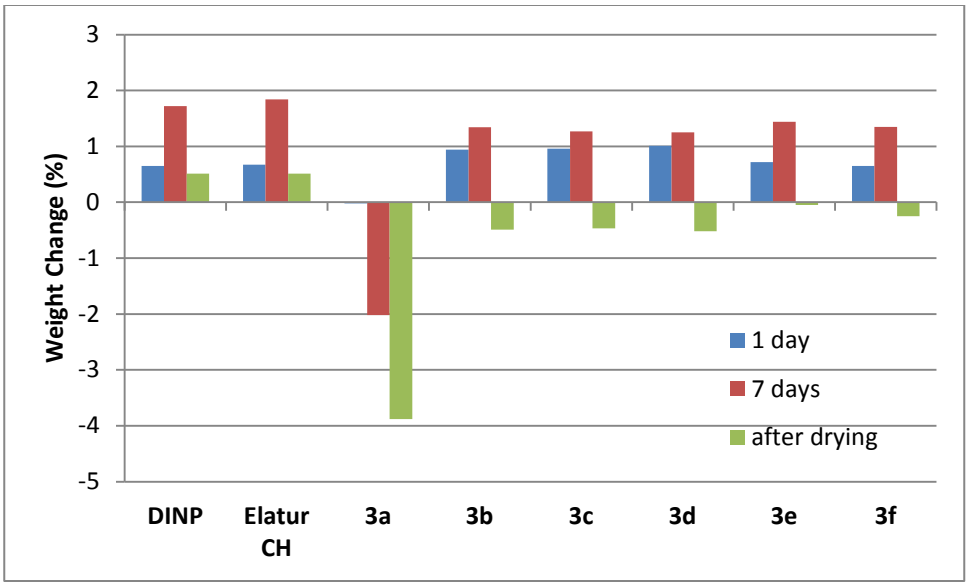


Figure 32 Water storage properties of PVC plastisols compounded with commercial and experimental plasticizers

The propensity of the plasticizers to exude from the plastisols indicates their compatibility and was measured by using a loop exudation test. In Table 19 the loop exudation results of the plastisols prepared from experimental and control plasticizers after one, seven, and fourteen days are tabulated and compared. As the table indicates, there was no exudation from plastisols prepared from the control plasticizers nor from the plastisols prepared from experimental plasticizers **3a-d** even after fourteen days. Plastisols prepared from the experimental plasticizers **3e** and **3f** showed moderate exudation after seven and fourteen days indicating significant compatibility issues with these plasticizers.

Table 19 Plastisol loop exudation test[1]

Plasticizer	1 day	7 days	14 days
DINP	0	0	0
Elatur CH	0	0	0
3a	0	0	0
3b	0	0	0
3c	0	0	0
3d	0	0	0
3e	0	2	2.5
3f	1	2	1.5

[1] ASTM D 3291
0 = no exudation, 0.5 = very little, 1.0 = slight, 2.0 = medium, 3.0 = heavy, >3.0 = extreme

The volatility of plastisols prepared with commercial and experimental plasticizers was compared by measuring the weight loss after holding at 100 °C for three and seven days. The results are shown in Figure 33. From the figure it can be seen that the plastisols prepared with experimental plasticizer **3c-f** had similar volatility to DINP but less than Elatur CH. The data for the experimental compounds **3a** and **3b** are not available.

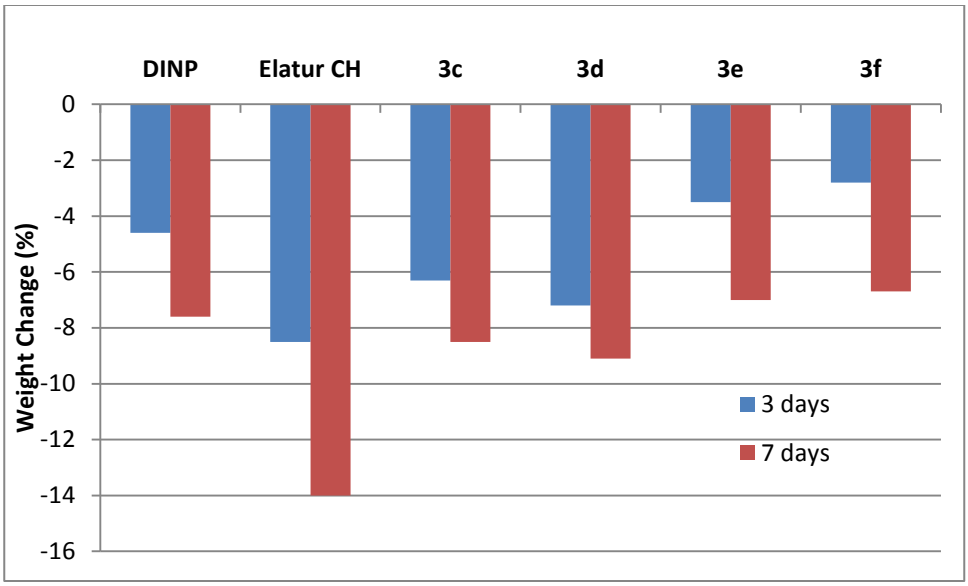


Figure 33 Volatility of PVC films compounded with commercial and experimental plasticizers.

7.6.Conclusions

A series of epoxy fatty acid ester estolides were synthesized from soybean oil as experimental plasticizers for PVC applications. The experimental plasticizers had varied polarity and molecular weight due to the ester headgroup size. The plasticizers were compounded with PVC to make plastisols and their functional properties were evaluated and compared to two commercial plasticizers. The lower molecular weight epoxy fatty acid ester estolides (methyl ester) had good gelation, efficiency, and compatibility with PVC as compared to the commercial controls. Its gelation properties indicate that it could be useful as a fast fuser in the formulations. However, the poor performance of greater water extraction and higher volatility limit its use as a stand-alone plasticizer. The medium molecular weight epoxy fatty acid ester estolides (*n*-butyl, *n*-pentyl and mixed pentyl) showed the best performance in volatility, gelation, efficiency, compatibility, and water extractability comparable or better than commercial controls. These medium

molecular weight fatty acid ester estolides would be useful as general purpose plasticizers in many PVC applications and are good candidates to replace the phthalates. The higher molecular weight epoxy fatty acid ester estolides (2-ethyl hexyl and isononyl) showed good volatility and low water extractability but had poor efficiency and compatibility limiting their usefulness as plasticizers.

Chapter 8: Overall Conclusions

In this study a number of vegetable oil derived fatty acid ester compounds having different functional groups were synthesized and evaluated as a potential replacement to the petroleum based phthalate plasticizers in PVC. The first series of compounds, fatty acid ester estolides, showed good plasticizer functionality. The fatty acid ester estolides with short acetoxy groups on the fatty acid back bone provided better performance with PVC than the longer laurate estolides. The acetoxy groups increased the polarity of the fatty acid ester estolides improving their compatibility with PVC. The ring opening of the epoxy groups on diepoxy fatty acid esters to produce estolides resulted in cyclic tetrahydrofuran ether estolides. Epoxy fatty acid ester estolides without the cyclic ethers were synthesized by using castor oil as the starting material. The presence of epoxy groups significantly improved the thermal stability of the plastisols prepared from these plasticizers. Partial epoxy ring opening to synthesize estolides effectively retained the epoxy group in soy epoxy fatty acid ester estolides and also reduced the formation of the cyclic ethers. The epoxy soy fatty acid ester estolides with moderate molecular weight with butyl and pentyl ester head groups showed the best plasticizer functionality and would be potential replacements to phthalate plasticizers in certain applications. They have the right combination of price, performance, and functionality to be general purpose plasticizers for many applications including flooring, wall covering and wire and cable coatings.

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Appendix A: Prior Art Related to Bioplasticizers

Patent/Application Number	Company
BR2009PI15488 20090709	Polyone Corporation, USA
CA2863431 A1	Emerald Kalama Chemical LLC, USA
CN 102285946 B	Guangzhou, Joel Ma plants Oil Co., China
DE 4433958 A1	Henkel Kgaa, Germany
EP 2470595 B1	Dow Global Technologies LLC, USA
EP1516865 B1	OXEA Deutschland GmbH, Germany
EP2039718 A2	Lanxess Deutschland GmbH, Germany
UA20160009673A1	Arkema Inc., USA
US 2008/0200595 A1	Gerflor, France
US 2010/0010127 A1	Resinas y Materiales, S.A. de C.V., Mexico
US 2010154292A1	Chevron U.S.A. Inc., USA
US 2012/0122745 A1	Segetis, Inc., USA
US 2012/0214920 A1	Galata Chemicals Llc., USA
US 20120289727A1	Npc Industrias Quimicas Ltda, Brazil
US 2013/0203907 A1	Arkema Inc., USA
US 20140102335 A1	Awi Licensing Company, USA
US 20140221538 A1	Nexoleum Bioderivados Ltda., Brazil
US 2015/0005420 A1	Dow Global Technologies Llc, USA
US 20150129279 A1	Dow Global Technologies Llc, USA
US 2624680	Daniel Swern
US 4124558	The United States Of America As Represented By The Secretary Of Agriculture
US 5075046	Henkel Kommanditgesellschaft Auf Aktien, Germany
US 6734241 B1	Danisco A/S, Denmark
US 6797753 B2	Battelle Memorial Institute, USA
US 6949597 B2	Danisco A/S, Denmark
US 8383708 B2	Polyone Coporation, USA
US 8552098 B2	Dow Global Technologies Llc, USA
US20150005420 A1	Dow Global Technologies Llc, USA
US20150361310A1	Celanese Acetate LLC, USA
WO 2009/033240 A1	Sgs Polimeros Ltda, Brazil
WO 2009138508 A1	Tissage Et Enduction Serge Ferrari Sa, France
WO 2011021107 A2	Danisco A/S, Denmark
WO 2011041380 A1	Dow Global Technologies Llc, USA
WO 2011046736 A2	Polyone Corporation, USA
WO 2012/173666 A1	Lubrigreen Biosynthetics, Llc, USA
WO 2013/055961 A1	Galata Chemicals Llc, USA
WO 2013/119402 A1	Dow Global Technologies Llc, USA
WO 2013123127 A1	Emerald Kalama Chemical LLC, USA
WO 2014093624 A1	Polyone Corporation, USA
WO 2014143902 A1	Emerald Kalama Chemical LLC, USA