

Epoxidized vegetable oil and bio-based materials as PVC plasticizer

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ABSTRACT: Phthalate esters received a considerable attention owing to its various applications and the harmful health effects resulting from phthalate exposure; thus, finding an alternative to phthalate derivatives became a necessity. Phthalate esters are commonly used as plasticizer in polymer formulation; in particular for poly(vinyl chloride) (PVC) formulation. According to the researches in the last 18 years, epoxidized vegetable oils are one of the alternatives that are strongly encouraged to substitute phthalate esters since they were proven to be valid in various applications, eco-friendly and sustainable resource. However, most of the production practices for epoxidized vegetable oil are via conventional epoxidation that concentrates on a catalyst that is homogeneous and non-reusable. This type of catalyst, however, causes several problems later in the process. Therefore, the selective epoxidation of vegetable oils process requires new catalytic systems that are more aligned with the green chemistry principles. This article reviews the harmful health effects associated with the exposure to phthalate esters products, explains the usage of oleochemicals resources as a substitute to phthalate esters and describes different approaches for the epoxidation of vegetable oils. Finally, it draws attention to the usage of epoxy and bio-based compounds as plasticizers in PVC manufacturing. © 2018 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2018**, 135, 46270.

KEYWORDS: chemoenzymatic epoxidation; phthalate esters; phthalate risks; plasticizer; PVC; vegetable oils

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INTRODUCTION

Over the last decade, poly(vinyl chloride) (PVC) has been one of the largest commodity thermoplastics used for numerous commercial and domestic applications, such as children toys, infants supply, medical supplies, packaging materials, and others.^{1,2} PVC has hard and brittle characteristics as a result of dipole present on each C—Cl bond, where an interaction among PVC chain exists that restricts chain motility.³ In order to enhance PVC characteristics, a compatible plasticizer is to be added to adjust its mechanical and thermal properties.^{4,5} This is performed via spacing out the PVC molecules to reduce the interaction between segments of polymer chains which leads to lowering the adhesion among molecules.^{2,3,6,7,11} Furthermore, adding a plasticizer to PVC lowers both the elasticity modulus and the glass transition point which leads to an enhancement in PVC processing properties.^{3,8,11} However, most plasticizers are not chemically bonded with PVC polymer chains; this allows them to leach from products into surrounding media.^{3,9} Hence, studying the exposure to these compounds has become an essential part of maintaining public health, and preventing associated adverse effects.¹⁰

There are many plasticizers used in PVC processing, one of those plasticizers is phthalate esters. Phthalate esters are petroleum-based products which are the most commonly used plasticizers in PVC processing. They represent more than 80% of PVC plasticizer market share.^{3,11} Phthalate esters group has a lot of members that are used in industry such as diisodecylphthalate (DIDP), di-2 ethyl hexyl phthalate (DEHP), di-octyl phthalate (DOP), and di-isononyl phthalate (DINP). All the industry-used members have very similar chemical and physical properties.¹² Most of phthalate plasticizers are well-known to be toxic, and may cause disorders in human reproduction system and endogenous hormone; owing to their migration from polymer matrix.^{3,13} Thus, it is recommended to use bio-compatible and sustainable alternative instead of phthalate esters. This would be from renewable resources and more secure materials than commercial phthalate.^{3,11}

This review article depicts the harmful health effects of using commercial phthalate esters plasticizers in PVC products. It also describes two approaches; the first is a conventional production approach that uses chemical catalyst to obtain ester or epoxy from substrates such as vegetable oils. The second approach is

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the chemoenzymatic approach. It is one of the environment-friendly approaches that use bio-catalyst to obtain ester or epoxy. In addition, this review article highlights the usage of bio-compatible and sustainable alternatives as a valid plasticizer in PVC products.

IMPACTS DUE TO PHTHALATE EXPOSURE

For more than 35 years, the harmful health effects of phthalates have been investigated.^{13–15} Various researches on phthalate exposure were carried in laboratories over rodents and humans.^{14–16}

There is a consensus from numerous studies that phthalate lowers testosterone levels and causes genital failure and deficiencies in performance of the metabolism. Kim *et al.*¹⁷ indicated that DEHP has a significant effect on new-born babies' weight by measuring DEHP metabolites concentrations in urine and blood samples. This study is compatible with other studies which agreed that there is a relation between kids' obesity and significant concentrations of phthalates.^{18,19} Other studies stated that newborn males and females are affected by different phthalate compounds and in different ways.²⁰ For instance, DEHP has a negative effect on female growth, where di-pentyl phthalate influence males.

Liang *et al.* investigated the effect of phthalate exposure on lung function. The results indicated that the decline of lung function is associated with phthalates exposure, which could lead to allergic diseases.²¹ This result is compatible with another study that relates specific phthalate esters concentration such as DEHP and *n*-butyl benzyl phthalate (BBP) in home dust with asthma, rhinitis, and eczema.²² Moreover, Columbia Center for Children's Environmental Health investigated the effect of pre-natal phthalates exposure on children's asthma.²³ The study included 300 mothers and their children between 5 and 11 years old. Urine samples were collected from mothers during the third trimester and children at the age of 3, 5, and 7. This study focused on children who were born to mothers having notable levels of phthalate at the time of pregnancy and others born to mothers who had imperceptible phthalate levels. The study showed that there is a strong relation between asthma and phthalates. The outcomes of this study are consistent with another study performed by European Chemical Agency (ECHA) in 2014.²⁴ Therefore, The European Union (EU) has prohibited different phthalate components such as di-isobutyl Phthalate, BBP, and others for specific applications.²⁵

Other studies explored the risks resulting from utilizing phthalate in many personal care products such as nail polish, perfumes, and medications.^{19,26,27} This could be a reason for diabetic adults.^{26–28} This was clearly illustrated by Tamarra *et al.* where the relation between phthalate concentration in urine and diabetes among women was studied. The study included 2530 women between 20 and 80 years old. It was indicated that the increased concentrations of phthalates in some women was a significant symptom for diabetes. Moreover, it was found that women could have the opportunity to foster diabetes when they have high concentrations of either mono-benzyl phthalate or mono-isobutyl phthalate or both of them in comparison to those who have low concentrations.²⁸

It is found that above a certain concentration phthalates compounds are considered hazards. Accordingly, due to regulations, PVC manufacturing companies were forced to limit the usage of phthalates in goods. Moreover, European Union illegalized the use of di-butyl phthalate, DEHP, and BBP, in kid's toys.²⁹ Thus, an alternative for phthalates plasticizer to produce free-phthalate goods became a must.

OLEOCHEMICALS OVERVIEW

There is a growing demand for petrochemical derivatives as population and economy are increasing rapidly, thus finding an alternative to these derivatives has become a necessity. Oleochemicals are analogues to petrochemicals derived from petroleum. They are generally chemicals obtained from plants and animal fats which makes them an appropriate alternative for some of petrochemical derivatives with a reduced carbon footprint. Therefore, it is applicable that vegetable oils^{30,31} could play a vital role for developing new valuable products resulting in achieving sustainable development.

Modifications of Oleochemical Compounds

In spite of all the advantages associated with using oleochemicals compounds as a valid renewable resource for healthy and

sustainable products, there is still a challenge in operation and modification processes to get the desired derivative that suits certain applications such as poor seed quality and inadequate supply of seeds.³² The characteristics of vegetable oils could be enhanced via changing fatty acid chains of triglycerides to improve oleochemical compounds processing properties.^{33,34} The transformation of triglycerides could be an effective way for performing modifications^{35,36} in order to obtain different monomers for making new compounds for various applications. There are many key aspects of oleochemicals modification depending on targeting specific sites to enable other processes such as polymerization. The concept behind developing oleochemical compounds depends on the activity of unsaturated centers in oils and fats, such as carboxyl groups which usually react independently.³⁷ Nevertheless, the most reactive sites in fatty acids are the carboxyl groups and double bonds, methylene adjacent to them is activated, leading to increasing the reactivity. Therefore, saturated chains rarely show reactivity.³⁸ Traditionally, oleochemicals industry focuses mostly on exploiting synthetic methods such as esterification, transesterification, hydrogenolysis, saponification, and acylation. These methods are applied to the carboxylic group of fatty acids to synthesize major industrial oleochemicals such as biodiesels,³⁹ fatty acids, glycerol, soaps, and so on.^{40,41}

Vegetables oils have a slight use as lubricants due to the presence of various unsaturation chains of fatty acids which lead to poor thermal and oxidative stability.^{31,42} To overcome these shortcomings, functional groups modification could be done.^{43,44} via creating stabilized function groups.⁴⁵ One of the most common processes for these modifications is "Epoxidation process", where various side chains derived from the mono- or di-epoxidation of the double or triple bonds present in the fatty acid could be performed.⁴⁶ Therefore, improvement of poor thermal stability could be achieved through the reduction of unsaturated chains.⁴⁷

Some examples for the chemical modification of oleochemical compounds are the unsaturated bonds in seed oils. This could be chemically modified to improve their physical properties in order to be used in various applications.^{48,49} Moreover, Secondary OH group, as in castor oil becomes vital industrial raw material due to the presence of hydroxyl group.^{50,51} A brief illustration for oleochemicals modification pathways are depicted in Figure 1, where numerous routes for oils and fats to develop multiple healthy green products from fats and oils via changing their physical and chemical aspects.

Epoxidation of Vegetable Oils

It has been found that most vegetable oils contain high contents of unsaturated fatty acids which can be transformed into epoxy fatty acid by different epoxidation methods. Epoxidation as a critical double bond addition reaction is commonly used. The term "Epoxides" refers to oxiranes, which includes cyclic ethers with reactive three-membered ring. Epoxide transformations can be performed via different methods like ketone rearrangement and hydrogenation.⁵² Therefore, various oleochemical compounds used for manufacturing different products are originated from epoxide through the reactions of open rings.

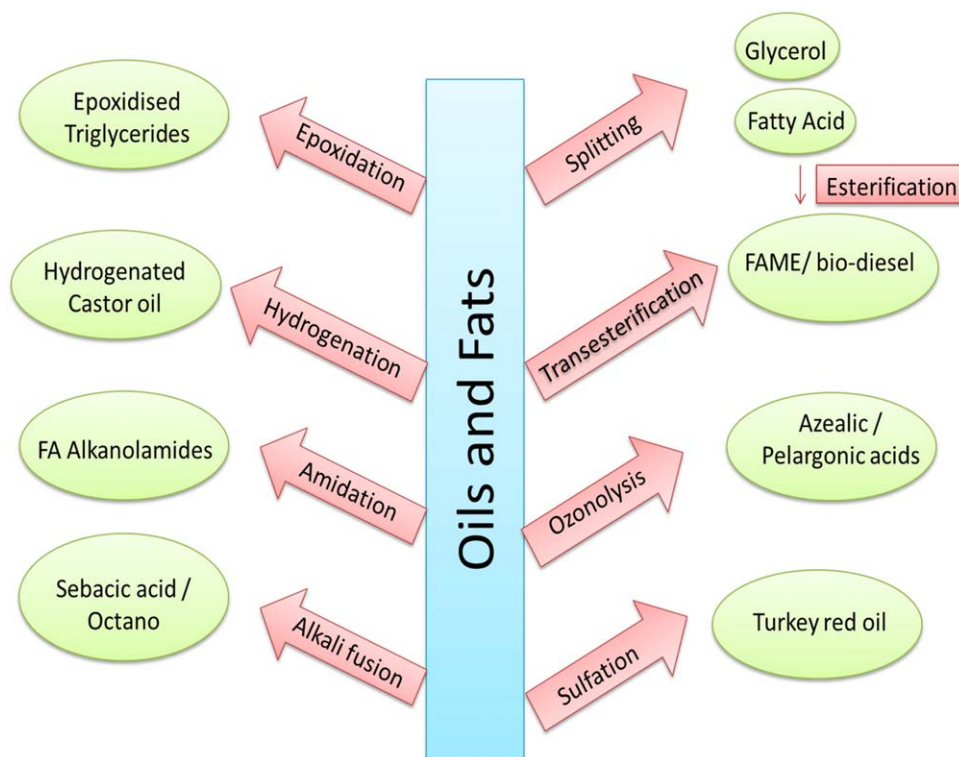


Figure 1. Pathways of oleochemical derivatives. [Color figure can be viewed at wileyonlinelibrary.com]

Epoxidation Methods of Vegetable Oils

Attention to the epoxidation of vegetable oils has grown exponentially in recent years in many industries since epoxidized vegetable oils are eco-friendly, decomposable, harmless, and sustainable compounds. Epoxidation of vegetable oils can be performed through different processes which vary only in the type of catalyst used. The prime catalysts used in the epoxidation of vegetable oils are peracids, metals, resins, and enzymes.⁵³

Nowadays, the largest proportion of epoxidation of vegetable oils is executed by conventional epoxidation approach, where the unsaturated chains transformed with the aid of peroxy acid.⁵⁴ Although this approach is commonly used, but it suffers from diverse impediments^{53,55} such as: (1) reduction in epoxides selectiveness that results from oxirane ring opening, (2) instability and explosiveness of peroxy acids, and (3) corrosion problems that arise significantly due to the acidic byproducts. Accordingly, there are several researches focusing on proposing new catalytic processes to overcoming such disadvantages. One of the proposed processes was the ion exchange resin which is an insoluble organic polymer with extremely small beads format and generally white or yellowish. This approach is used in epoxidation using peroxy acid with the resin, where the resin traps the peroxy acid ions along with releasing other ions. Thus, in this process, the resin pores are filled with peroxy ions and vegetable oils are unable to enter the pores. This results in decreasing the oxirane decomposition.⁵³ In addition to this process, there is a more advanced one that has been used in the epoxidation of vegetable oils using diverse metal catalysts such as tungsten, titanium, and molybdenum. Metal catalyst process

succeeded to enhance the epoxidation reaction performance and enlarge the oxirane content; but in some cases, it lowered the conversion of epoxidized vegetable oil that could be achieved compared with using the conventional approach.³³ In all these processes, the conversion hardly exceeds 80% of the desired products selections in industrial plants. Furthermore, the process is associated with undesired components which are not compatible with sustainable development requirements and with hazards to operators.⁵⁶

Consequently, it became a must to discover new approaches using sustainable catalysts to increase the selectivity criteria in the epoxidation reaction. Hence, the chemoenzymatic approach emerged as a legitimate alternative to the chemical approach, which aims to shun the side reactions and create a green rout in epoxidation. Biocatalyst will be used in this process and added gradually to avoid the deactivation that can be happen due to the presence of oxygen donor.⁵⁷ Also, there are many advantages accompanied by the latter process over the chemical process,⁵⁸ which can be clarified: the chemoenzymatic epoxidation needs a medium temperature meaning that it helps to save heat in comparison with the other chemical process. In addition, the chemoenzymatic epoxidation process does not need a solvent and requires a neutral pH. This means, downstream processes for separating the targeted products are not costly like that in the chemical processes. An obvious comparison between all processes is depicted in Table I. Also Figure 2 shows a block flow diagram for the chemoenzymatic and chemical approaches which was inspired from this reference [59].

Table 1. Comparison between Different Epoxidation Processes

| Processes/parameters | Conventional epoxidation | Epoxidation using ion exchange resin | Epoxidation using metal catalyst | Chemoenzymatic epoxidation solvent-free system | Chemoenzymatic epoxidation with solvent |
|-----------------------|--|--|---|---|--|
| Example for catalysts | Formic acid, hydrogen peroxide and sulfuric acid | Amberlite IR-120 hydrogen form | tungsten, titanium and molybdenum | Lipases | Lipases (Solvent): hydrophilic ionic liquid, toluene |
| Operating temp. (°C) | (80–160) | (50–75) | (40–60) | (25–55)C | 20–60 °C |
| % wt of catalyst | ≥1% | ≥1% | ≥3% | ≤1% | ≤1% |
| Conversion % | 80–90% | 65–78% | 70–85% | 85–94% | 67–90% |
| Health risks | Traces of the catalyst such as sulfurs may remain in the product | None | Traces of the metal catalyst may remain in the product | None | Traces of the solvent may remain in the product |
| Impact to environment | High ^a | Moderate ^b | High ^a | Low ^c | Moderate ^b |
| References | Danov <i>et al.</i> ⁵³ and Waskitoaji <i>et al.</i> ⁶⁰ | Saurabh <i>et al.</i> ⁴⁶ and Zeleke and Ayana ⁶¹ | Saurabh <i>et al.</i> ⁴⁶ , Abdullah and Salimon ⁶² , and Sharifah Nafisah <i>et al.</i> ⁶³ | Kuo <i>et al.</i> ⁵⁷ and Mustafa <i>et al.</i> ⁶⁴ | Milchert <i>et al.</i> ⁶⁵ |

^a Require high temperature to operate, risk of explosion of peroxy acids, corrosion problem to the process and non-recyclable catalyst.

^b In ion exchange resin method: There are some problems associated with the safe disposal for the deactivated catalyst after reusing it several times, in chemoenzymatic epoxidation method, the problem is with the disposal of the solvent.

^c No significant impact to the environment when using enzymes in solvent-free system.

Chemoenzymatic Epoxidation of Vegetable Oils

Chemoenzymatic epoxidation is the reaction which combines the flexibility of chemical epoxidation and the exquisite selective properties for enzymes in reaction.⁶⁶ The reaction mechanism of chemoenzymatic epoxidation consists of two consequent reactions⁶⁷: the first is the conversion of unsaturated fatty acids or esters, where the enzyme reacts with hydrogen peroxide to form unsaturated peroxy carboxylic acid. The second is the conduction of intermolecular pathway epoxides without enzyme participation. Based on the above mentioned mechanism, Orellana-Coca *et al.*⁶⁷ performed chemoenzymatic epoxidation of oleic acid and methyl ester using hydrogen peroxide and immobilized lipase from *Candida antarctica* under solvent free conditions. They found that the conversion of oleic acid was about 90%. While Zanette *et al.*⁶⁸ studied chemoenzymatic epoxidation of oleic and linoleic acid with hydrogen peroxide using *C. antarctica* lipase immobilized in organogels which is considered as a semi-solid catalyst that can be easily isolated from the product. The H₂O₂ addition rate was tested. Surprisingly, when the total amount of H₂O₂ was added at the beginning of the reaction, it resulted in the highest reaction yield which was opposing to the other commercial immobilized enzymes. The phenomenon occurs because enzyme being protected by hydroxyl-propyl-methyl cellulose organogel. The reaction conversion yield was relatively low when compared to another chemoenzymatic epoxidation as it was 56% mono-epoxy octadecanoic acid and 28% di-epoxy octadecanoic acid.

Zhang *et al.*⁶⁹ examined the influence of enzyme load, reaction time, agitation speed, H₂O₂ addition, usage of different organic solvent, and reaction temperature on the chemoenzymatic epoxidation of *Sapindus mukurossi* fatty acids catalyzed with *Candida sp.* 99–125 lipase. It was observed that besides solvent-free system, *N*-hexane was the only solvent among the organic solvents: toluene, tert-butanol, acetone, and acetonitrile; which led to a higher oxirane value. In addition, the optimum reaction condition for chemoenzymatic process yielding 83% reaction conversion was achieved by H₂O₂ addition with a frequency of 13.8 μL/min, enzyme load of 15 wt %, agitation speed of 350 rpm, and reaction temperature of 30 °C for 6 h followed by 35 °C for 2 h. Compared to the Novozym 435, a shorter reaction time was required for the epoxidation reaction at a lower temperature and in a free solvent media, achieving an approximately similar conversion when using *Candida sp.* 99–125. Sun *et al.*⁷⁰ also investigated chemoenzymatic epoxidation of *Sapindus mukorossi* seed oil depending on H₂O₂ and stearic acid as deoxidizing agents. They found that 90.3% of epoxidized *S. mukorossi* was reached. The optimum conditions were 50 °C as operating temperature, 1:4 molar ratio of C=C/H₂O₂, lipase B was. 2 wt % relative to the oil weight and the duration of the reaction was 7 h. It is found that the epoxidation of unsaturated fatty acids based on H₂O₂ and carboxylic acids via the chemoenzymatic method is faster than that of vegetable oils.

Yang *et al.*⁷¹ reported the comparison between the chemical epoxidation process and chemoenzymatic epoxidation process of Karanja oil with respect to the following parameters: temperature, rpm, H₂O₂ amount, type of solvents (toluene, benzene, and hexane), and catalyst. It was found that the optimum

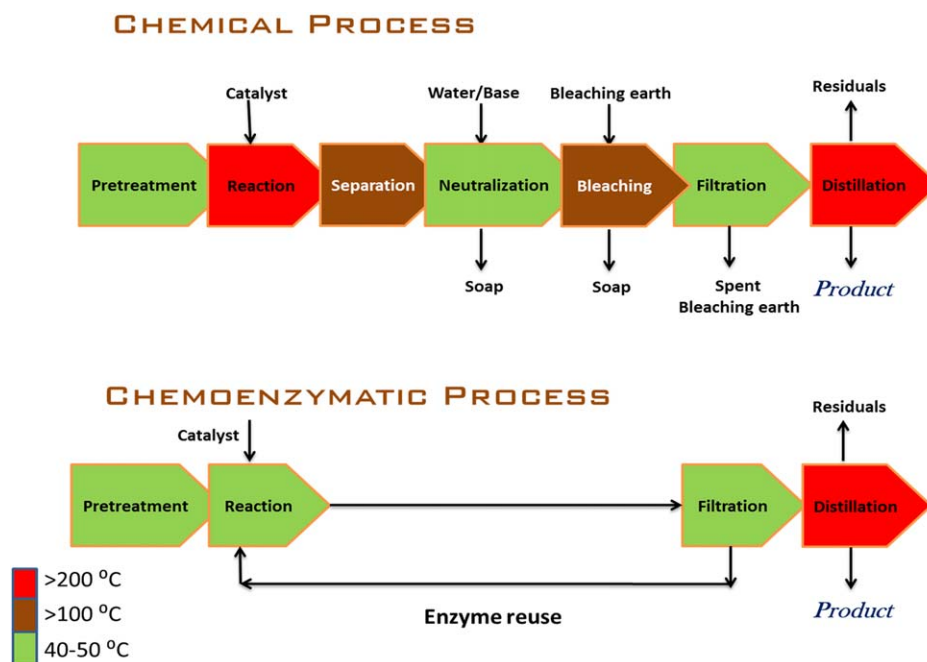


Figure 2. Aspects of conventional and chemoenzymatic epoxidation processes. [Color figure can be viewed at wileyonlinelibrary.com]

conditions for chemoenzymatic epoxidation process were when the temperature is 30 °C, mole ratio (H_2O_2 : unsaturation bond) is 1.25, biocatalyst concentration (Novozyme 435) is 4% and toluene solvent mass is 5.5 g. Bajwa *et al.*⁷² also tested the effect of benzene, toluene, and hexane as different solvent in chemoenzymatic epoxidation process of Karanja oil. It was found that conversions of 82 and 72% were achieved when toluene and benzene were used, respectively; while lower conversion of 64% was achieved using hexane. From the previously mentioned conditions it is obvious that chemoenzymatic epoxidation process required approximately three times less temperature and six times less rpm than chemical epoxidation process. Moreover, less amount of H_2O_2 was chemically needed in comparison to chemical epoxidation process.

Vleck *et al.*⁷³ studied chemoenzymatic epoxidation of soybean oil using hydrogen peroxide, oleic acid and catalyzed by Novozyme 435. They found that epoxidation rate of oil was highly affected by the concentration of lipase biocatalyst and the catalytic efficiency. Törnvall *et al.*⁷⁴ studied the effect of various parameters on lipase activity and operation life time during chemoenzymatic epoxidation of fatty acids. For instances, toluene, and water mixture as solvent, hydrogen peroxide as oxidant, oleic acid, perpalmitic acid, and stearic acid. In their study, they incubated immobilized *C. antarctica* lipase B at temperature between 20 and 60 °C followed by measurement of residual enzyme activity. They concluded that activity of enzyme was not affected by using water/toluene mixture for oleic acid or perpalmitic acid. Epoxy stearic acid slightly deactivated the enzyme when temperature reached 50 °C. Further, the increase in concentration of hydrogen peroxide and temperature affects the enzyme activity. These findings are consistent with the other researches, Goodwin *et al.*⁷⁵ proved that hydrogen peroxide

deactivate oxalate oxidase during the oxidation of oxalate to carbon dioxide. In addition, Milchert *et al.*⁷⁶ reviewed the effect of different parameters on chemoenzymatic epoxidation process of vegetable oils. This study indicated that increasing the concentration of hydrogen peroxide leads to enzyme inactivation. Moreover, increasing the process temperature also leads to enzyme inactivation. Therefore, temperature and hydrogen peroxide concentration should be monitored to avoid enzyme deactivation.

Méndez-Sánchez *et al.*⁷⁷ studied the production of twelve epoxides using *Rhizomucor miehei* lipase (RML); several parameters influence on the enzyme was reported. Thirty percent of hydrogen peroxide in presence of decanoic acid with water and dichloromethane mixture as a solvent was used for epoxidation of cyclohexane, but deactivation of RML was observed leading to 4% conversion after 24 h at 30 °C. Dimethyl carbonate was used as a peracid precursor, but it also led to negligible results. Urea-hydrogen peroxide (UHP) complex was used instead of hydrogen peroxide with decanoic acid in the presence of different solvents such as tetrahydrofuran, 2-methyltetrahydrofuran, and tert-butylmethyl ether where they led to a conversion of 4, 16, and 16%, respectively. The effect of replacing decanoic acid by phenylacetic acid, benzoic acid, stearic acid, lauric acid, and butanoic acid was also investigated. The highest conversion 31% was obtained when Lauric acid was used. The reaction temperature and alkene concentration were studied at 30, 37, 45 °C using lauric acid and UHP in acetonitrile with a substrate concentration of 0.33 M. The highest conversion 31% was achieved at 30 °C after 5 h. At the optimum temperature 30 °C, the substrate concentration was doubled to 0.66 M and the conversion was measured after 5, 13, and 24 h the highest conversion of 85% was achieved after 24 h. The influence of different loads of

RML in the presence of UHP and lauric acid concentration were reported. The highest conversion 91% was achieved when 50 mg of RML was used with 1.1 equivalents and 2 equivalents of lauric acid and substrate concentration of 0.66 M for 24 h. Increasing lauric acid to 3 equivalents under the same conditions resulted in reducing the conversion to 68%. Reducing lauric acid concentration to 1.1, reduced the conversion to 85% under the same reaction conditions. The epoxidation of cyclic substrates as cyclohexene, 2-methylcyclohexene, and cycloheptene occurred in a quantitative yield after 24 h. Dihydronaphthalene derivatives products were mainly obtained for conversion up to 83%, while styrenes derivatives products were mainly obtained for conversion up to 54%. Finally, they investigated the use of lipase for the indirect oxidation of (S)-carvone and limonene in order to form preacid. It was found that 18% conversion of internal alkene bond was oxidized in limonene and 78% conversion was achieved in exocyclic double bond in (S)-carvone.

Silva and Nascimento⁷⁸ studied the chemoenzymatic epoxidation of citronellol and different parameters affecting the operation such as several types of enzymes, types and number of oxidizing agents, types, and amount of acyl donor, types and effect of organic medium as well as reaction time. The effect of various enzymes such as lipases M Amano 10, PS Amano IM, Lipozyme IM, Amano 12, Lipases PS-C Amano I, F-AP15, AY Amano 30, Lipases PS Amano SD, PS Amano, AK, PS-C Amano II, Lipozyme RM IM, and CAL-B were investigated in the presence of Octanoic acid and acetonitrile at the same reaction conditions. Highest yields of conversion 70% citronellol oxide 2 and 30% citronellol oxide 3 were achieved when CAL-B enzyme was used followed by 26% citronellol oxide 2 and 3% citronellol oxide 3 when Amano I was used. Some enzymes showed no conversion while other enzymes showed low yield of <10%. Regarding the reaction time, the yield was measured after 2, 4, 6, 8, 10, and 24 h. It was found that the highest yields of citronellol oxide 2 and citronellol oxide 3 were obtained after 24 h. In addition to that, the effect of amount of UHP from 0 to 10 mmol on chemoenzymatic epoxidation of citronella was studied. It was observed that product conversion increased as amount of UHP increased up to 5 mmol. After that, a minor change in the yield was observed. Similar results were obtained when 30% H₂O₂ was used as oxidizing agent under the same reaction conditions. Different acyl donor C6–C16 were examined, the highest yield 71% was achieved when octanoic acid was used. The yield product of citronellol oxide 2 and citronellol oxide 3 were found to be function in amount of octanoic acid. As the amount of octanoic acid increases up to 0.5 mmol, citronellol oxide 2 increases up to 70–74% after that it remained constant. The effect of temperature on chemoenzymatic reaction rate was studied in a range 15–40 °C. It was observed that the highest yields of citronellol oxide were 80 and 77% and were obtained at 20 and 25 °C. As the temperature increased in the range 30–40 °C, citronellol oxide 2 yield decreased to 63% and citronellol oxide 3 increased to 37%. The effect of different solvents such as hexane, chloroform, *t*-butanol, *t*-butyl methyl ether, dichloromethane, ethyl acetate, ethanol, methanol, and a mixture of *n*-hexane and *t*-butyl methyl

ether or chloroform were tested and it was found that higher yields were obtained using ionic liquids.

Hilker *et al.*⁷⁹ used linseed oil, hydrogen peroxide, and water in recirculating reactor with separation of immobilized lipase B. The outcomes of this study were that the deactivation of immobilized lipase in the organic phase was reduced. Furthermore, studying the rate of reaction supports future research resulting in that the stability of enzyme relied on the hydrogen peroxide concentration and reaction temperature.

Warwel *et al.*⁸⁰ examined the lipase activity in the epoxidation of unsaturated fatty acids reaction. They succeeded to elongate the usage of lipase to 15 cycles as the reaction time was 8 h cycle and at cycle number 15 they found the lipase activity to be 25% of its original activity. Therefore, many reactions were carried out using unsaturated compounds, hydrogen peroxide, lipase as biocatalyst and hydrophobic solvents in order to maintain the lipase activity as much as possible. The outcome from this study was that the solvent polarity has an undesired effect on lipase stability because of the contest between the enzymatic protein and the solvent for water.⁸¹ Accordingly, hydrophobic solvents are not preferred to be used for lipase catalyzed reactions and to open the way towards many intermediate polarities compounds which could be used as solvents.^{82–85} De Abr u *et al.*⁸⁶ considered PSCI-Amano lipase for the epoxidation of oleic acid instead of *C. antarctica* which was used in the previous mentioned studies. They found that the epoxidized oleic acid yield reached to 88% when reaction duration was 3 h, 0.2% hydrogen peroxide used as solvent, and the enzyme content was 10% of the sample weight.

COMPARISON BETWEEN COMMERCIAL AND BIO-BASED PLASTICIZERS FOR PVC

PVC is thermoplastic compounds that is composed of PVC resin combined with diverse ranges of petroleum compounds such as plasticizers, fillers, stabilizers and manufacturing aids. Phthalate esters represent the gigantic proportion of the petroleum compounds that used in synthesizing flexible PVC compounds since it is responsible for softening PVC and enhancing the flexibility of the compound. Phthalate esters are versatile compounds that are used in multiple applications such as pharmaceutical capsules, baby toys, paints, fishing lures, textiles, shampoo, soaps, conditioners, glues, cosmetic products, drug delivery systems, and so on.^{2,87} Each application relies on the physical characterizations of certain type of phthalate ester, particularly the length and branching of the side chains. According to the previously mentioned harmful effects, replacing phthalate esters with bio-based compounds have attracted attention in the last decade. For PVC applications, several investigation methods are required to ensure the suitability of such alternatives to the commercial petroleum phthalate plasticizer. For example, mechanical properties, thermal stability, and flame retardant are fundamental aspects to evaluate PVC performance.

Li *et al.* synthesized epoxidized cardanol butyl ether (ECBE) and showed that using the epoxidized compounds as a PVC plasticizer instead of petroleum products such as DOP had enhanced the thermal and mechanical properties for PVC

Table II. Mechanical Properties for PVC Materials⁸⁸

| Sample | Elongation at break | Tensile strength |
|--------|---------------------|------------------|
| F0 | 340.40 ± 9.13 | 21.23 ± 0.71 |
| F1 | 356.91 ± 14.12 | 21.66 ± 1.28 |
| F2 | 377.88 ± 9.98 | 21.88 ± 0.12 |
| F3 | 401.15 ± 19.22 | 25.14 ± 0.98 |
| F4 | 385.32 ± 5.38 | 23.10 ± 0.70 |

materials.⁸⁸ Glass transition temperature (T_g) was decreased from 38.78 to 33.02 °C, when the plasticizer mixture was 70% for DOP and 30% for ECBE. In addition, thermal stability of PVC blends with different DOP and ECBE ratios and constant plasticizer content at 40 phr were examined via conducting thermogravimetric analysis (TGA). TGA gives details for degradation steps of various types of plasticized PVC matrixes. The initial degradation temperature for PVC matrix when plasticized with 100% DOP was 241.1 °C and increased to 256.4 °C when 40 wt % of EBCE substituted DOP. A similar increase was obvious in different degradation steps proving that EBCE improves the thermal stability of the PVC materials. With regards to mechanical properties, this research relied on testing elongation at break and tensile strength and they found that mechanical properties improved while increasing ECBE content resulting from the structure of alkyl group of ECBE and chain polarity. Table II illustrated the mechanical properties behavior starting from neat DOP (F0) till substituting DOP with 40 wt % of ECBE (F4).

Omrani *et al.*,⁸⁹ synthesized methyl 10-(2-methoxy-2-oxoethanesulfonyl) and ethyl 10-(2-ethoxy-2-oxoethanesulfonyl) from oleic acid and thioglycolic acid with the use of facile and scalable method of thiol-ene coupling. The plasticizing effects of the synthesized plasticizers in PVC as plastisol viscosities, thermal stability, glass transition, tensile properties, hardness, migration stability, exudation loss, and volatility stability were measured and compared to DOP. Ismail⁸⁹ reported that the weight loss of prepared PVC films using methyl 10, ethyl 10, and 2-ethylhexyl phthalate were 0.112, 0.098, and 0.176%, respectively, which indicated that both synthesized plasticizers are more compatible with PVC than DOP. In addition, migration was found to be lower than DOP when measuring the volatility at 180 °C for 30 min due to the higher molecular weight of synthesized plasticizers and the availability of higher polar groups in their structure. Moreover, ethyl 10 plasticizer had decreased glass transition temperature (T_g) for PVC blend to 36.26 compared to 40.14 °C when DOP was used as plasticizer. Accordingly, thermal characteristics of PVC matrix's plasticized with these green plasticizers (methyl 10 and ethyl 10) have been improved when compared with commercial one (DOP) because of the presence of the double ester bond, long chain fatty acid, and sulfone group. With reference to mechanical properties, this study defined the plasticizing effects of these bio-based plasticizers via conducting tensile test and shore hardness. It was found that the tensile strength, elongation at break, shore hardness, and modulus of elasticity are approximately similar to synthesized plasticizers and DOP, indicating that the synthesized

plasticizers had the ability to soften PVC and diffuse between chains.

Jia *et al.* (2017), synthesized phosphorous containing castor oil derivative, propargly ether EAMR-DOPO which was linked to PVC-N₃ as plasticizer. They studied the chemical structure and properties of different PVC plasticizer blends samples (PVC-A, PVC-B, and PVC-C). The mentioned samples were varying in weight ratios of PVC-N₃, propargly ether EAMR-DOPO, cuprous bromide, and 5,5-dimethyl-2,2-dipyridyl. The thermal properties for all PVC samples (PVC-A, PVC-B, and PVC-C) were investigated through conducting TGA and measuring the glass transition temperature (T_g). It was found that the thermal degradation of all samples began above 200 °C and by increasing the propargly ether EAMR-DOPO ratio in the compound, thermal stability increased at around 345–600 °C although it was unstable under 200–345 °C. This improvement in thermal stability was a result of raising the buildup of char remnant at above 345 °C which overcome the instability under 200–345 °C due to the disintegration of propargly ether EAMR-DOPO. Moreover, glass transition temperatures (T_g) for PVC-C, PVC-B, and PVC-A were 66.6, 53.2, and 46.4 °C, respectively; and it was noted that glass transition decreased from 87.6 to 46.4 °C when propargly ether EAMR-DOPO amount increased. In addition to measuring the thermal properties, degree of migration on all PVC samples (PVC-A, PVC-B, and PVC-C) were studied by testing the effect of different solvents (distill water, 10% (v/v) ethanol, 30% (v/v) acetic acid, and petroleum ether) on the samples.⁹⁰ Zero migration was observed in all samples using the previous solvents, ensuring that propargly ether EAMR-DOPO is a valid alternative for commercial plasticizer.

Chen *et al.*⁹¹ developed an epoxidized cardanol phenyl phosphate (ECPhP) and examined the thermal, mechanical properties, and migration resistance of five different PVC blends as secondary plasticizer. The composition of total plasticizer content in five samples (F0, F1, F2, F3, and F4) was 40 phr, where ECPhP and dioctyl terephthalate (DOTP) contents varied in each sample. For the first sample (F0), while the total plasticizer content was pure DOTP, the second sample (F1) contained 4 phr ECPhP and 36 phr DOTP, the third sample (F2) contained 8 phr ECPhP and 32 phr DOTP, the fourth sample (F3) contained 12 phr ECPhP and 28 phr DOTP, and finally the fifth sample (F4) was purely ECPhP. Regarding thermal characteristics, the glass transition temperature for F0, F1, F2, F3, and F4 was 47.2, 44.3, 43.9, 47.7, and 55 °C, respectively. These results indicated that by increasing ECPhP content to 12 phr, glass transition temperature decreased. This was due to ECPhP chemical structure which caused the existence of more polar group and longer alkyl chain. In addition, it was observed that PVC degradation occurred in two steps: the first step was dehydrochlorination and formation of macromolecules with conjugated double bond and the second step was transformation of this macromolecules into linear or cyclic structure via cracking and pyrolysis. Moreover, degradation time, balance torque and dynamic thermal stability time was measured for each sample. It was found that (F4) has the highest degradation time with 58.7 min and longest thermal stability time of 49.6 min. While (F0) has the lowest degradation time with 11.7 min and the

Table III. Sample Codes and Ratios⁹³

| Sample | PVC (g) | DOP (g) | PSOPE (g) |
|--------|---------|---------|-----------|
| A | 30 | 0 | 0 |
| B | 30 | 12 | 0 |
| C | 30 | 9 | 3 |
| D | 30 | 6 | 6 |
| E | 30 | 3 | 9 |
| F | 30 | 0 | 12 |

shortest thermal stability time of 9.6 min, these results show the ECPhP improved dynamic thermal stability of PVC. Concerning mechanical characteristics, this study investigated tensile properties and hardness of PVC blends. The elongation percent of the film increased from 376.7 till 389.4% as ECPhP content increased till it reached 12 phr (F3). Further increase in ECPhP content led to a decrease in elongation to 282.4% due to higher molecular weight and aromatic ring structure of ECPhP. In construct to that, a decrease in tensile strength was first observed till ECPhP content of 12 phr then tensile strength increased as the ECPhP content increased. As for shore hardness, they were all approximately similar. Finally, migration stability of PVC films was investigated using petroleum ether, soybean oil, and distilled water. Poor migration resistance was observed in all samples when petroleum ether and soybean oil were used in the following order $F4 > F3 > F2 > F1 > F0$ compared to distilled water, it showed that migration resistance is highly dependent on molecular weight.

Analysis for synthesizing acetyl soybean oil polyol ester (SOPE-1, SOPE-2) and epoxy acetyl soybean oil polyol ester (ESOPE-1, ESOPE-2) was carried out in 2016 as internal plasticizer for PVC. Eight PVC blends (PVCD, PVCE, PVC1, PVC2, PVC3, PVC4) were prepared using different plasticizer as DOP, ESO, SOPE-1, ESOPE-1, SOPE-2, and ESOPE-2, respectively.⁹² This research aimed to check the validity of the proposed plasticizers with PVC matrix through investigating the thermal and mechanical properties for the eight blends. With respect to thermal properties, glass transition temperature (T_g) was measured for all plasticized PVC blends showed a lower glass transition temperature than non-plasticized PVC which was 84.2, 43.1, 47.5, 44.6, 42.2, 44, and 34.3 for PVC, PVCD, PVCE, PVC1, PVC2, PVC3, and PVC4, respectively. In addition, an improvement in thermal stability for plasticized PVC blends compared with non-plasticized PVC. In terms of mechanical properties, modulus of elasticity, elongation at break, and tensile strength were measured. The findings out of these measurements were that PVC4 has the lowest tensile strength with 26.6 Mpa, while the highest was observed in non-plasticized PVC. Furthermore, the percent of elongation at the break of PVC2 was the highest of 598.79% and the lowest percentage was observed for non-plasticized PVC.

Jia *et al.*⁹³ synthesized phosphaphenanthrene group containing soybean oil polyol ester and investigated its effect on thermal stability, flame retardant performance as well as mechanical property of PVC-blend samples. Six PVC blends samples were

prepared by mixing PVC resin with DOP and phosphaphenanthrene group containing soybean oil polyol ester (PSOPE) at different weight ratios. All samples contained the same amount plasticizers with different ratios and the same amount of PVC as illustrated in Table III.

In terms of the decomposition temperature, as the weight content of PSOPE increases in PVC blend samples, the thermal degradation temperature increases. Accordingly, the thermal stability of PSOPE is higher compared to DOP indicating more flame retardant. In addition, limit oxygen index (LOI) values for PVC blends were investigated. As PSOPE content increased, LOI values decreased from 48 till 36.2% which indicate a self-extinguishing behavior. The results from this study is depicted in Figure 3. This finding was consistent with another research⁹³ carried out in 2015 that used epoxidized castor oil as plasticizer for PVC blend. The results from this study is depicted in Figure 3. LOI value increased from 23.6 to 36.7% for the PVC materials, this behavior was due to the formation of thick carbonization zone which acts as a preventing layer to O_2 .

Regarding the mechanical properties, tensile strength, elongation as well as modulus of elasticity were studied for PVC blends samples. For pure PVC blend (a) higher tensile strength, modulus of elasticity, and low elongation at the break were observed at 26.6, 197.11, and 167.21%, respectively. When DOP was introduced in PVC blend the tensile strength, modulus of elasticity decreased to 13.08 and 98.93 MPa, while elongation at break increased to 405.35%. Upon the increasing PSOPE content and decreasing DOP gradually for the rest of the samples, tensile strength as well as modulus of elasticity increased to 22.84 and 181.26 Mpa, respectively; while the elongation decreased to 278.39%.

Jia *et al.*⁹⁴ prepared a green plasticizer using a castor oil containing phosphaphenanthrene groups (PCOPE) as an additive to PVC. The results showed several important differences between using bio-plasticizer and petroleum based plasticizers. It was found that PVC molecules were more stable at high temperatures and the performance in inhibiting the outbreak of fire was increased. Moreover, when all petroleum-based plasticizers were completely substituted with bio-plasticizer in PVC blends, the TGA and difference thermogravimetric parameters values:

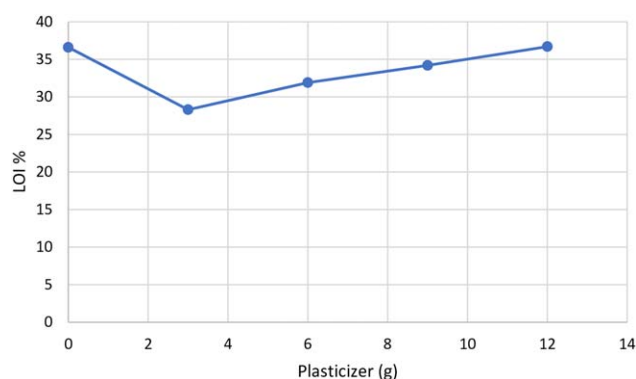


Figure 3. Relation between LOI and plasticizer content.⁹⁴ [Color figure can be viewed at wileyonlinelibrary.com]

T_b , T_{50} , T_{p1} , and T_{p1} reached 289.4, 318.2, 293.8, and 444.3 °C, respectively.⁹⁴ This study suggested the replacement of commercial phthalate plasticizer either partially or completely with a biocompatible and sustainable resources. Bondeson studied the epoxidation of vegetable oils such as soybean, sunflower, and safflower are good replacements for DINP in PVC materials used for indoor applications.⁹⁵ Moreover, the rate of crosslinking is positively correlated with the degree of epoxidation of the epoxidized vegetable oils.

Yin *et al.*⁹⁶ prepared and evaluated the mechanical and thermal properties of three bio-based PVC plasticizers (glucose, hexanoate, esters) from Glucose and compared them to α -D(+)-glucose pentaacetate (GPA) and D-(+)-sucrose octaacetate (SOA). The three green plasticizers (GH9h, GH12h, and GH24h) were obtained by adding glucose (18 g, 0.1 mol), surplus of hexanoic acid (97 g, 0.8 mol) catalyzed by di-butyl tin oxide (0.14, 0.6 mmole) at different reactions time 9, 12, and 24 h, respectively. PVC blends were prepared for each plasticizer using two plasticizer compositions 20 and 40 wt %. Yin reported that as the reaction time increases, several numbers of hexanoate substituents per glucose molecule increase. It was observed that the highest number of hexanoate substituents per glucose was achieved in GH24h while lower similar results were observed for both GH9h and GH12h. With regards to thermal properties, a single glass transition temperature (T_g) was observed for all blends as it was decreased by increasing the plasticizers percentage in the blend, except for PVC blends with GH9h 40 wt %, SOA 40 wt %, and GPA 40 wt % plasticizers which showed two glass transition temperatures. These results indicate that GHs plasticizers had a good miscibility with PVC. The transparency of PVC film for different plasticizers (GH12h, GPA, and SOA) with 40 wt % was also investigated. It was observed that the best transparency appeared in GH12h followed by SOA and then GPA. By comparing the three green plasticizers together, they all looked similar. With regards to the mechanical properties of PVC blends, they were studied by measuring stress, strain, and elastic modulus. As the amount of plasticizer increase from 20 to 40 wt %, the elastic modulus and stress at the break decreases while the strain at the break increases for PVC blends except for GPA plasticizer blend. By comparing GHs plasticizers effects, better performance was achieved for GH12h and GH24h compared to GH9h.

All the previous researches and studies bring the light to bio-compatible plasticizer for PVC blends; particularly the epoxidized vegetable oils. According to Zio market research company, the worldwide consumption of PVC in 2015 was 43,662.0 kilotons which valued at 57.06 billion USD and it is predicted to rise to 78.90 billion USD in 2021. The proportion of the phthalate addition in PVC varied from 20 to 50% according to the flexibility requirements for each product, which means that phthalate demand in 2015 was 8732–21,831 kilotons. The cost of DOP is around 1300 \$per ton, while the cost of epoxidized vegetable oil is around 1500 \$per ton. This difference in prices is not significant but the impacts difference between the traditional plasticizer and the bio-based one is significant if the priority are the health concerns or environmental issues.

CONCLUSIONS

This article aims to review bio-compatible and sustainable alternatives for commercial phthalate esters. Since commercial phthalate esters have serious health risks particularly on children and women, searching for healthy phthalate alternatives has become a necessity. One of the most distinguished methods in producing bio-compatible plasticizer is the epoxidation of vegetable oils and fatty acid. There are several processes for the epoxidation such as chemical and chemoenzymatic processes. Chemoenzymatic process is recommended to be used in epoxidation for two reasons: (1) low environment impact during processing and (2) safety of produced product. The challenge in using chemoenzymatic process is in scaling up the enzyme production process in order to produce enzymes economically. Moreover, the investigation of physical and mechanical properties for synthesized PVC using bio-compatible plasticizer are promising indicating equivalent properties to synthesized commercial phthalate PVC. All the above-mentioned studies and results in this article give great motivation for replacing petroleum based plasticizers with bio-compatible plasticizers in PVC.

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