Synthesis of Flame Retardant Phosphorus Containing Polyols from Canola Oil

by

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ABSTRACT

Phosphorus containing polyols were synthesized from canola oil. Epoxidized canola oil was transesterified with 1,3 propanediol to introduce one reactive primary hydroxyl group. Incorporation of phosphorus into these structures was explored using three different epoxy ring opening reactions – reaction with phosphoric acid, ethyl phosphates and dibutyl phosphate. The phosphate ester structures initially formed were found to be unstable, ultimately leading to the formation of cyclic dioxaphospholane structure. The effects of these chemical changes on the characteristics of the polyols for polyurethane preparation were studied. The reactive flame retardant canola oil based polyol was successfully replaced all of the polyol content used for the preparation of rigid polyurethane foams with biocontent of more than 90%. These were shown to have significantly improved flame retardancy and were self-extinguishing.

DEDICATION

I dedicate this work to my father, Liew Nyuk Chong and my mother, Chia Jun Moi, who are no longer with us, for their sacrifice and dedication to raise me up and make me the person I am today.

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Praise and glory to Lord Jesus Christ, for His blessings and provisions.

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AN	Acid number
ASTM	American Society for Testing and Material
C-OH	Hydroxyl group
DBP	Dibutyl phosphate
EIC	Extracted Ion Chromatogram
eFAPE	Hydroxypropyl ester of epoxidized canola oil
eFAPE-DBP	Phosphorus containing polyol obtained from reaction between eFAPE and dibutyl phosphate
eFAPE-EP	Phosphorus containing polyol obtained from reaction between eFAPE and ethyl phosphate
eFAPE-PA	Phosphorus containing polyol obtained from reaction between eFAPE and phosphoric acid
EP	Ethyl phosphate
ESI+/-	Electrospray Ionization (positive/negative mode)
FTIR	Fourier Transformed Infrared Spectroscopy
GPC	Gel permeation chromatography
LCMS	Liquid chromatography mass spectrometry
LOI	Limiting Oxygen Index
NMR	Near Magnetic Resonance
OHV	Hydroxyl value
OOC	Oxirane oxygen content
P-OH	Phosphoric acid functional group
PUR	Polyurethane
TIC	Total ion count

CHAPTER 1: INTRODUCTION

1.1 Background

1.1.1 Polyurethane (PUR)

Polyurethane (PUR) is a polymer composed of various monomers joined by urethane bonds, which result from the reaction between isocyanate groups (-NCO) and hydroxyl groups (C-OH) as shown in Figure 1.1. It is one of the most useful and widely used commercial polymers[1]. Due to the possibility to use wide range of raw material components i.e. di/tri-isocyanates, polyols and chain extenders used for synthesis of PUR, the properties of PUR can be customized, leading to the presence of other functional groups such as urea, esters, aromatics and ethers in the PUR structure. This wide range of compositions and versatile properties enables PUR to be extensively used in many commercial applications such as thermoplastics, thermorigids, foams, coatings, adhesives, sealants, synthetic leathers, membranes, fibers, elastomers and many applications in biomedical field. Major industries where PUR is used are furniture and upholstery, automotive and building (as insulations)[1] [2][4][5][6].

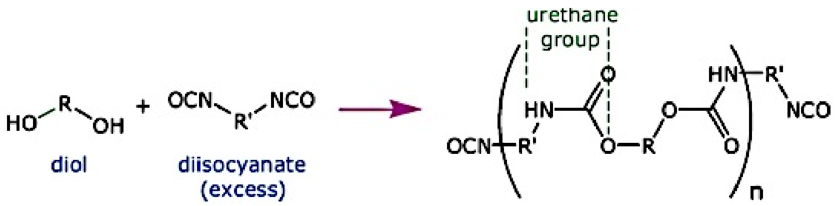


Figure 1.1 Reaction between diisocyanate and diol to form urethane bond[5]

1.1.1.1 Polyurethane Foams

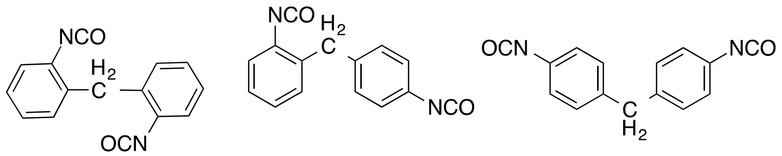
PUR foam can exist in rigid or flexible form. Rigid PUR foams are widely used for thermal insulation such as building insulation and in energy saving appliances such as refrigerators, freezers, insulated truck, and as buoyancy for boats. Rigid PUR foams have a closed cell structure whereas flexible PUR foams have an open cell structure. Flexible PUR foams are used for cushioning in furniture, transportation and the packaging industry.

PUR foam is composed of solid-gas material in which the continuous phase is the PUR polymer and the discreet phase is gas phase. Rigid PUR foams are hard and contain high crosslink density, resulted from reaction between polyol with high functionality and lower molecular weight with isocyanate. Flexible foams are soft and contain lower crosslink density, obtained from crosslinking between low functionality and high molecular weight polyol with isocyanate.

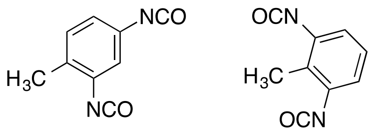
1.1.1.2 PUR Foams Preparation

PUR can be prepared from reaction between isocyanate and polyol having at least two isocyanate and C-OH groups, respectively. The basic components used for making PUR foams are polyols, isocyanates, catalysts, blowing agents and surfactants. Flame retardants, fillers, colorants and epoxides are used as auxiliary or optional materials depending on the desired features or characteristics of the foams[7].

The most commonly used isocyanates (Figure 1.2) in commercial PUR manufacturing are aromatic isocyanates, toluene diisocyanate (TDI), diphenyl methane diisocyanate (MDI) and polymeric diphenyl methane diisocyanate (pMDI). Aliphatic isocyanates such as hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI) and 4,4’-methylene bis(cyclohexyl isocyanate) (HDMI) are also used but in some special applications[6].



MDI isomers



TDI isomers

Figure 1.2: Molecular structure of MDI and TDI

Normally tertiary amines and/or organometallics, often containing tin, lead or mercury are used as catalysts in the reaction between the C-OH groups from the polyols or water with isocyanate groups of the isocyanates to form a cross-linked network. Gas is introduced into the PUR structure by mean of reaction of isocyanate with water, which produces CO_2. In addition to that, auxiliary blowing agents (materials with low boiling point) such as cyclopentane are also used. The reaction between isocyanate and polyol is exothermic, producing heat which will cause the CO_2 gas and the auxiliary blowing agent to diffuse and expand into nucleated bubbles and aid in the foam expansion[6][8].

Surfactants is added to lower the surface tension, emulsify incompatible ingredients, initiate nucleation of bubbles during mixing, stabilize the rising foam, to prevent coalescence of the cells until they are strong enough to becoming self-supporting, thus preventing shrinkage.

Several techniques used in PUR making include the prepolymer technique, quasiprepolymer technique and “one shot” technique. The latter is the most commonly used technique that consists of very efficient mixing of all the ingredients in one step and very short time. Prior to mixing, compound A, which is a mixture of components that do not react with each other (all ingredients except isocyanate) is prepared. The second component is. isocyanate, also called as compound B. Efficient contact between the isocyanate component and the polyolic component leads to formation of PUR[6].

1.1.1.3 Flammability of PUR foams

Due to its organic nature, just like other polymers, vegetable oil based PUR foams are flammable. They burn easily and completely when subjected to fire and pose fire hazards in applications where fire safety and regulations are required. Flammability of PURs poses threats to both the integrity of the products and human health/safety. Thus, flame retardancy or resistance is a desired property in PUR. It is critical to incorporate flame retardant in manufacturing of PURs for applications in some industries such as construction, transportation, electrical and electronic industries[9]

Flammability is related to the tendency of a material to form gaseous and flammable products during thermal decomposition. It is characterized by the ignitability, flame spread rate and heat release of the material under fire condition, which can be measured by cone calorimetry. This has to do with the energy required for thermal decomposition to happen, tendency to form flammable products and the amount and rate of heat release during combustion [5], [10], [11]. Flammability of a polymer is also commonly measured by less sophisticated methods such as the Limiting Oxygen Index (LOI) and UL94, which measures the ignitibility and flame spread of a specimen exposed to small flame and groups materials under categories based on their flammability. LOI is the most commonly used method. LOI is expressed as $([O_2]/([O_2] + [N_2]) \times 100$. Fire resistant material will require more O_2 to sustain combustion, thus, will give higher LOI. The O_2 content in air is 21% so any material with LOI above 21% is considered as self-extinguishing because the combustion cannot be maintained at ambient temperature without contribution from external source. LOI is measured by passing a mixture of oxygen and nitrogen over a burning specimen, and reducing the oxygen level until a critical level is reached. Materials with LOI below 21% are considered as flammable[10], [11].

Generally, PUR has relatively low thermal stability due to the presence of urethane bonds. Depending on the substituents of the polyol and isocyanate side, the onset on urethane bond dissociation lies between 150°C and 220°C

Several studies conducted on the thermal stability of vegetable oils based PURs concluded that vegetable oils based PURs degrade in multiple stages of thermal degradation. PURs synthesized from vegetable oil based polyols (castor, soybean, sunflower, safflower, canola, peanut, olive and corn) with diphenyl methane diisocyanate showed better oxidative thermal stability as compared to PUR from a commercial polyol, Acrol LG-168, which is a polyoxypropylene triol. However, in the absence of oxygen, vegetable oil PURs are less stable as compared to the Acrol based PUR[12]. Studies also concluded that vegetable oil based polyols containing primary C-OH groups resulted in PURs with better thermal stability than polyols with secondary C-OH groups. PURs with high urethane group concentration are less stable than those that have lower concentration of urethane bond[5], [12], [13]. This is directly related to the C-OH functionality of the polyols, which is defined by number of reactive C-OH group per molecule of polyols available for forming cross-links with isocyanate to form urethane bonds.

It has been reported that the thermal decomposition of vegetable oil based PUR happens in a complicated two or three step process, starting with the degradation of urethane bonds into isocyanate and alcohols, primary or secondary amines, olefins and CO_2[5], [12], [13]. The second stage is attributed to ester bond decomposition through chain scission. The third stage happens at higher temperature could be due to C-C bond cleavage. Depending on the chain length of the diisocyanate or polyol used, products generated from degradation of PURs differ from one to another[5], [12], [13]. It is also reported that thermal stability of vegetable oil based PURs depends strongly on the number of urethane group per unit volume. Generally, PUR with high crosslink density have better thermal stability in both inert and oxidation environment as more thermal energy is required to break down the additional bonds with increasing crosslink density before the break down of the total network take place[5][12]. In contrast, Monteavaro et. al.[13] reported that the initial weight loss (weight loss at first stage of degradation at 210ºC) increased with increasing amount of urethane groups in the PURs in soybean oil based PUR foams. The contradicting findings regarding the thermal stability of PUR in relation to urethane bond density could also be affected by other factors such as foam density, polyol structure etc. PUR foams are also known to produce large quantity of vision obscuring corrosive smoke and toxic gases such as carbon monoxide and hydrogen cyanide during combustion[14].

1.1.2. Flame Retardants

Basically, there are three essential elements required for combustion of a material to be sustainable – heat, oxygen and fuel (combustible masses). When PUR foam is subjected to heat, various polyurethane linkages are broken at different temperatures. In the presence of sufficient oxygen, combustion occurs producing combustible gases, non-combustible gases, entrained solid particles (smoke) and carbonaceous char. The heat resulting from the combustion raises is transferred by radiation from the combustion zone to adjacent materials leading to further decomposition and ignition, thus, flame propagation[11], [14].

The main function of flame retardant is to inhibit flame spread or to make the material self extinguishing in the event of fire. Strategies to improve PU against fire including interrupting the combustion process at one of more of its complex stages, aiming to inhibit ignition, reducing burning rate and/or change the combustion mechanism as well as to suppress production of smoke and toxic gases. Basically, fire is inhibited or by excluding one or more of the three essential elements of substantial combustion cycle [10], [11].

In order to enhance the flame retardancy of PUR foams, several approaches can be employed via (1) incorporation of additives flame retardants by simple mechanical mixing at the PUR preparation stage; (2) incorporation of reactive flame retardant, compounds containing functional groups such as C-OH, which will be chemically bound to the polymer chain; and (3) coating the foam surface with flame retardant materials. Coating is only useful for spray-applied foam where low vapour permeability is desired. Use of reactive flame retardants has many advantages over additives because the flame retardant actually take part in the foaming reaction and become part of the polymer. It can retain the flame retardancy for a longer period of time and the distribution of flame retardant compound is more even over the entire foam. Additive flame retardants often have adverse effects on the physical properties of the foams such as discoloration, decrease in closed cell content & strength, increased in water absorption and migration to the surface during foam preparation and over a long period of time, thus leads to loss flame retardancy properties[10], [11], [14]

1.1.2.1 Phosphorus Containing Flame Retardants (PFRs)

The most widely used flame retardants are halogenated FR such chlorinated and brominated FRs However, due to growing concerns over their persistency, bioaccumulation and toxicity to the environment and human health, there have been stricter regulations, restrictions, bans and voluntary phase out in use of halogens as FR in some countries[11].

Phosphorus containing compounds are becoming alternative as FRs in many polymers due to their versatility, less toxicity and efficiency as FR[11], [15][14]. PFRs are incorporated either as additives or reactive FRs, in form of inorganic compounds such as red phosphorus and ammonium polyphosphate; as well as phosphorus containing organic compounds such organophosphates, phosphines and phosphonates.

PFRs are known to primarily inhibit flame propagation in the condense phase via formation of protective char layer. Upon thermal decomposition, phosphorus in the burning polymer forms anhydrides of phosphoric acid and other related acids, which act as dehydrating agents to form C=C in the polymer. At elevated temperature, the C=C will cross-link and form a char layer. In addition to that, the acids also form a thin glassy liquid protective layer in the condensed phase. These protective layers lower oxygen diffusion, heat and mass transfer between the condensed phase and the gas phase. Finally, the acids also decrease the heating process (as heat sink) by retarding the oxidation of carbon and oxygen to carbon dioxide[11], [14]. In addition to that, additive PRFs are also found to exhibit free radical trapping properties in the gas phase[11].

Incorporation of phosphorus into PUR foams at as low as 0.5% (w/w) of the total foam formulation was found to effectively increase the LOI to 21.8%. It was reported that incorporation of phosphorus at up to 1.5% in the total formulation proved to be effective but that further increases seemed to give no further benefit[14].

Several studies on the synthesis of additive phosphorus containing FRs from biobased materials such as itaconic acid[16], fatty acid derivatives[17] and phoroglucinol[18] were reported. Reactive PFR polyols (as opposed to additive PFRs, these phosphorus containing polyols that cross link with isocyanate to form PUR, thus, the phosphorus element is chemically bound into the PUR structure) for PUR application were synthesized from epoxidized soybean oil[19] and palm oil[20] based on reaction with ortho-phosphoric acid as reported by Guo et al[21]. The resulting product derived epoxidized oils had high molecular weight (>3,800 g/mole)[21] and high acid number[19]. Zhang et al[22] synthezied PFR polyol from epoxidized castor oil by incorporating phosphorus into the polyol structure via reaction with diethyl phosphate, by employing toluene as solvent and catalyzed by triphenylphosphine.

1.1.3 Polyols

Polyol is molecule containing two or more C-OH groups and it is one of the two main components of PUR. In PUR manufacturing industry, only a few types of isocyanates are used such as MDI, TDI and pMDI, thus the thermal and mechanical properties of PUR depend mainly on the characteristics of polyols.

One of the most important characteristics of polyol for PUR application is hydroxyl value (OHV). OHV represents the amount of reactive C-OH group available for isocyanate reaction. It is determined by a wet analytical method and is expressed as mgKOH/g, based on the reaction between the C-OH gr oup with organic anhydrides. The acidic carboxyl groups resulting from this reaction are then neutralized with equimolecular quantity of potassium hydroxide (KOH)[23].

Functionality of a polyol is defined as the average number of C-OH site per molecule of polyol. A polyol must have functionality of at least two to be able to cross-link with isocyanate to form a PUR. The physical and mechanical properties of PURs are affected by density of cross-linking in the structure. Polyol functionality affects the cross-linking density if a PUR. The higher the functionality, the more reactive sites are available for cross-linking with isocyanate, thus, resulting in PURs with higher cross-linking density. Generally, a lower amount of cross-linking will result in more elastic PUR and higher cross-linking will result in more rigid PUR [24][6]. Similarly, polyols with low molecular weight result in rigid PUR and higher molecular weight, flexible PUR. Vegetable oil based polyols consist of macromolecules with a wide distribution of molecular weights[6], [24].

Reactivity of the C-OH groups is particularly important for the preparation of PUR foams. Fast reaction between isocyanate and C-OH group is always preferred especially in preparation of spray foam. Thus, primary C-OH group which is 3-3.3 times more reactive towards reaction with isocyanate than secondary hydroxyl group is desired[25][6].

Parameters such as viscosity and acid number are also important factors impacting the processing and production effectiveness in preparation of PUR. Viscosity gives indication of processability of a polyol. All polyols should be in liquid form at low temperature (30-60°C). Polyols with relatively low viscosity 0.1-10 Pa.s at 25°C are preferred for better mixing[6].

The acid number (AN), expressed in mgKOH/g is a number arising from wet analytical method corresponds to milligram of potassium hydroxide required to neutralize the residual acidity of one gram polyol. The presence of residual acidity in polyol decreases the catalytic activity of tertiary amines by acid-base neutralization, thus polyol with low acid number is desired[6] [16].

1.1.3.1 Vegetable Oil Based Polyols

Traditionally, polyols for PUR are derived from petroleum or natural gas based chemicals [4]. However, due to various environmental issues such as greenhouse gas emission and depletion of non-renewable resources, there has been extensive and emerging interest in research and development of bio-based isocyanates and polyols for PUR applications. Bio-based polyols can be synthesized from oil and fats particularly vegetable oils[9], [27]–[32], protein[9], lignocellulosic biomass[9], and cardanol.

Abundantly available, inherently biodegradable, low toxicity and low cost, plant oils have gained much interest from both academic and industry research as platform materials for PURs. Several characteristics that make vegetable oils more attractive as biomaterials including the possibility that (1) their structure can be modified such as through chemical reactions at the double bond, ester and allylic H to become monomers for polymeric materials; (2) their hydrophobic nature makes them suitable for the synthesis of hydrophobic polymers that will complement other biomaterials such as carbohydrates and proteins; and (3) they are suitable for the synthesis of monomers with structure similar to petrol-based monomers[30]. Vegetable oils consist of triglyceride of fatty acids which of linear hydrocarbon chains, structure similar to those of petrochemicals.

Oils extracted from plants such as soybean, oil palm, canola, corn, flax seed etc contain mainly triglyceride molecules where the C-OH functions of the glycerin are esterified with fatty acids as presented in Figure 1.3. The fatty acid chains, R_1, R_2 and R_3 could correspond to mono- (one double bond) or poly-unsaturated (two or more double bonds) or saturated (no double bonds) C12-24 carbon chain. The most common unsaturated fatty acids present in vegetable oils are C18:1 (oleic acid), C18:2 (linoleic acid) and C18:3 (linolenic acid). The composition of fatty acids varies depending on the source of oil[29][33][34]. The ester groups, allylic carbons and the double bonds in plant oils (Figure 1.4) are reactive groups that enable functionalization of vegetable oils based on several well-known chemical reactions, some examples are shown in Figure 1.5.

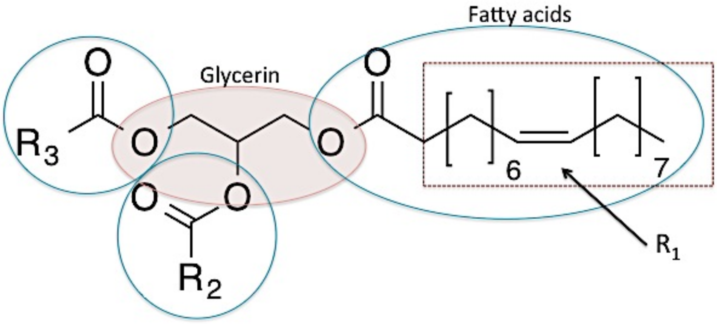


Figure 1.3: Triglyceride structure with R_1, R_2 and R_3 aliphatic fatty acid chains, with R_1 corresponding to oleic acid.

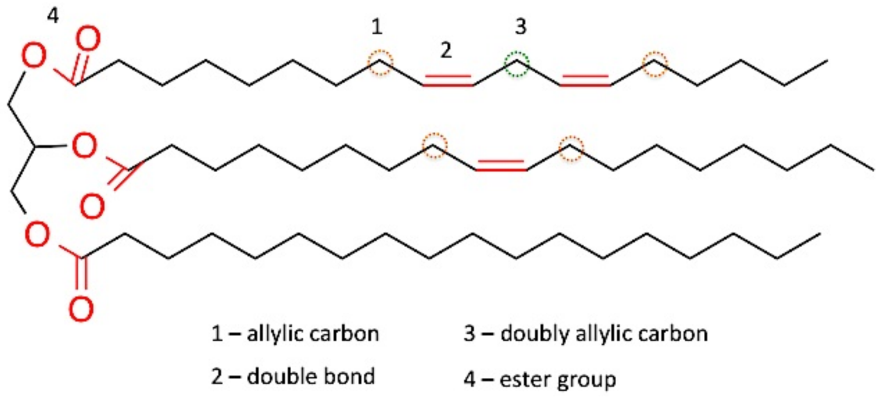


Figure 1.4: Reactive sites in triglyceride molecule of vegetable oils

With the exception of castor oil, natural plant oils have no alcoholic C-OH group, thus the C-OH groups have to be introduced into the oil structure for synthesis of polyols. The carbon-carbon double bonds and ester groups are two reactive sites most commonly used for synthesis of polyols. The most common pathways for synthesis of polyols for PURs applications from vegetable oils are (a) epoxidation and oxirane ring opening; (b) hydromylation and hydrogenation; (c) ozonolysis; (d) thiol-ene coupling and (e) transesterification/amidation[9][28] (Figure 1.5)

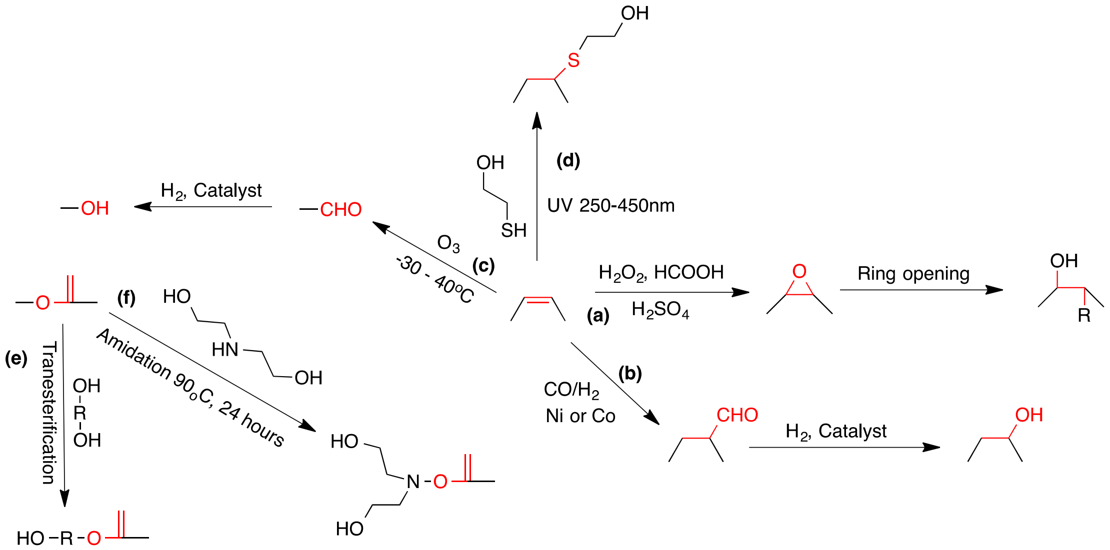


Figure 1.5: Various pathways for synthesis of vegetable oil based polyols (a) epoxidation and oxirane ring opening (b) hydromylation and hydrogenation (c) ozonolysis (d) thiol-ene coupling (e) Tran esterification (f) admiration

C-OH groups can be introduced into the fatty acid structure via transesterification with diol or polyol such as glycerol, 1,2-propanediol or 1,3-propanediol in the presence of acid or alkaline catalysts[22], [27], [30], [35]. In addition to this, transesterifcation also remove two fatty acids from the triglyceride molecule resulting in product with relatively lower molecular weight, which is desirable for lower viscosity. Generally, it is hard to obtain polyol from vegetable oils with OHV higher than 250 mgKOH/g with low viscosity at the same time. Due to the limited number of double bonds, the number of C-OH group that can be introduced to the structure via epoxidation and ring opening is also limited. However, an additional transesterifcation step with diols or polyol could increase the functionality as well as to reduce the molecular weight (consequently the viscosity) at the same time[27], [35].

The most important route for synthesis of polyol is via epoxidation of double bonds followed by ring opening with various reactants. The selection of type of reactants will later determine the functional groups incorporated into the polyol structure. Vegetable oil double bonds can be converted to epoxy group by peroxyacetic or peroxyformic acid formed *in situ* by reaction of hydrogen peroxide with acetic or formic acid in the presence of catalyst such as sulfuric acid[30]. Oxirane ring opening can be performed via reaction with nucleophilic compounds, such as water, alcohols and acids resulting in addition of at least one C-OH group.

1.1.4 Oxirane Ring Opening Reaction with Phosphoric Acid and Its Derivatives.

In the presence of acid catalysts, oxirane ring can be opened by water or alcohols, forming two secondary C-OH groups or an ether bond and a secondary C-OH respectively, via a nucleophilic substitution reaction. Since the reaction resulted in formation of C-OH, formation of C-OH terminated oligomers may occur. Generally, the reactions under such condition are summarized in Figure 1.6[21].

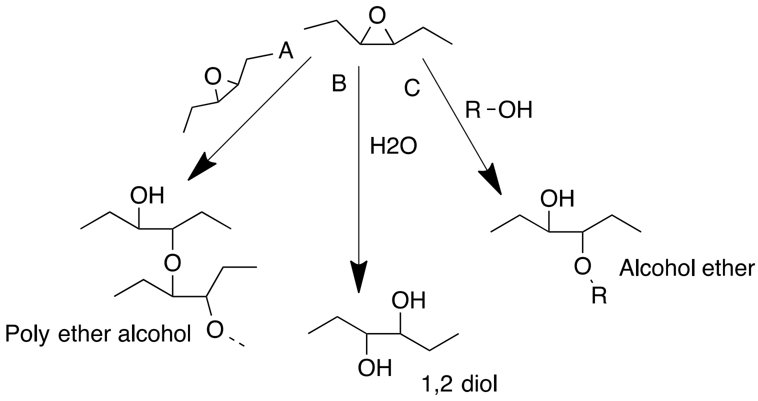


Figure 1.6: Ring opening pathways of oxirane in the presence of acid catalysts

Phosphoric acid, containing three acidic P-OH having $pKa_1 = 2.15$, $pKa_2 = 7.09$ and $pKa_3 = 12.32$ was reported to act as catalyst and reactant is ring opening of epoxide, resulting in a mixture of mono-, di- and tri-ester phosphate, with formation of one secondary C-OH for each oxirane ring opened by P-OH, as shown in Figure 1.7[21], [36]–[38].

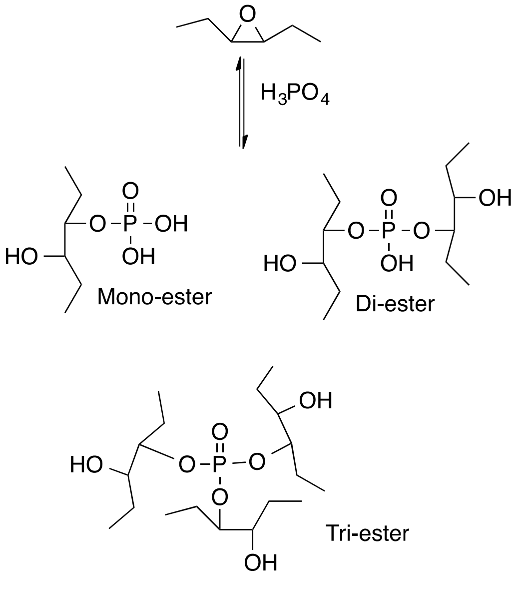


Figure 1.7: Formation of phosphate esters from reaction with epoxy ring and phosphoric acid

This reaction had been employed to incorporate phosphorus into fatty acids of vegetable oil for synthesis of bio-based flame retardant polyol[19], [39],[20], [40] for oleo-based pressure sensitive adhesives[41], [42] and lubricant additive[43].

1.2 Motivations and Overview

Just like its petrol-based counterpart, PUR made from bio-based polyol is flammable by nature. Due to the wide application of PUR foams in building insulation and household upholstery, strict regulations require PUR foams to meet fire safety standards and regulations. Addition of flame retardants to PUR should give permanent flame retardant effect, minimum emission of toxic fumes, remain economical and have no adverse effect on the processing and properties of the PUR. It is more challenging however, if the PURs are made of renewable materials such as vegetable oils due to the fact that the renewable polymer industry is fairly new and compatible flame retardant is yet to be available. The complexity of the vegetable oil chemistry makes it difficult to incorporate flame retardant elements without affecting the qualities and properties of PUR materials.

Phosphorus, inorganic and organophosphorus compounds, which are generally less toxic, has become an excellent alternative as flame retardant. In commercial manufacturing of PUR foams, phosphate based FRs are added into the polymer as additives. Additive flame retardants are more likely to migrate to the surface (loss of permanent effect and likelihood to be released into the environment), because they are not chemically bound to the polymer structure. They could also be inhomogeneously distributed in the polymer as they are physically mixed into the polymer. Incorporation of phosphorus or phosphate into the PUR structure by using phosphorus containing polyols could overcome these disadvantages by having the FR element chemically bound to the structure.

This research was proposed to explore the possibilities of development of bio-based polyols with flame retardant properties from vegetable oils for PUR foam applications via simple, environmental friendly and low cost synthesis routes. Specifically, the study aimed to synthesis polyols (i) containing sufficient number of hydroxyl group for cross linking of PUR foam, with (ii) maximum amount of phosphorus chemically bound in its structure to effectively reduce the flammability of the foam. Physical and chemical properties of the polyols such as viscosity, acidity and molecular weight are also taken into consideration, as these properties are important in affecting the processing and properties of the PUR foam.

It is well established that unsaturated vegetable oils can be derived into epoxides and further functionalization can be carried out via opening of the epoxy ring with compounds containing various functional groups such as hydroxyl groups to yield polyols. Additional C-OH can also be introduced to each fatty acid via transesterification, the reaction that will also reduce the triglyceride to fatty acid ester containing multiple C-OH groups with lower molecular weights, characteristics of polyol desirable for PUR foam preparation. Phosphoric acid and its derivatives containing one to three P-OH groups were found to not only function as catalyst in epoxy ring opening but also participate as reagent in the nucleophilic ring opening reaction yielding phosphate ester bond and a secondary hydroxyl group. Thus, phosphorus can be grafted into vegetable oil epoxide to yield polyol, which can function as reactive FR in PUR foam.

To test this hypothesis, reaction of hydroxypropyl ester of epoxidized fatty acid derived from canola oil with phosphoric acid was studied, as described in

Chapter 2. It was found that phosphoric acid reacts with the epoxy ring resulting in formation of mono-, di- and tri-ester phosphates, and also oligomeric ethers in the presence of water and alcohols. Reaction with monobasic phosphoric acid (diester phosphate) potentially will be able to minimize formation of diester and triester phosphate, and maximize formation of monoester phosphate. In order to obtain the optimum chemically bound phosphorus content in the polyol structure, formation of diester phosphate, triester phosphate and oligomers should be avoided. Thus, reactions with dibutyl phosphate and ethyl phosphates were also studied. PUR foams were synthesized from the resulting polyols and tested to demonstrate their effects on the flammability and thermal behavior of the PUR foams, as described and discussed in Chapter 3.

A discussion of the background, issues and previous work on PUR, biobased polyols and phosphate FRs are presented in this Chapter 1. The overall findings of this work, conclusions, limitations and recommendations for future work are presented in the final chapter.

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CHAPTER 2: MATERIALS AND METHOD

2.1 Preparation of Polyol

2.1.1 Materials

Food grade canola oil (Safeway®) was obtained from a local store. Formic acid (≥85%), hydrogen peroxide (≥35%), and sodium sulfate were provided from Univar (AB. Canada). Analytical grade methanol and ethyl acetate were purchased from Fluka Analytical Sigma-Aldrich (ON, Canada), with 1,3-propanediol purchased from DuPont Tate. Dibutyl phosphate (>97%) and phosphorus pentoxide and phosphoric acid (99.999% trace metals basis) were purchased from Sigma Aldrich. *Tert*-butanol, ethanol anhydrous and phosphoric acid (85%) were purchased from Fisher Scientific.

2.1.2 Synthesis of hydroxypropyl ester of epoxidized canola oil fatty acids (eFAPE)

2.1.2.1 Epoxidation of canola oil

Canola oil was epoxidized by formic acid and hydrogen peroxide. About 4000g of canola oil was mixed with 2800 g hydrogen peroxide (35% w/w in water) in a 6-L glass reactor equipped with an overhead mechanical stirrer and water heating/cooling system. The temperature was kept at ~25 °C and the mixture stirred at the speed of ~ 350 rpm. 246g formic acid (85% w/w) was slowly added to the reactor while the reaction mixture was continuously stirred. After the addition of formic acid completed, the temperature was increased to 50 ± 5°C gradually at the rate of ~ 10 °C per 10 min. Due to the exothermic nature of the epoxidation reaction, the temperature of the reaction mixture was controlled by a water cooling/heating system to avoid overheating. The oxirane oxygen content (OOC) of the reaction mixture was measured and the reaction was stopped when the oxirane oxygen content reached the maximum. The reaction took about 52 hours to complete. After epoxidation, the mixture was cooled down to room temperature, and ~ 2 L ethyl acetate was added to the mixture and subsequently the mixture was washed with saturated salty water by adding ~ 1.5 L saturated sodium chloride (NaCl) solution. The washing step was repeated until the pH ~5-6. Approximately 2000 g sodium sulfate was added to the organic phase to remove residual remaining water. The organic phase was filtered through Whatman paper filter No. 1 before the solvent was removed using rotary evaporator. The resulting epoxidized oil was stored in a container with closed cap at room temperature until the next step.

2.1.2.2 Transesterification of epoxidized canola oil with 1,3 propanediol

Transesterification reaction was carried in a 6-L reaction vat equipped with an overhead mechanical stirrer and water heating/cooling system. About 2000g of the canola oil epoxide resulted from reaction described in section 2.1.2.1 was transferred into the vat. The catalyst, sodium methoxide (30g) which was diluted in ~1000mL acetone and then mixed with 1600g 1,3-propanediol before added into the vat containing the canola oil epoxide. The reaction was carried for 4 hours at 60°C ± 5°C with continuous stirring at ~350 rpm. After reaction was completed, the mixture was cooled to room temperature before 1000mL of ethyl acetate was added. Subsequently the mixture was neutralized with sulfuric acid, and washed with saturated NaCl solution. The washing step was repeated 3 times. Residual water was removed from the organic phase by adding ~1000g sodium sulfate. The organic phase was then filtered with Whatman filter paper No 1 and finally, the ethyl acetate was removed using rotary evaporator. The resulting eFAPE was stored in a closed cap bottle at room temperature.

2.1.3 Oxirane ring opening with dibutyl phosphate (DBP)

The starting material, eFAPE was melted at ~50ºC and cooled to ~30ºC, weighed and transferred to a conical flask and stirred with magnetic stirred. DBP was added dropwise into the flask, with continuous stirring for 12 hours. The molar ratio of oxirane oxygen in eFAPE to DBP was 1:0.5, 1:0.75, 1:0.95, 1:1 and 1:1.5. A washing step to remove the remaining DBP was carried out by first diluting the mixture in diethyl ether (1:1 vol/vol) and washing with 0.5M NaOH solution until the pH is 7, followed by three time washing with saturated NaCl solution. Residual water was removed using sodium sulfate. The organic phase was then filtered with Whatman Filter paper No. 1 or centrifuged to remove the sodium sulfate. Finally, the diethyl ether was removed using rotary evaporator.

2.1.4 Oxirane ring opening with ethyl phosphates (EP)

The ethyl phosphates was prepared by reacting with anhydrous ethanol at 80ºC at molar ratio of phosphorus pentoxide to ethanol of 1:8. About 37 g of ethanol was transferred into a conical flask. The flask was partially submerged in an ice bath to control the temperature due to the exothermic nature of the reaction. An amount of 29 g of phosphorus pentoxide was slowly added into the ethanol with continuous stirring using magnetic stirrer. The conical flask was then connected to a condenser and the mixture heated to 80ºC in an oil bath for 12 hours with continuous stirring. Excess ethanol was removed using rotary evaporator and the final weight of the resulting product was recorded.

The resulting ethyl phosphates was reacted with eFAPE at a molar ratio of 1 mole of oxirane oxygen to 0.25, 0.5 and 0.75 moles of phosphorus in the mixture at ~30ºC. The reaction was carried out for 5 hours with continuous stirring.

2.1.5 Oxirane ring opening with phosphoric acid

eFAPE was mixed in *tert*-butanol (1:1 w/w) in a 3-neck round bottom flask and heated to ~40ºC in oil bath. The flask was attached to a condenser and overhead mechanical stirrer. Phosphoric acid was added slowly into the mixture, while stirring. When the addition of PA was completed, the temperature was increased to 70ºC with continuous stirring at ~350 rpm until the oxirane rings were all consumed or reached plateau. The mixture was then transferred to a round bottom flask and the *tert*-butanol was removed using a rotary evaporator.

2.1.6 Characterisation of polyols

2.1.6.1 Hydroxyl Value (OHV), Acid Number (AN) and Oxirane Oxygen Content (OOC) Measurements

Hydroxyl value (OHV) was determined using the single sample FTIR method[1]. The OOC and AN were measured by ASTM method D1652-11 and D4662-98 respectively. OHV, AN and OOC values were reported as the average value and standard deviation for triplicates.

2.1.6.2 Gel Permeation Chromatography (GPC)

Gel permeation chromatography was carried out on a Styragel HR1 column (300 mm × 7.8 mm id.) with 5 µm particle size (Styragel HR1, Waters Corporation, USA) coupled with an evaporative light scattering detector (ALLtech ELSD 200, Mandel Scientific Company Inc, Canada) and an isocratic Agilent 1100 pump (Agilent Technologies, CA, USA). Tetrahydrofuran (THF) was used as a mobile phase at flow rate of 0.5 mL/min. The sample (1 mg/ml in THF) was injected into the column at the volume of 10 μL. The detector was run at temperature of 60°C and nitrogen gas flow at 2.5 bar.

2.1.6.3 Viscosity

An AR 2000 (TA Instrument, DE, USA) TA Advanced Rheometer with a plate-plate system 25 mm in diameter and a gap of 0.2 mm was used to measure the viscosity of the polyols using a constant shearing rate of 51.6 s^{-1} at temperature of 25°C.

2.1.6.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra was recorded using a Bruker Alpha FTIR spectrophotometer (Bruker Optics, Esslingen, Germany) equipped with an ATR single-bounce diamond crystal. Spectra was collected over the range of 410-4000 $cm^{-}1$, at resolution of 4 cm^{-1}. A total of 16 scans were acquired and averaged using OPUS software version 6.5 provided by Bruker. Background spectrum of the clean ATR crystal was collected prior to collection the sample spectrum.

2.1.6.5 Mass Spectrometry Analysis

An Agilent 1200 series HPLC system coupled to a QSTAR Elite mass spectrometer (AB SCIEX, Concord, ON, Canada) with electrospray ion source (ESI) under positive and negative mode was used to analyze sample solutions. The ESI ion source temperature was held at 300ºC. The other instrumental parameters were as follows: curtain gas 25; auxiliary gas 40; nebulizing gas 60 in arbitrary unit. In all cases, high purity of nitrogen was used. The ion spray voltage, declustering potential (DP), focus potential (FP), and DP2 were 5200V, 50V, 150V and 15V under positive mode and -4500V, -50V, -150V and -15V under negative mode, respectively. Under positive mode, the mass spectrometer was tuned using the ion at *m/z* 879.9723 at a resolution of above 10,000 full width at half maximum by infusing porcine renin substrate tetradecapeptide into ESI ion source and calibrated from 50 amu to 1300 amu. Taurocholic acid was used to calibrate the instrument from 50 amu to 1300amu under negative mode. Collision energy from 25 eV to 45 eV was employed for MS/MS analysis depending on the compound to make sure that both fragment ions and protonated molecular ions were observed. Analyst QS 2.0 was used for data acquisition and analysis.

The separation was carried out on silica 150mm × 2.1 mm column, 3 μm particle size. The mobile phase A was hexanes and B was isopropanol. The gradient was as follows: 0–0.1 min, 2% B; 0.1–18min, from 2% to 18% B; 18-25min, from 18% to 40%B, keep at 40% B for 5 minutes, then back to 2% B at 30.1 minute for 5 minutes to re-equilibriate the column prior to the next injection. The flow rate of mobile phase was 200 μl/minute. The injection volume was 2 μl and the cycle time was 35 min/injection. A post-column addition of 40mM ammonium acetate in methanol at 0.1ml/min was used to enhance the ionization efficiency.

The sample was prepared by dilution with chloroform to 0.1mg/mL solution.

2.1.6.6 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR spectra of was recorded on a Varian Inova 400MHz at 399.95 MHz for ^{1}H and at 161.90 MHz for ^{31}P. Sample was analyzed in deuterated chloroform at 25°C. The chemical shifts are expressed in ppm in the δ scale.

2.1.6.7 Phosphorus Content

Total phosphorus content was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Microwave-assisted nitric acid digestion was performed on the polyol sample using 5 mL of trace-metal grade HNO_3 and diluted to a final total volume of 25mL.

2.2 Preparation of flame retardant polyurethane foams

2.2.1 Materials

The isocyanate, pMDI was purchased from Bayer Corporation, Pittsburg, PA, USA. Its NCO content was 31.5% and the functionality was 2.5. The blowing agent, cyclopentane was purchased from Thermo Fisher Scientific Company. Amine catalyst Polycat 30 from and tin catalyst Dabco T120 were purchased from Air Products & Chemicals Inc, Detroit, Michigan, USA. Surfactant used this experiment was B8404 purchased from Evonik Industries AG, Essen, Germany.

Two non-phosphorus containing polyols were used in combination with the phosphorus containing polyols. Commercial polyol Mannich 425 was purchased from Carpenter Company (VA, USA) and 3GP polyol was derived from canola oil via transesterification and epoxide ring opening with 1,3 propanediol, based on method described by Hossein[2]. The OHV, AN and phosphorus content of the polyols used for PUR foams in this chapter is listed in Table 2.1.

Table 2.1: Hydroxyl Value (OHV), Acid Number (AN) and calculated phosphorus content in the polyols used for preparation of PUR foams

Polyol (oxirane: DBP/PA)		OHV (mg KOH/g)	AN (mg KOH/g)	%P
eFAPE-DBP1	(1:0.95)	185	22.94	5.73
eFAPE-DBP2	(1:0.75)	193	7.34	4.94
eFAPE-DBP3	(1:0.5)	192	3.64	3.72
eFAPE-PA	(1:0.25)	260	3.60	1.97*
Mannich 425	-	425	-	0
3GP	-	345	-	0

** Actual value determined by ICP-OES*

2.2.2 Preparation of PUR foam

2.2.2.1 PUR foam from eFAPE-PA (PU1, PU2, PU3)

PUR foams were prepared by a one-shot technique, where all ingredients were mixed simultaneously. Prior to mixing with MDI, a fixed amount of catalysts, surfactant and blowing agents were weighed and mixed with 3GP and/or eFAPE-PA. The mixtures were stirred with a propeller stirrer for ~ 2 minutes at ~450rpm to ensure homogenous mixing. For all of the foams the composition of all ingredients was fixed except for the polyols, which was adjusted between 3GP and eFAPE-PA to produce foams containing different phosphorus content. The mixtures were then mixed with MDI and stirred at high speed of 2000 rpm until they began to change from a liquid to a creamy state and start to subsequently expand; the time (cream time) to reach this state was recorded. The time for the foam to reach its maximum height (rise time) was also recorded. In the preparation of foam for LOI, TGA analysis and burning test, each mixture was poured into an 8 x 8 x 2 inches (203 x 203 x 51mm) mold immediately after the mixture reached creamy state. The NCO/OH ratio was 1.1:1.0. The PUR foams were left to cure at room temperature for 12 hours. Foam containing no phosphorus was prepared by using 100% 3GP polyol as reference. The compositions of the foams are shown in Table 3.5.

2.2.2.2 PUR foam from eFAPE-DBP

PUR foams were prepared by a one-shot technique, where all ingredients were mixed simultaneously. Prior to mixing with MDI, a fixed amount of catalyst, surfactant and blowing agents was weighed and mixed with Mannich 425 polyol and eFAPE-DBP. The mixture was stirred with propeller stirrer for ~ 2 minutes at ~450rpm to ensure homogenous mixing. For all the foams the composition of all ingredients was fixed except for the polyols, which was adjusted between Mannich 425 and eFAPE-DBP to produce foams containing different phosphorus content. Each mixture was then mixed with MDI and stirred at high speed of 2000 rpm until it started to cream. Both the cream time and rise time were recorded. The NCO/OH ratio was 1.1:1.0. Foam containing no phosphorus was prepared by using 100% 3GP polyol as reference. The compositions of the foams are shown in Table 3.5.

2.2.3 Characterization of PUR foam

2.2.3.1 Thermogravimetric Analysis (TGA)

TGA was carried out using TGA Q50 (TA Instrument, DE, USA) following method ASTM D3850-94. Each foam sample was ground into fine powder and 4-5 mg of the sample was loaded into a ceramic pan before it was put into the furnace.

The sample was then heated from 25°C to 600° at heating rate of 10°C/min under 100ml/min flow nitrogen atmosphere.

2.2.3.2 Limiting Oxygen Index (LOI)

The flammability of the foams was tested by Limiting Oxygen Index (LOI) test based on ASTM2863 method, measuring the minimum concentration of oxygen required to maintain the burning flame. The specimens dimension used for this test was 10mm x 10mm x 150mm (thickness x height x length).

2.2.3.3 Burning Test

A simple burning test was conducted in a fume hood. PUR specimens PU1, PU2 and PU3 (10mm x 20mm x 85mm H x W x L) was subjected to Bunsen flame and removed from the flame once ignition occurred. The burning specimen was held horizontally until the fire self-extinguish. The time from ignition to the time the flame went out was recorded.

2.2.3.4 Density

The density of the foams was measured by the weight/volume ratio of the samples.

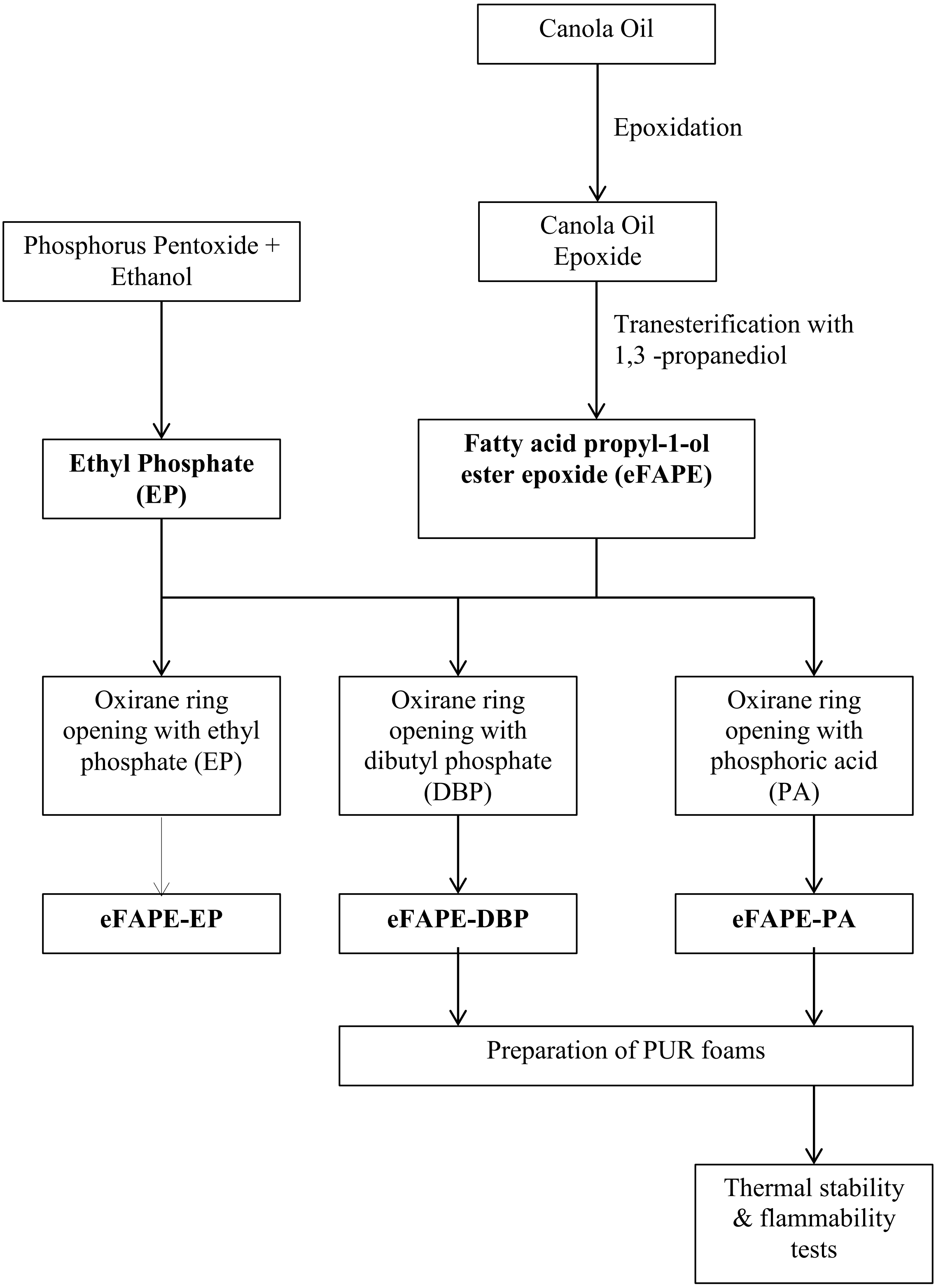


Figure 2.1: Overview of experiment in this thesis

Reference

[1] M. H. Tavassoli-Kafrani, J. M. Curtis, and F. R. van de Voort, “A single-sample method to determine the hydroxyl values of polyols using mid-FTIR spectroscopy,” *Eur. J. Lipid Sci. Technol.*, vol. 117, no. 1, pp. 65–72, Jan. 2015.

[2] M. H. Tavassoli Kafrani, “Vegetable Oil-based Polyols and Some Novel Analytical Techniques Used in Their Development,” University of Alberta, 2016.

CHAPTER 3: RESULT AND DISCUSSION

3.1 Synthesis of phosphorus containing polyol from canola oil

3.1.1 Synthesis of canola oil hydroxypropyl ester of epoxidized canola oil fatty acids (eFAPE)

First, epoxidation of the double bonds in the fatty acid component of the canola oil was achieved using performic acid formed from reaction between formic acid and hydrogen peroxide. Then, the glycerol backbone was removed from the triglyceride and replaced with 1,3 propanediol in a transesterification step, introducing to the structure of the fatty acid epoxide one primary terminal C-OH group, as shown in Figure 3.1. Finally, glycerol, the catalyst and excess 1,3 propanediol were removed via the washing step as described in Chapter 2, section 2.1.2.2.

The measured hydroxyl value (OHV) and oxirane oxygen content (OOC) of eFAPE were 155 $\pm$ 3mgKOH/g and 5.43 $\pm$ 0.005g/100g respectively. The increase in OOC and OHV indicates the formation of epoxy rings and addition of C-OH group from the 1,3 propanediol, respectively. The fatty acid composition and iodine value (IV) of the canola oil were measured and listed in Table 3.1, with C18:1 being the major fatty acid, followed by C18:2, representing ~63% and ~19% of the total fatty acids respectively[1]. Thus, the resulting products from this reaction sequence were hydroxypropyl esters of epoxidized fatty acids of canola oil (eFAPE) with, the major compounds being the hydroxypropyl ester of epoxidized oleic acid and hydroxypropyl ester of epoxidized linoleic acid, with molecular weights of 357 g/mol and 371 g/mol respectively, as shown in mass spectra (ESI +ve) in Appendix I.

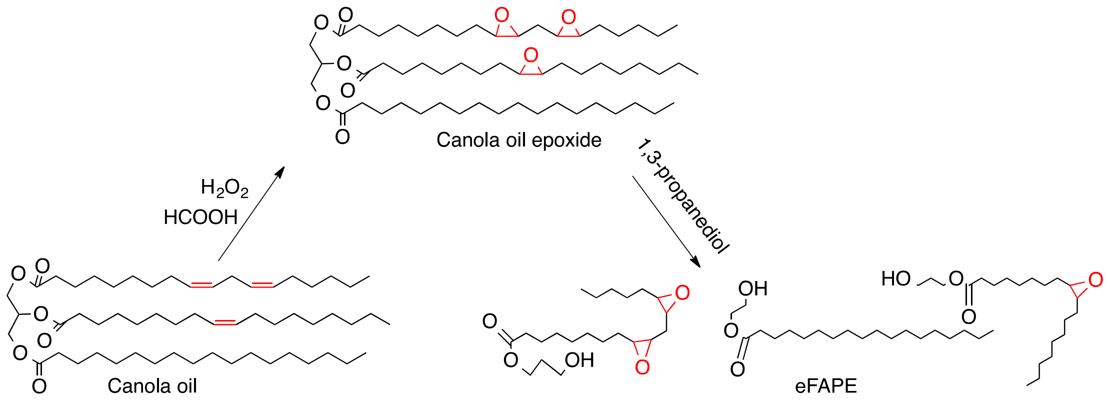


Figure 3.1: Schematic illustration of synthetic route of the starting material, hydroxypropyl ester of epoxidized fatty acid (eFAPE) from canola oil

Table 3.1: Fatty acid composition and Iodine Value of canola oil[1]

	Fatty Acid (%)					Iodine Value
	Saturated	C18:1	C18:2	C18:3	C20:1	
Canola Oil	6.6	62.8	19.3	8.9	1.2	119

The transesterification step removed glycerol from the epoxidized triglyceride of canola oil and attached the 1,3 propanediol of each fatty acid via ester bond, converting the epoxidized canola oil into hydroxypropyl ester of fatty acid epoxides. This resulted in a starting material with lower molecular weight for the subsequent ring opening reactions. The number average molecular weight (M_n) of eFAPE was ~338 g/mol, compared to M_n of canola oil, which was ~892 g/mol, as shown in Figure 3.2. The molecular weight (MW) resulting eFAPE is about three times lower than the MW of epoxidized soybean oil reported by Heinen et al[2], thus the MW of the resulting phosphorus containing product from the reaction with phosphoric acid or diester phosphates is also expected to be lower.

This is favorable for producing polyol with relatively low viscosity as compared to polyols produced from epoxidized vegetable oils as reported by Guo et al [3] and Heinen et al[2]. The resulted eFAPE was used as starting material for all the synthetic routes in this study. In addition to that, transesterification with 1,3 propanediol also gave eFAPE an extra primary hydroxyl group. This is a more reactive C-OH group towards forming cross links with isocyanates during PUR foam preparation as compared to the phosphate polyols made directly from epoxidized oil and which contain only secondary C-OH, as reported in Guo et al[3].

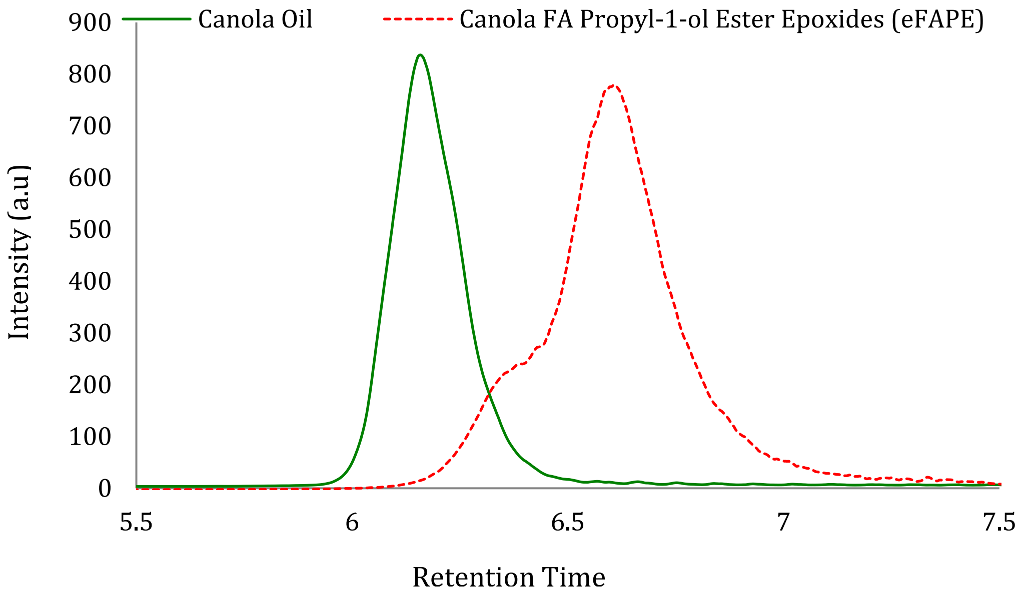


Figure 3.2: The GPC trace of canola oil (RT 6.15 min) and eFAPE (RT 6.58 min) resulted from epoxidation followed by transesterification with 1,3 propanediol

3.1.2 Oxirane ring opening reactions

Phosphoric acid is a tribasic acid with three functional P-OH groups[4]. Phosphoric acid and its primary and secondary esters, containing two and one acidic P-OH groups are reported to react with oxirane rings to form a phosphate bond and a secondary C-OH group[3], [5]–[9]. The physical products obtained from these reactions were transparent light yellow liquid with viscosities ranged from 0.3 to 8.2 Pa.s. The reaction between eFAPE and phosphoric acid (PA), ethyl phosphate (EP) and dibutyl phosphate (DBP) resulted in each of the oxirane rings being opened to form a phosphate ester and an extra secondary C-OH. The FTIR spectra (Figure 3.3) of the products of reaction between eFAPE with PA, DBP and EP show decreased intensity in absorbance at 762-862cm^{-1}, which corresponds to stretching of C-O-C bond of oxirane groups. The oxirane oxygen content (OOC) measured by ASTM titration method D1652-11dropped from 5.43% to < 0.5% in all of eFAPE-PA, eFAPE-DBP and eFAPE-EP, attributed to consumption of the oxirane rings.

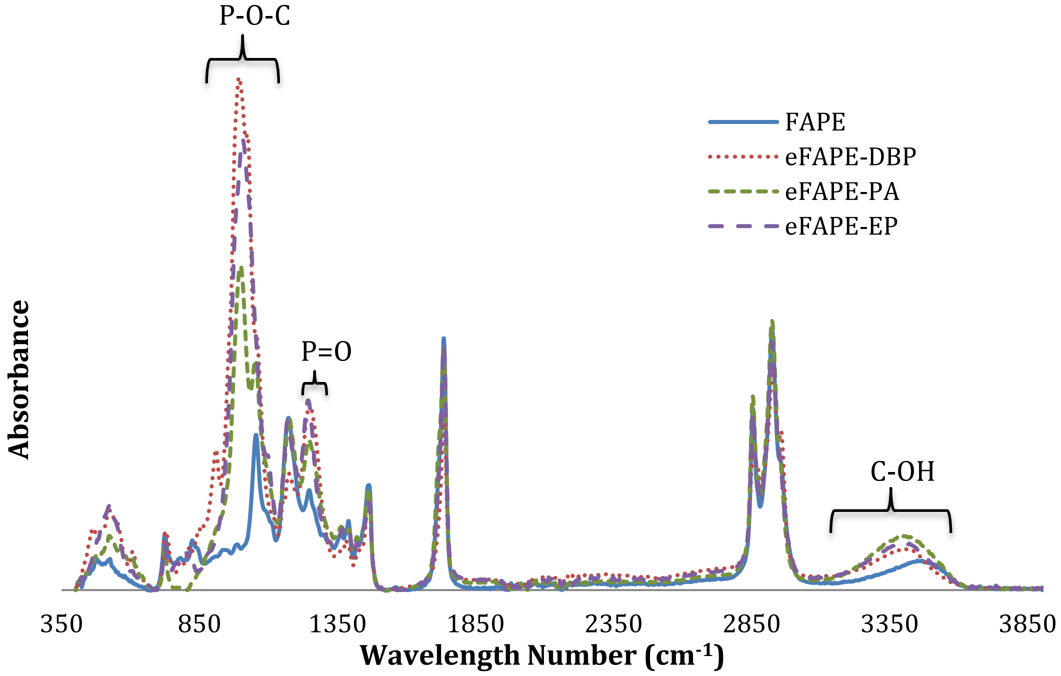


Figure 3.3: IR spectrum of the starting material (eFAPE) and the phosphorus containing polyols (eFAPE-DBP, eFAPE-PA and eFAPE-EP)

At the same time, there is an increased intensity in absorbance at 940 – 1100cm^{-1}, 1215 – 1277cm^{-1} and 3240-3600cm^{-1} regions corresponding to stretching of P-O-C, P=O and OH of hydroxyl groups respectively. This resulted in formation of phosphate bonds and secondary C-OH groups. The measured hydroxyl value (OHV) increased from 155 mgKOH/g to ~190 – 260 mgKOH/g, attributed to formation of secondary C-OH group at the one of the carbons where the epoxy ring was.

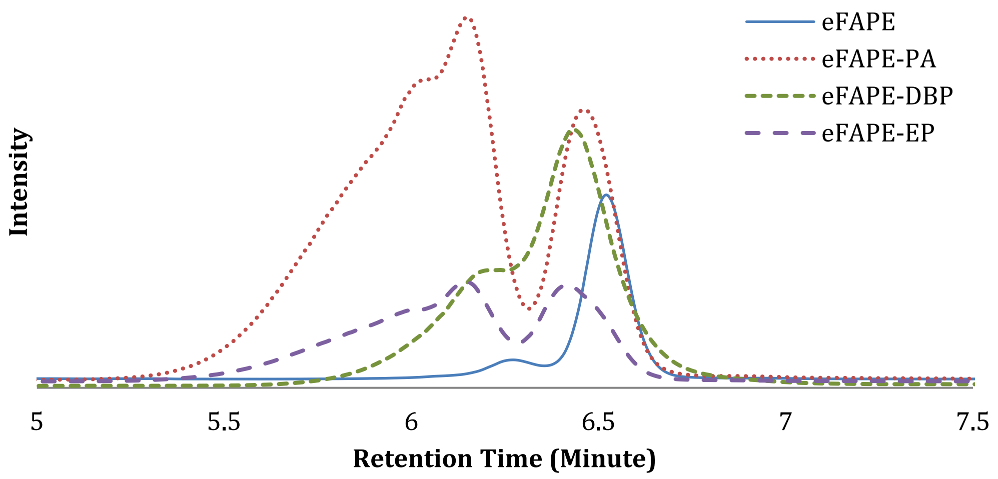


Figure 3.4: GPC chromatograms of the starting material (eFAPE) and the phosphorus containing polyols (eFAPE-DBP, eFAPE-PA and eFAPE-EP)

Gel Permeation Chromatography (GPC) analysis as shown in Figure 3.4 shows that the products from all the reactions eFAPE-PA, eFAPE-DBP and eFAPE-EP have higher molecular weight than the starting materials, indicating incorporation of the phosphate adducts into the eFAPE structure and also formation of dimers and diester phosphate.

3.1.3 Oxirane ring opening with dibutyl phosphate (DBP)

Dibutyl phosphate (DBP) is mono-basic phosphate compound containing one P-OH group and two butyl esters. It is moderately acidic having dissociation constant, pK_a of 2.32 at 25°C and often used in industrial applications such as rare earth extraction and atomic energy recovery[10]. DBP was used in this reaction because it only contain one P-OH which is expected to react with only one fatty acid propyl ester epoxide to form a mono-ester phosphate. The existing two butyl phosphate groups prevent the formation of di- and tri-ester phosphate with eFAPE, leading to incorporation of one phosphorus to each oxirane group in the starting material. The objective of using DBP is to maximize the covalent phosphorus content in the final product by minimizing formation of di- or triester phosphate. Theoretically, if each mole of oxirane reacts with one mole of DBP to form a phosphate ester bond, the phosphorus content in eFAPE-PA could reach ~6%. However, oligomerization or formation of di- and triester phosphates will reduce the phosphorus content in the product. The expected reaction is as shown in Figure 3.5.

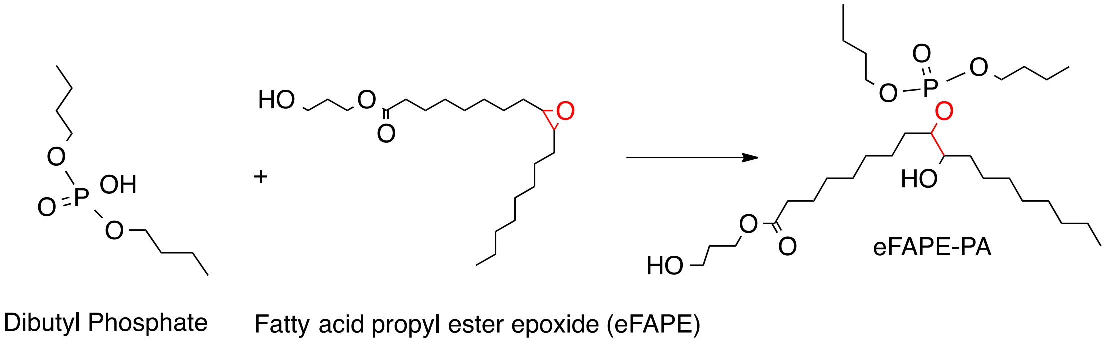


Figure 3.5: Schematic illustration of oxirane ring opening reaction by DBP

Preliminary reactions were carried out using eFAPE with DBP at a molar ratio of oxirane: DBP of 1:1, with and without *tert*-butanol as solvent (*tert*-butanol to eFAPE ratio of 1:1 *w/w*), at 80°C for 4 hours. The amount of DBP required for a specific oxirane:DBP molar ratio was calculated based on the mole of oxirane in eFAPE per unit weight. An example of the calculation is given in Appendix II.

The resulting products had high viscosities of more than 30.0 Pa.s, too high to be suitable for PUR applications. Reactions at low temperature (~25°C) were also carried out without using solvent. The eFAPE was melted at ~40°C and DBP was added drop wise to the starting material and stirred. The OOC of reaction at a molar ratio of oxirane:DBP at 1:1.5 decreased from 5.43% to ~ 0.30% in 15 minutes. The viscosity of the product prior to washing was 1.2 Pa.s. However, due to excess amount of DBP added, there was need to remove the excess DBP. The mixture was diluted in diethyl ether (1 part:1 part) and washed with 0.5M sodium hydroxide solution and followed by saturated sodium chloride solution. The residual water was removed using anhydrous sodium sulfate, filtered through Whatman paper No. 1 and the diethyl ether removed using rotary evaporator. However, the washing step resulted in inconsistent (appearance and physical properties such as sticky and highly viscous, or sometime soluble in aqueous phase) and high acid products, as explained in Section **3.1.3.2,** Figure 3.17.

To avoid the need to remove excess DBP, reactions were carried out using an oxirane:DBP molar ratio of 1:<1 . A series of reactions was carried out using one mole oxirane to 0.5, 0.75 and 0.95 mole DBP . The OHV, AN and viscosities of the resulting products are as shown in Table 3.2.

Table 3.2: Hydroxyl value (OHV), acid number (AN), oxirane oxygen content (OOC) and viscosity of products from reaction between eFAPE and dibutyl phosphate (DBP) at different oxirane:DBP molar ratio

Oxirane:DBP ratio	OHV (mgKOH/g)	AN (mgKOH/g)	OOC (%)	Viscosity (Pa.s)
1:0.5	192 + 4	3.64 ± 0.33	1.44 ± 0.01	0.341 ± 0.003
1:0.75	193 ± 2	7.34 ± 0.24	0.28 ± 0.03	1.196 ± 0.154
1:0.95	185 ± 1	22.94 ± 0.27	0.27 ± 0.04	1.919 ± 0.120

The total phosphorus content in eFAPE-DBP obtained from reaction at oxirane:DBP molar ratio of 1:0.95 as measured by ICP-EOS was 5.91±0.08%.

3.1.3.1 LCMS/MS analysis of Structure of eFAPE-DBP

Figure 3.6 shows the total ion chromatogram (TIC) under positive (a) and negative (b) for sample with ratio of oxirane: DBP at 1:0.5. Two major peaks at retention time 11.8 minutes and 12.9 minutes (+ve) and 11.4 minutes and 12.5 minutes (-ve) were observed. The mass spectra of peak at RT 11.8 minutes under positive mode showed the ion at *m/z* 567, while the ion at *m/z* 625 observed under negative mode at RT 11.4 minutes. The molecular weight can be identified as 566 g/mol with protonated ion at *m/z* 567 under positive and acetic acid adducts of $[M+CH_3COO^-]$ at *m/z* 625. A structure was proposed as **1a** (Figure 3.7), which is formed when DBP opens the oxirane ring of oleic acid propyl ester epoxide to give a hydroxyphosphate adduct containing a secondary C-OH group. Due to the possibility of DBP attached to position 9 or 10 on the epoxide fatty acid chain, there are two unresolved peaks observed at retention time 11.8 minutes.

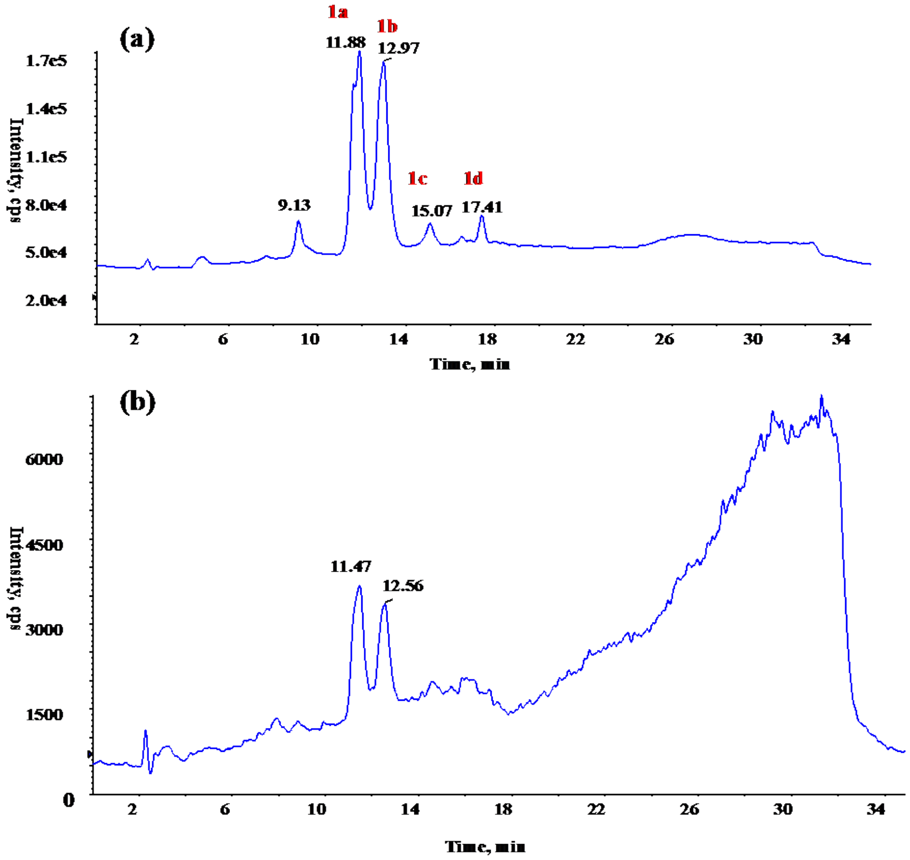


Figure 3.6: Total ion chromatogram (TIC) of eFAPE-DBP obtained by reacting eFAPE with DBP at oxirane:DBP molar ratio 1:0.5 (a) positive (b) negative mode

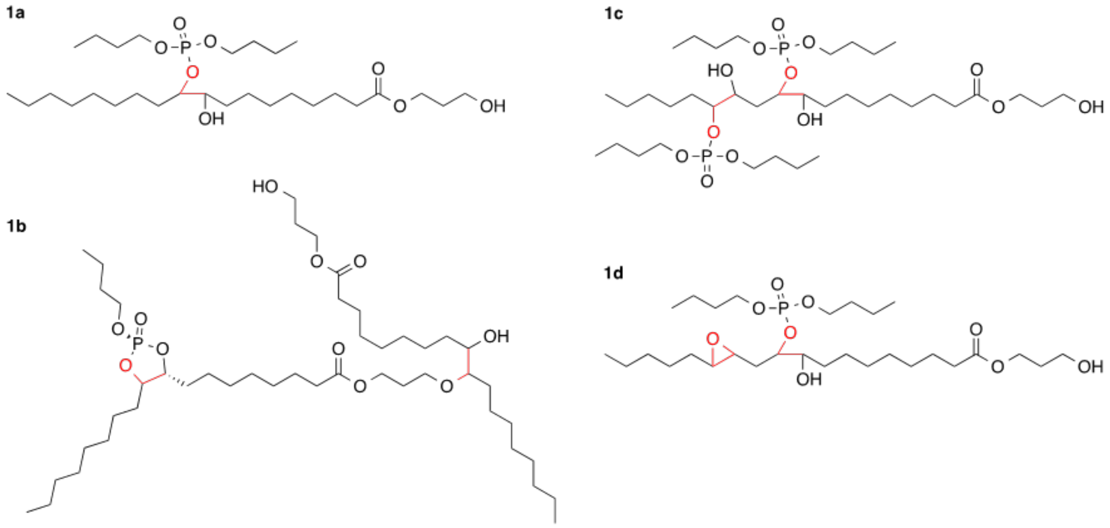


Figure 3.7 Structure of compounds **1a-d** in eFAPE-DBP as detected by LCMS/MS

Similarly, the molecular weight of peak at RT 12.9 minutes (Figure 3.6) was identified as 848 g/mol from the mass spectra (Appendix III) in positive ion mode at *m/z* 849 ($[M+H]^+$), *m/z* 866 ($M+NH_4^+$) and in negative ions at *m/z* 907 ($[M+acetic\ acid-H]^-$). A structure was proposed in Figure 3.7 as **1b**. The tandem mass spectra of the ion at *m/z* 866 and 849 gave rise to ion at *m/z* 493 and 357 (explained in Appendix III), while negative tandem mass spectra of ion at *m/z* 907 gave rise to fragment ion at *m/z* 551 (acetic acid adduct). Furthermore, the fragment ion of DBP was not observed at both positive and negative mode for this compound, consistent with structure **1b**. Meanwhile, a high intensity ion of *m/z* 493 was observed which formed by loss of a butanol from compound 1 to form a 5-cyclic, dioxaphospholane structure. An ether bond was formed by reaction of the terminal C-OH from the hydroxypropyl ester group to an oxirane site on another molecule, resulting in dimer formation between two epoxidized fatty acid esters.

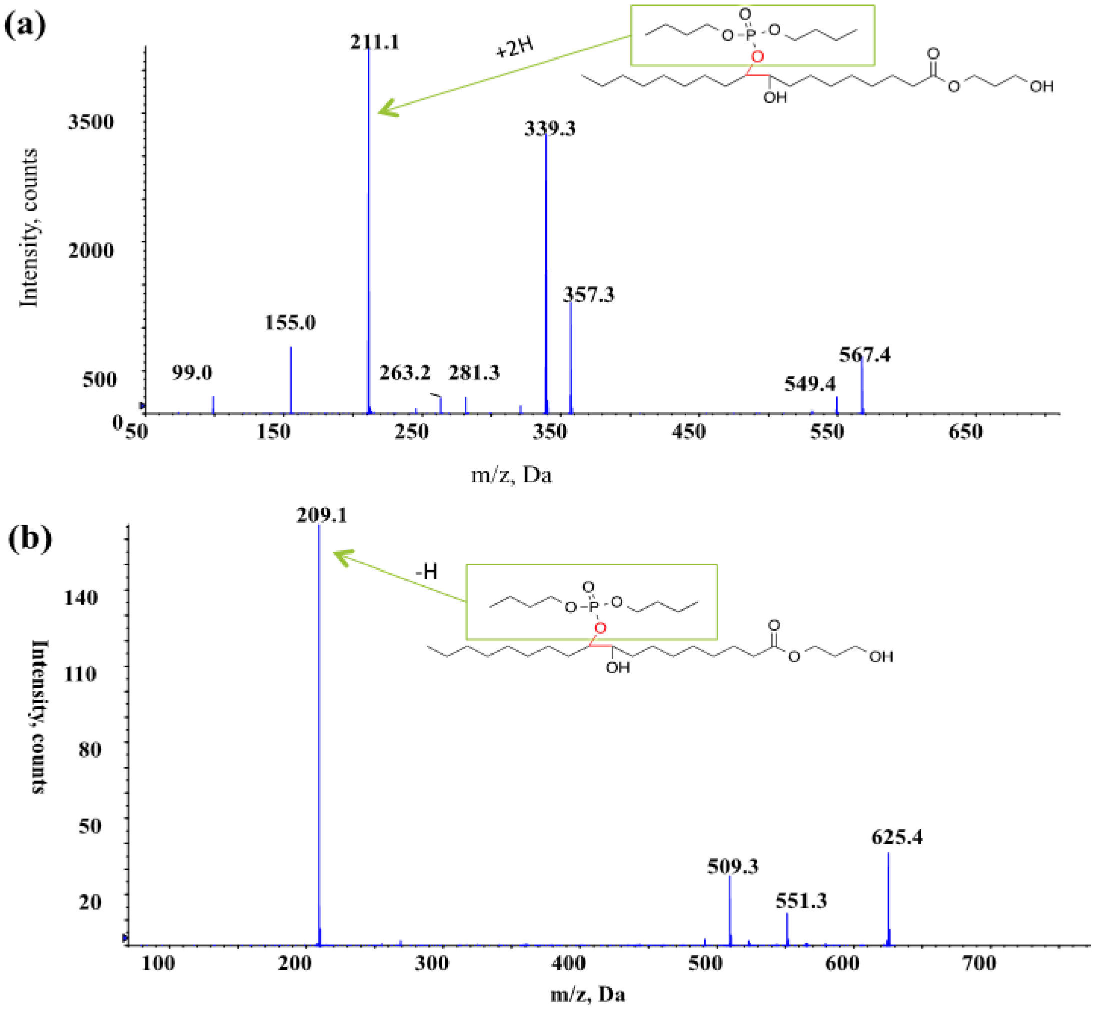


Figure 3.8: Tandem mass spectra of ion at *m/z* 567 (ESI+) (a) and ion at *m/z* 625 (ESI-)

In addition to these two compounds, another three peaks in Fig. 3.6(a) were observed as well. The peak at RT 9.14 minutes was the starting material of epoxide with molecular weight of 356 g/mol, corresponding to epoxidized hydroxypropyl ester of oleic acid, the major fatty acid naturally found in canola oil. The peak at RT 15.0 minutes was proposed to originate from epoxidised linoleic acid hydroxypropyl ester, with both oxirane rings opened by DBP, forming two hydroxy dibutyl phosphate adducts and two secondary C-OH groups (**1c**) (Figure 3.7).

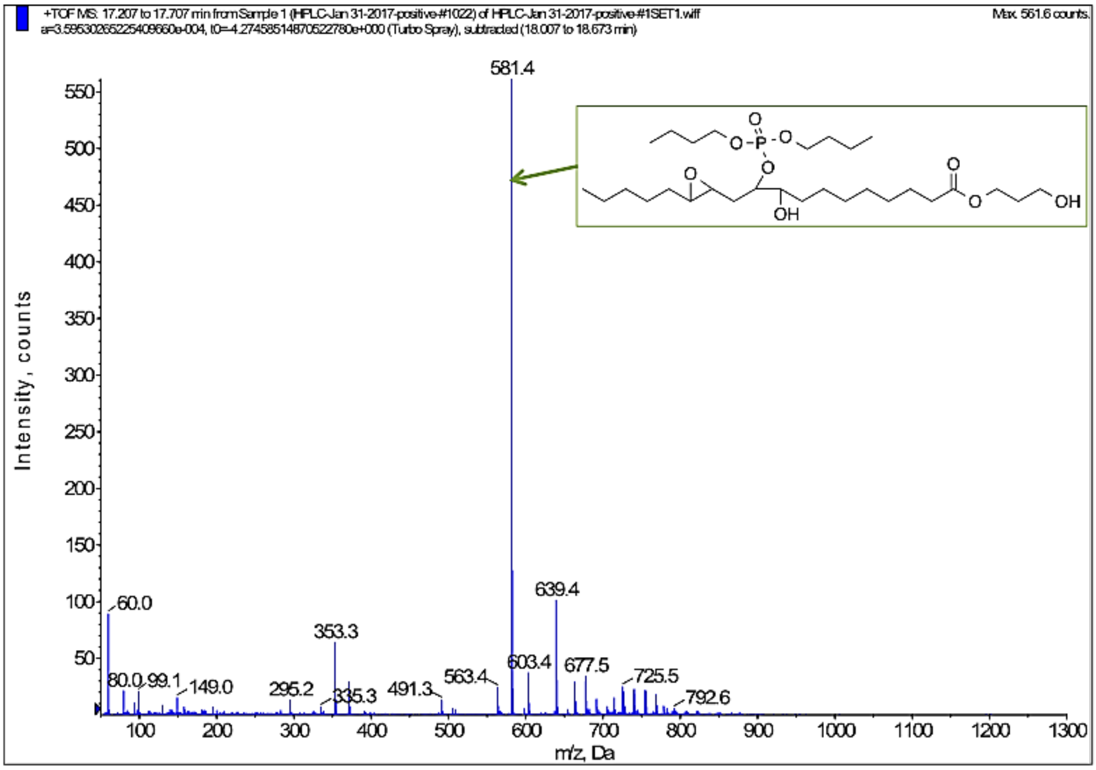


Figure 3.9: Mass spectra (ESI+) of peak at RT 17.4 minute (**1d**).

Figure 3.9 and Figure 3.10 show the mass spectra of peak at RT 17.4 minutes and tandem mass spectra of ion at *m/z* 581 respectively. The fragment ion at *m/z* 211 from Fig. 3.10 indicated the incorporation of DBP into epoxide ring, forming hydroxyphosphate adduct. The likely structure is a derivative of epoxidised linoleic acid in which one of the two oxirane groups is opened by DBP, giving **1d** or an isomer, as shown in Figure 3.7.

3.1.3.2 Conversion of hydroxyphosphate structure to dioxaphospholane

It was observed that over a period of time there was a simultaneous decrease in the abundance of compound **1a** and increase in **1b** in eFAPE-DBP. Changes in the relative peak area percentages derived from extracted ion chromatography (EIC) between **1a** and **1b** plotted over time are shown in Figure 3.11.

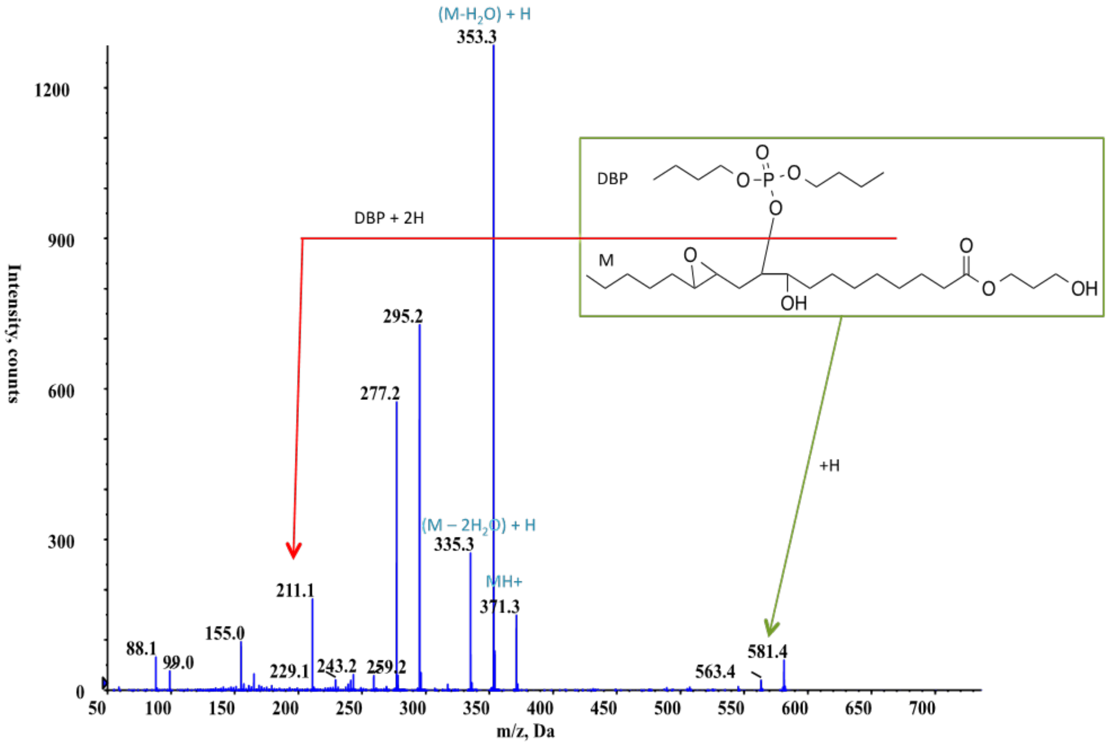


Fig. 3.10: Tandem mass spectra of ion at *m/z* 581 (ESI+)

Conversion from **1a** to **1b** resulted in formation of one molecule of free butanol. In order to validate this, eFAPE_DBP stored for one month was analyzed with gas chromatography coupled with flame ionization detector and was found to contain ~16% butanol. Monitoring eFAPE-DBP by FTIR over the course of a week showed a decrease in the P-O-C region (~1050 cm^{-1}) and increase in absorbance signal at ~600cm^{-1} region, which could corresponds to the formation of dioxaphospholane adduct (Figure 3.12). The rate of this conversion is seemingly affected by the molar ratio of oxirane:DBP used – the higher the amount of DBP used per mole of oxirane, the more **1a** was converted to **1b** as indicated by the increased relative peak area percentage of EIC of the samples as shown in Figure 3.13.

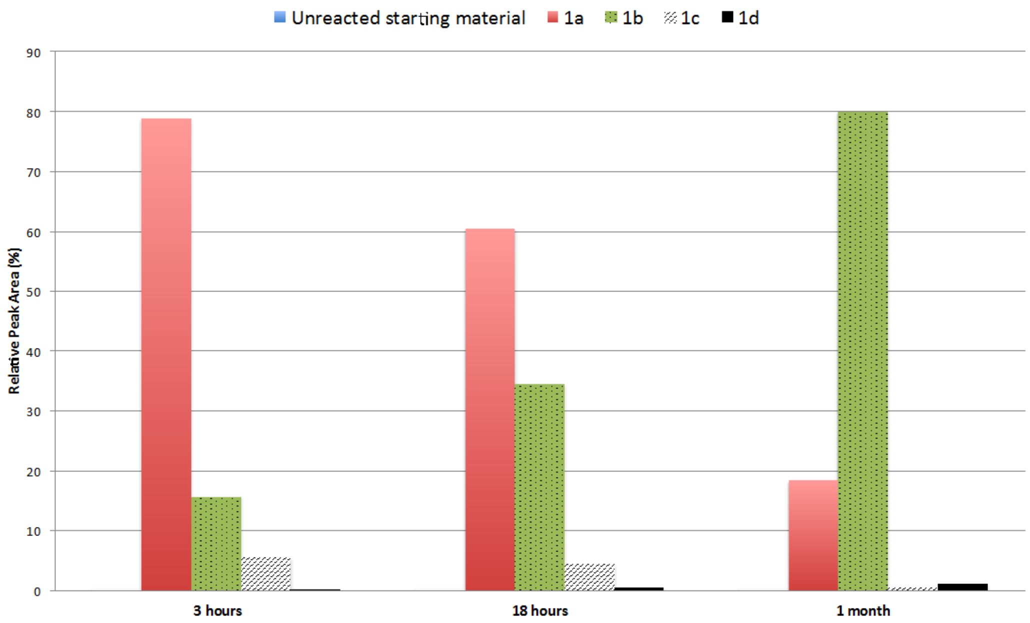


Figure 3.11: Relative peak areas from EIC of eFAPE:DBP (oxirane:DBP 1:0.95) at different time after addition of DBP

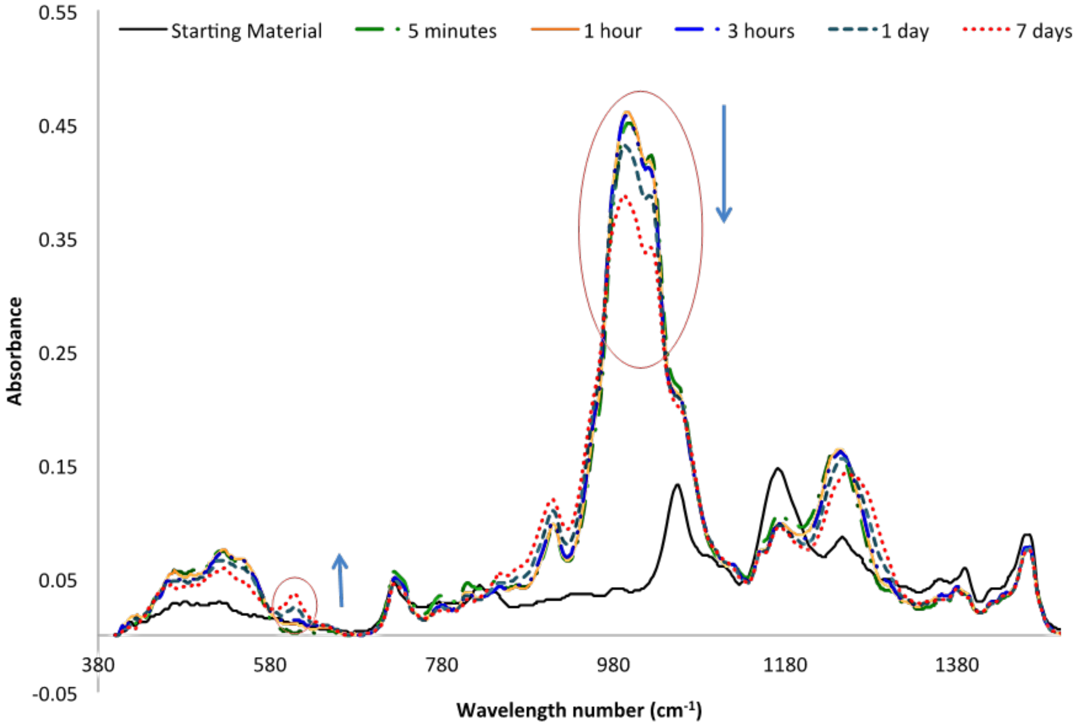


Figure 3.12: FTIR spectrum of ring opening of eFAPE with DBP at different times after addition of DBP

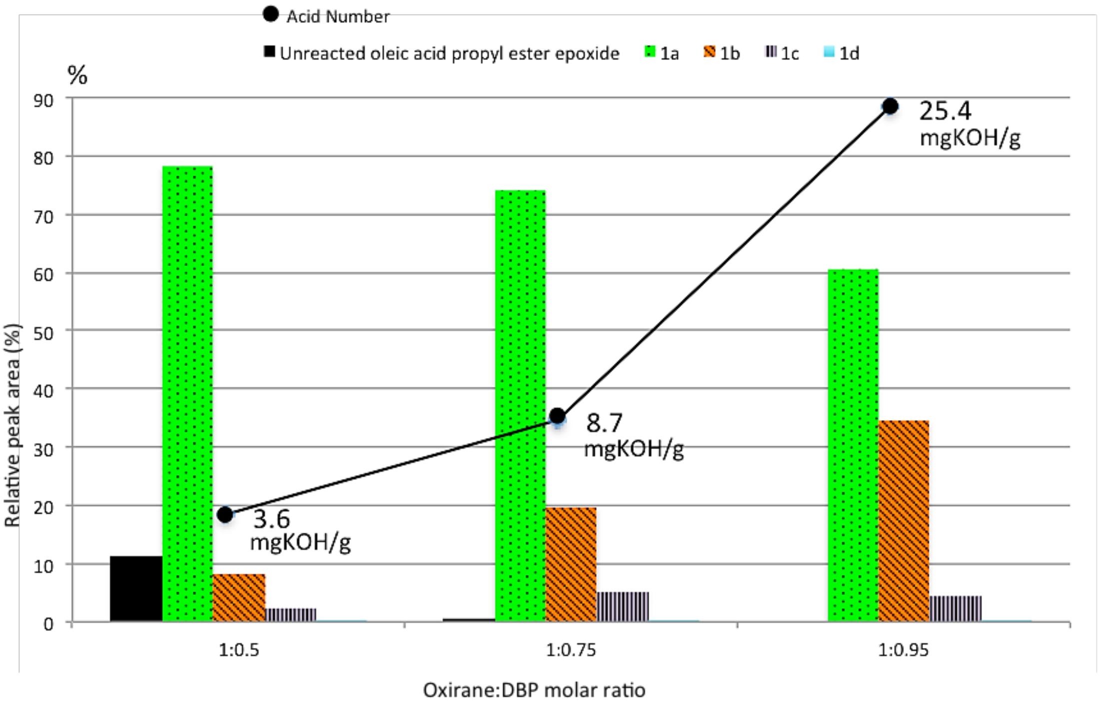


Figure 3.13: Relative EIC peak area percentage and acid number of phosphated product of reactions at different molar ratios (oxirane:DBP 1:0.5 – 0.95) 18 hours after addition of DBP

Conversion of **1a** to the dioxaphospholane form of **1b** can be explained by mechanism suggested by Derouet et al[11], as illustrated in Figure 3.14. The dioxaphospholane adduct was formed as a result of internal condensation reaction between a butylphosphate group and the secondary C-OH group of the initial hydroxyphosphate adduct (**1a**). Naturally, unsaturated fatty acids of vegetable oil are *cis* fatty acids, forming *cis*-epoxide groups when the double bonds are epoxidized. Ring opening of *cis*-epoxide and *trans*-epoxide by DBP resulted in dioxaphospholane adducts and hydroxyphosphate adducts as the main products, respectively. The configuration of the hydroxyphosphate adduct resulted from initial ring opening of a *cis*-epoxide by DBP is unstable and consequently it rearranges into a more stable *trans* configuration occurs around the C-C bond. This results in the C-OH group being brought closer to the phosphate group, making the formation of dioxaphospholane via cyclization with elimination of butanol more likely. Should the starting material be *trans*-epoxide, the final product would be composed of the hydroxyphosphate form as the main product, due to the fact that it is already in a stable configuration and rearrangement around the C-C bond is not likely to occur.

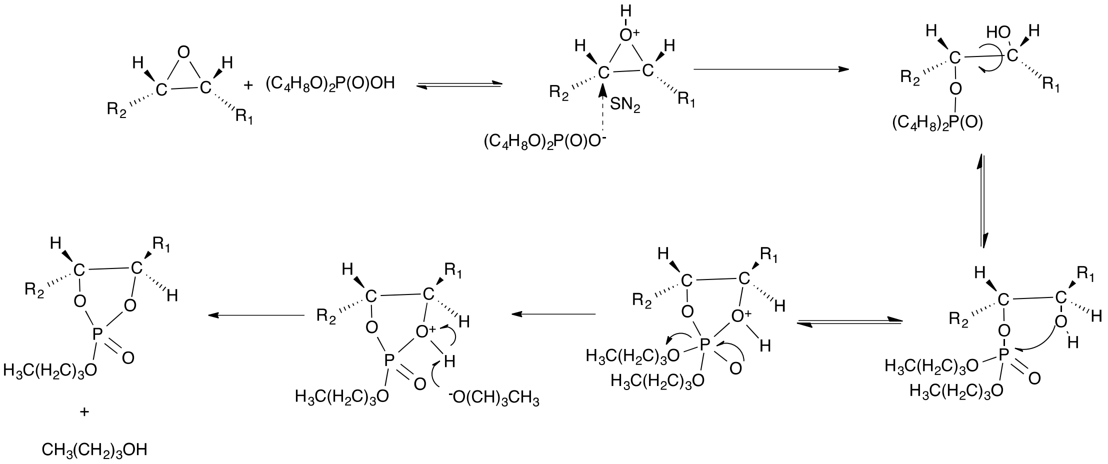


Figure 3.14: Schematic illustration for mechanism of dioxaphospholane formation (*trans*-isomer) from *cis* epoxide [11]

The conversion of **1a** to **1b** also involves the attack on the P-O-C bond of a dibutyl phosphate adduct by the terminal -OH group of a hydroxypropyl ester to yield a dimer bridged by an ether bond (**1b**). This results in the release of a free DBP molecule. GPC analysis of eFAPE-DBP stored after one year showed that there was formation of dimer over time (Figure 3.16).

It is not known which reaction (formation of dioxaphospholane ring or the attack on the P-O-C bond by the terminal C-OH to form dimer) occurred first, but the release of DBP could explain the increase of acid number in eFAPE-DBP over a period of time. The freshly prepared eFAPE-DBP at 1:0.95 molar ratio (oxirane:DBP) had an acid number (AN) of 23 mgKOH/g and its value increased to 43 mgKOH/g after one month. Except for the reaction at molar ratio of 1:0.5, the OOC of all the eFAPE-DBP products were < 0.5% indicating that most oxirane rings had been opened, thus opening of epoxides by the terminal C-OH could not happen. Furthermore, the conversion of **1a** to **1b** in eFAPE-DBP reaction at 1:0.5 was lower than that of 1:0.75 and 1:0.95 indicating that the terminal C-OH groups did not open the oxirane ring directly but rather this proceeds via displacement of structures similar to **1a** shown in Fig 3.15, liberating DBP as indicated by the increase in AN.

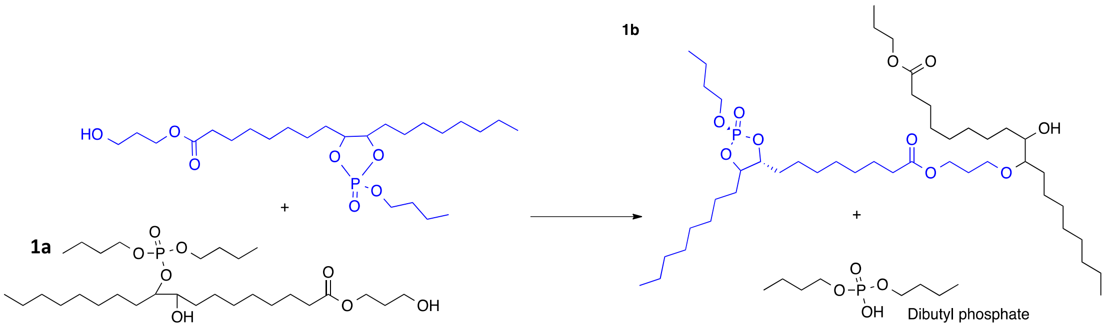


Figure 3.15: Schematic illustration for formation of dimer (**1b**)

The GPC trace of eFAPE-DBP (Figure 3.16) obtained at 1 week and 1 year after reaction also shows increase in compounds with higher molecular weight from 26.8% to 45.1% of the total peak area, presumably due to dimer formation.

Phosphate esters, the dioxaphospholane ring and its exocyclic groups are all susceptible to hydrolysis[4], [11]. The hydrolysis mechanism of linear and cyclic phosphates, as suggested by Penczek et al [4] , is shown in Fig 3.17 where both possibilities result in the formation of one P-OH group. This could explain the increase in acidity of the eFAPE-PA after the washing step.

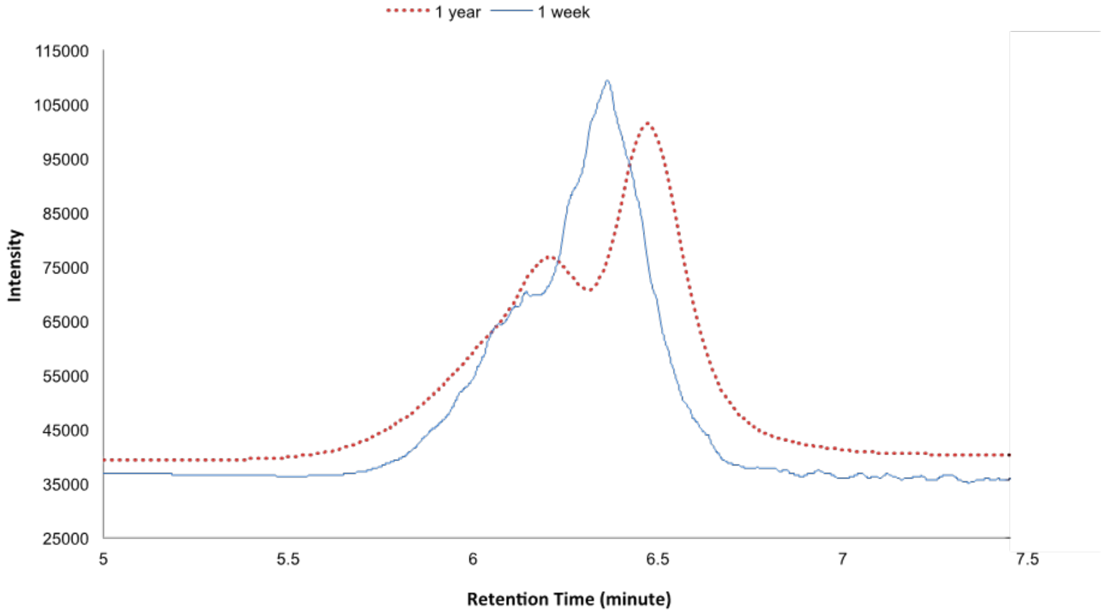


Figure 3.16: GPC trace of eFAPE-DBP at one week and one year after reaction

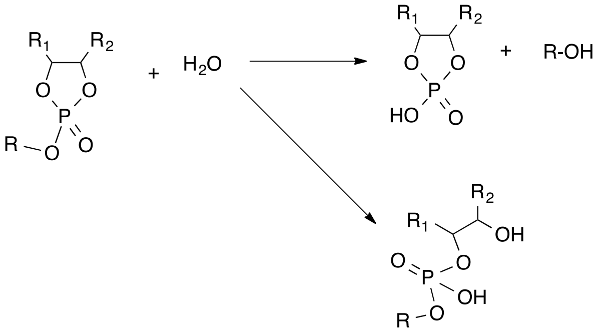


Figure 3.17: Schematic illustration of hydrolysis of alkyl phosphate

3.1.4 Oxirane ring opening with ethyl phosphates (EP)

The objective of the experiment is similar to that of eFAPE-DBP i.e. to maximize the covalent phosphorus content while maintaining relatively low viscosities by using mono or di functional phosphoric acid (diethyl or mono-ethyl phosphate) to minimize formation of di or tri-ester phosphate with the fatty acid propyl esters. The use of ethyl phosphate to open the oxirane ring of eFAPE is expected to produce polyol with relatively lower molecular weight as compared to dibutyl phosphate, thus, increase the covalent phosphorus content and higher OHV. The reaction between phosphorus pentoxide and ethanol to form ethyl phosphate is also less toxic compared to process with $POCl_3$ and also more economical[4].

Zhang et al[12] synthesized flame retardant polyol from epoxidized castor oil tranesterified with glycerol and carried out the ring opening at 70-75°C in toluene and triphenylphosphine as catalyst, for application in preparation of rigid PUR foam. The experiment described in this chapter used a simpler ring opening reaction and was carried out at room temperature and without solvent or catalyst or washing step to remove the catalyst or solvent.

3.1.4.1 Reaction of P_4O_{10} with ethanol

The oldest and cheapest method to form phosphate esters is by reacting phosphorus pentoxide with alcohols to form a mixture of primary and secondary esters, and phosphoric acid [4], [7], [13]. Phosphorylation of ethanol gives mixture of $C_2H_5OP(O)(OH)_2$, $(C_2H_5)_2OP(O)(OH)$ and H_3PO_4.

In this experiment, P_4O_{10} was reacted with excess of ethanol at the ratio of one mole phosphorus to >6 moles of ethanol. The reaction was carried out by adding P_4O_{10} into ethanol in a water bath to control the temperature because the reaction is exothermic, with constant stirring until all the P_4O_{10} was dissolved. The mixture was then heated to 80°C for 12 hours, excess ethanol was removed with rotary evaporator and the weight loss was recorded to calculate the final phosphorus content in the mixture.

The final phosphorus content (mole P/g mixture) in the mixture was calculated based on the amount of P_4O_{10} used in the reaction per unit weight of the final product after removal of excess ethanol. Example of calculation is given in Appendix IV.

The resultant mixture contained 0.007 mole phosphorus per gram mixture, and the acid number was 708 ± 2mgKOH/g. After the reaction was completed and ethanol removed, the final weight showed about 6 moles of ethanol reacted with one mole P_4O_{10} (equivalent to 6 moles ethanol to 4 moles phosphorus). The calculation is given in Appendix IV.

Mono- and diethyl phosphate esters were detected via direct infusion into the mass spectrometer ESI -ve as *m/z* 153 and 125 respectively (Appendix V). Mono and diethyl pyrophosphate were also present as *m/z* 233 and 261 respectively. However, the composition of this EP mixture was not determined.

3.1.4.2 Oxirane ring opening with ethyl phosphates (EP)

The eFAPE was reacted with EP at molar ratio of one mole oxirane to 0.25, 0.5 and 0.75 mole phosphorus, calculated based on the phosphorus content in the mixture. EP was added to eFAPE drop wise while constant stirring with magnetic stirrer, at room temperature (~25ºC). The reaction was exothermic. The resulting eFAPE-EP was a light yellow transparent liquid with viscosities from 1.20 to 5.26 Pa.s. The OHV, AN and viscosities of the eFAPE-EPs measured 18 hours after reaction are as shown in Table 3.3.

The increase of OHV indicates that new C-OH had been formed, by opening of the ring by the either mono-, diethyl phosphate or phosphoric acid in the EP mixture. GPC of the eFAPE-EP (Figure 3.4) shows that there is more than one peak, indicating a mixture of compounds with wide range of molecular weights.

The calculated phosphorus content in eFAPE-EP from reaction at oxirane:phosphorus molar ratio of 1:0.25, 0.5 and 0.75 are 2.34%, 4.10% and 7.07% respectively. However, at 1:0.75 the AN was high and not suitable for preparation of polyurethane where amine catalysts are used. The high acid number in eFAPE-EP due to high content of acidic P-OH group which will react with the amine catalyst and consequently reduce the efficiency of the catalyst to catalyze the cross-link formation between isocyanate and R-OH as well as isocyanate with water to form CO_2 for blowing agent[14].

Table 3.3: Hydroxyl value (OHV), acid number (AN) and viscosity of products (eFAPE-EP) of reaction between eFAPE and ethyl phosphates (EP) at different oxirane:phosphorus ratio

Oxirane:EP ratio	OHV (mgKOH/g)	AN (mgKOH/g)	Viscosity (Pa.s)
1:0.25	191 ± 6	2.66 ± 0.08	1.200 ± 0.020
1:0.5	222 ± 6	9.95 ± 0.67	5.260 ± 0.024
1:0.75	226 ± 2	51.43 ± 1.31	3.046 ± 0.012

FTIR spectra of eFAPE-EP as shown in Figure 3.3 indicates the opening of oxirane rings, with subsequent formation of P-O-C bond and C-OH group. The OOC of the eFAPE-EP from reaction of eFAPE with EP at oxirane:phosphorus molar ratio of 1:0.25 dropped from 5.43% to 1.67%. Simultaneous addition of 1.3-propanediol at oxirane:phosphorus:1,3-propanediol molar ratio of 1:0.25:0.5 resulted in further consumption of the oxirane rings, with OOC of 0.36% and OHV of 338mgKOH/g. The structure of hydroxypropyl ester of epoxidized oleic acid opened by 1,3 propanediol was shown by peak at RT 16.58 minutes in the TIC obtained from LCMS/MS analysis of the sample reacted with EP and 1,3-propanediol. Addition of more 1,3-propanediol for example at oxirane:phosphorus:1,3-propanediol molar ratios of 1:0.25:0.75 showed that 1,3-propandiol was more reactive in opening the oxirane rings than EP, indicated by higher AN of 5.53 mgKOH/g.

Fig. 3.18 showed the LCMS (TIC) trace for products from the reaction of epoxides, and the ethyl phosphate (EP) mixture and 1,3 –propanediol. 4 major peaks were observed. The first peak was starting material epoxides with the ion at *m/z* 357, corresponding to hydroxypropyl ester of epoxidized oleic acid.

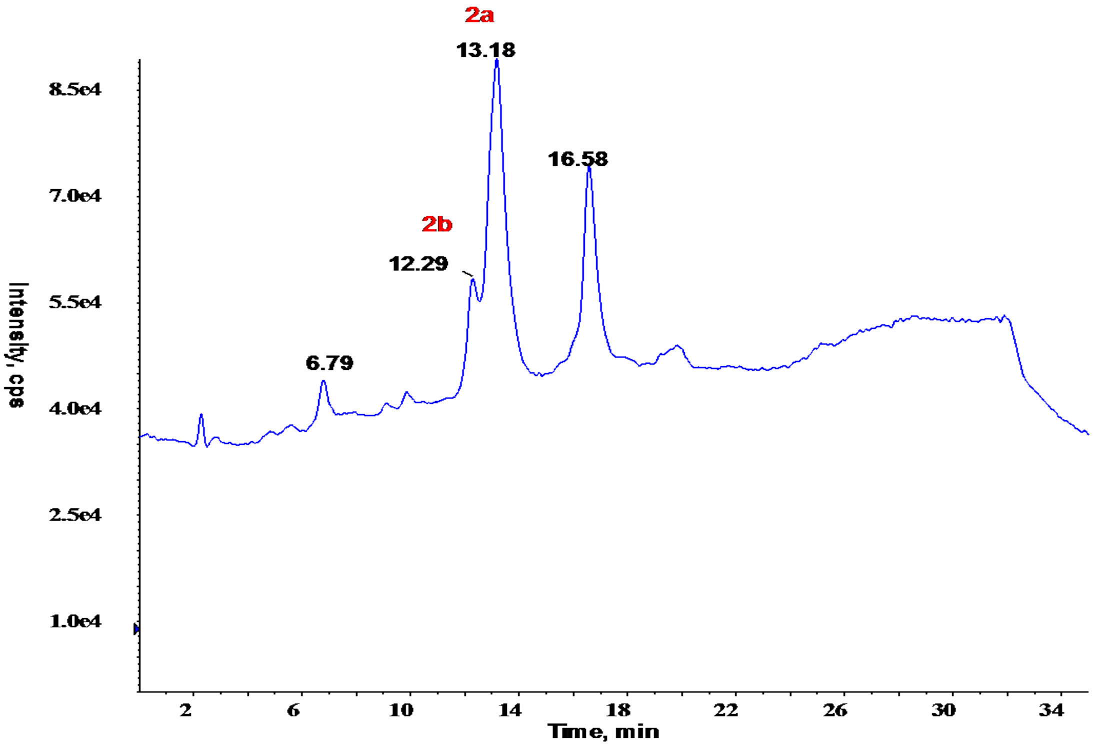


Figure 3.18: TIC of eFAPE reacted with EP and 1,3-propanediol

The peak at RT 13.1 minute was identified as **2a** (Figure 3.19). It was formed by one diethyl phosphate opened the oxirane ring of oleic acid propyl ester epoxide. The mass spectra gave rise to ion at *m/z* 511 (+H), 533 (+Na) and 569 under positive and ion at *m/z* 569 (acetic acid adducts) under negative mode. Therefore, the molecular weight was 510 g/mol. Dioxaphospholane structure with loss of one ethanol was observed at peak 12.2 mins (**2b** in Fig.3.19). The positive mass spectra of this peak gave rise to ion at *m/z* 465 (+H), 487(+Na). The fragment ion at *m/z* 155 (diethyl phosphate) was observed from ion at *m/z* 511 not 465, indicating stability of the oxaphospholane structure proposed for **2b**. The full scan mass spectra and MS/MS of **2a** and **2b** are as shown in Appendix VI and Appendix VII respectively.

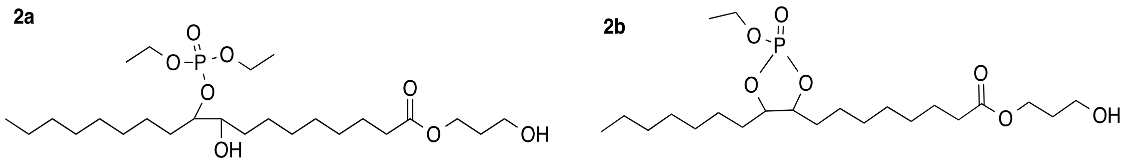


Figure 3.19: Proposed structure of major compounds in eFAPE-EP

Contrary to what was observed with eFAPE-DBP reaction, formation of dimer via ether bond between the terminal C-OH with oxirane did not occur. The compound with dioxaphospholane structure **2b** was eluted before **2a**, which was more polar than **2b**, consistent with the order of elution based on polarity in the normal phase liquid chromatography, based of freshly prepared eFAPE-DBP at oxirane:phosphorus:1,3-propanediol of 1:0.5:0.5. Changes to the eFAPE-EP over time were not studied and thus, whether the formation of the dimer via replacement of the ethyl phosphate adduct by the terminal C-OH of the eFAPE (reaction as illustrated in Figure 3.15) occurs (as was the case for eFAPE-DBP) is not known.

3.1.5 Oxirane ring opening reaction by phosphoric acid (PA)

Phosphoric acid reacts with epoxides to form phosphate ester linkages, resulting in a mixture of mono-, di- and triester phosphate. However, at the same time when nucleophilic alcohols or water are present, formation of ether crosslinks, catalyzed by acidic conditions provided by the phosphoric acid will also occur[3], [5], [7][15], [16]. This will result in formation of oligomeric ethers with terminal C-OH. Several studies had been conducted to utilized the reaction between phosphoric acid and epoxides to incorporate phosphorus into the oil structure[3] for various applications such for pressure sensitive adhesive[5], phosphorylated polyol for coatings[17] and polyols for polyurethane (PUR) applications[2], [18]–[20]. In all of the studies related to the synthesis of phosphorus containing polyols for PUR applications, phosphoric acid, containing 85% H_3PO_4 and 15% water was used to react with either epoxidized soybean oil[2] or palm oil[18]–[20]. Water in the 85% phosphoric acid will react with the epoxides and form diols, which subsequently in the presence of phosphoric acid and diols and/or terminal hydroxyl groups, will lead to formation of ether linkages and thus, oligomeric ethers. This is not favorable if the polyol is to be used as a component for PUR foam preparation. The formation of oligomeric ethers, in addition to the already relatively high molecular weights of vegetable oil epoxides in the triacylglyceride form, will result in polyols with high molecular weights, high viscosities and low OHV.

Furthermore, the previous use of epoxidized soybean or palm oil as starting material resulted in phosphorus containing polyol with no primary C-OH groups. In this experiment epoxidized canola oil was transesterified with 1,3 propanediol to incorporate one primary C-OH into the fatty acid epoxide ester structure, giving the polyol more reactivity for crosslinking reactions with isocyanates. This is desirable for the preparation of PUR foam requiring shorter curing times, such as in spray foam where high reactivity is required.

In addition to this, phosphorus containing polyol was synthesized from canola oil epoxide transesterified with 1,3 propanediol, having considerably lower molecular weight than the triglyceride form. In order to minimize formation of oligomers by ether crosslinks, crystalline anhydrous (99.999% trace metal basis) phosphoric acid was used. The same reaction was also carried out by using 85% H_3PO_4 in order to compare outcome of the reaction with the absence and presence of water. *Tert*-butanol was used as solvent because its low nucleophilicity which promotes higher degree of reaction between H_3PO_4 but not taking part in the oxirane ring opening reaction[3]. H_3PO_4 was added into the eFAPE at 40ºC and the temperature was raised and kept at 70ºC until the OOC reached < 0.5%. The yield of product after removal of solvent via vacuum evaporation was ~ 86%.

Table 3.4 shows the comparison between eFAPE-PA from reaction with crystalline anhydrous PA and 85% PA. eFAPE-PA. Reaction with 85% phosphoric acid containing water showed consumption of the oxirane ring at relatively higher rate than reaction with crystalline anhydrous phosphoric acid. Higher acidity and viscosity but lower OHV in product from reaction with 85% phosphoric also indicates that formation of oligomeric ethers occurred when the epoxide was reacted with PA in the presence of water. Higher acidity in the product also indicates lower rate of ring opening by P-OH group, leaving higher amount of free P-OH groups which contribute to the high acid number. The GPC trace of both products showed that reaction in presence of water resulted in a greater percentage of high molecular weight compounds, *ie* oligomers (Figure 3.20). In the figure, this is seen by a higher peak area ratio of the high MW to low MW peaks.

The phosphorus content of eFAPE-PA obtained from reaction with crystalline anhydrous phosphoric acid was found to be $1.98 \pm 0.01\%$. Figure 3.22 shows the TIC of product from reaction between eFAPE and the phosphoric acid from LCMS. Three main peaks were observed. The first peak at RT 9.18 minutes was the starting material at ion at *m/z* 357, corresponding to the hydroxypropyl ester of epoxidized oleic acid, the major compound found in eFAPE. The second peak at RT 16.03 minutes was attributed to the hydroxypropyl ester of epoxidized oleic acid opened by water forming a diol with ion at *m/z* 375 (**3a** in Figure 3.21). Two compounds were found in the third peak at RT 19.08 minutes, ions at *m/z* 793 and 811 corresponding to hydroxyl phosphate diester (**3b** in Figure 3.21) and the dimer with dioxaphospholane structure (**3c** in Figure 3.21).

Table 3.4: Acid number (AN), hydroxyl value (OHV), oxirane oxygen content (OOC) and viscosity of eFAPE reacted with crystalline anhydrous (99.999% trace metals basis) phosphoric acid (PA) and 85% phosphoric acid

Molar ratio (Oxirane: PA)	AN (mg KOH/g)	OHV (mg KOH/g)	OOC (%)	Viscosity (Pa.s)
eFAPE + 99.999% PA (1:0.25)	4.1 ± 0.6	260 ± 1	0.5 ± 0.1	8.2 ± 0.1
eFAPE + 85% PA (1:0.25 + H_2O)	10.2 ± 0.4	241 ± 3	0.2 ± 0.1	15.2 ± 0.1

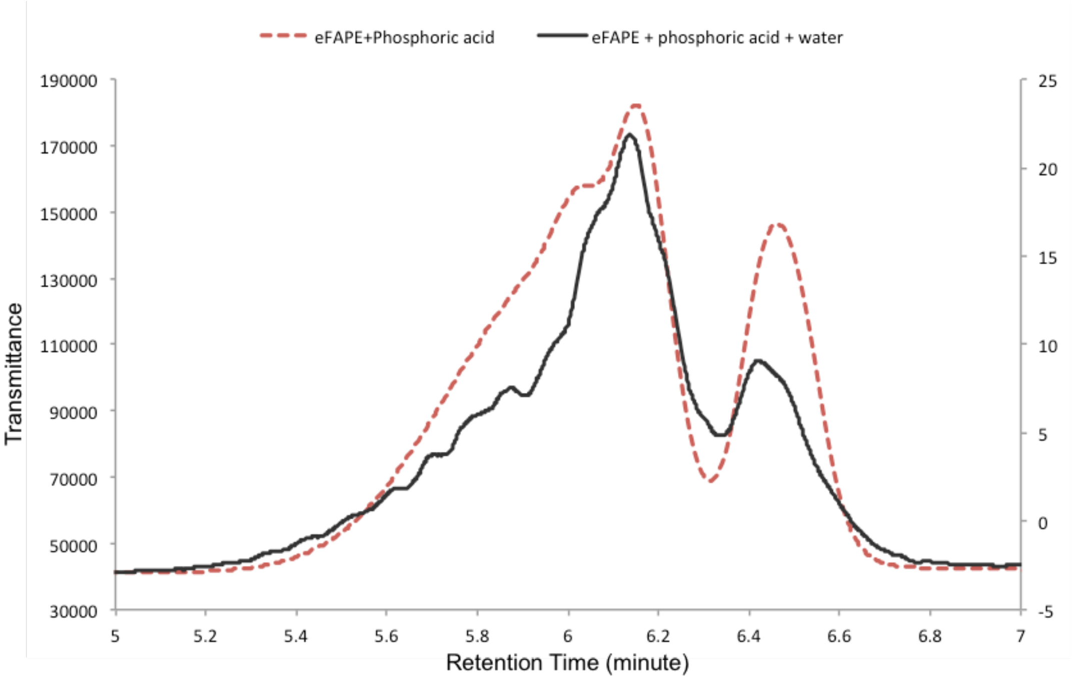


Figure 3.20: GPC of eFAPE reacted with phosphoric acid with water and without water

The ^{1}H-NMR analysis of eFAPE-PA indicated a transformation of eFAPE to polyol. The signals characteristic of the phosphate groups are localized between 4.00 to 4.40 ppm. **3c** is characterized in ^{1}H-NMR by signal at 4.22 ppm corresponding to the hydrogen -CH-O-P of the dioxaphospholane cycle. **3b** is characterized by the signals of -CH- hydrogen groups at 3.70 and 4.13 ppm corresponding respectively to the hydrogen of the hydroxyl group and that of phosphate diester group (Figure 3.23). Chemical shifts in 14.0-15.6 ppm and 0-0.5 ppm region in ^{31}P-NMR attributed to the characteristic of dioxaphospholane structure and the hydroxyphosphate structures respectively, indicating that both structures are present (Figure 3.24). These chemical shifts are consistent with those reported by Derouet et al [11]. In contrast, Zhang et al[8] and Heinen et al[2] reported that ^{31}P-NMR chemical shifts at 14-15ppm are characteristic of phosphonate structures in their polyols formed by reaction of soybean oil epoxides with phosphoric acid or diethyl phosphate. However, under the conditions described in their experiments it appears that this would more likely be attributed to dioxaphospholanes [13].

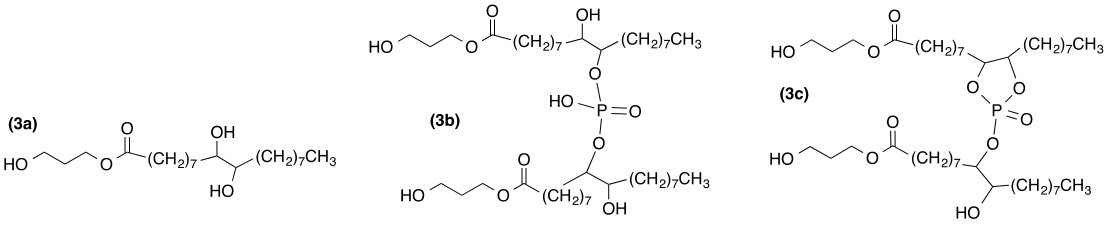


Figure 3.21: Proposed structure of compounds found in eFAPE-PA **(3a)** propyl ester of oleic acid epoxides opened by water to form diol **(3b)** two propyl ester of oleic acid epoxides opened by phosphoric acid to form hydroxyphosphate diester **(3c)** two propyl ester of oleic acid epoxides to form dimer with one dioxaphospholane ring structure and one hydroxyphosphate.

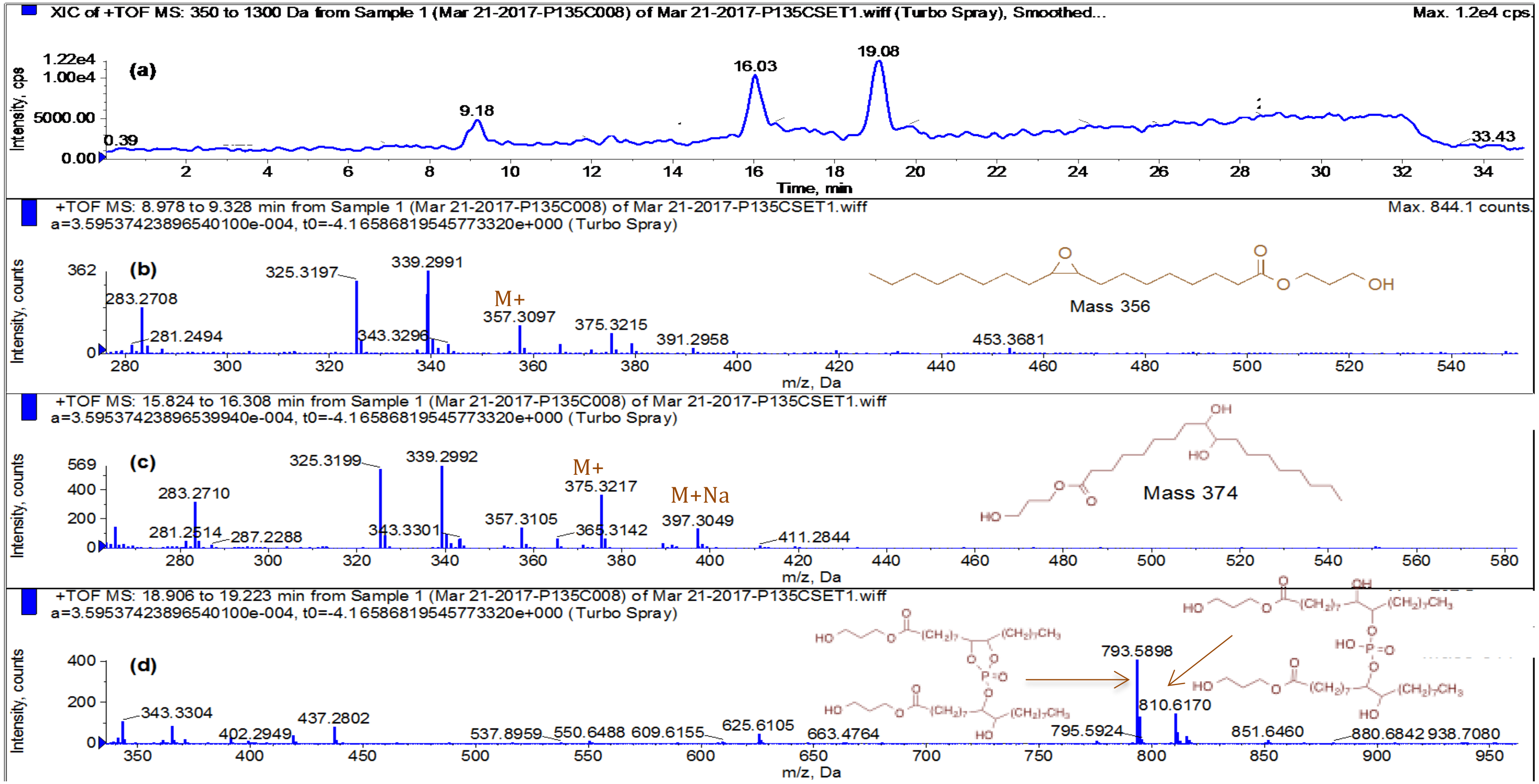


Figure 3.22: (a) LCMS TIC of eFAPE-PA (b) Mass spectra of peak at RT 9.18 minute (c) Mass spectra of peak at RT 16.03 minute and (d) Mass spectrum of peak at RT 19.08 minute

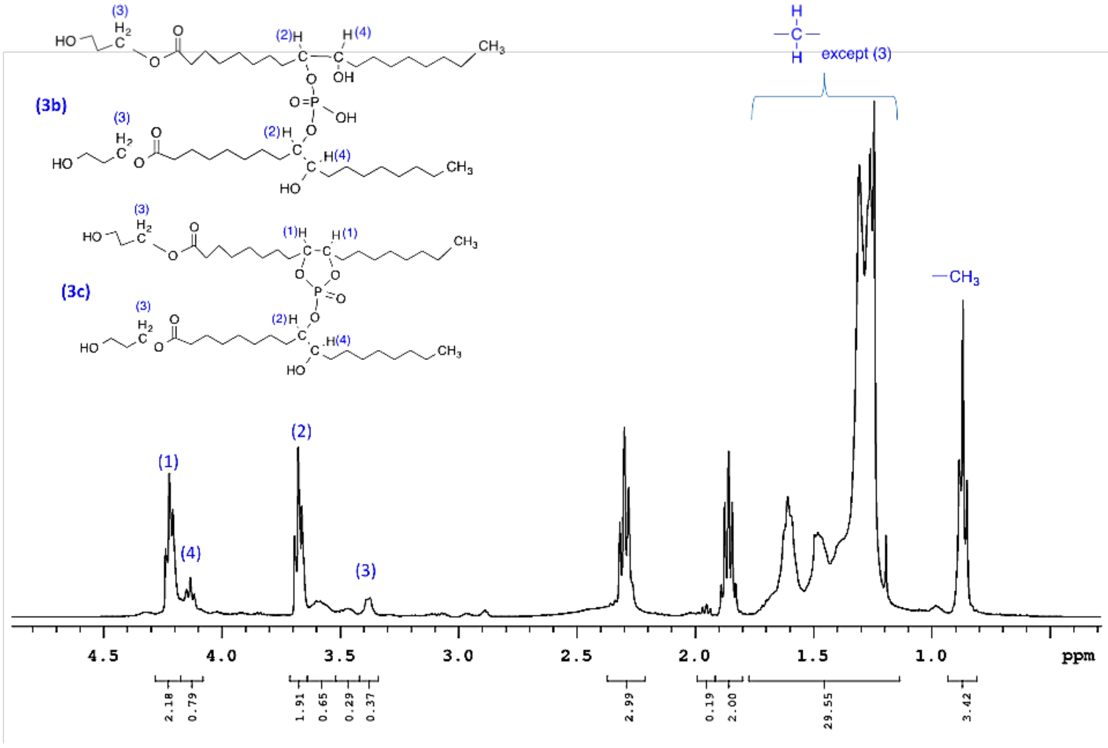


Figure 3.23: ^{1}H-NMR characterization of **3b** and **3c**

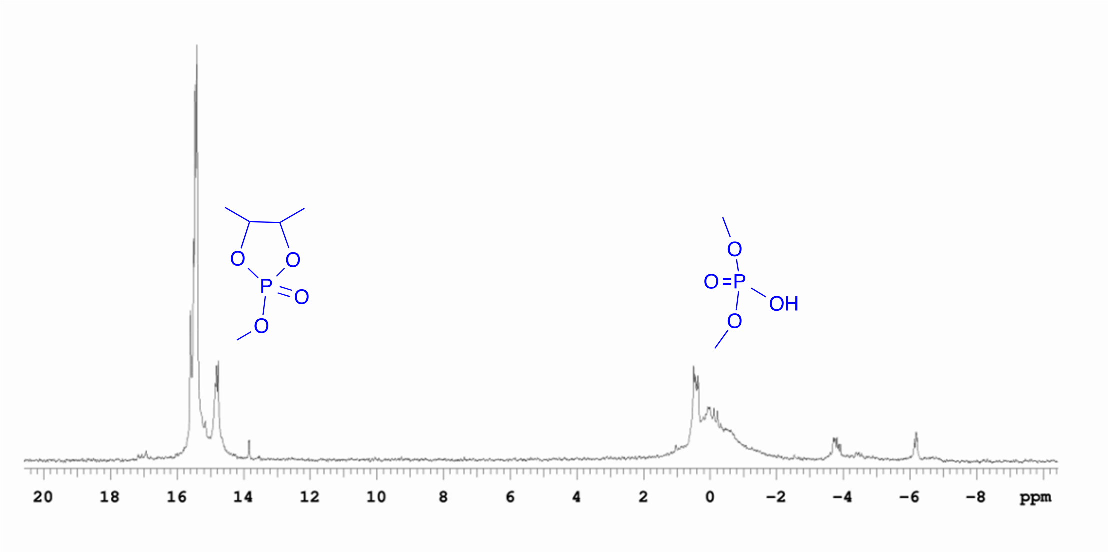


Figure 3.24: ^{31}P-NMR of eFAPE-

Although no water was available in the reaction with crystalline anhydrous (99.999% heavy metals basis) phosphoric acid, structures with diols were found in the products (**3a**), indicating that water was released during the formation of the dioxaphospholane ring (**3c**) from the hydroxyphosphate diester (**3b**) (Figure 3.25). As discussed earlier, based on the mechanism suggested by Derouet et al[11], opening of an oxirane ring by phosphoric acid or a P-OH group forms a phosphate ester bond and a secondary C-OH (hydroxyphosphate). Due to the unstable *cis* configuration, C-C rotation to a more stable *trans* position brings the C-OH group closer to the phosphate center leading to formation of the cyclic dioxaphospholane structure. In the case of phosphoric acid, internal condensation also occurs to release one water molecule, which is available to open an oxirane ring resulting in a diol (**3a**). Conversion of **3b** to **3c** also resulted in loss of the remaining P-OH in the initial **3b** structure, which means a decrease in acid value of the product should be observed. The high temperature employed in the reaction may help to speed up the conversion, however, in this experiment the reaction was stopped once the OOC reached < 0.5% before all **3b** was converted to **3c**. A prolonged reaction time may lead to conversion of more **3b** to **3c**. To observe the stability or changes in the product, it was stored at 50°C and the acid number (AN) measured after one month. The AN dropped from 4.09±0.58 mgKOH/g to 1.53±0.01 mgKOH/g, indicating the instability of the hydroxyphosphate structure and consistent with the continuous conversion to the stable cyclic dioxaphospholane structure.

3.1.6 Formation of dioxaphospholanes from hydroxyphosphate and the effects of this reaction on the resulting phosphorus containing polyols for PUR preparation.

The conversion of hydroxyphosphate structures in the polyols to dioxaphospholane structures when phosphoric acid was used for oxirane ring opening is advantageous over reactions involving mono or di-functional phosphoric acid, such as DBP or any alkyl or aryl phosphates. When phosphoric acid was used, formation of the ring through internal condensation occurs, resulting in release of water and loss of the remaining P-OH group, which results in reduced acidity. This is favorable for PUR preparation where an amine catalyst is used, as explained earlier in section 1.1.3. The water released may then open remaining oxiranes to form diols, which in turn increases the OHV of the polyol. At the same time, the reduced acidity may lower the possibility of formation of acid catalyzed ether links after the diols are formed, thus oligomerization is unlikely to happen. However, excess water may be a disadvantage as it may cause hydrolysis of P-O-C bonds as explained in Figure. 3.17. The ratio of oxirane:H_3PO_4 can be optimized so that the water released is completely consumed in the formation of diols and the reaction time can be optimized to ensure complete conversion of all the hydroxyphosphate to dioxaphospholane to obtain a stable product. Although a secondary hydroxyl group is lost due to the conversion from **3b** to **3c** (Figure 3.25), in the case of eFAPE-PA, the functionality of **3c** is still three and the OHV of eFAPE-PA is 260 mgKOH/g and suitable for many PUR applications.

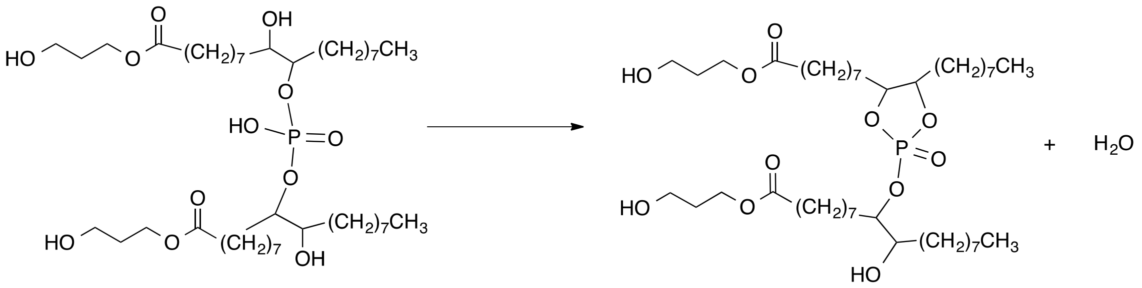


Figure 3.25: Schematic illustration of conversion of compound **3b** to **3c**

On the other hand, use of dialkyl phosphate will release free mono alcohol (as illustrated by example in Figure 3.26), which will be a chain terminator during PUR preparation via reaction with isocyanate. When a starting material like eFAPE is used, formation of the dioxaphospholane monomer reduced the functionality of the product to only one, and in eFAPE-DBP formation of dimer released free DBP and consequently the covalently bound phosphorus content was reduced and acidity was increased.

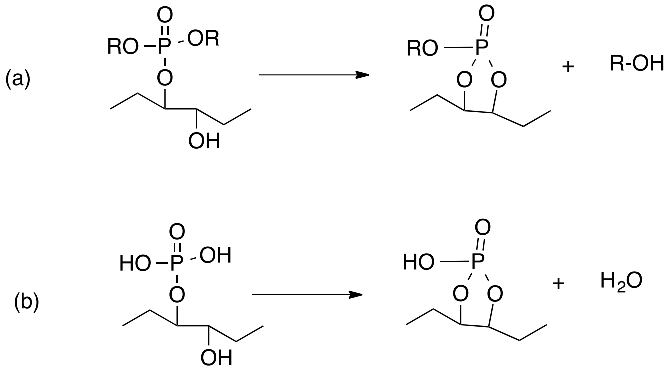


Figure 3.26: Schematic illustration of conversion of hydroxyphosphate structure formed via reaction of oxirane ring with (a) dialkyl phosphate and (b) phosphoric acid to dioxaphospholanes

In summary, the conversion from hydroxyphosphate structure to the dioxaphospholane is very likely to occur due to the natural occurrence of *cis*-double bonds in most vegetable oils. Although the consequences of this conversion have significance to the structures and properties of vegetable oil based polyols synthesized in this manner, none of the previously reported studies [2], [8], [18]–[20] have addressed this issue. Knowledge of this instability in the hydroxyphosphate structure towards conversion to dioxaphospholanes, along with resulting byproducts and changes in AN, OHV and other properties, provides insight when selecting phosphorus containing ring-opening reagent for synthesis of fire retardant polyols from vegetable oils.

3.2 Preparation of PUR foams from phosphorus containing polyol

3.2.1 PUR foams from eFAPE-DBP

PUR foams were prepared from 50% eFAPE-DBP with different phosphorus contents and 50% Mannich polyol. Our preliminary studies showed that attempts to prepare PUR foams from 100% eFAPE-DBP polyols resulted in long cream time and raise time, which indicates the low reactivity of the polyols [21]. The addition of Mannich 425 polyol increased the reactivity of compound A with the MDI thus, decreased the cream time and rise time. However, foams prepared from Mannich 425: eFAPE-DBP at a ratio of less than 1:1 resulted in PUR foams with undesirable qualities – brittle, yellowish color, and shrunken. Shrinking is due to an imbalance between the rate of foam expansion and the rate at which cross-links are formed[22]. Heat that is generated by the reaction between isocyanate and polyol resulted in expansion of CO_2 and blowing agent, thus, expansion of the foam. After some time, when the heat is gone, the gases contract and if there are insufficient urethane crosslinks formed to support the cell structure, the foam structure collapses and shrinks. The formulations, densities, their cream times and raise times of the some foams (PU4 – PU6) prepared from eFAPE-DBP are as shown in Table 3.5.

The low reactivity of eFAPE-DBP could be attributed to the formation of dioxaphospholane that depletes the secondary C-OH group from the structure, reducing the functionality of eFAPE-DBP. In addition to that, formation of the dimer structure (**1b)** also depletes another primary C-OH. The major component of eFAPE-DBP (**1b** in Figure 3.7) has functionality of two.

1-butanol and free DBP resulted from formation of oxaphospholane ring and dimers also contributed to the low reactivity of eFAPE-DBP. 1-butanol, which acted as chain terminator, competed with the polyols to react with isocyanate, forming only one urethane bond and unable to form cross-links because it contains only one C-OH group. This depleted the NCO groups available for cross-linking with the polyols, resulting in a weak cell structure. In addition, free DBP, with one P-OH is acidic, which may react with the amine catalyst, resulting in less effective catalyst function.

Addition of Mannich polyol into the PUR formulation increased the reactivity by providing more reactive primary C-OH groups for cross-linking with isocyanates. However, the because of the continuous conversion of hydroxyphosphate to dioxaphospholanes, resulting in an increase of 1-butanol content, dimerization of the polyol and increased AN, preparation PUR foams with reproducible characteristics was not possible.

3.2.2 PUR foams from eFAPE-PA

Polyol prepared from ring opening with phosphoric acid however, showed better reactivity and PUR foam was prepared using 100% of eFAPE-PA. As shown by LCMS/MS analysis, the major compound has the functionality of 3, with 2 primary C-OH and one secondary C-OH. Because higher temperature (70°C) was used during preparation eFAPE-PA, most of the ydroxyphosphate was converted to the more stable dioxaphospholane structure, resulting in formation of water. This is indicated by the presence of diols, compounds, which resulted from opening of ring by water. In the formulations shown in Table 3.5, the cream time was ~11 seconds and raise time was 20 seconds.

Three foams with different phosphorus content were prepared by using different concentration of eFAPE-PA in combination with 3GP polyol. Foam prepared with 100% eFAPE-PA (PU3) contained ~1.09% phosphorus, and foam prepared from 50% eFAPE-PA and 50% 3GP contained 0.52% phosphorus (PU2). The control foam containing 0% phosphorus was prepared from 100% 3GP (PU1).

The foams made using eFAPE-PA have density of 2.6 – 2.8 lbs/ft^3. These foams have relatively better appearance in term of color (lighter) and consistency as compared to foams prepared using eFAPE-DBP.

3.2.2.1 Derivative Thermogravimetric Analysis (DTGA) and Thermogravimetric Analysis (TGA) of PUR foams

Thermogravimetric analysis was carried to study the thermal decomposition of PU1, PU2 and PU3. Table 3.6 shows the corresponding values of thermograms, while Figure 3.27 and Figure 3.28 show the TGA and DTGA thermograms of polyurethane foams with different phosphorus contents.

Under an N_2 environment, PU foams modified by addition of the phosphorus containing polyol decreased the onset temperature for weight loss but increased char formation. Thermal degradation of all the foams composed of two main stages as shown by the DTGA thermograms.

Table 3.5: Formulations for PUR foams prepared from eFAPE-PA and eFAPE-DBP polyols and their characteristics

Ingredient	Parts					
	PU1	PU2	PU3	PU4	PU5	PU6
eFAPE-PA	-	50	100	-	-	-
eFAPE-DBP1	-	-	-	50	-	-
eFAPE-DBP2	-	-	-	-	50	-
eFAPE-DBP3	-	-	-	-	-	50
Mannich	-	-	-	50	50	50
3GP	100	50	0	-	-	-
B8404	1.1	1.1	1.1	1.1	1.1	1.1
Polycat 30	2	2	2	2	2	2
Dabco T120	0.2	0.2	0.2	0.4	0.4	0.4
Water	1.2	1.2	1.2	1.2	1.2	1.2
Cyclopentane	10	10	10	4	4	4
MDI	110	110	110	110	110	110
Density (lbs/ft^3)	2.4	2.6	2.8	3.4	3.4	3.3
% Phosphorus	0	0.52	1.09	1.37	1.18	0.89
Cream time (sec)	12	11	11	17	12	10
Raise Time (sec)	20	20	20	30	30	30

Table 3.6: The parameters of TGA and DTGA of PU1, PU2 and PU3

	Stage One			Stage two			Carbon residue (%)
	Onset (°C)	Td$_{max}$ (°C)	R$_{max}$ (%/°C)	Onset (°C)	Td$_{max}$ (°C)	R$_{max}$ (%/oC)	
PU1	278	336	0.89	361	429.	0.29	10.3
PU2	266	314	0.75	351	451	0.51	11.9
PU3	252	305	0.66	334	444	0.54	15.7

TGA and DTGA thermograms from thermogravimetric analysis of PU1, PU2 and PU3 showed the following:

Addition of the phosphorus containing eFAPE-PA polyol into the PU foams resulted in (i) lower onset temperatures for both stages of decomposition, (ii) lower decomposition or weight loss rates in the first stage but (iii) higher decomposition or weight loss rate in the later stage, (iv) lower temperatures at which the maximum decomposition rate occurred in first stage, (v) higher temperatures at which the maximum decomposition rate occur in the second stage (vi) lower weight loss in the first stage, (vii) lower temperatures at which the final stage occurred (plateau in TGA thermograms) and (viii) higher carbonic residues at the end of decomposition process.

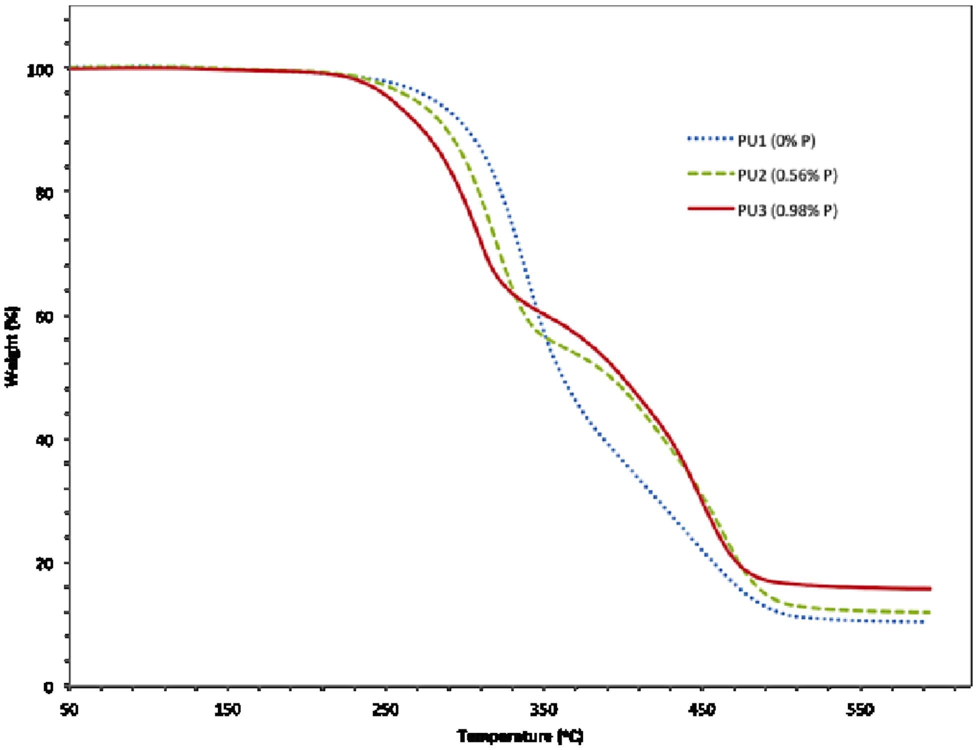


Figure 3.27: TGA thermograms of polyurethane foams PU1, PU2 and PU3

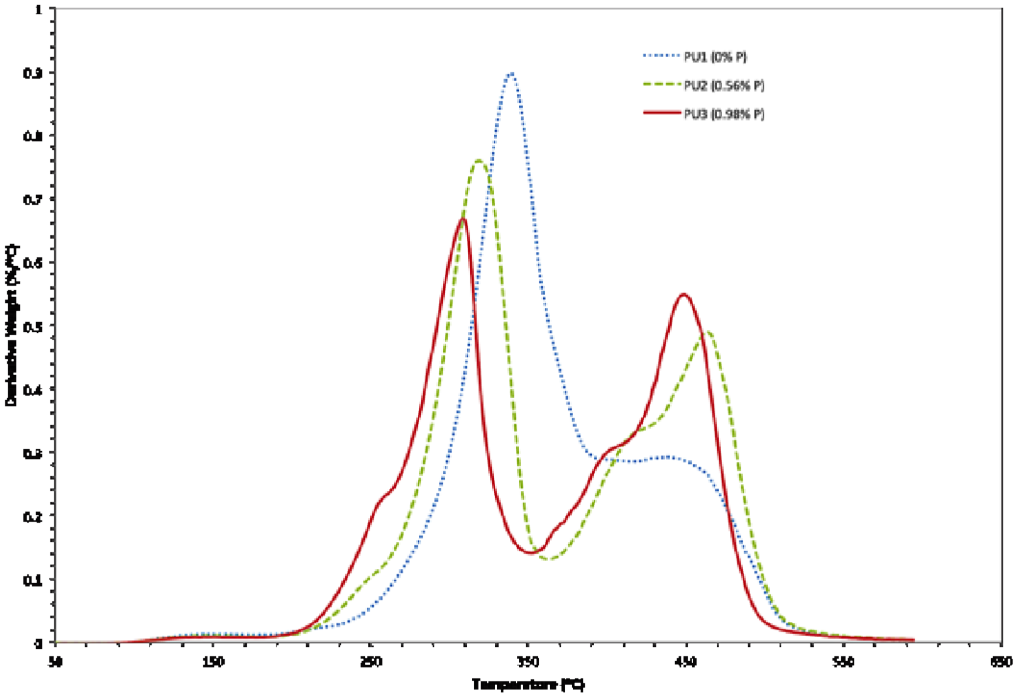


Figure 3.28: DTGA thermograms of polyurethane foams PU1, PU2 and PU3

The pure foam (PU1) begun to decompose at 278°C and the maximum weight loss was at 336°C. In the first stage of decomposition, about 62% of its weight was lost. It then further decomposed leaving about 10.3% of carbon residue at 600°C. The onset temperatures for PU2 and PU3 were shifted to lower temperatures of 266.5°C and 252.6°C, with the maximum weight loss at 314.8°C and 305.8°C respectively. The maximum degradation rate for the pure foam was 0.89 % / °C, and the rates decreased in foams containing increasing amount of eFAPE-PA polyol in the first stage to 0.75 and 0.66 for PU1 and PU2 respectively. In the first stage, only 45% and 40% of weight was lost for PU2 and PU3 respectively compared to 62% for the control foam.

The second stage of decomposition started at 411.3°C, 359.8°C and 352°C for PU1, PU2 and PU3 respectively. The trend for maximum degradation rates were reversed however, during the second stage, with PU3 being the highest at 0.54 compared to 0.51 and 0.29 for PU2 and PU1 respectively.

Thermal degradation of PU foams is known to occur in at least two stages of degradation [2], [8], [23]–[27]. Generally, the thermal degradation starts with dissociation of urethane bonds, dehydration, carbon dioxide and isocyanate evaporation, followed by decomposition of PU hydrocarbon chains. The temperatures at which these stages occur vary depending on many factors such as density of crosslinking, structure and type of chemical bonds in the hydrocarbon chains, presence of additive or reactive flame retardant etc. Ding et al[28] reported that decomposition of phosphorus containing moieties in PUR starts at 200-300°C. Urethane bonds decompose at 200-283°C followed by hydrocarbon chains of polyols at temperature 283-400°C[24].

The initial thermal stability of PURs containing phosphorus was reduced due to lower thermal stability of P-O-C bonds [28] [8], [23], [29]. In PU2 & PU3, a small shoulder prior to the main peak of the first decomposition stage shown by DTGA thermograms, indicating that at the very early stage decomposition of some P-O-C may occur, followed by urethane bonds. The reduced decomposition rates in PU2 & PU3 may also indicate that some flame retardant mechanisms are at work, resulted in lower weight loss and delayed decomposition of the samples. Decomposition of P-O-C bonds thus resulted in formation of products that promote formation of char residue, which then protect the samples from further degradation. The relatively higher residue in PU2 & PU3 at the final stage of TGA in comparison to PU1 indicates formation of char. The carbon residue in the PU2 and PU3 at 600°C was improved to 11.9% and 15.7% respectively relative to pure foam PU1 (10.3%), demonstrating the roles of the phosphorus containing eFAPE-PA polyol as reactive flame retardant in PU2 and PU3.

The IR spectra of the gaseous decomposition products released during thermal decomposition of PUR foams made from soy-based phosphorylated polyol and MDI was carried out by Heinen et al [2]. These foams are fairly similar to the PUR foams prepared in this study. At 472°C a band from P=O compound was observed, together with bands corresponding to C-O-C, C-C and C-H. Some phosphorus containing FRs work not only by producing anhydrides of phosphoric acid and related acids when decomposed (which acts as catalyst to the formation of char) but also take part in forming a phosphorus containing protective layer in the condense phase[30], [31]. Ding et al [28] reported that P=O groups (1250 cm^{-1}), and P-O-C groups (1080 cm^{-1}) existed in the FTIR spectrum of PUR char, indicating that the phosphate segments from flame retardant polyols probably decomposed leaving these cross-linked phosphoric acid derivatives, which could promote the formation of char residues.

Since the weights after the first stage of decomposition of PU2 and PU3 were higher than PU1, at higher temperatures (>350°C), further decomposition of remaining P-O-C bonds (perhaps in the char structure) and C-O-C, C-C and C-H bonds, make the decomposition rates for PU2 and PU3 appear higher than for PU1. The shoulder peaks at around 350°C – 400°C could be attributed to decomposition of P-O-C bonds, which are less thermally stable than C-O-C, C-C and C-H.

3.2.2.2 Limiting Oxygen Index (LOI)

The flammability of the PUR foams prepared from eFAPE-PA polyol (PU2 & PU3) was evaluated with oxygen index (LOI) method[32]. The Limiting Oxygen Index (LOI) test is a standard test to quantify the resistance to ignition of a polymeric material. LOI is expressed as $([O_2]/([O_2] + [N_2]) \times 100$. A fire resistant material will require more O_2 to sustain combustion, thus, will give a higher LOI. The O_2 content in air is 21% so any material with LOI above 21% is considered as self-extinguishing because the combustion cannot be maintained at ambient temperature without contribution from external source. Materials with LOI below 21% are considered as flammable[32], [30].

The reference foam (PU1) containing no phosphorus was prepared from 100% 3GP polyol, which is also derived from canola oil. The amount of all of the other components such as catalysts, surfactant and blowing agent were fixed.

The LOIs of PU1, PU2 and PU3 containing no phosphorus, 0.52% and 1.09% phosphorus respectively are as shown in Table 3.7. LOI increased with increasing concentration of eFAPE-PA in the foams, showing an obvious trend of flame retardant properties and fire performance improvement in foam containing eFAPE-PA.

Table 3.7: Limiting Oxygen Index and phosphorus content of polyurethane foams PU1, PU2 and PU3

PUR foam	Phosphorus content (%)	Limiting Oxygen Index (%)
PU1	0	19.1
PU2	0.52	20.1
PU3	1.09	21.1

3.2.2.3 Burning Test

A simple burning test was performed on PU1, PU2 and PU3 as described in section 2.2.3.3. Upon exposure to the Bunsen flame, all of the foams ignited almost immediately. Foam prepared from 100% 3GP (PU1), once ignited the fire spread across the foam and consumed almost all of the foam, leaving 0.0825g (~9% of initial weight) of char residue after it burned out in 43 seconds. PU2 ignited and the fire spread across the specimen, consuming on the upper layer of the foam then eventually self-extinguished after 85 seconds. PU3 ignited and the fire slowly spread up to about 20% of the foam and self-extinguished in 20 seconds. Figure 3.29 shows the residues of PU1, PU2 and PU3 after the fire self extinguished and Figure 3.30 shows the foams at different times after ignition.

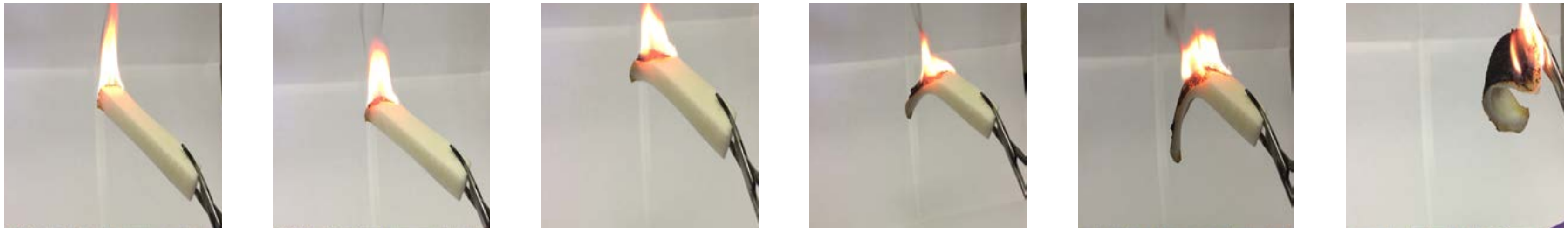
The fire performance of the foams was significantly improved with increasing phosphorus content in the foams. This was evaluated qualitatively based on the relatively lower rate of the fire spread, higher residue after the fire extinguished and also self-extinguishing nature of the phosphorus containing foams as compared to the control specimen. The fire spread in foam containing 50% eFAPE-PA (0.52% phosphorus) at almost half the rate of the foam prepared from 100% 3GP, PU1 (Figure 3.30). Furthermore, only the upper part of the foam was consumed. Char residue was formed covering the area at which the fire spread, protecting the lower part of the foam from burning, indicating the condensed phase mechanism of the flame retardant. In the foam prepared from 100% eFAPE-PA (PU3), the fire spread at almost the same rate as PU2 but self extinguished after only 20 seconds, consuming only about 20% of the foam. Char residues were also formed at the area where the fire spread, however the fire did not spread further across the foam, which suggests the gas phase mechanism of the flame retardant. The above burning experiments were performed twice with similar results.

Figure 3.29: Char residues of PU1, PU2 and PU3 after burning test

(a)

5 secs 10 secs 20 secs 30 secs 40 secs

(b)



5 secs 10 secs 20 secs 30 secs 40 secs 80 secs

(c)

5 secs 10 secs 20 secs

Figure 3.30: (a) PU1, (b) PU2 and (c) PU3 at different times after ignition

Reference

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CHAPTER 4: CONCLUSIONS AND FUTURE WORKS

4.1 Conclusions

Phosphorus has been successfully incorporated into canola oil based polyol *via* epoxy ring opening by reacting hydroxypropyl esters of epoxidized canola oil fatty acids (eFAPE) with phosphoric acid (PA), ethyl phosphates (EP) and dibutyl phosphate (DBP). Thus, biobased phosphorus containing polyols have been successfully prepared from canola oil. The synthetic routes to these biobased phosphorus containing polyols were simple. Preparation of eFAPE-DBP and eFAPE-EP was carried without solvent at room temperature and no washing step was employed to remove excess reagent because the molar ratio of oxirane to DBP or EP was lower than 1. As for eFAPE-PA, *tert*-butanol was employed and removed by vacuum. No additional washing step was required, and the butanol can be reused.

The use of monofunctional phosphoric acid (dialkyl phosphate) was able to prevent formation of diester or triester phosphate. The phosphorus content of the polyol from reaction with dibutyl phosphate (eFAPE-DBP) was as high as 5.91%.

A important finding of this work is that the use of high purity phosphoric acid, minimized the formation of oligomers and resulted in a polyol with lower acid number and lower viscosity along with a higher hydroxyl value, when compared to the more commonly use of 85% phosphoric acid[1]. This is likely due to the absence of water in the reaction. The phosphorus containing polyol produced in such a way has low viscosities and were shown to be suitable for the preparation of polyurethane foams.

The hydroxyphosphate structure that was formed from epoxy ring opening by phosphoric acid or alkyl phosphate esters was unstable and converted to cyclic dioxaphospholane structure. This led to the loss of one secondary C-OH group and the liberation of water in the case of ring opening by phosphoric acid. Ring opening by dialkyl phosphate results in release of an alcohol. These changes have significant effects on the compatibility of the resultant polyols as components for PUR preparation. This finding provides important new insight for future work in selection of synthetic processes, process parameters and the phosphate derivatives used for synthesis of phosphorus containing polyols employing ring opening reactions from epoxidized vegetable oils.

In this study, a canola oil based phosphorus containing polyol was prepared from hydroxypropyl esters of epoxidized canola oil by reaction with phosphoric (eFAPE-PA). This was found to have the most promising attributes for PUR foam applications, with a viscosity of 8.24 Pa.s, acid number 4.09 mgKOH/g and hydroxyl value of 260 mgKOH/g. Also, the major compound has a functionality of three (two primary C-OH and a secondary C-OH group).

The reaction between phosphoric acid and eFAPE formed hydroxyphosphate diester which subsequently converted to the cyclic dioxaphospholane ring. This resulted in chemical changes advantageous to the formation of crosslinking in PUR foam preparation.

PUR foams were also successfully prepared from eFAPE-DBP (50% of polyol component) and eFAPE-PA (up to 100% of polyol component) polyols. However, due to instability of eFAPE-DBP, the chemical changes negatively affected cross-link formation between the polyol and isocyanate, these are considered not to be suitable for PUR applications.

PUR foams prepared from eFAPE-PA were evaluated for their fire performance (Limiting Oxygen Index, LOI and a simple burning test) and their thermal degradation behavior (thermogravimetric analysis, TGA). There was a significant improvement in the flame retardancy of the foams prepared from eFAPE-PA:

(1) 10% increment in LOI from 19.1% of the foam with no phosphate polyol to 21.1% for foam prepared from eFAPE-PA (100% eFAPE-PA as polyol in compound A, 1.09% phosphorus in the foam).

(2) When subjected to an open flame, the same foam self-extinguished after 20 seconds having burned only about 20% of the initial foam volume. This compares to the control PUR foam for which the entire foam was burnt leaving only 9% of the original weight as residue.

(3) Addition of eFAPE-PA into PUR foam decreased the onset temperature for thermal degradation in TGA. However, at the end of heating there was 50% more residual char compared to the same experiment with the control PUR foam.

Thus, flame retardant canola oil based PUR foam was successfully prepared from canola oil based phosphorus containing polyol with biocontent of more than 90%, via a simple, green and low cost synthesis route.

4.2 Recommendations for Future Works

4.2.1 Oxirane ring opening reaction with phosphoric acid

The molar ratio between phosphoric acid to oxirane in eFAPE employed in this experiment was 1:4, or 0.25 and the final phosphorus content was 1.97%. From the LCMS analysis, the main product was diester phosphate, which means one mole of phosphoric acid will consume two moles of oxirane rings. The LCMS analysis also detected remaining unreacted eFAPE. With conversion of hydroxyl phosphate ester to the cyclic ring on one of the phosphate-oxirane sites, one mole of water will be released, and will open one mole of oxirane. For every mole of phosphoric acid, 3 moles of oxirane ring are consumed. Thus, there is room for higher molar ratio of PA to oxirane, up to 1:3 or 0.3 in order to optimize the consumption of all the oxirane and consequently increase the phosphorus content, while maintaining the viscosity, acid number and hydroxyl value within the acceptable range. Increased phosphorus content will increase the flame retardant capacity of the polyol.

Use of solvent reduces oligomerization thus reduce the viscosity[2], however the optimum amount of solvent should be determined in order to have a more economical and environment friendly process. The optimum time and temperature were not studied in this experiment. The kinetics of the reaction in terms of conversion from the hydroxy phosphate structures to the dioxaphospholane should be studied to ensure that full conversion occurs in order to obtain a stable product.

4.2.2 Oxirane ring opening reaction with DBP and EP

In the reaction between eFAPE-DBP, formation of dioxaphospholane resulted in release of butanol and the formation of an ether linked dimer by replacement of the existing DBP adduct by the terminal C-OH from another fatty acid, resulting in release of free DBP and high acid number over time. The formation of dimers, however was not observed in eFAPE-EP, but in this experiment the changes in eFAPE-EP during storage was not studied. The formation of a dioxaphospholane ring leads to consumption of the adjacent C-OH group, thus, reducing the hydroxyl value and functionality of the product. In the case of eFAPE-EP, the major product with the cyclic ring structure contains only one C-OH group, and in the case of eFAPE-DBP, the dimer has two C-OH groups.

In this study, the changes from phosphate ester to dioxaphospholane were observed only in the oleic acid derivatives and what happened in linoleic acid epoxides (two epoxides) was unknown. It would be worth looking into the effect of the number of oxirane groups per molecule on the formation of dioxaphospholane as the mechanism for formation of dioxaphospholane as suggested by Derouet et al[3] was due to rotation around the C-C bond where there is only one epoxide. The effect of overall stereochemistry on the formation of dioxaphospholane structure should also be looked into.

eFAPE-DBP and eFAPE-EP may not be compatible for PUR foam preparation (where reactive C-OH is required), they maybe useful in other applications such as PUR coatings and pressure sensitive adhesive, should also be studied.

4.2.3 Mechanical and physical properties of PUR foams prepared from eFAPE-PA polyol

Optimization of the PUR formulation using eFAPE-PA polyol was not carried out in this experiment. Thus, further optimization of the formulation could be studied in order to produce flame retardant PUR foams having the desired mechanical and physical properties.

4.2.4 Fire behavior of PUR foams prepared from eFAPE-PA polyols

A comprehensive study on the fire behavior and pyrolysis profile such as heat release rate, total heat release etc, as well as gases released during combustion of flame retardant foams prepared from eFAPE-PA should also be studied.

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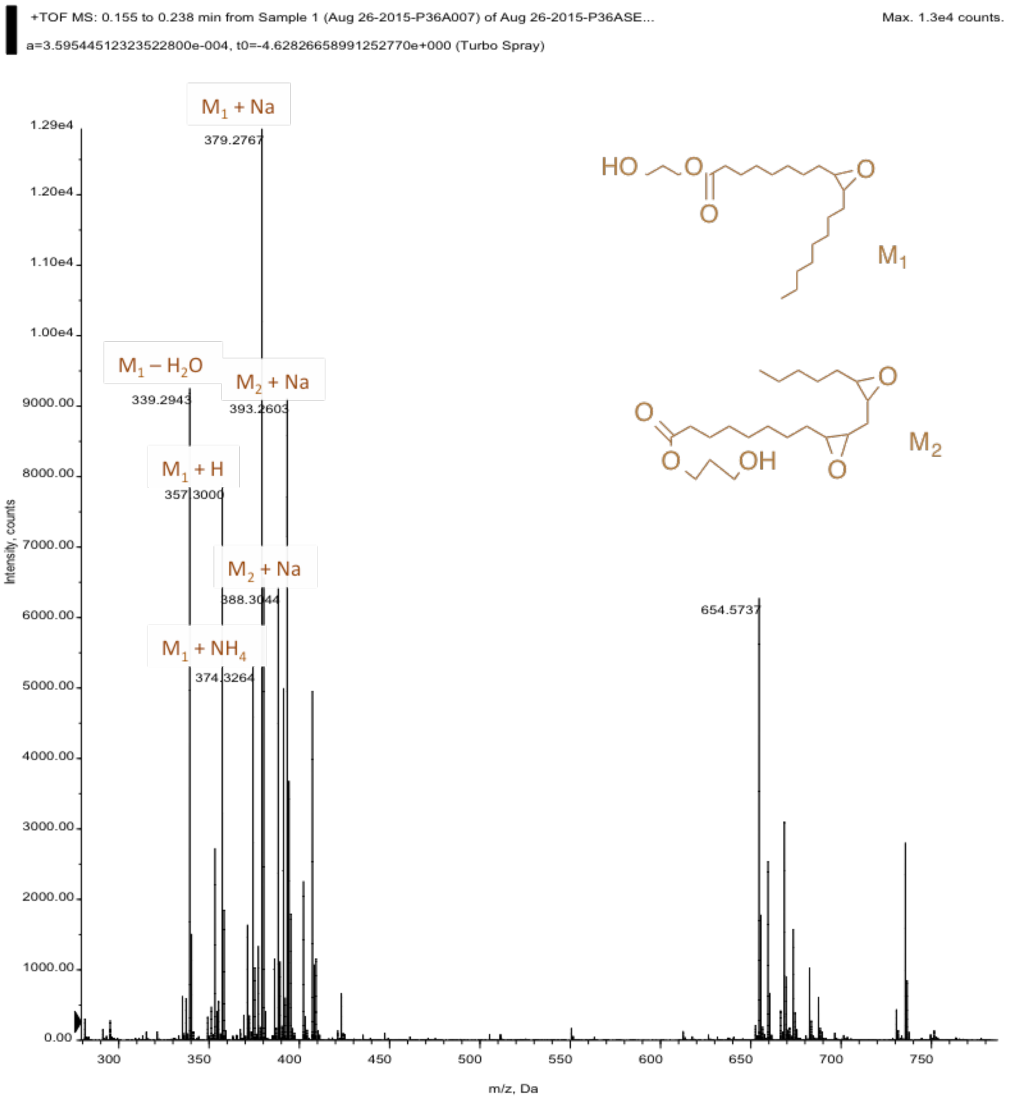
Appendix I: TIC (ESI+) of eFAPE



Appendix II: Calculation of amount of dibutyl phosphate (DBP) required for reaction with eFAPE

The theoretical calculation of the DBP required for one mole of oxirane group to a one mole of DBP is as below:

Epoxy content of eFAPE = 5.43g/100g

Molecular weight of DBP = 210g/mole

Purity of DBP = 97%

Atomic mass of oxygen = 16 amu

Mole of oxirane oxygen in 100g of eFAPE = 5.43/16 = 0.34 mole per 100g

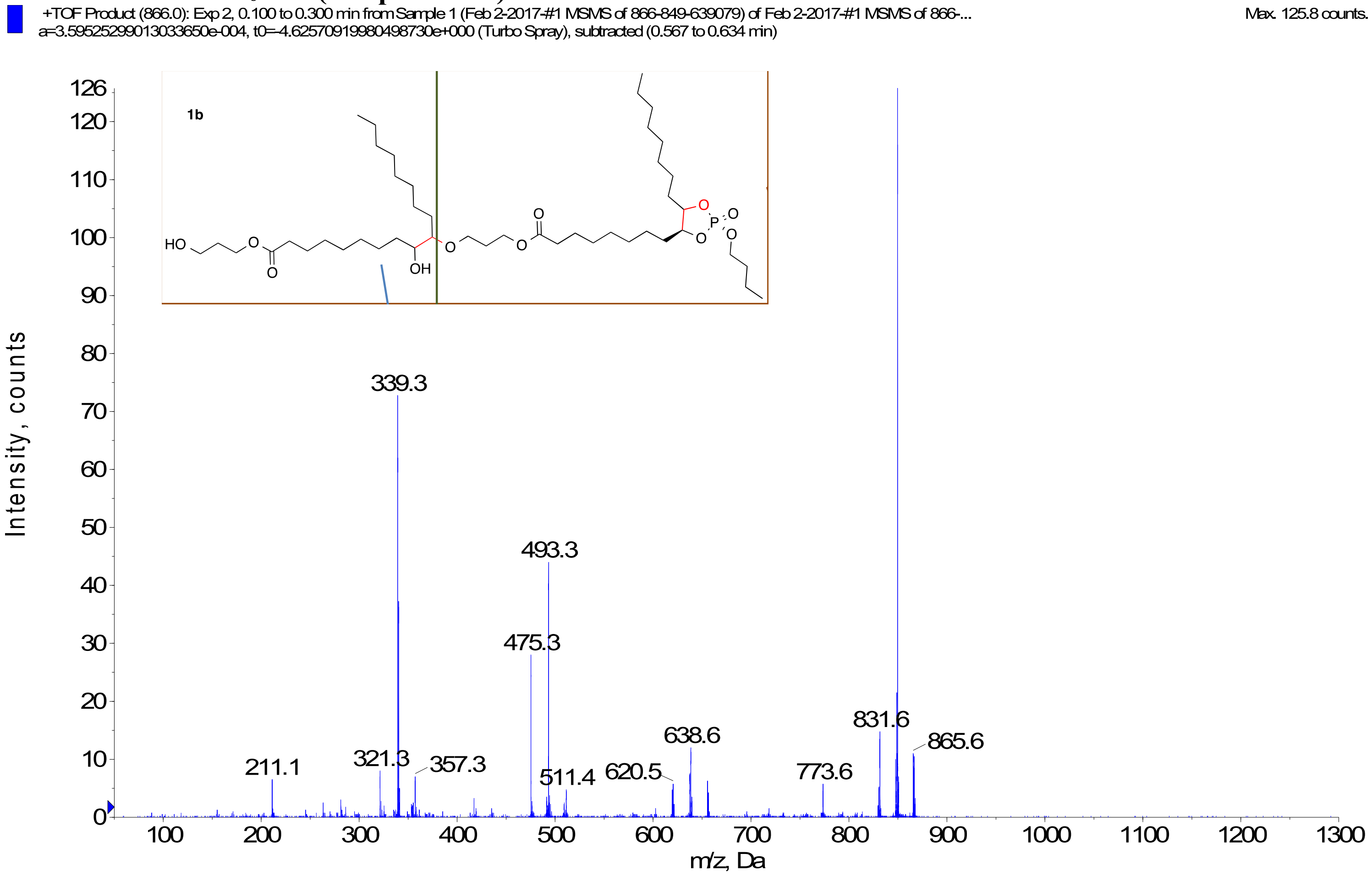
Thus, for molar ratio of 1 mole oxirane: 1 mole DBP based on 100g eFAPE, we need (0.34 x 210)/0.97 = 73.6g DBP.

Theoretical phosphorus content in eFAPE-PA at molar ratio oxirane:DBP of 1:1

= (31/210 x 73.6g x 100)/(73.6g + 100g)

= 6.25%

Appendix III: Tandem MS of *m/z* 866 (compound 1b)



Appendix IV: Calculation of phosphorus content in EP mixture and oxirane:phosphorus molar ratio for reaction between eFAPE and EP

(1) Calculation of phosphorus content in EP mixture

Mole phosphorus per gram P_4O_{10} = 4/284 = 0.014mole/g (1 mole of P_4O_{10} gives 4 moles P)

Molecular weight of P_4O_{10} = 284 g/mole

Amount of P_4O_{10} added for the reaction = 29g

$$\text{Mole P per gram EP mixture} = \frac{(0.014 \text{ x weight of } P_4O_{10} \text{ added})}{\text{Final weight after removal of excess ethanol}}$$

$$= (0.014 \text{ x } 29\text{g})/55\text{g}$$

$$= 0.0074 \text{ mole P/g}$$

(2) Calculation of mole of ethanol reacted with P_4O_{10}

Amount of P_4O_{10} added = 29g/284* = 0.1 mole

Final weight of mixture = 55g

Ethanol reacted = (55g – 29g)/46 = 0.6 mole

(3) Calculation of amount of EP mixture for reaction at molar ratio of *oxirane:phosphorus at 1:0.5*

Mole phosphorus per gram EP mixture = 0.0074

Oxirane oxygen content in eFAPE = 5.43g/100g

Atomic mass of oxygen = 16 amu

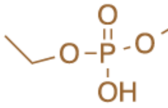
Mole of oxirane oxygen in 100g of eFAPE = 5.43/16 = 0.34 mole per 100g

Thus, for molar ratio of 1 mole oxirane: 0.5 mole P based on 100g eFAPE, we need [(0.34x0.5)/0.74] x 100 = 23g

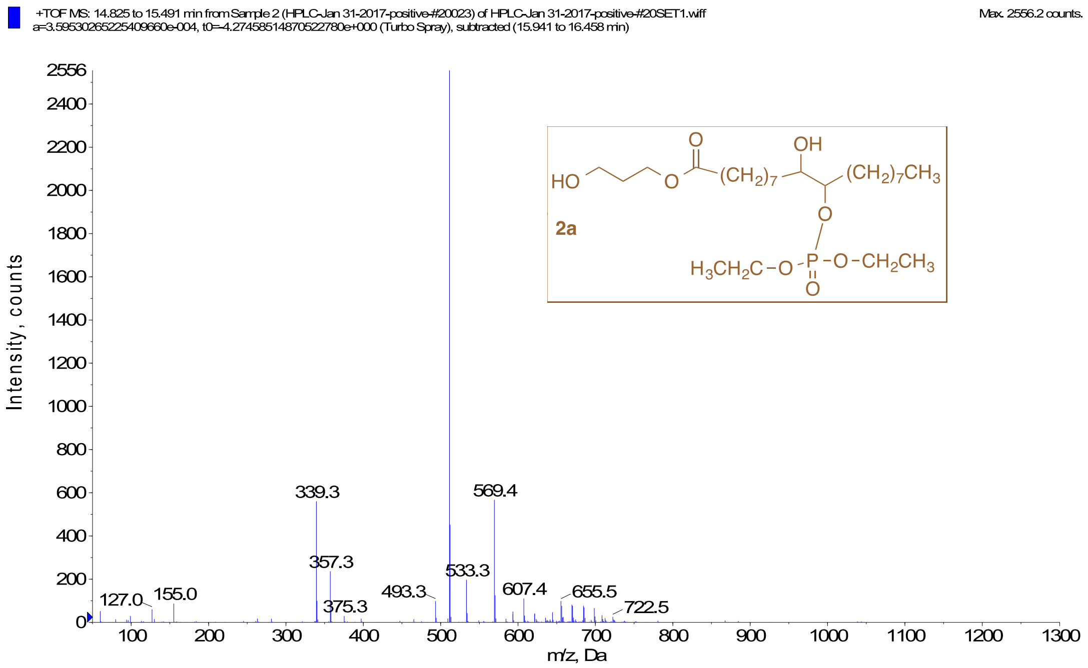
Appendix V: TIC (ESI-) of EP mixture

M_4 - H

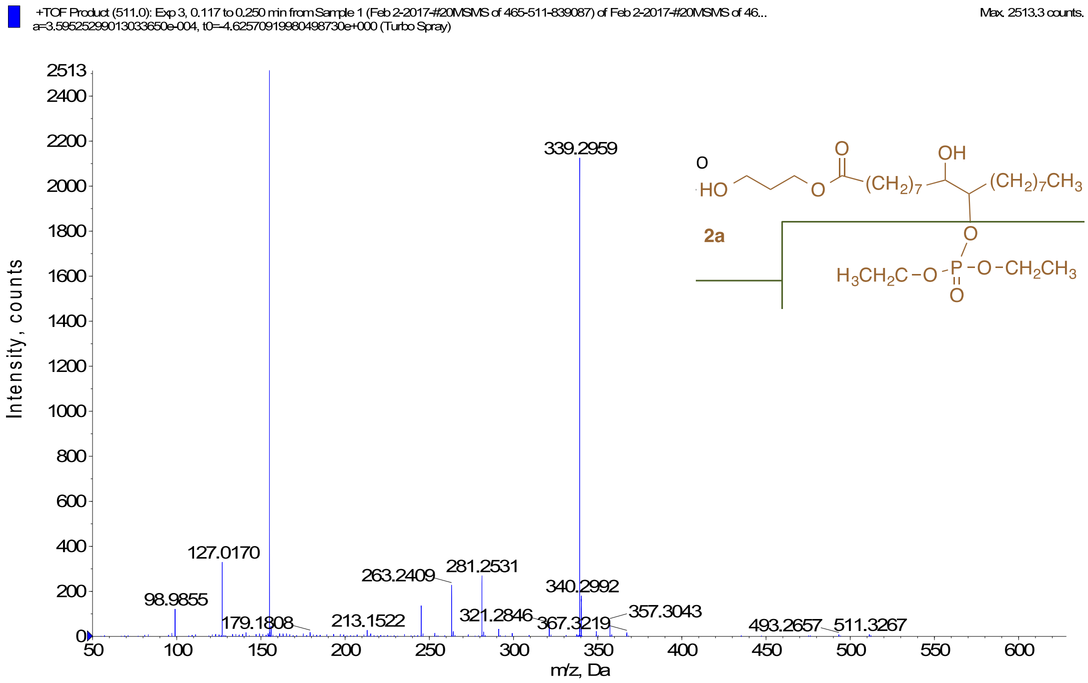
M_3 - H


M_4

Appendix VI: TIC (ESI+) of compound 2a and MS/MS *of m/z* 511

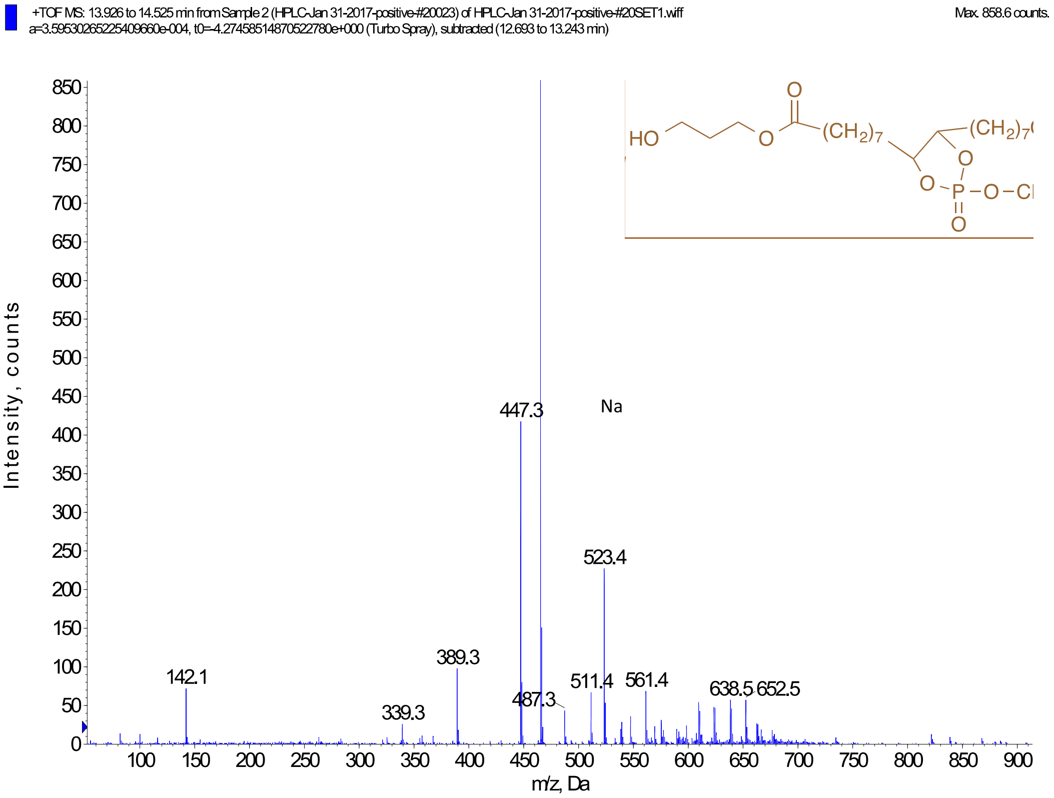


TIC (ESI+) of compound **2a** (Mass = 510 g/mol)

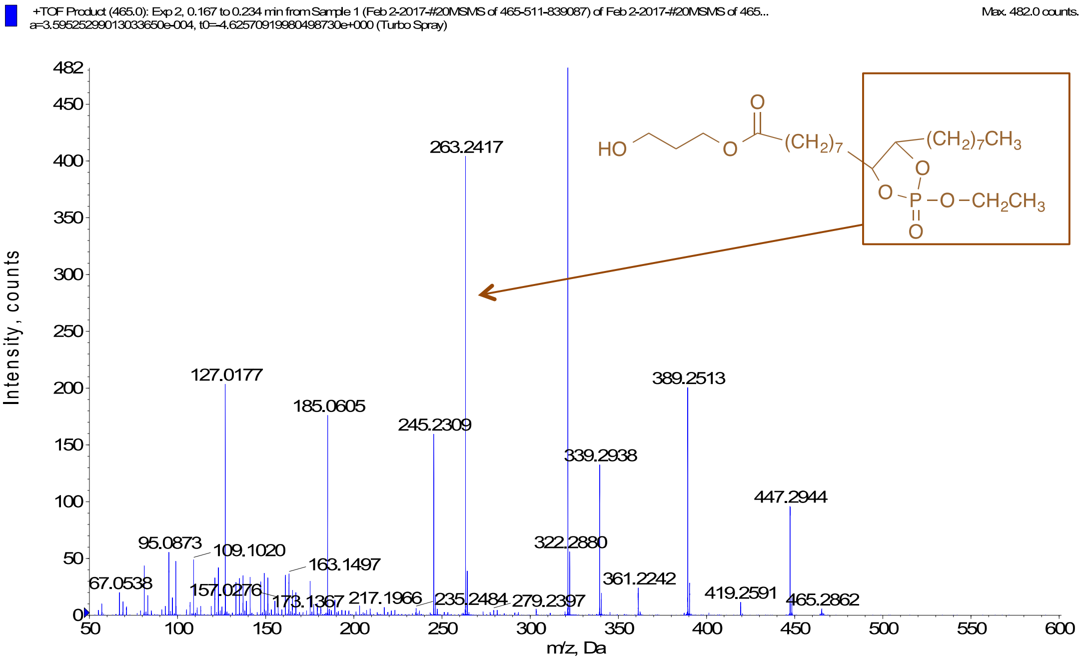


MS/MS (ESI+) of *m/z* 511

Appendix VII: TIC (ESI+) of compound 2b and MS/MS of *m/z* 465

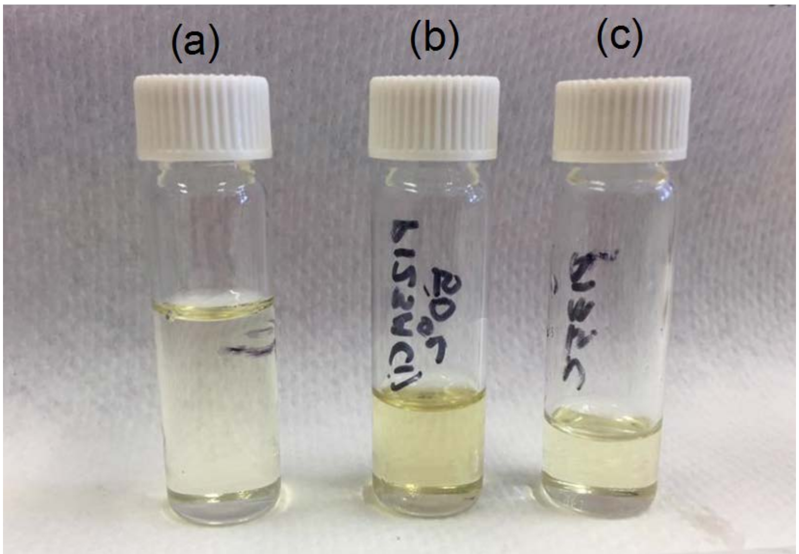


TIC (ESI+) of compound **2b** (Mass = 464 daltons)



MS/MS (ESI+) of *m/z* 465

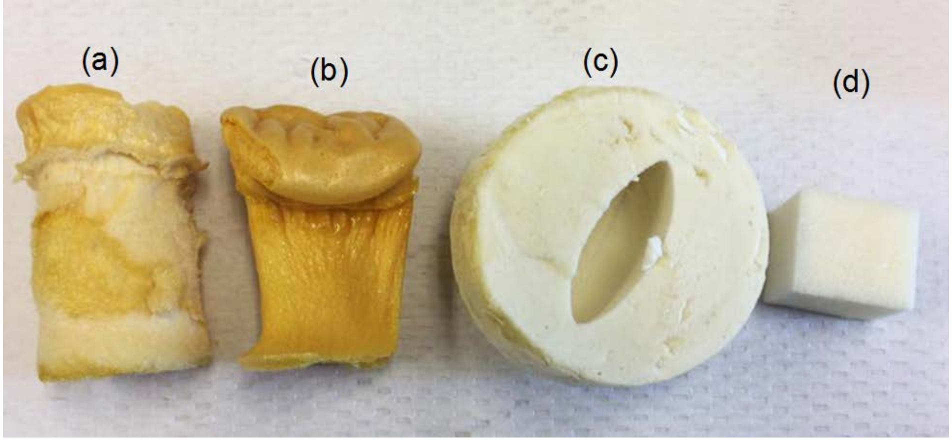
Appendix VIII: Products from reactions



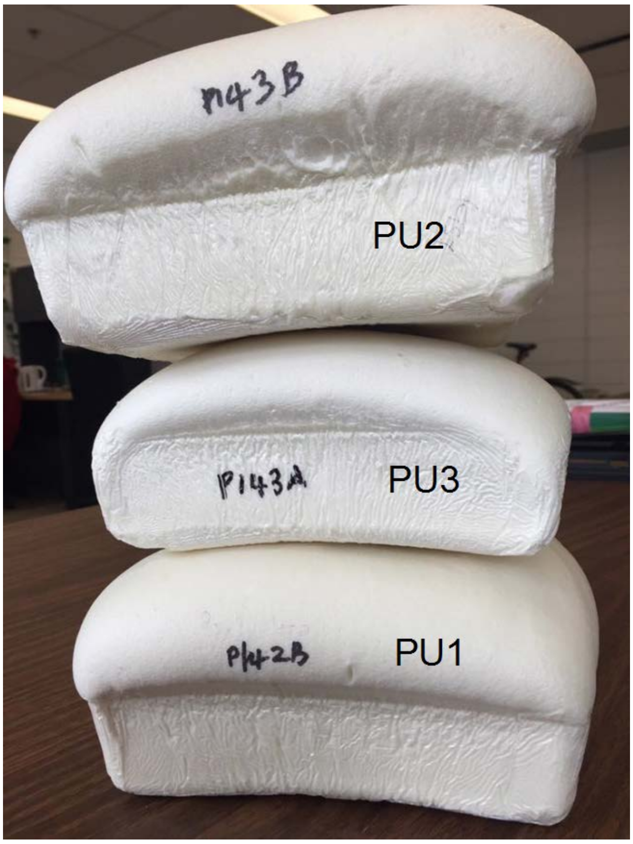
(a) eFAPE-DBP (b) eFAPE-EP (c) eFAPE-PA

EP mixture obtained from reaction between P_4O_{10} and ethanol

Appendix IX: Foams prepared from phosphorus containing polyols from canola oil



Foams prepared from eFAPE-DBP (a) brittle (b) shrinkage (c) formation of air pocket (d) foam with acceptable properties



Foams prepared from eFAPE-PA and 3GP: PU1 = 100% 3GP (0% P), PU2 = 50% 3GP + 50% eFAPE-PA (0.5% P), PU3 = 100% eFAPE-PA (1% P)